A Framework for Environmental Impact Assessment of Carbon Dioxide Utilisation Processes

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Summary

World agreements have stipulated that global temperature should be kept below 2 degrees Celsius above pre-industrial levels to reduce the risks of climate change. However, there is no one path, technology or solution to achieve this. One potential solution is a range of processes known as carbon dioxide utilisation. With this process, CO_2 from waste streams can be captured and used to produce other chemicals.

This research focuses on measuring the potential of these conversion processes to avoid enviromental impacts and be part of the carbon mitigation agenda. Currently, there is no consensus on how to evaluate these impacts and interpret them in a way that allows for comparison. Therefore, a multi-disciplinary environmental impact assessment framework with specific guidelines for carbon dioxide utilisation processes was developed. To test this new framework, two case studies were chosen: methanol and urea synthesis.

Results for the methanol case study showed at best a carbon neutral scenario when methanol is produced through catalytic hydrogenation of CO_2 with renewable H_2 compared to methanol from natural gas (0.1 kg of CO_2 avoided/kg methanol). For urea, the best scenario sees up to 1.3 kg of CO_2 avoided/kg of urea produced in a scenario where an electrolyser connected to wind power supplies H_2 for ammonia synthesis is compared to ammonia produced from fossil fuels. System expansion was used to allocate emissions in all case studies.

Twenty indicators were used for scenario analysis and ranking of each process. Six different rankings were used to analyse impacts. For both case studies, the highest utilisation potential was calculated with a combination of CO_2 capture and an utilisation process based on renewable energy. This framework is a decision making tool that can help guide CO_2 chemical transformation processes towards reaching environmental targets and contribute to lessening the effects of climate change.

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List of Abbreviations

ADP: Abiotic depletion potential

AHP: Analytical hierarchy process

AP: Acidification potential

BEIS: Department for Business, Energy and Strategy

CCC: Committee on Climate Change

CCS: Carbon capture and storage

CCU: Carbon capture and utilisation

CDU: Carbon dioxide utilisation

DAC: Direct air capture

DMC: Dymethylcarbonate

EG: Ethylene glycol

EOL: End of life

EP: Eutrophication potential

EPD: Environmental product declaration

EU ED: European Union Industrial Emissions Directive

EU ETS: European Union Emissions Trading System

FAET: Freshwater ecotoxicity

FAETP: Freshwater ecotoxicity potential

FD: Fossil depletion

FDP: Fossil depletion potential

FD: Fossil depletion

GHG: Greenhouse gases

GW: Global warming

GWP: Global warming potential

HTP: Human toxicity potential

ISO: International Organization for Standardization

IPA: Isopropyl alcohol

IPCC: Intergovernmental Panel on Climate Change

LCA: Life cycle assessment

LCI: Life cycle inventory

LCIA: Life cycle impact assessment

LCOE: Levelised cost of electricity

MAET: Marine aquatic ecotoxicity

MAETP: Marine aquatic ecotoxicity potential

MCDA: Multi criteria decision analysis

MEA: Monoethanolamine

MVAT: Multi value attribute theory

NGCC: Natural gas combined cycle

NGO: Non-governmental organization

NMVOC: Non-methane volatile compounds

ODP: Ozone depletion potential

PC: Pulverised coal

PMF: Particulate matter formation

PM: Particulate matter

POCP: Photochemical ozone creation potential

PSA: Pressure swing absorption

SDGs: Sustainable Development Goals

SMART: Simple multi attribute rating technique

SMR: Steam methane reforming

SNG: Synthetic natural gas

TAET: Terrestrial ecotoxicity

TAETP: Terrestrial ecotoxicity potential

TBL: Triple bottom line

TEG: Triethylene glycol

TRL: Technology readiness level

UNFCCC: United Nations Framework Convention on Climate Change
VOC: Volatile organic compound

VSA: Vacuum swing absorption

WFD: Waste Framework Directive

WTO: World Trade Organization

1 Introduction

As living species in this planet, everything that we do has a consequence to our home. This consequence can be good or bad, like this we have survived for millions of years. Nature has a way of finding a balance, whether it is through the carbon cycle, the nitrogen, the water cycle, etc. However, as humans we have been pushing the barrier of these cycles with our anthropogenic activities (Olah, Prakash and Goeppert, 2011). How do we know when is it too much or too little? How can we measure our impact in this world, the bad and the good? Moreover, particularly, how can we have a sustainable life that will not compromise the future of next generations?

There are many efforts to reduce the negative aspects caused by our standard of living. Accepting that we will always have an impact is a first step towards managing these. From finding less carbon intensive energy sources, optimising resources, recycling materials, tightening environmental regulations etc., as a society there is much more awareness than ever before in what a sustainable life means (Moldan, Janouskova and Hak, 2012). Still, there is much work to do in this area.

Climate Change is without a doubt one of the most discussed environmental changes in the 21st Century. It is an issue set at global scale that will affect natural and human systems. Some of the observed impacts by the Intergovernmental Panel on Climate Change (IPCC) include (IPCC, 2014):

- Change in precipitation or melting snow that modify hydrological systems. This also includes permafrost warming and thawing and shrinking of glaciers.
- Changes in the way animal species react in response to climate change. Including migration patterns, seasonal activities, abundances and geographical ranges.
- Uneven development that will affect marginalised societies the most.
- Climate related extremes such as, droughts, floods, cyclones, wildfires, heatwaves, etc.
- Violent conflict that leads to increased climate vulnerability.

To prevent further impacts, the Intergovernmental Panel on Climate Change (IPCC) set a carbon budget to limit global temperature rise to 2 degrees C above pre-industrial levels. The world responded in 1992 by joining an international treaty, creating the United

Framework Convention on Climate Change. By 1995, the Kyoto Protocol was signed legally binding countries to comply with emission reduction targets. Since then, the convention includes 197 parties and 192 of these have signed the Kyoto Protocol.

More recently, in September 2015 world leaders adopted the 17 Sustainable Development Goals (SDGs) of the 2030 Agenda for Sustainable Development. These goals address several social needs including health, social protection, education, addressing climate change and environmental protection amongst others. While these goals are not legally binding, countries are expected to implement their own national frameworks, monitor, review and report progress. Goal number 13 is set to take urgent action to combat climate change and its impacts. It emphasises in acknowledging that the United Nations Framework Convention on Climate Change is the primary international, intergovernmental forum for negotiating the global response to climate change. The targets of this goal include (United Nations, 2015):

- Strengthen resilience and adaptive capacity to climate-related hazards and natural disasters in all countries.
- Integrate climate change measures into national policies, strategies and planning.
- Improve education, awareness-raising and human and institutional capacity on climate change mitigation, adaptation, impact reduction and early warning.
- Promote mechanism for raising capacity for effective climate change-related planning and management in least developed countries and small island developing States, including focusing on women, youth and local and marginalised communities.
- Implement the commitment undertaken by developed-country parties to the United Nations Framework Convention on Climate Change to a goal of mobilising jointly $100 billion annually by 2020 from all sources to address the needs of developing countries in the context of meaningful mitigation actions and transparency on implementation and fully operationalise the Green Climate Fund through its capitalisation as soon as possible.

While these commitments to tackle climate change are set at a large scale, small ideas, local improvements and new technologies can make an overall difference. Through this work, we focus on the potential of a technology to reduce anthropogenic CO_2 emissions: CO_2 utilisation, also known as carbon capture and utilisation (CCU).

There is a focus on carbon dioxide chemical transformation processes because if successful, it can be part of the carbon mitigation agenda. With this technology, carbon dioxide can be captured from various sources and used to produce other chemicals. Ideally, these chemicals would have lower environmental impacts if CO_2 was supplied from waste rather than using virgin materials as feedstock. While this is a promising technology, the potential for avoiding environmental impacts is still unknown. Without further knowledge of this potential, it is difficult to predict the success of CO_2 utilisation as a carbon mitigation technology. Finding this research gap gave purpose to this work; there is a need to assess the environmental benefit (in particular CO_2 avoidance) of CO_2 based products.

There are many ways to assess the impact of an anthropogenic activity, whether it is a product or a process. While these methods have been available for decades (Moldan, Janouskova and Hak, 2012), newer processes sometimes need tailored methods. Through this work, we explore the possibilities of an environmental impact assessment framework that can address the challenges of a product that does not use a raw feedstock. These challenges include allocating emissions between capture, CO_2 transformation and use, dealing with lack of data and processes not easily modelled, separating the carbon benefit and other environmental impacts, amongst others.

With these in mind, the research questions, aim and objectives were the following:

- Do CO_2 utilisation processes have less environmental impacts than non-CO_2 utilisation processes? In particular, climate change and fossil depletion?
- How can available sustainability assessment methods be adapted to include CO_2 utilisation processes?
- What are the main challenges of these adaptations and how can they be overcome?
- Can these adapted assessments be standardised for better comparison between CO_2 utilisation routes?
- Are there specific products that can be assessed that would give an overview of CO_2 utilisation processes and can be used as baseline cases?

- What should be the structure of an environmental impact assessment for CO_2 utilisation? What is the scope?

The aim of this work is to develop an environmental impact assessment framework for CO_2 utilisation processes. To achieve this, a series of objectives were proposed:

1. Create a framework that englobes the design of the CO_2 utilisation process, locational availability of renewable energy, the impact assessment and other aspects of CO_2 utilisation into one study.
2. Present the framework in a practical way, where results can easily be compared with other studies.
3. Explain the differences between assessing a process that uses waste streams instead of raw materials and a conventional product/process.
4. Deliver study cases that support the applicability of the framework.
5. Determine the limitations of assessing carbon dioxide utilisation routes.

The framework follows the life cycle assessment (LCA) technique. The definition of the term life cycle assessment from the International Organization for Standardization (ISO) in 1997 is (Sadhukhan, Ng and Hernandez, 2014):

"Compilation and evaluation of the inputs, outputs and the potential environmental impacts of a product system throughout its life cycle."

This methodology is based on four main phases: Goal and scope definition, inventory analysis, impact assessment and interpretation. The International Organization for Standardization has then published several documents on how these life cycle assessments principles and phases are to be applied. These documents are (Sadhukhan, Ng and Hernandez, 2014):

- ISO 14040 Life cycle assessment-principles and framework (June 1997, now confirmed from 2006)
- ISO 14041 Life cycle assessment-goal and scope definition and inventory analysis (October 1998)
- ISO 14042 Life cycle assessment-life cycle impact assessment (March 2000)
- ISO 14043 Life cycle assessment-life cycle interpretation (March 2000)
- ISO/TS 14048 Life cycle assessment-data documentation format (2002)

Using this life cycle assessment (LCA) technique, the aims and objectives are achieved throughout the next eight chapters. In each one, a specific part of the developed framework is discussed.

To begin, there is an overview of what does it mean to transform CO_2 chemically. **Chapter 2** discusses the basic theory behind these processes from a supply chain perspective. This leads to a cradle to gate approach that is seen for most of the work. The main phases include CO_2 capture and CO_2 utilisation. Other aspects include CO_2 treatment, transportation, energy source, product, etc. This chapter lays the groundwork for the case scenarios selected for this work: methanol and urea production. Methanol has been studied extensively by the CO_2 utilisation community and as a result there is more data available than for most of the other CO_2 utilisation processes. Because of this, it was feasible to develop an environmental impact assessment framework around this process and use it worked example. The framework could then be tested on a urea production method researched internally.

The focus then moves to reviewing the assessment work available for CO_2 utilisation. There was a specific interest in searching for life cycle assessment (LCA) work, as this was the methodology considered as basis. In this review, it was found that a large amount of information exists, but it is often scattered or presented inconsistently. Some of the studies did present life cycle assessment (LCA) results or guidelines, but no work was found that took a general approach to sustainability issues and CO_2 utilisation. This opened the possibility of creating such framework, in a way that could address the problems associated with a CO_2 based product

A final section in **Chapter 3** analyses policies related to utilisation technologies. Currently it is unclear what role it will have in the mitigation agenda and what regulations are attached to it. An assessment is made on the options available for the technologies under study, particularly in the UK. The framework was developed in **Chapter 4** and divided into four main sections:

1. Design of the CO_2 utilisation process: Addresses the problems with obtaining a life cycle inventory (LCI) when processes are not at commercial scale or with undefined outputs/inputs. This includes ways to use process simulations as alternatives to traditional life cycle inventory databases.

2. Environmental impact assessment: Assesses the technical data using life cycle assessment (LCA) methodology. Adaptations are made to allocate carbon dioxide emissions by using the system expansion method. It uses global warming and fossil depletion, carbon avoided, and carbon utilised as the main indicators. However, all other impacts categories under the CML-IA method are also assessed.
3. Locational availability of renewable energy: This is an aspect that needs to be revised constantly throughout the framework. The potential of any CO_2 utilisation project will depend on the CO_2 sources available within a region as well as the renewable energy mix also available. These two variables are not time-fixed thus creating alternative scenarios gives a wider overview of the impacts. The geographical section includes mapping of CO_2 sources and energy outlooks up to 2050 as examples.
4. Other aspects: This includes a glimpse of other characteristics that affect CO_2 utilisation. While there is less information available, there is also more ground to improve and create useful guidelines. In this work, there is an introduction to:
    - Utilities costs
    - Energy projections
    - Human health issues
    - Aspects that will affect future generations
    - CO_2 utilisation potential markets

This section outlines the initial requirements so in the future a life cycle costing model for can be created. The results from this section are shown as 20 indicators for the assessment of carbon dioxide and utilisation.

The direct interpretation of un-aggregated results can be challenging when there are many process alternatives to consider. To simplify the interpretation of CO_2 based products at an initial screening level, a multi criteria decision analysis method (MCDA) was proposed to rank the indicators. This allowed better comparisons between processes under the same CO_2 chemical transformation conditions. The simple multi attribute ranking technique (SMART) method was also used to determine the indicator weights and analyse how different weights will affect the final interpretation.

After the framework was outlined, **Chapter 5 to 8** tested its application. **Chapter 5** uses methanol production through catalytic hydrogenation of CO_2 as the utilisation process. This worked example is created with collected data and available models. The results are compared to other similar studies for sensitivity analysis and to check the accuracy of the assessment method. The same steps are then implemented to another product in **Chapter 6**. The process is urea production from ammonia using ‘green hydrogen’ and captured CO_2. In collaboration with another research group by the University of Sheffield, the life cycle inventory (LCI) is provided for a pilot plant that will produce urea at a rate of 250 kg/day. Both case studies use five baseline scenarios for comparison.

In **Chapter 7**, the results from both case studies are used to create energy scenarios to 2050 in the UK. National Grid projections and UK renewable data are used to calculate these scenarios. Other aspects such as cost of utilities and market potential are also assessed with current background data. This chapter concludes with the summary of all indicator results for each case and for each scenario.

The decision analysis method is applied in **Chapter 8**. This includes an equal weights approach and a specific CO_2 utilisation weighting scheme for sensitivity analysis. For the latter, global warming and fossil fuel depletion are the impact categories considered with the most weight at an initial screening level. Ten fundamental questions for utilisation processes were created to determine the weights of each impact. With these results, final recommendations on the potential of each route were made. This also includes policy recommendations and suggestions for process improvement for utilisation routes. Through this work, the benefits, opportunities and challenges of evaluating CO_2 utilisation processes such as methanol and urea are assessed.

This framework presents other opportunities to continue finding paths to show environmental results in simpler and practical ways. The search to finding less carbon intensive and more environmentally friendly processes will not stop; therefore, finding ways to prove the success of these processes will also be as relevant and as important as the processes itself.

1.1 Chapter one reference list

IPCC (2014) *Summary for policymakers. In: Climate Change 2014: Impacts, Adaptation, and Vulnerability Part A: Global and Sectoral Aspects. Contribution of Working Group II to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*.

Moldan, B., Janouskova, S. and Hak, T. (2012) ‘How to understand and measure environmental sustainability: Indicators and targets’, *Ecological Indicators*, 17, pp. 4–13. doi: 10.1016/j.ecolind.2011.04.033.

Olah, G. a, Prakash, G. K. S. and Goeppert, A. (2011) ‘Anthropogenic chemical carbon cycle for a sustainable future.’, *Journal of the American Chemical Society*, 133(33), pp. 12881–98. doi: 10.1021/ja202642y.

Sadhukhan, J., Ng, K. S. and Hernandez, E. M. (2014) *Biorefineries and Chemical Processes: Design, Integration and Sustainability Analysis*. Chichester, UK: John Wiley & Sons, Ltd. doi: 10.1002/9781118698129.

United Nations (2015) *Sustainable Development Goals: 17 goals to transform our world*.

2 Overview of Chemical Transformations of CO_2 for Utilisation

This chapter reviews the pathways of capturing CO_2 from anthropogenic sources and direct air capture to transform it chemically into a product. This review covers potential CO_2 sources; the capture options currently available and the routes to utilising captured CO_2. While these are the main aspects of carbon dioxide utilisation, they are not the only ones. Additional processes such as: the removal of impurities, compression and transportation of CO_2, the use of the final product, and the use of renewable energy for CO_2 utilisation are also discussed. This is a brief overview of some of the processes that can be used to chemically transform CO_2; understanding what drives these processes is fundamental for developing an environmental impact assessment framework for them.

2.1 Carbon sequestration for greenhouse gases (GHG) mitigation

While fossil fuels continue to be available as a source of energy, it is necessary to optimize extraction, production and consumption. This is a fundamental step to exploit this resource with in its natural limits. This also includes finding new ways to lessen the impacts to the carbon cycle by maintaining a balance between carbon uptakes and releases. The aim is to stay within its natural rates as possible. CO_2 utilisation is amongst the developing technologies that push towards an efficient fossil fuel economy. It is an option that can contribute to CO_2 emission reductions by utilising carbon dioxide through chemical transformations. While the carbon dioxide would eventually be emitted again, it can displace new raw fossil fuels and their associated impacts (IPCC, 2005). CO_2 utilisation (also referred to as carbon dioxide and utilisation) and abbreviated as CDU is frequently linked to carbon capture and storage (CCS). However, the similarities between CDU and CCS end after the capture of carbon dioxide from emission sources. With carbon utilisation, a useful product can be introduced to the market, while carbon capture and storage will only demand economical investment with no revenues. Carbon capture and storage is considered a storage solution for CO_2 and not a mitigation technology (IPCC, 2005). As for carbon utilisation, its role as a mitigation process is still unclear.

Utilising carbon dioxide at industrial scale would require high investments but so would carbon capture and storage.

Carbon capture and storage has a large upstream supply chain, but an almost inexistent downstream chain**.** For CO_2 utilisation its supply chain map would include a capture phase as seen in **Figure 2.1,** plus the utilisation unit and a downstream supply chain. Because of these extra processes, it is more complex to form a life cycle inventory for CO_2 utilisation than for carbon capture and storage. **Sections 2.1.1** to **2.4** further discuss the life cycle of carbon capture and CO_2 utilisation supply chains.

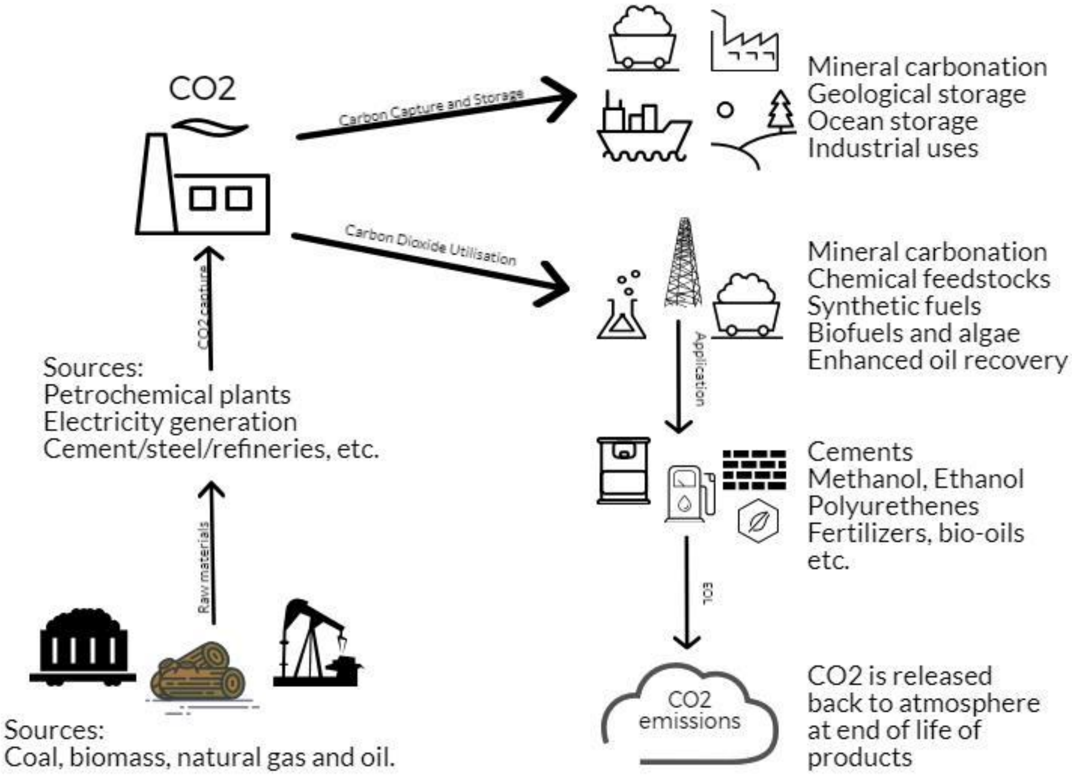


Figure 2.1 Supply chain of carbon capture and storage and CO_2 utilisation, based on IPCC (2005)

2.1.1 CO_2 capture routes

The first step towards chemically transforming CO_2 is securing a carbon dioxide supply (von der Assen *et al.*, 2016). In terms of sustainability, the first step is ensuring that this CO_2 stream does not deplete fossil reserves any further by using an energy intensive capture process. In efforts to achieve better environmental performances, many capture routes have been studied through CCS (carbon capture and storage) technologies. Although initially popular, low public acceptance, high costs and other problems lead carbon capture and storage (CCS) development to stall in the UK (House of Commons and Committee, 2016).

Although currently there are no large-scale carbon capture and storage projects in the UK, capture technologies are still investigated with the aim of finding ways to lower carbon emissions. These capture routes are fundamental for a successful utilisation of CO_2. Carbon dioxide use is not necessarily limited by the capture step; it can also be used directly from a mixture of gases. This is known as direct flue gas utilisation (Zhang *et al.*, 2013; Connect, 2014). While using direct gases is still a new research area, there are processes such as mineralisation that are much more advance. The main carbon capture routes are discussed below.

Carbon dioxide can be captured from several industrial sources, such as:

- Coal and gas fired power plants
- Cement manufacturing
- Ammonia and fertiliser production
- Steel industry
- Oil and gas refineries

Overall, in EU countries, the energy generation sector is the highest emitter of greenhouse gases and the largest carbon dioxide source, followed by transportation (Eurostat, 2017). Although transportation comes in second contributing to 23% of greenhouse gases (GHG) emissions in a year, the capture of these emissions is not yet feasible as most developments have focussed on fixed point emission sources.

This leaves energy generation, industrial processes, agriculture and waste management as industrial sectors were carbon capture could be deployed (Eurostat, 2017). Each sector emits CO_2 at different rates, concentrations and conditions. These differing parameters determine which utilisation options are applicable as well as the optimum carbon capture method.

A typical CO_2 composition from a coal-fired power generation after SO_2 scrubbing can range from 7 to 15% (Wattanaphan *et al.*, 2013). Capture technologies are commonly divided into three categories depending on the carbon capture point: Pre-combustion, post-combustion and oxy-fuel capture (**Figure 2.2**).

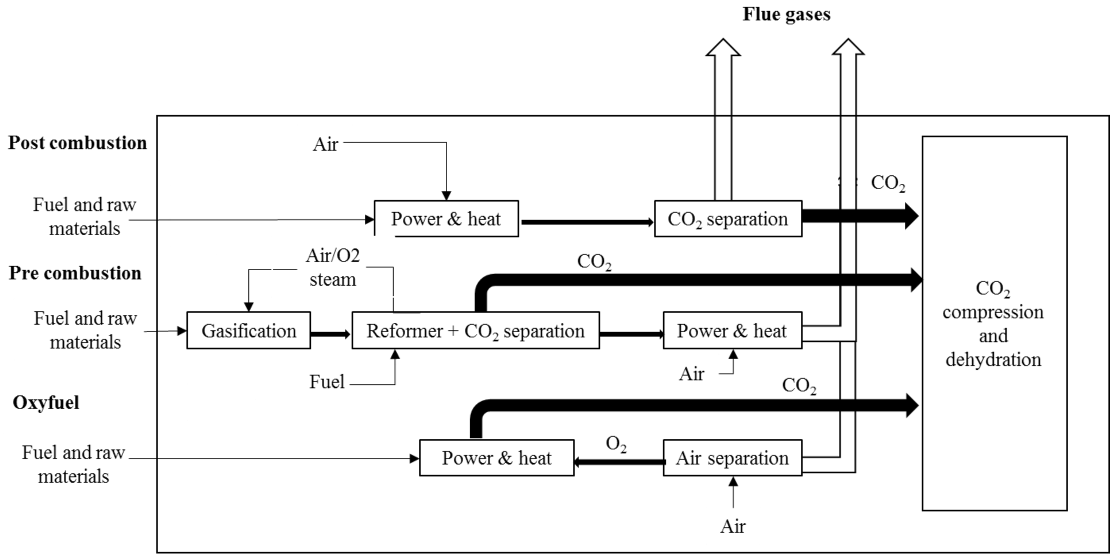


Figure 2.2 Carbon dioxide capture routes, based on diagram by IPCC (2005)

Pre-combustion and oxy-fuel capture can be integrated into new plants; post-combustion capture can be retrofitted to existing technologies. Currently, post-combustion is the most accessible carbon capture process but generally remains prohibitively expensive. (IEA Greenhouse Gas R&D Programme, 2008; Kolding, Fehrmann and Riisager, 2012; Srisang *et al.*, 2017). Post-combustion capture processes use solvents to strip carbon dioxide from flue gases from power plants. They are designed to treat high volumes of gas due to low carbon dioxide concentrations at low pressures (NETL, 2013). This project focuses on post-combustion as the capture method, based on data availability and scope of the project.

In general, separation processes can be either physical or chemical. These methods include the following processes for CO_2 capture: absorption, adsorption, chemical looping combustion, gas separation membranes and low temperature separation. Each process has different characteristics, potential and use (Pires *et al.*, 2011; Sadhukhan, Ng and Hernandez, 2014). Over the next 10-20 years, solvent scrubbing, (including ionic liquids), oxy-fuel combustion, chemical looping and calcium looping are processes that are expected to grow within CCS (Boot-Handford *et al.*, 2014). The separation processes for carbon capture are described below.

Absorption processes

Absorption works by stripping the CO_2 from the flue gas by using solutions that bind CO_2 (Troy, Schreiber and Zapp, 2016). The process operates in an absorption column at low temperatures with water used for scrubbing (Petrescu *et al.*, 2017). **Figure 2.3** shows the basic configuration of an absorption column. Amine-based is the most common absorption solution and is mentioned often in CSS studies (Ho, Allinson and Wiley, 2011; Zoannou, Sapsford and Griffiths, 2013; Basavaraja and Jayanti, 2015; Petrescu *et al.*, 2017; Srisang *et al.*, 2017; Van der Giesen *et al.*, 2017). Part of the success with amines is its applicability at industrial scale for gas treating. Other advantages of using amines include: low reboiler regeneration energy, low power for CO_2 compression, low cost for ammonia and a high capacity to carry CO_2 (Versteeg and Rubin, 2011). To this date, amines such as monoethanolamine (MEA), diethanolamine (DEA) and methyl diethanolamine (MDEA) have had the most success. Out of the above amines, monoethanolamine (MEA) currently has the highest potential for industrial applications, with MEA being known for having a good affinity for CO_2 resulting in good capture properties (Pirngruber and Leinekugel-le-cocq, 2013; Xu *et al.*, 2013; Sadhukhan, Ng and Hernandez, 2014).

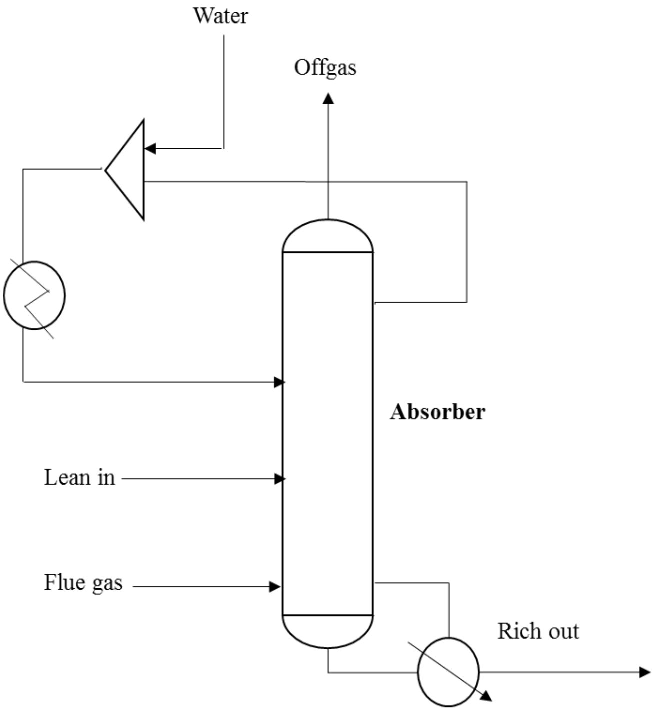


Figure 2.3 Block diagram of absorber used for CO_2 capture, based on Abu-Zahra, Schneiders, *et al.* (2007)

Much of the ongoing research in this area is dedicated to the use of amines beyond pilot scale. Finding better solvents that regenerate at lower cost, energy and at a less frequent rate is priority. If research succeeds in reducing energy penalties and costs of solvent regeneration, then amines will continue to be the most feasible of carbon capture technologies. Alternatively, there are also other, less-explored absorption processes that can be considered. Chilled ammonia, carbonation/calcination cycles and amino-acid salt solutions are all alternatives technologies for absorptive carbon capture. However, these are still less developed than amines with less performance data/information available (Pires *et al.*, 2011).

Even though solvents are a widely studied and popular option for carbon capture, they still have disadvantages. Solvents have limited CO_2 recycling loading capacity. For monoethanolamine (MEA) there is net consumption of approximately > 1.4 kg per tonne of CO_2 captured (Pirngruber and Leinekugel-le-cocq, 2013). After the saturation point is reached, the solvent must be replaced requiring extra energy. Overall, energy requirements increase from 70-80% in a coal fired power plant with capture while total energy penalties range from 25% to 40%. (Zhai and Rubin, 2013; Hopkinson *et al.*, 2014). Solvent is also lost by evaporation, leading to increased negative environmental impacts (increased pollution, toxicology). There are also issues with equipment corrosion and a large increase in water consumption for the plant. For example, in a coal fired power plant with a post-combustion capture system with amines, water consumption rates double (Zhai and Rubin, 2013). **Table 2.1** shows examples of baseline power plant parameters with and without CO_2 capture from literature.

Table 2.1 Examples of baseline power plant parameters with and without CO_2 capture process

Plant parameters	**Reference studies**			
	(Troy, Schreiber and Zapp, 2016)	(Xu *et al.*, 2013)	(NETL, 2015)	(NETL, 2015)
	Supercritical coal power plant w/o capture	Supercritical coal power plant with capture	Supercritical coal power plant with capture	NGCC power plant with capture[1]
Plant net output (MW)	555	570	550	550
Net plant efficiency (%)	46	40	32	46
Live steam pressure (bar)	300	242	241	165
Live steam temperature (°C)	600	566	593	566
Output CO_2 (g/kWh)	N/A	781	873	360
Auxiliary power (MW)	N/A	30	91	42
Capture rate (%)	N/A	90	90	90

[1] Natural gas combined cycle power plants

The highest energy penalties and operating cost are associated with the regeneration column (Alie *et al.*, 2005; Versteeg and Rubin, 2011; Hopkinson *et al.*, 2014). The rest of the auxiliary power is mainly divided between various pumps and heat exchangers. Absorption costs are high due to elevated energy requirements; however alternative processes are being studied to reduce these (Karimi, Hillestad and Svendsen, 2011; Versteeg and Rubin, 2011). An example of this is chilled ammonia. Ammonia has lower heating absorption and lower compression needs for a liquid CO_2 stream than for a CO_2 gas stream, which could make it less energy intensive (Pires *et al.*, 2011). Water requirements are still high but several companies are currently testing this process at pilot scale (IEA Greenhouse Gas R&D Programme, 2008).

Currently, the most common physical absorption processes are Selexol ^{TM} and Rectisol ^{TM} (Sadhukhan, Ng and Hernandez, 2014). The Rectisol ^{TM} technology uses refrigerated methanol as the solvent to remove the contaminants and produce ultra-clean syngas (Sadhukhan, Ng and Hernandez, 2014). It is typically used to remove sulphur for the production of chemicals such as methanol and ammonia (Olajire, 2010; Sharma *et al.*, 2016). Its use in CO_2 capture is favoured because of its commercial availability and its performance at high partial pressures when compared to other solvents (Sharma *et al.*, 2016). The main drawback of this process is the high energy penalties associated for the capture of CO_2, according to Sharma *et al.* (2016) and Yang *et al*. (2016), the higher the capture rate, the higher the energy penalty. The high energy penalty limits CO_2 capture rate to 60-70 % (Yang, Qian and Yang, 2016).

The Selexol^{TM} process is used when fuel gas specifications are not as rigorous and is less energy intensive than the Rectisol ^{TM} technology (Sadhukhan, Ng and Hernandez, 2014). The benefits of this process is its technological maturity with over 110 commercial Selexol^{TM} processes operating around the world (Im *et al.*, 2015). It is also the conventional process used to recover CO_2 and H_2S simultaneously operating at high pressures > 20 atm (Sadhukhan, Ng and Hernandez, 2014; Im *et al.*, 2015; Kapetaki *et al.*, 2015). As it is the case with Rectisol ^{TM}, the economics of the Selexol^{TM} process need to improve for its large scale use in CO_2 capture (Im *et al.*, 2015).

Adsorption processes

Adsorption process is based on the use of a solid adsorbent to capture one or more components from a gaseous mixture (Sadhukhan, Ng and Hernandez, 2014). There are some benefits of using adsorption over absorption processes. Regeneration of adsorbents is less energy intensive and there is also less pollution since chemicals are not released to the environment (Pires *et al.*, 2011). The main two processes are pressure swing adsorption (PSA) and vacuum swing adsorption (VSA) (Haghpanah *et al.*, 2013). The first one is a process that relies on solid sorbents thus avoiding liquid handling issues. Costs are also similar to adsorption with monoethanolamine (MEA). Vacuum swing adsorption processes work at ambient temperature and pressures, desorbing at lower pressures (Liu *et al.*, 2012). This leads to lower power consumption and increased ease of operation compared to other methods (Liu and Green, 2013). Both technologies have potential if suitable adsorbents are selected such as zeolites (Labus and Machnikowski, 2014).

There are however, several disadvantages to adsorption processes. Pressure swing absorption requires positive and strong partial pressure difference between adsorption and desorption. To achieve high CO_2 recovery a pressure feed of at least 7 bar is necessary, increasing energy consumption and costs for the capture process (Pirngruber and Leinekugel-le-cocq, 2013). With vacuum swing adsorption, extra compression stages and vacuum blower trains are needed due to low pressure. Compression will also increase costs (Pirngruber and Leinekugel-le-cocq, 2013). There are other associated costs with flue gas drying and cooling for both pressure swing adsorption/pressure vacuum adsorption (PSA/VSA) (Pires *et al.*, 2011) . Finally, one of the major problems with absorption is scale up. According to Pirngruber & Leinekugel-le-cocq (2013) the largest vacuum swing adsorption plants for are six times smaller than the minimum required for a large scale, industrial project. Pirngruber & Leinekugel-le-cocq (2013), Labus & Machnikowski (2014) and Liu *et al.* (2011) amongst others, are working towards feasible solutions to overcome these barriers.

Gas separation membranes

Membranes are not as widely in industry as processes such as amine or PSA separation (Labus & Machnikowski, 2014). But, they offer advantages such as requiring easy installation and low energy consumption for a low purity stream (Pires *et al.*, 2011; Pera-Titus, 2014). Membrane systems can also be fitted to a compact space by using high packing density. As is the case with adsorption processes, selecting the correct adsorbent or membrane can determine the separation (and therefore capture) rate. Thus, reaching a balance between membrane properties (selectivity and permeability) is fundamental for post-combustion capture (Zhai & Rubin, 2013). As the search to find more advanced and better carbon capture and storage methods, investment in technologies like gas separation membranes is increasing. These include optimizing installations of carbon capture and storage plants with membranes in supercritical plants and comparing chemical absorption models to membranes (Kotowicz, 2012; Skorek-Osikowska, Janusz-Szymańska and Kotowicz, 2012).

There are several disadvantages to existing membrane separation systems. Compared to absorption with amines, carbon dioxide capture rates are not as high in post-combustion capture. The purity of CO_2 is also lower than that produced by amine separation with single or two stage membrane systems. Although this technology is successful in other areas such as industrial gas purification, there is still a lack of technological advancement in carbon capture. There are also questions regarding costs – both capital costs and costs associated with its operation beyond pilot scale and auxiliary equipment (Favre, 2011; Troy, Schreiber and Zapp, 2016). Ultimately there is a necessity for further techno-economic studies as well as studies that combine materials and engineering aspects to evaluate membrane feasibility (Favre, 2011; Zhai and Rubin, 2013).

Chemical looping combustion

This process uses calcium oxide as a high temperature sorbent and carrier of CO_2 between a steam gasifier and an oxygen-fired generator as shown in **Figure 2.4** (Sadhukhan, Ng and Hernandez, 2014). It mainly consists of two reactors, an air reactor and a fuel reactor with the oxygen carrier supplying oxygen from the air to the fuel while avoiding contact between the materials during the transfer (Tian *et al.*, 2013; Li *et al.*, 2017). According to Nandy *et al.* (2016) the primary fuel can be either liquid, solid or gas and the type of reactor design can be, alternating packed or fluidized-bed reactors, two or more interconnected fluidized-bed or moving bed reactors and rotating reactors.

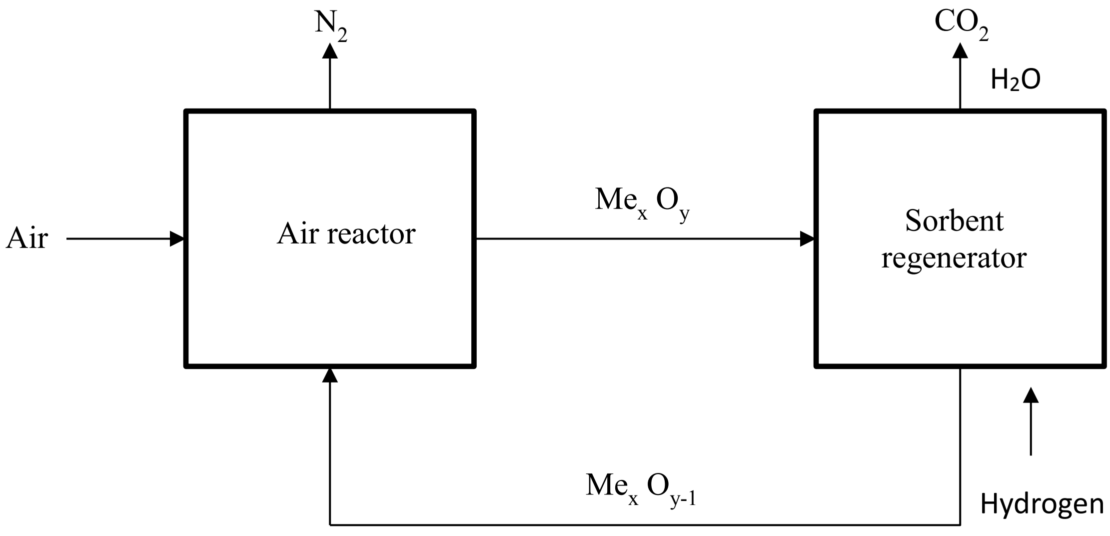


Figure 2.4 Chemical looping combustion schematic, based on Sadhukhan *et al.* (2014)

One of the benefits of this process is that carbon capture can be achieved without having to add on technologies that will lead to new process steps. These new steps can create additional costs and increase energy penalties (Sadhukhan, Ng and Hernandez, 2014). By being an integrated system, both CO_2 and H_2 can be separated from the N_2 gas stream whilst sustaining high efficiencies of heat and power generation with an electrical efficiency up to 52 – 60% based on process simulations (Li *et al.*, 2017).

Amongst the drawbacks, a main challenge for commercialisation is ensuring an adequate oxygen carrier that can have a long-term performance over the system cycles and can deal with the harsh conditions of chemical looping combustion (Bhavsar and Veser, 2013; Tian *et al.*, 2013; Sadhukhan, Ng and Hernandez, 2014; Mukherjee *et al.*, 2015; Li *et al.*, 2017). The oxygen carriers often investigated are copper (Cu), nickel (Ni), manganese (Mn), iron (Fe) and CO based carriers (Li *et al.* 2017; Bhavsar & Veser 2013; Tian *et al.* 2013).

Other hurdles to overcome include the extra costs to reach the optimum process performance, competing with more established CO_2 capture routes, CO_2 capture efficiency and technical barriers to provide reliable operation at large scale (Nandy *et al.*, 2016; Li *et al.*, 2017). Despite these challenges, according to Nandy *et al.* (2016), in the last 10 to 15 years there have been enough important technological advancements that guarantee that chemical looping combustion will be relevant in the future.

The lime enhanced gasification sorption process is another capture process that is integrated and consists of two main reactors. In this process CaO is used as the carrier between the two reactors as a high temperature sorbent (Sadhukhan, Ng and Hernandez, 2014). The two reactors are a steam gasifier and an oxygen-fired regenerator (**Figure 2.5**), where H_2 is produced in the gasifier and the sorbent is calcined in the sorbent regenerator generating a rich CO_2 stream ready for storage (Weimer *et al.*, 2008; Sadhukhan, Ng and Hernandez, 2014). According to Abanades *et al.* (2015) this process is less developed and has more challenges to overcome than other variants that use coal as a fuel.

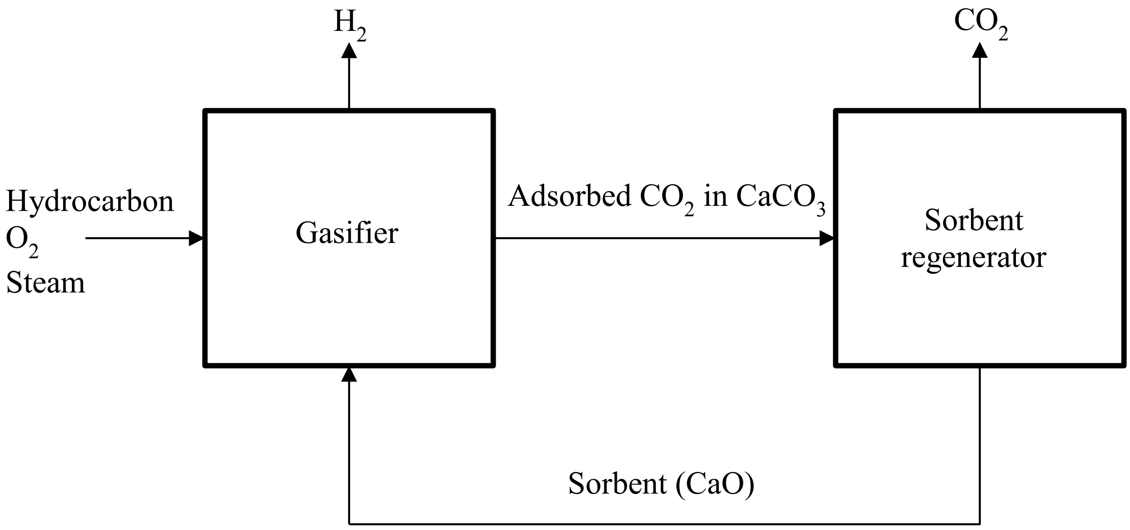


Figure 2.5 Lime enhanced gasification sorption schematic, based on Sadhukhan *et al.* (2014)

Low temperature capture technologies

Low temperature capture processes refer to the separation of CO_2 by direct cooling and physical separation (Berstad, Anantharaman and Nekså, 2013). With this process the temperature of a H_2 and CO_2 mixture is lowered enough that the CO_2 can be condensed and easily removed from the mixture with phase separation (Sadhukhan, Ng and Hernandez, 2014; Xu *et al.*, 2014). In a review by Berstad *et al*. (2013) it is mentioned that low temperature processes have not been researched as intensively for being too energy intensive, too expensive or having limited application compared to other capture technologies.

Cryogenic distillation

The term “cryogenic” capture or separation is often used to refer to CO_2 capture by cooling and phase separation in the literature (Berstad, Anantharaman and Nekså, 2013). This process is also fit for post-combustion capture, with the process using packed beds that separate CO_2 and H_2O directly without using solvents and high pressures (Pires *et al.*, 2011; Xu *et al.*, 2014; Yuan, Pfotenhauer and Qiu, 2014). Cryogenic distillation occurs at ambient pressures, thus after CO_2 is separated it will require compression before it can be transported. There are disadvantages to using packed beds in post-combustion capture. Plugging by ice and refrigerant costs are issues to consider. According to Xu *et al*. (2014) one of the major challenges to overcome is the lower levels of CO_2 purity obtained with cryogenic distillation. The impurities can range from 2 % to 5 % which prevent the use of CO_2 in most industrial processes (Xu *et al.*, 2014). In general, there is lack of information of this process applied directly to carbon capture compared to other separation methods. Most research dedicated to cryogenic distillation discusses alternative uses such as separation of acid gases from natural gas (Pires *et al.*, 2011) and isotope separation (Dumitrache, Inoan and De Schutter, 2014).

Direct air capture

Direct air capture (DAC) is a technology that removes CO_2 directly from air. Ambient air flows through a chemical sorbent that separates the CO_2. The sorbent is regenerated and the CO_2 depleted air is returned to the atmosphere (Socolow, R. H.; Desmond, 2011). If successful, it could be a mitigation process that removes emissions instead of only avoiding them (Zeman, 2014). Because of its potential as a carbon negative process, it is often mentioned and discussed in the field of CO_2 utilisation research. While it is a promising technique, there is still little research published. Most information available is at bench scale, focusing on specific process units and metrics (kJ energy per mol CO_2) (Baciocchi, Storti and Mazzotti, 2006; Keith, Ha-Duong and Stolaroff, 2006; Zeman, 2007). There are also many concerns about the elevated costs of a capturing CO_2. According to American Physical Society (APS), capturing 1 tonne of CO_2 has a cost of USD 518, value higher than post combustion capture (Socolow, R. H.; Desmond, 2011). However, there are environmental benefits of capturing carbon from air that might offset costs if energy penalties can be minimised. A direct air capture plant can operate where necessary, this can eliminate the need for CO_2 transportation. It also means that it can capture the emissions of a fixed point source without having to be near it (Van der Giesen *et al.*, 2017). According to the American Physical Society (APS), the scale of a direct air capture plant is small when compared to other capture plants available. For a general air contactor, 20 tons of CO_2 are captured per year for one square meter of area in which air flows. While this technology is not yet suitable for large-scale capture, it is an option to consider for small scale processes.

The main process found in literature for direct air capture is thermal regeneration. This process can be utilise sorbents such as lime, titanium and solid amines (Zeman, 2014). However, most of the research found focuses on using sodium hydroxide as a sorbent (Baciocchi, Storti and Mazzotti, 2006; Keith, Ha-Duong and Stolaroff, 2006; Zeman, 2007, 2014; Socolow, R. H.; Desmond, 2011). Using sodium hydroxide and calcium hydroxide cycles for CO_2 capture is a well-known technology, thus favouring its use for direct air capture simulations over other studies. In this process, NaOH is used as a sorbent to capture CO_2 and then it is converted to a solution of sodium carbonate (Na_2CO_3). Evaporating the water from the solution is highly energetic, therefore; the solution is first converted to calcium carbonate ($CaCO_3$) by adding calcium hydroxide ($Ca(OH)_2$). In this step, NaOH is regenerated and sent back to the absorber. The $CaCO_3$ is then decomposed in the calciner into CO_2 and CaO. The decomposition reaction is endothermic and requires high-temperature heat to release the CO_2 (Socolow, R. H.; Desmond, 2011). **Figure 2.6** shows the process flow diagram of a basic direct air capture plant that uses NaOH as the absorber.

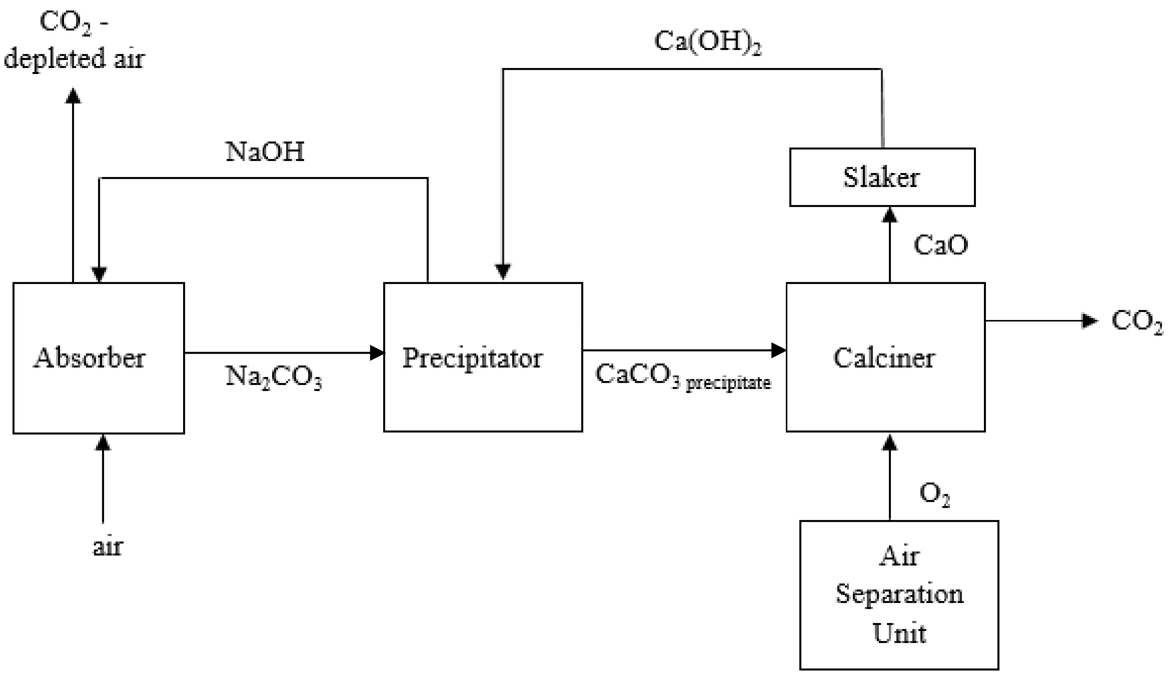


Figure 2.6 Diagram of CO_2 capture using sodium hydroxide as sorbent based on Socolow, R. H. & Desmond (2011)

While using NaOH as a sorbent is a proven technology, its regeneration has a high-energy penalty. The American Physical Society (APS) presents an ideal scenario where the CO_2 emitted in the kiln would be captured by the plant. By eliminating emissions associated with thermal energy, only electricity emissions are accounted for. Most recently, other capture technologies have tried to reduce energy penalties by trying regeneration alternatives. Humidity-swing direct air capture consists in drying the sorbent by evaporating at ambient temperatures, driving air through filters. But its performance is linked to weather conditions (Lackner, 2013). A similar technology, temperature-swing direct air capture uses low-grade heat to cycle the sorbent. Both processes theoretically require less electrical and thermal power (Van der Giesen *et al.*, 2017). Although the technology readiness level of direct air capture is still low, understanding its environmental impacts and improving its energy requirement is fundamental for the future of this capture technology.

2.2 CO_2 utilisation for greenhouse gases (GHG) mitigation

Carbon dioxide utilisation processes extend the supply chain further than CO_2 storage. This is done by using the carbon stream instead of sequestering it. This has the potential to not only reduce carbon emissions but also convert a waste into a chemical feedstock. While carbon capture and storage would only bring environmental benefits, utilising could also present new economic opportunities.

There are many ways to utilise carbon dioxide and transform it to useful products, these technologies are typically at different R&D phases (with a small number of commercial technologies). For example, processes like Enhanced Oil Recovery (EOR) are already used at industrial scale in the US (Godec, Kuuskraa and Dipietro, 2013; Ng, Zhang and Sadhukhan, 2013; Compernolle *et al.*, 2017). The main processes and products according to Styring & Jansen (2011) are shown in **Table 2.2**.

Table 2.2 Examples of CO_2 utilisation options and CO_2 based products

CO_2 utilisation options	Example of products
Chemical feedstock and synthetic fuels Carbon dioxide can be used in the production of a range of chemicals (from simple alcohols & acids to complex polymers), including various hydrocarbons typically used as traditional fuels (light and heavy fuel oils). The carbon dioxide reaction mechanism varies depending on the product and the synthesis process utilised, for some products direct reaction of carbon dioxide is possible with the correct catalyst and reaction conditions (e.g. urea, methanol, formic acid), but for other products the carbon dioxide must be converted to carbon monoxide through the reverse water gas shift reaction to produce a syngas.	Inorganic carbonates Cyclic carbonates Polycarbonate monomers Formic acid Carboxylic acids Hydrocarbons Methanol Methane Cyclic carbamates Organic carbamates Poly-carbamate monomers
Mineral carbonisation A process in which carbon dioxide is reacted with materials containing group II metal oxides (typically that of calcium and to a lesser extent magnesium) to form a stable carbon dioxide containing product - a metal carbonate. Example materials include fly ash, cement kiln dust & quarry fine and paper ash. Mineralisation not only utilises carbon dioxide but allows for it to be trapped in a product for a longer timescale than most chemical CO_2 based products.	Silica Metals Chemicals Cements Construction materials Remediation of waste materials
Enhanced recovery CO_2 is injected into deep oil/gas reservoirs and is used as the working fluid to benefit further energy production. Once CO_2 is injected it goes through trapping mechanisms to ensure storage within the reservoir (Safi, Agarwal and Banerjee, 2016).	Enhanced oil recovery Enhanced gas recovery Enhanced geothermal recovery
Biofuels and algae A biochemical approach to the conversion of CO_2 that attempts to mimic the CO_2 reduction in nature (Aresta, Dibenedetto and Angelini, 2014). Conversion of biofuels implies a two-step procedure: formation of biomass and a processing step for conversion to products.	Ethanol Microalgae Fertilisers Fuels Chemicals and bio oils

As research continues in this area, less energy intensive CO_2 capture routes are being studied. One of these alternatives is utilisation of CO_2 direct from flue gas without using a capture step. It is expected that by eliminating the capture step, the environmental burden of a CO_2 utilisation process can be reduced. However, published literature suggests that this goal has not been achieved yet (Zhang *et al.* 2013). Understanding the environmental burden of a CO_2 utilisation process is important to ensure that developing processes are indeed better for the environment. Thus, life cycle assessment (LCA) studies are fundamental to determine benefits or drawbacks of any potential utilisation route. Carbon dioxide utilisation embrace many areas and therefore require a multidisciplinary approach. To obtain a life cycle inventory (LCI), stages and boundaries must be well defined. The following diagram shows the life cycle of a supply chain for a CO_2 based product (**Figure 2.7**).

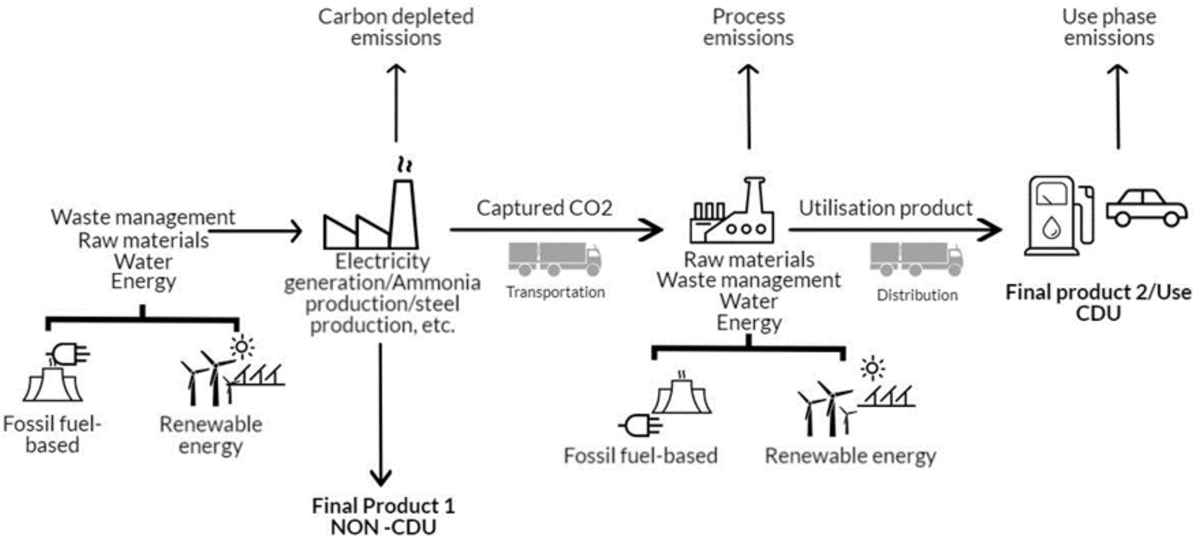


Figure 2.7 Life cycle of a product from CO_2 utilisation

The CO_2 based products that fall under the scope of this study are methanol (as part of synthetic fuels) and urea production. A brief description of both products and their role in CO_2 utilisation is given in the sections below.

2.2.1 Synthetic fuels production from CO_2 capture

Synthetic fuels can be produced through the chemical transformation of CO_2. These fuels can be blended at different concentrations with traditional fossil fuel-based products if necessary. Through this process, CO_2 is obtained from flue gases and used as a raw material to produce fuels like methanol (Olah, Goeppert and Prakash, 2009; Tang *et al.*, 2017). From a life cycle assessment approach, using carbon dioxide for synthetic fuel production could lower net emissions if associated energy penalties could be reduced. An example of these barriers is the large supply of hydrogen needed to produce methanol from CO_2 (Boretti, 2013). For it to be environmentally feasible, hydrogen must come from renewables such as geothermal, solar, nuclear, wind, tidal, etc. (Sayah and Sayah, 2011; Styring and Jansen, 2011; Suleman, Dincer and Agelin-Chaab, 2015) however this is currently not economically viable (in most instances).

Companies like Carbon Recycling International (CRI) have taken research and development of synthetic fuels to industrial scale. CRI produces methanol through hydrogenation of CO_2 using geothermal power. The first pilot plant was introduced in 2007 producing up to 0.5 million litres of methanol per year. The first commercial plant started running in at Svartsengi, Iceland with a capacity of 5 million litres per year. However, the success of this plant is linked directly to its access to geothermal energy (CRI, 2017). This model cannot be replicated in most of the world. Therefore, the problems with CO_2 utilisation processes are far from solved.

Methanol

Methanol is typically produced by natural gas steam reforming which relies on four basic steps: syngas generation, compression, methanol synthesis and distillation (Bermúdez *et al.*, 2013). BASF Company use a ZnO/Cr_2O_3 based catalyst in the production process developed in the 1920's. Since then, finding better catalysts has been an objective of many studies and improving catalysts is still a major factor in improving methanol production (C.-J. Yoo *et al.*, 2013). Methanol is a chemical widely used as an industrial feedstock to produce formaldehyde, acetic acid, methyl-tertiary-butyl ether (MTBE), dimethyl ether (DME), esters, olefins, and other chemical that are used for varied purposes (Methanol Institute, 2011a). Methanol can also be used as an alternative fuel and as a chemical energy carrier. According to Yang & Jackson (2012) China's increasing methanol consumption rates are directly related to gasoline-methanol blends and DME-Liquefied petroleum gas (LPG) making it the number one producer and consumer in the world, with a share of global methanol production that is greater than 20%. It is also considered as an alternative option to hydrogen as a fuel due to advantages in operational and infrastructural costs. Methanol can be used in internal combustion engines with minor changes and dimethyl ether (DME) can be used for water heaters and household stoves (Olah, Goeppert and Prakash, 2009). Yang & Jackson (2012) also support "methanol economy" as an easier transition when compared to a hydrogen one, partly due to it being a more feasible option for use in existing available infrastructure.

A green methanol economy is a concept pursued since the 1990s (Olah, 2005). The aim is to reduce carbon emissions from fossil fuels while introducing a carbon dioxide stream to the markets which can be used for methanol production.

Catalytic hydrogenation of CO_2 is considered as a 'green route' to produce methanol (Kar *et al.*, 2018). This route utilises recycled CO_2, a low carbon source of H_2 and a catalyst; where ideally the only other co-product is water vapour (Li *et al*. 2014). **Equation 2.1** and **Equation 2.2** show the reactions for methanol synthesis from CO_2:

$$CO_2 + 3H_2 = CH_3OH + H_2O$$

Equation 2.1

$$H_2O \rightarrow {}^{1}/_{2}\, O_2 + H_2$$

Equation 1.2

Equation 2.1 rearranged in mass terms:

$$1.4\, kg\, CO_2 + 0.2\, kg\, H_2 \rightarrow 1.0\, kg\, CH_3OH + 0.6\, kg\, H_2O$$

Equation 2.3

Where to produce 1 kg of methanol, 0.2 of kg H_2 and 1.4 kg of CO_2 are required.

The main limitations with this process are energy penalties from hydrogen production and catalyst performance efficiency (percentage of feed converted to desired product) (Esmaili, Dincer and Naterer, 2015).

A significant research effort is invested towards finding better and more stable catalysts that can overcome water vapour interference. Some of the best performing catalysts under study include Zr-doped Cu-Zn-Zr-Al (CZZA) and CuO-ZnO-Al_2O_3 (Zhang, Zhang and Chen, 2012; Bansode and Urakawa, 2014; Li, Yuan and Fujimoto, 2014). One alternative to existing systems found is to use high-pressure conditions with co-precipitated catalysts. However, these conditions still result in high energy penalties, thus further research is still required (Bansode and Urakawa, 2014).

For methanol production, the supply of economically viable renewable hydrogen is the biggest challenge. The enthalpy change for catalytic hydrogenation of CO_2 equals -11.9

kcal/mol (at 298 K); while for water electrolysis is 68.3 kcal/mol (at 298 K) (Boretti, 2013). Wind or solar energy have been suggested as the only renewable sources capable of generating enough energies; 53 kWh are needed to produce 1 kg of hydrogen (Boretti, 2013). This equals to 190.8 MJ of electric energy per 120.1 MJ of fuel energy produced. **Table 2.3** shows general energy requirements to produce 1 kg of methanol.

Table 2.3 Main energy requirements for 1 kg of methanol produced through catalytic hydrogenation of CO_2, based on Boretti (2013)

Processes/units	Energy requirements (MJ/kg methanol)
H_2 production	46.5
Compressor	10.0
Distillation	1.7
Reaction Heat	-1.5
Total	56.7

2.2.2 Production of urea as a CO_2 based product

Studies such as Bose *et al*. (2015) have proposed producing urea (carbamide) from a CO_2 recovery process. This includes coupling CO_2 from a capture process and a supply of 'green hydrogen' to produce NH_3 through the Haber-Bosch process. The configurations to obtain these two feedstocks can vary, but the process is the same. Commercial urea is produced by the reaction of CO_2 with NH_3. These react to form ammonium carbamate which is then dehydrated to urea (Xiang *et al*., 2012).

The reactions to produce urea are as follows (**Equation 2.4 to 2.6**):

Ammonia synthesis $$N_2 + 3H_2 \leftrightarrow 2NH_3$$

Equation 2.4

Ammonium carbamate formation $$2NH_3 + CO_2 \leftrightarrow NH_2COONH_4$$

Equation 2.5

Urea formation $$NH_2COONH_4 \leftrightarrow H_2O + NH_2CONH_2$$

Equation 2.6

Where producing 1 kg of NH_2COONH_4 requires 0.73 kg of CO_2, 1.23 kg of NH_3 and 23.4 MJ of natural gas for a fossil fuel-based process (Althaus *et al.*, 2007). **Figure 2.8** shows a basic diagram of what urea production from ammonia powered by wind and CO_2 capture would look like.

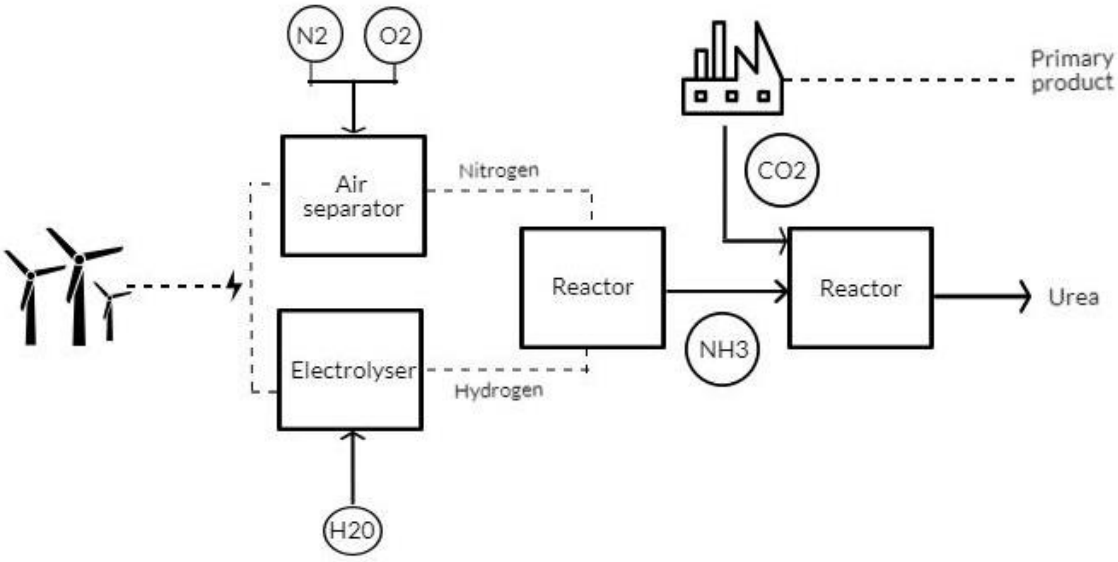


Figure 2.8 Block diagram of urea and ammonia synthesis coupled with CO_2 capture and hydrogen production

Few studies were found that consider carbon dioxide utilisation routes for urea and ammonia synthesis. In a conventional process, ammonia synthesis supplies the CO_2 required for carbamide production (Xiang *et al.*, 2012). Therefore, there is already a case for CO_2 utilisation. However, there is also potential for a case that involves eliminating carbon emissions from ammonia synthesis by sourcing hydrogen from non-fossil sources and using other available CO_2 emissions.

Table 2.4 summarises the studies found that use carbon utilisation routes to produce N-based fertiliser. Of these studies, Reese *et al*. (2016) has the most similar set-up and simulation process to the one assessed in this work. The process consists of a small-scale Haber-Bosch set-up where wind power (1.65 MW turbine) is used for hydrogen production in ammonia synthesis. There is no discussion of CO_2 supply, but it is assumed that it would have to be provided from a carbon capture route. Their results showed the feasibility of this process at small scale, although there has been no demonstration on a larger scale.

Table 2.4 Technical studies related to coupling CO_2 utilisation and urea synthesis

Reference studies	**CO_2 supply**	**H_2/NH_3 supply**	**Final products**	**Stage**
(Kempka, Plotz, *et al.*, 2011)	Underground coal gasification	Underground coal gasification	Urea, carbon sequestration	Design
(Bose *et al.*, 2015)	Coal gasification	Coal gasification	Urea, electricity	Design
(Reese *et al.*, 2016)	N/A*	Water electrolysis	Ammonia	Pilot plant

*Non-applicable

Some of the collaborations between industry and academia working on green ammonia and/or green urea include:

- SIEMENS electric ammonia synthesis and energy storage system. A pilot scale plant is to run until December 2017. SIEMENS are working in collaboration with the University of Oxford, Cardiff University and Science & Technology Facilities Council.
- The University of Minnesota created a renewable hydrogen and ammonia pilot plant in 2013. At that time, it was set to be the first of its kind in the world. The pilot plant uses wind energy to power ammonia synthesis using Haber-Bosch technology. Future work is set to focus on reducing costs and energy consumption.
- Power to – Ammonia project in the Netherlands by Nuon Heat and Delft University of Technology. This ten-year program started in 2016 with the goal of converting surplus wind energy into liquid ammonia and using gas-fired power plants as storage facilities for renewable energy.

2.3 Other projects at pilot/commercial scale

Although still a ‘young’ technology, there are efforts to push it to a commercial scale. The Smart CO_2 transformation project (SCOT, 2017) recorded 212 projects worldwide by companies/academia that are working on processes at pilot, commercial scale or research phase. From these projects, the following product applications were found:

- CO_2 to fuels: methanol, biofuels, DME, methane, syngas, diesel
- CO_2 to chemicals: hydrogels, acrylic acid, polyols, plastic chlorinated polypropylene, cyclic carbonates, formic acid, oxalic acid, acetic acids, carbon monoxide, succinic acid and butadiene
- CO_2 mineralisation: sodium bicarbonate, calcium carbonates, graphene, enriched precast concert products

Most of these projects are based on Europe, with 138 of the 212 identified worldwide. North America comes in second with 59 projects. Many of these projects are not yet economically feasible; however, some processes are more commercially successful than others. Companies such as Covestro and Sunfire have taken CO_2 transformation to the next level, promoting their success story beyond the more traditional known mineralisation route. An example of companies and their CO_2 product by sector is shown in **Table 2.5**.

Table 2.5 Example of industries by the CO_2 utilisation sector

Company	**Covestro**	**Carbon Clean Solutions**	**Carbonfree Chemicals**	**Sunfire**	**Calera**	**Calera**
Sector	Chemicals	Mineralisation	Mineralisation	Fuels	Mineralisation	Mineralisation
Product	Polyurethane foam	Soda ash	Sodium bicarbonate	Synthetic fuels	Calcium carbonate	Calcium carbonate
CO_2 source	Chemical facility	Power plant	Chemical and power plant facilities	Direct Air Capture	Power plant	Power plant
Scale	Commercial	Commercial	Commercial	Pilot Commercial	Pilot Commercial	Pilot Commercial

2.4 Additional processes down and up the CO_2 utilisation chain

2.4.1 CO_2 purification

After CO_2 is captured, several treatments to reduce impurities are needed before transportation and utilisation occurs. Impurities in the carbon dioxide stream will differ depending on the capture process. This work emphasises on CO_2 purification from post-combustion capture. The main impurities found in literature that interfere with the carbon dioxide stream are water and oxygen (Pipitone and Bolland, 2009; Abbas, Mezher and Abu-Zahra, 2013a) and are summarised in **Table 2.6**. To achieve permissible water and oxygen levels there are several deep removal technologies that can be applicable (**Table 2.7**).

Table 2.6 Stream composition vs permissible levels, adapted from Abbas *et al.* (2013a)

Component	**Range of product stream composition (mol %)**	**Range of stream composition levels required (mol %)**
CO_2	79.0-92.0	> 95.0
H_2O	2.8-7.3	< 0.005
Ar	$1.0 \times 10^{-3} - 2.0 \times 10^{-3}$	< 4.00
N_2	$2.0 \times 10^{-2} - 0.1$	< 4.00
O_2	$1.0 \times 10^{-3} - 3.0 \times 10^{-2}$	< 0.001
SO_2	1.0×10^{-3}	< 0.005

Table 2.7 Deep removal technologies for flue gas impurities based on Abbas *et al.* (2013)

Oxygen removal treatments	**Water removal treatments**
Cryogenic distillation Catalytic oxidation of carbon monoxide/propane/methanol/hydrogen Oxidation of coal Chemisorption of oxygen	Absorption using EG/TEG[1] Adsorption on silica gel/molecular/sieves/ activated Alumina Refrigeration Condensation

[1] EG = Ethylene glycol, TEG = Triethylene glycol

According to Abbas *et al*. (2013a), the most promising oxygen removal technology is catalytic oxidation of H_2. For water removal, refrigeration and condensation are considered the best process due to low costs. Catalytic oxidation of CO for oxygen removal and ethylene glycol absorption for water are considered the least promising technologies.

The CO_2 purification method will depend on the capture process and final usage of the carbon dioxide stream. A starting point is to consider acceptable transportation impacts/costs regardless of transformation or storage. Currently, processes that use ethylene or triethylene glycol (EG/TEG) are readily available and could contribute to CO_2 capture. If these technologies can get cleaner and cheaper, they could be an option for CO_2 transformation technologies.

After purification and before transportation, carbon dioxide is compressed to supercritical form (80-150 bar) lowering its density (Pires *et al.*, 2011). Compression makes transportation more efficient. However, according to Aspelund & Jordal (2007), costs and energy penalties are high ranging from 90 to 120 kWh/ton of CO_2.

2.4.2 CO_2 transport

Transportation of carbon dioxide is also part of the upstream chain in CO_2 utilisation. There are pipeline infrastructure similarities between carbon dioxide and other gases. New pipelines require large investments, thus re-using infrastructure is the best option to lower costs. This can avoid additional investment (Pires *et al.*, 2011). The main drawbacks to using existing pipelines is the level of uncertainty associated with transporting carbon dioxide. There are also no set conclusions on how different these pipelines would be from natural gas. Aspects to assess include (Koornneef *et al.*, 2010):

- Higher failure rates in smaller pipelines versus larger diameters
- Crater formation on the release of CO_2
- Effects of release of supercritical CO_2 from a pipeline
- Environmental impacts of impurities on release, mainly CO and H_2S
- Cooling of CO_2 and thermal stress in pipeline and adjacent materials
- Overpressure from sudden expansion

Even with uncertainties, CO_2 transportation by pipeline is the safest and most cost-effective option compared to ship or tanker trucks for short distances (Pires *et al.*, 2011; Global CCS institute, 2014). It is also a transportation method already used successfully for Enhanced Oil Recovery. A way to addressing transportation issues within a 'carbon management platform' could ensure that all aspects are considered throughout the supply chain. This includes capturing, transporting, storing and/or utilising (Middleton, Keating, *et al.*, 2012). Specific infrastructure models such as *Sim*CCS (Middleton, Kuby, *et al.*, 2012) and general chemical engineering programs such as Aspen Hysis® and Aspen Plus® are fundamental to carbon management. If transportation is required for more than 1,000 km then the IPCC (2005) recommends shipping as the cheapest option. There are also suggestions to ship after 500 km with a break-even point at 200-300 km (B.-Y. Yoo *et al.*, 2013). Carbon dioxide shipment is still at pilot scale. Total shipping cost of carbon dioxide would need to reduce to reach commercial scale. Shipping costs include liquefaction plant, temporary storage and carbon dioxide carriers (B.-Y. Yoo *et al.*, 2013).

There is a limited amount of pipeline infrastructure information available to the public, complicating life cycle inventories. In general, costs are rarely reported. One of the available reports shows capital costs of carbon dioxide pipelines according to terrain type. These costs can be used for general assessments. **Table 2.8** replicates the values founds. Other guidelines by the Department of Energy (2012) estimate fixed operational and maintenance costs of USD 8,454 per mile/year.

Table 2.8 Capital costs of CO_2 pipelines according to type of terrain, adapted from Global CCS institute (2014)

Terrain	Capital cost (USD/inch-diameter/mile)
Flat, dry	50,000
Mountainous	85,000
Marsh, wetland	100,000
River	300,000
High population	100,000
Offshore (150-200 feet, 45-60 meters depth)	700,000

In the UK, four projects related to CO_2 transportation are described below. Two of these projects were stated as in ‘planning stage’ and two others have been cancelled (**Table 2.9**), with the Longannet and Kingsnorth proposals shelved due to the closure of the associated coal fired power plants.

Table 2.9 CO_2 pipeline projects in the UK, adapted from Global CCS institute (2014)

Project name	Status	Length (km)	Capacity (Mt/y)	Onshore/offshore	Sink
Peterhead	Proposed	116	10	Both	Depleted oil/gas field
Longannet	Cancelled	380	2	Both	Depleted oil/gas field
White Rose	Proposed	165	20	Both	Saline aquifer
Kingsnorth	Cancelled	270	10	Both	Depleted oil/gas field

2.4.3 Hydrogen supply for carbon dioxide utilisation processes

Hydrogen can be produced from many different sources including: water, methane, ammonia, methanol, biomass, coal and H_2S (López Ortiz, Meléndez Zaragoza and Collins-Martínez, 2016; Dincer and Acar, 2017). Any fossil-fuel based feedstock is generally considered unsustainable for any CO_2 transformation route and other options must be explored. For non-fossil routes the associated “energy penalty” is a key part in the assessment/selection of a hydrogen generation process.

Reducing energy penalties in hydrogen production is fundamental for the success of CO_2 utilisation. According to Nikolic *et al.* (2010), the economics of hydrogen production via electrolysis are dictated by the cost of electrical power. Where with an electricity efficiency of 30 to 40% (primary energy sources) the overall efficiency of an electrolyser is below 40%. However, driving towards a hydrogen economy is part of the transition to lessen dependency on fossil fuels and there are many alternatives to achieve this.

There are over 90 hydrogen production routes that can be divided in biological, chemical, electrochemical and thermal (Stojić *et al.*, 2003). Of these, five subcategories are studied as alternative sustainable production routes that could reduce high energy penalties according to Dincer & Zamfirescu (2012). The objective is to find an alternative to hydrogen supply from natural gas (via steam methane reforming) which to date comprises 90% of the global market (Bičáková and Straka, 2012). These alternative routes are based on five methods to extract hydrogen: electric, thermal, photonic, nuclear and biochemical.

The following methods lead to potentially sustainable pathways for hydrogen production: Water splitting, fossil hydrocarbons decarbonisation, hydrogen sulphide decomposition, biomass conversion, extraction from waste materials. These options can all be supported by a renewable energy source. The sources can then be divided by their generation potential: Low, medium and high. Dincer & Zamfirescu (2012) present 24 sustainable ways to produce hydrogen, of which water splitting was the most promising. Bičáková & Straka (2012) also studied hydrogen production from sustainable routes. This study presented an overview of available technologies considering environmental, economic and resource impacts. Water cracking (electrolysis, thermolysis and photo-electrolysis) is mentioned as the best alternative process. Once again, electrolysis has the highest potential.

Of the literature reviewed, water splitting is also mentioned the most. Water electrolysis only represents 4% of the world hydrogen production (Zeng and Zhang, 2010), but it is fundamental for many utilisation processes if CO_2 emissions are to be avoided. Some of the advantages of producing hydrogen from water electrolysis include its simple process, high H_2 purity, low CO_2 emissions and compatibility with different power sources. The main drawback is its energy consumption of 4.5 to 5 kWh/m^3H_2 (Stojić *et al.*, 2003; Wang *et al.*, 2014).

Other studies use process simulations or background data to analyse hydrogen production methods and their environmental impacts (Smitkova, Janíček and Riccardi, 2011; Dufour *et al.*, 2012; Bhandari, Trudewind and Zapp, 2013; Suleman, Dincer and Agelin-Chaab, 2015; Bicer and Dincer, 2016). The data obtained was then used to complete a life cycle assessment (LCA) comparing environmental impacts between hydrogen production routes. The results from these studies are very useful to CO_2 utilisation. By assessing the impacts of hydrogen production, the assessment of the supply chain for several CO_2 utilisation processes can be completed. In this work, both methanol and urea synthesis depend on the provision of sustainably produced hydrogen. The impacts of H_2 production are further discussed in **Chapter 3**.

2.4.4 Final use for utilisation product

Methanol as synthetic fuel

After utilisation, methanol can either be transported to a refinery to blend with gasoline or transported directly to gasoline distribution terminals. For the second process, methanol is blended when tanks are loading. For this, gasoline must be treated previously for optimum performance. Blending concentrations will be regulated differently throughout regions in the world (Methanol Institute, 2011b).

Blended gasoline with methanol will have a lower distillation point. This property can influence cold engine drivability performance by either improving it or by maintaining the same levels as unblended gasoline. Storing conditions would also have to be considered. To prevent excessive water in the fuel, fixed roof tanks would be used for storing methanol and blended gasoline, as well as using alternative methods to clean pipes without using water. Fuel filters would be replaced more frequently at gasoline dispenser pumps and filter openings for smaller microns. Routine checks would also be necessary to ensure that water bottoms do not occur at underground tanks, water detection paste would also have to change to detect alcohol-gasoline blends (Methanol Institute, 2011b). To understand fully the supply chain for methanol as a synthetic fuel, environmental aspects should also be considered. In terms of carbon reductions, emissions from methanol produced from natural gas are 6 % lower than gasoline and 10 % lower than bio-ethanol. Utilising CO_2 as raw material instead of natural gas could potentially lower further carbon emissions. Research throughout the supply chain is still necessary to determine total emission reductions (Commission, 2014).

Urea as fertiliser

The case of urea use is simpler than with methanol. The final product is the same whether it is from ammonia synthesis from natural gas or from renewable hydrogen. Urea will have the same purity and same use from a conventional route as from a route that uses recovered CO_2. This also means that environmental impacts at use point are the same. This includes ammonia volatilisation losses. Ammonia that stays in the atmosphere is oxidised by hydroxyl radicals to different nitrogen gases (Byrnes, 1990). The rate of ammonia volatilisation will depend on the type of crop that fertiliser is applied to. Further studies are required to determine whether there is an overall positive benefit from applying urea from CO_2 utilisation routes. However, in terms of demand and supply, the outlook is positive. Over 80% of synthetic urea produced is for fertiliser use (Stamicarbon, 2017).

Nitrogen has a direct impact on yield, growth and quality of a crop. Most agricultural soils do not contain enough nitrogen to meet the crop requirements in a season (DEFRA, 2015). According to the FAO (2015) projections, nitrogen based fertiliser demand is expected to continue growing worldwide up to 2018. The total demand is projected to be around 119,400,000 tonnes for 2018. With South Asia, East Asia and Latin America & Caribbean being the regions with highest fertiliser increased consumption from 2014-2018.

2.5 Chapter two summary

This chapter gives an initial overview of the carbon dioxide utilisation supply chain. This includes a CO_2 source, transportation of CO_2 source, chemical transformation of CO_2 into a useful product and final use of this product. The CO_2 can either be captured or used directly depending on the process. The most widely commercially utilised capture route until now is absorption with solvents like monoethanolamine (MEA) used most frequently (Vasudevan *et al.*, 2016). Although the technology is well understood, solvent regeneration costs remain high. After the CO_2 is captured, the stream will go through an impurity removal process, primarily water and oxygen (Abbas, Mezher and Abu-Zahra, 2013b). The CO_2 is compressed and transported to its utilisation site. Once it reaches the chemical factory, it is ready to be transformed. Common final products include synthetic fuels, chemicals, mineralisation or fertilisers (SCOT, 2017). Throughout this work, there is a focus on methanol and urea production from recovered CO_2. Methanol is produced through a catalytic hydrogenation of CO_2 process that relies on hydrogen and captured CO_2 (Boretti, 2013). The hydrogen must be sourced from decarbonised sources to avoid extra carbon emissions. A similar situation is seen with urea production, where ammonia is synthesised with green hydrogen (Reese *et al.*, 2016). Finally, both products have commercial applications which make them attractive CO_2 utilisation options. Methanol can be blended with gasoline and diesel; urea can be used directly as fertiliser. These are the basic components of a CO_2 utilisation supply chain; however, each final product has a specific set-up and requirements for productions. The following chapters discuss further the implications of producing a product from a waste stream with CO_2.

2.6 Chapter two reference list

Abanades, J. C., Arias, B., Lyngfelt, A., Mattisson, T., Wiley, D. E., Li, H., Ho, M. T., Mangano, E. and Brandani, S. (2015) ‘Emerging CO2 capture systems’, *International Journal of Greenhouse Gas Control*, 40, pp. 126–166. doi: 10.1016/j.ijggc.2015.04.018.

Abbas, Z., Mezher, T. and Abu-Zahra, M. R. M. (2013a) ‘CO2 purification. Part I: Purification requirement review and the selection of impurities deep removal technologies’, *International Journal of Greenhouse Gas Control*. Elsevier Ltd, 16, pp. 324–334. doi: 10.1016/j.ijggc.2013.01.053.

Abbas, Z., Mezher, T. and Abu-Zahra, M. R. M. (2013b) ‘CO2 purification. Part II: Techno-economic evaluation of oxygen and water deep removal processes’, *International Journal of Greenhouse Gas Control*. Elsevier Ltd, 16, pp. 335–341. doi: 10.1016/j.ijggc.2013.01.052.

Abu-Zahra, M. R. M., Schneiders, L. H. J., Niederer, J. P. M., Feron, P. H. M. and Versteeg, G. F. (2007) ‘CO2 capture from power plants’, *International Journal of Greenhouse Gas Control*, 1(1), pp. 37–46. doi: 10.1016/S1750-5836(06)00007-7.

Alie, C., Backham, L., Croiset, E. and Douglas, P. L. (2005) ‘Simulation of CO2 capture using MEA scrubbing: a flowsheet decomposition method’, *Energy Conversion and Management*, 46(3), pp. 475–487. doi: 10.1016/j.enconman.2004.03.003.

Althaus, H., Chudacoff, M., Hischier, R., Jungbluth, N., Osses, M., Primas, A. and Hellweg, S. (2007) ‘Life cycle inventories of chemicals. ecoinvent report No.8, v2.0.’, *Final report ecoinvent data …*, (8), pp. 1–957.

Aresta, M., Dibenedetto, A. and Angelini, A. (2014) ‘Catalysis for the Valorization of Exhaust Carbon: from CO 2 to Chemicals, Materials, and Fuels. Technological Use of CO 2’, *Chemical Reviews*, 114(3), pp. 1709–1742. doi: 10.1021/cr4002758.

Aspelund, A. and Jordal, K. (2007) ‘Gas conditioning—The interface between CO2 capture and transport’, *International Journal of Greenhouse Gas Control*, 1(3), pp. 343–354. doi: 10.1016/S1750-5836(07)00040-0.

von der Assen, N. and Bardow, A. (2014) ‘Life cycle assessment of polyols for polyurethane production using CO2 as feedstock: insights from an industrial case study’, *Green Chemistry*, 16(6), p. 3272. doi: 10.1039/c4gc00513a.

von der Assen, N., Jung, J. and Bardow, A. (2013) ‘Life-cycle assessment of carbon dioxide capture and utilization: avoiding the pitfalls’, *Energy & Environmental Science*, 6(9), p. 2721. doi: 10.1039/c3ee41151f.

von der Assen, N., Müller, L. J., Steingrube, A., Voll, P. and Bardow, A. (2016) ‘Selecting CO2 Sources for CO2 Utilization by Environmental-Merit-Order Curves’, *Environmental Science and Technology*, 50(3), pp. 1093–1101. doi: 10.1021/acs.est.5b03474.

von der Assen, N., Voll, P., Peters, M. and Bardow, A. (2014) ‘Life cycle assessment of CO2 capture and utilization : a tutorial review’, *Chem Soc Rev*, 43, pp. 7982–7994. doi: 10.1039/C3CS60373C.

Azapagic, A. and Cue, R. M. (2015) ‘Carbon capture , storage and utilisation technologies : A critical analysis and comparison of their life cycle environmental impacts’, 9, pp. 82–102.

Baciocchi, R., Storti, G. and Mazzotti, M. (2006) ‘Process design and energy requirements for the capture of carbon dioxide from air’, *Chemical Engineering and Processing: Process Intensification*, 45(12), pp. 1047–1058. doi: 10.1016/j.cep.2006.03.015.

Bansode, A. and Urakawa, A. (2014) ‘Towards full one-pass conversion of carbon dioxide to methanol and methanol-derived products’, *Journal of Catalysis*. Elsevier Inc., 309, pp. 66–70. doi: 10.1016/j.jcat.2013.09.005.

Basavaraja, R. . and Jayanti, S. (2015) ‘Comparative analysis of four gas-fired, carbon capture-enabled power plant layouts’, *Clean Technologies and Environmental Policy*, 17(8), pp. 2143–2156.

Baumann, H. and Tillman, A.-M. (2004) *The Hitch Hiker’s Guide to LCA*. Studentlitteratur.

Bermúdez, J. M., Ferrera-Lorenzo, N., Luque, S., Arenillas, a. and Menéndez, J. a. (2013) ‘New process for producing methanol from coke oven gas by means of CO2 reforming. Comparison with conventional process’, *Fuel Processing Technology*. Elsevier B.V., 115, pp. 215–221. doi: 10.1016/j.fuproc.2013.06.006.

Bernard, O. (2009) ‘Policy Analysis Life-Cycle Assessment of Biodiesel Production from Microalgae’, pp. 6475–6481.

Berstad, D., Anantharaman, R. and Nekså, P. (2013) ‘Low-temperature CO2 capture technologies – Applications and potential’, *International Journal of Refrigeration*, 36(5), pp. 1403–1416. doi: 10.1016/j.ijrefrig.2013.03.017.

Bhandari, R., Trudewind, C. a. and Zapp, P. (2013) ‘Life cycle assessment of hydrogen production via electrolysis – a review’, *Journal of Cleaner Production*. Elsevier Ltd, 85, pp. 151–163. doi: 10.1016/j.jclepro.2013.07.048.

Bhavsar, S. and Veser, G. (2013) ‘Bimetallic Fe–Ni Oxygen Carriers for Chemical Looping Combustion’, *Industrial & Engineering Chemistry Research*, 52(44), pp. 15342–15352. doi: 10.1021/ie400612g.

Bičáková, O. and Straka, P. (2012) ‘Production of hydrogen from renewable resources and its effectiveness’, *International Journal of Hydrogen Energy*. Elsevier Ltd, 37(16), pp. 11563–11578. doi: 10.1016/j.ijhydene.2012.05.047.

Bicer, Y. and Dincer, I. (2016) ‘Life cycle assessment of nuclear-based hydrogen and ammonia production options: A comparative evaluation’, *International Journal of Hydrogen Energy*. Elsevier Ltd, pp. 1–12. doi: 10.1016/j.ijhydene.2017.02.002.

Bicer, Y., Dincer, I., Vezina, G. and Raso, F. (2017) ‘Impact Assessment and Environmental Evaluation of Various Ammonia Production Processes’, *Environmental Management*, 59(5), pp. 842–855. doi: 10.1007/s00267-017-0831-6.

BIS (2015) ‘Industrial Decarbonisation & Energy Efficiency Roadmaps to 2050: Cross Sector Summary’, (March), p. 31.

Björklund, A. E. (2002) ‘Survey of approaches to improve reliability in lca’, *The International Journal of Life Cycle Assessment*, 7(2), pp. 64–72. doi: 10.1007/BF02978849.

Boot-Handford, M. E., Abanades, J. C., Anthony, E. J., Blunt, M. J., Brandani, S., Mac Dowell, N., Fernández, J. R., Ferrari, M.-C., Gross, R., Hallett, J. P., Haszeldine, R. S., Heptonstall, P., Lyngfelt, A., Makuch, Z., Mangano, E., Porter, R. T. J., Pourkashanian, M., Rochelle, G. T., Shah, N., Yao, J. G. and Fennell, P. S. (2014) ‘Carbon capture and storage update’, *Energy & Environmental Science*, 7(1), p. 130. doi: 10.1039/c3ee42350f.

Boretti, A. (2013) ‘Renewable hydrogen to recycle CO2 to methanol’, *International Journal of Hydrogen Energy*. Elsevier Ltd, 38(4), pp. 1806–1812. doi: 10.1016/j.ijhydene.2012.11.097.

Bose, A., Jana, K., Mitra, D. and De, S. (2015) ‘Co-production of power and urea from coal with CO2 capture: Performance assessment’, *Clean Technologies and Environmental Policy*. Springer Berlin Heidelberg, 17(5), pp. 1271–1280. doi: 10.1007/s10098-015-0960-7.

Burgess, A. A. and Brennan, D. J. (2001) ‘Application of life cycle assessment to chemical processes’, 56, pp. 2589–2604.

Butlin, J. (1989) ‘Our common future. By World commission on environment and development. (London, Oxford University Press, 1987, pp.383 £5.95.)’, *Journal of International Development*, 1(2), pp. 284–287. doi: 10.1002/jid.3380010208.

Byrnes, B. H. (1990) ‘Environmental effects of N fertilizer use - An overview’, *Fert.Res.*, 26, pp. 209–215. doi: 10.1007/BF01048758.

Carbon Capture & Storage Association (2017) *CCS Policy and Regulation*.

Cetinkaya, E., Dincer, I. and Naterer, G. F. (2012) ‘Life cycle assessment of various hydrogen production methods’, *International Journal of Hydrogen Energy*. Elsevier Ltd, 37(3), pp. 2071–2080. doi: 10.1016/j.ijhydene.2011.10.064.

Commission, C. E. (2014) *Low carbon fuel standard*.

Committe on Climate Change (2016) *The Climate Change Act and UK regulations*.

Compernolle, T., Welkenhuysen, K., Huisman, K., Piessens, K. and Kort, P. (2017) ‘Off-shore enhanced oil recovery in the North Sea: The impact of price uncertainty on the investment decisions’, *Energy Policy*, 101, pp. 123–137. doi: 10.1016/j.enpol.2016.11.034.

Connect, S. (2014) *Carbon dioxide sequestration by direct mineral carbonation with carbonic acid*.

Corsten, M., Ramírez, A., Shen, L., Koornneef, J. and Faaij, A. (2013) ‘Environmental impact assessment of CCS chains – Lessons learned and limitations from LCA literature’, *International Journal of Greenhouse Gas Control*. Elsevier Ltd, 13, pp. 59–71. doi: 10.1016/j.ijggc.2012.12.003.

CRI (2017) *Reduction of Carbon Emissions*.

Cuéllar-Franca, R. M. and Azapagic, A. (2014) ‘Carbon capture, storage and utilisation technologies: A critical analysis and comparison of their life cycle environmental impacts’, *Journal of CO2 Utilization*, 9, pp. 82–102. doi: 10.1016/j.jcou.2014.12.001.

DECC (2011) ‘UK Renewable Energy Roadmap’, *Carbon*, 5(July), pp. 293–298. doi: 10.1021/es00108a605.

DEFRA (2015) ‘The British Survey of Fertiliser Practice - Fertiliser use on farm for the 2014 crop year’, (April), p. 6.

Department of Energy, N. E. T. L. (2012) *NETL Life Cycle Inventory Data – Unit Process: CO2 Pipeline Construction. U.S.*

Dincer, I. and Acar, C. (2017) ‘Innovation in hydrogen production’, *International Journal of Hydrogen Energy*. Elsevier Ltd, 42(22), pp. 14843–14864. doi: 10.1016/j.ijhydene.2017.04.107.

Dincer, I. and Zamfirescu, C. (2012) ‘Sustainable hydrogen production options and the role of IAHE’, *International Journal of Hydrogen Energy*, 37(21), pp. 16266–16286. doi: 10.1016/j.ijhydene.2012.02.133.

Dufour, J., Serrano, D. P., Gálvez, J. L., González, A., Soria, E. and Fierro, J. L. G. (2012) ‘Life cycle assessment of alternatives for hydrogen production from renewable and fossil sources’, *International Journal of Hydrogen Energy*, 37(2), pp. 1173–1183. doi: 10.1016/j.ijhydene.2011.09.135.

Dumitrache, D. C., Inoan, I. and De Schutter, B. (2014) ‘An analytic model for a isotope separation process by cryogenic distillation’, *Journal of Process Control*, 24(5), pp. 463–474.

doi: 10.1016/j.jprocont.2013.12.005.

Edrisi, A., Mansoori, Z. and Dabir, B. (2016) ‘Urea synthesis using chemical looping process - Techno-economic evaluation of a novel plant configuration for a green production’, *International Journal of Greenhouse Gas Control*. Elsevier Ltd, 44, pp. 42–51. doi: 10.1016/j.ijggc.2015.10.020.

Environment Agency (2012) ‘Guidance on The Legal Definition of Waste and Its Application’, (August), p. 69.

Esmaili, P., Dincer, I. and Naterer, G. F. (2015) ‘Development and analysis of an integrated photovoltaic system for hydrogen and methanol production’, *International Journal of Hydrogen Energy*, 40(34), pp. 11140–11153. doi: 10.1016/j.ijhydene.2015.04.077.

European Commission (2010) *International Reference Life Cycle Data System (ILCD) Handbook -- General guide for Life Cycle Assessment -- Detailed guidance, Constraints*. doi: 10.2788/38479.

European Commission (2017a) *Research and Innovation, technical background*.

European Commission (2017b) *The EU Emissions Trading System (EU ETS)*.

Eurostat (2017) *Greenhouse gas emission statistics*.

Fantke, P., Jolliet, O., Evans, J. S., Apte, J. S., Cohen, A. J., Hänninen, O. O., Hurley, F., Jantunen, M. J., Jerrett, M., Levy, J. I., Loh, M. M., Marshall, J. D., Miller, B. G., Preiss, P., Spadaro, J. V., Tainio, M., Tuomisto, J. T., Weschler, C. J. and McKone, T. E. (2015) ‘Health effects of fine particulate matter in life cycle impact assessment: findings from the Basel Guidance Workshop’, *The International Journal of Life Cycle Assessment*, 20(2), pp. 276–288. doi: 10.1007/s11367-014-0822-2.

FAO (2015) *World fertilizer trends and outlook to 2018, Food and Agriculture Organization of United Nations*.

Favre, E. (2011) ‘Membrane processes and postcombustion carbon dioxide capture: Challenges and prospects’, *Chemical Engineering Journal*, 171(3), pp. 782–793. doi: 10.1016/j.cej.2011.01.010.

Van der Giesen, C., Meinrenken, C. J., Kleijn, R., Sprecher, B., Lackner, K. S. and Kramer, G. J. (2017) ‘A Life Cycle Assessment Case Study of Coal-Fired Electricity Generation with Humidity Swing Direct Air Capture of CO 2 versus MEA-Based Postcombustion Capture’, *Environmental Science & Technology*, 51(2), pp. 1024–1034. doi: 10.1021/acs.est.6b05028.

Global CCS institute (2014) *CO2 pipeline infraestructure*.

Godec, M. L., Kuuskraa, V. A. and Dipietro, P. (2013) ‘Opportunities for Using Anthropogenic CO 2 for Enhanced Oil Recovery and CO 2 Storage’, *Energy & Fuels*, 27, p. 4183−4189.

Guinée, J. B., Gorrée, M., Heijungs, R., Huppes, G., Kleijn, R., De Koning, A., Van Oers, L., Sleeswijk, A. W., Suh, S. and Udo de Haes, H. A. (2001) *Life Cycle Assessment-An operational guide to the ISO standards Part 2A*.

Haghpanah, R., Majumder, A., Nilam, R., Rajendran, A., Farooq, S., Karimi, I. A. and Amanullah, M. (2013) ‘Multiobjective Optimization of a Four-Step Adsorption Process for Postcombustion CO 2 Capture Via Finite Volume Simulation’, *Industrial & Engineering Chemistry Research*, 52(11), pp. 4249–4265. doi: 10.1021/ie302658y.

Hasler, K., Broring, S., Omta, S. W. F. and Olf, H.-W. (2015) ‘Life cycle assessment (LCA) of different fertilizer product types’, *European Journal of Agronomy*, 69, pp. 41–45.

Heijungs, R., Huppes, G. and Guin??e, J. B. (2010) ‘Life cycle assessment and sustainability analysis of products, materials and technologies. Toward a scientific framework for sustainability life cycle analysis', *Polymer Degradation and Stability*, 95(3), pp. 422–428. doi: 10.1016/j.polymdegradstab.2009.11.010.

Heijungs, R. and Lenzen, M. (2014) 'Error propagation methods for LCA - A comparison', *International Journal of Life Cycle Assessment*, 19(7), pp. 1445–1461. doi: 10.1007/s11367-014-0751-0.

Ho, M. T., Allinson, G. W. and Wiley, D. E. (2011) 'Comparison of MEA capture cost for low CO2 emissions sources in Australia', *International Journal of Greenhouse Gas Control*. Elsevier Ltd, 5(1), pp. 49–60. doi: 10.1016/j.ijggc.2010.06.004.

Hopkinson, D., Luebke, D., Li, Z. and Chen, S. (2014) 'Solvent Optimization of Conventional Absorption Processes for CO 2 Capture from Postcombustion Flue Gases', *Industrial & Engineering Chemistry Research*, 53(17), pp. 7149–7156. doi: 10.1021/ie403869y.

Houghton JT, Y, D., DJ, G., M, N., PJ, van der L., X, D., K, M. and C, J. (2001) 'Climate Change 2001: The Scientific Basis', *Climate Change 2001: The Scientific Basis*, p. 881. doi: 10.1256/004316502320517344.

House of Commons, E. and C. C. and Committee (2016) *Future of carbon capture and storage in the UK, Second Report of Session 2015–16*.

Huang, Y., Rebennack, S. and Zheng, Q. P. (2013) 'Techno-economic analysis and optimization models for carbon capture and storage: a survey', *Energy Systems*, 4(4), pp. 315–353. doi: 10.1007/s12667-013-0086-0.

IEA Greenhouse Gas R&D Programme (2008) *CO 2 CAPTURE IN THE CEMENT INDUSTRY*.

Im, D., Roh, K., Kim, J., Eom, Y. and Lee, J. H. (2015) 'Economic assessment and optimization of the Selexol process with novel additives', *International Journal of Greenhouse Gas Control*, 42, pp. 109–116. doi: https://doi.org/10.1016/j.ijggc.2015.08.001.

IPCC (2005) *Carbon Dioxide Capture and Storage*.

ISO (1998) *ISO 14041 Environmental Management-Life Cycle Assessment-Goal and Scope Definition and Inventory Analysis*.

ISO (2000) *ISO 14042:2000 Environmental management--Life cycle assessment-Life cycle impact assessment*.

ISO (2006a) *ISO 14040 Environmental Management- Life Cycle Assessment-Principles and Framework*.

ISO (2006b) *ISO 14044 Environmental management--Life Cycle Assessment--Requirements and guidelines*.

Kahrl, F., Li, Y., Su, Y., Tennigkeit, T., Wilkes, A. and Xu, J. (2010) 'Greenhouse gas emissions from nitrogen fertilizer use in China', *Environmental Science and Policy*. Elsevier Ltd, 13(8), pp. 688–694. doi: 10.1016/j.envsci.2010.07.006.

Kapetaki, Z., Brandani, P., Brandani, S. and Ahn, H. (2015) 'Process simulation of a dual-stage Selexol process for 95% carbon capture efficiency at an integrated gasification combined cycle power plant', *International Journal of Greenhouse Gas Control*, 39, pp. 17–26. doi: https://doi.org/10.1016/j.ijggc.2015.04.015.

Kar, S., Sen, R., Goeppert, A. and Prakash, G. K. S. (2018) 'Integrative CO 2 Capture and Hydrogenation to Methanol with Reusable Catalyst and Amine: Toward a Carbon Neutral Methanol Economy', *Journal of the American Chemical Society*, 140(5), pp. 1580–1583. doi: 10.1021/jacs.7b12183.

Karimi, M., Hillestad, M. and Svendsen, H. F. (2011) ‘Capital costs and energy considerations of different alternative stripper configurations for post combustion CO2 capture’, *Chemical Engineering Research and Design*. Institution of Chemical Engineers, 89(8), pp. 1229–1236. doi: 10.1016/j.cherd.2011.03.005.

Keith, D. W., Ha-Duong, M. and Stolaroff, J. K. (2006) ‘Climate strategy with CO2 capture from the air’, *Climatic Change*, 74(1–3), pp. 17–45. doi: 10.1007/s10584-005-9026-x.

Kempka, T., Plotz, M.-L., Schluter, R., Hamman, J., Deowan, S. A. and Azzam, R. (2011) ‘Carbon dioxide utilisation for carbamide production by application of the coupled UCG-urea process’, *Energy procedia*, 4, pp. 2200–2205.

Kempka, T., Plötz, M. L., Schlüter, R., Hamann, J., Deowan, S. A. and Azzam, R. (2011) ‘Carbon dioxide utilisation for carbamide production by application of the coupled UCG-Urea process’, in *Energy Procedia*. doi: 10.1016/j.egypro.2011.02.107.

Kolding, H., Fehrmann, R. and Riisager, A. (2012) ‘CO2 Capture technologies: Current status and new directions using supported ionic liquid phase (SILP) absorbers’, *Science China Chemistry*, 55(8), pp. 1648–1656. doi: 10.1007/s11426-012-4683-x.

Koornneef, J., Spruijt, M., Molag, M., Ramírez, A., Turkenburg, W. and Faaij, A. (2010) ‘Quantitative risk assessment of CO2 transport by pipelines--a review of uncertainties and their impacts.’, *Journal of hazardous materials*, 177(1–3), pp. 12–27. doi: 10.1016/j.jhazmat.2009.11.068.

Kotowicz, J. (2012) ‘Optimisation of the connection of membrane CCS installation with a supercritical coal- fi red power plant’, 38(x), pp. 118–127. doi: 10.1016/j.energy.2011.12.028.

Kuramochi, T., Ramírez, A., Turkenburg, W. and Faaij, A. (2012) ‘Comparative assessment of CO2 capture technologies for carbon-intensive industrial processes’, *Progress in Energy and Combustion Science*. Elsevier Ltd, 38(1), pp. 87–112. doi: 10.1016/j.pecs.2011.05.001.

Labus, K. and Machnikowski, J. (2014) ‘Separation of Carbon Dioxide from Coal Gasi fi cation-Derived Gas by Vacuum Pressure Swing Adsorption’.

Lackner, K. . (2013) ‘Thermodynamics of direct air capture of carbon dioxide’, *Energy*. doi: 10.1016/j.energy.2012.09.012.

Li, C., Yuan, X. and Fujimoto, K. (2014) ‘2014’, *Applied Catalysis A: General*. Elsevier B.V., 469, pp. 306–311. doi: 10.1016/j.apcata.2013.10.010.

Li, J., Zhang, H., Gao, Z., Fu, J., Ao, W. and Dai, J. (2017) ‘CO 2 Capture with Chemical Looping Combustion of Gaseous Fuels: An Overview’, *Energy & Fuels*, 31(4), pp. 3475–3524. doi: 10.1021/acs.energyfuels.6b03204.

Liu, Z., Grande, C. a., Li, P., Yu, J. and Rodrigues, A. E. (2011) ‘Multi-bed Vacuum Pressure Swing Adsorption for carbon dioxide capture from flue gas’, *Separation and Purification Technology*. Elsevier B.V., 81(3), pp. 307–317. doi: 10.1016/j.seppur.2011.07.037.

Liu, Z. and Green, W. H. (2013) ‘Experimental Investigation of Sorbent for Warm CO 2 Capture by Pressure Swing Adsorption’, *Industrial & Engineering Chemistry Research*, 52(28), pp. 9665–9673. doi: 10.1021/ie303534u.

Liu, Z., Wang, L., Kong, X., Li, P., Yu, J. and Rodrigues, A. E. (2012) ‘Onsite CO 2 Capture from Flue Gas by an Adsorption Process in a Coal-Fired Power Plant’, *Industrial & Engineering Chemistry Research*, 51(21), pp. 7355–7363. doi: 10.1021/ie3005308.

López Ortiz, A., Meléndez Zaragoza, M. J. and Collins-Martínez, V. (2016) ‘Hydrogen production research in Mexico: A review’, *International Journal of Hydrogen Energy*, 41(48), pp. 23363–23379. doi: 10.1016/j.ijhydene.2016.07.004.

Makhlouf, A., Serradj, T. and Cheniti, H. (2015) ‘Life cycle impact assessment of ammonia production in Algeria: A comparison with previous studies’, *Environmental Impact Assessment Review*. Elsevier Inc., 50, pp. 35–41. doi: 10.1016/j.eiar.2014.08.003.

Martinez-Hernandez, E., Sadhukhan, J. and Campbell, G. M. (2013) ‘Integration of bioethanol as an in-process material in biorefineries using mass pinch analysis’, *Applied Energy*, 104, pp. 517–526. doi: 10.1016/j.apenergy.2012.11.054.

Mendoza Beltrán, A., Guinée, J. and Heijungs, R. (2014) ‘A statistical approach to deal with uncertainty due to the choice of allocation methods in LCA’, *9th International Conference LCA of Food*, p. 10.

Methanol Institute (2011a) *Methanol Basics*.

Methanol Institute (2011b) *Methanol gasoline blends: Alternative Fuel for Today’s Automobiles and Cleaner Burning Octane for Today’s Oil Refinery*.

Middleton, R. S., Keating, G. N., Viswanathan, H. S., Stauffer, P. H. and Pawar, R. J. (2012) ‘Effects of geologic reservoir uncertainty on CO2 transport and storage infrastructure’, *International Journal of Greenhouse Gas Control*. Elsevier Ltd, 8, pp. 132–142. doi: 10.1016/j.ijggc.2012.02.005.

Middleton, R. S., Kuby, M. J., Wei, R., Keating, G. N. and Pawar, R. J. (2012) ‘A dynamic model for optimally phasing in CO2 capture and storage infrastructure’, *Environmental Modelling & Software*. Elsevier Ltd, 37, pp. 193–205. doi: 10.1016/j.envsoft.2012.04.003.

Morales Mora, M. a., Vergara, C. P., Leiva, M. a., Martínez Delgadillo, S. a. and Rosa-Domínguez, E. R. (2016) ‘Life cycle assessment of carbon capture and utilization from ammonia process in Mexico’, *Journal of Environmental Management*. Elsevier Ltd, 183, pp. 998–1008. doi: 10.1016/j.jenvman.2016.09.048.

Mukherjee, S., Kumar, P., Yang, A. and Fennell, P. (2015) ‘A systematic investigation of the performance of copper-, cobalt-, iron-, manganese- and nickel-based oxygen carriers for chemical looping combustion technology through simulation models’, *Chemical Engineering Science*, 130, pp. 79–91. doi: https://doi.org/10.1016/j.ces.2015.03.009.

Nandy, A., Loha, C., Gu, S., Sarkar, P., Karmakar, M. K. and Chatterjee, P. K. (2016) ‘Present status and overview of Chemical Looping Combustion technology’, *Renewable and Sustainable Energy Reviews*, 59, pp. 597–619. doi: https://doi.org/10.1016/j.rser.2016.01.003.

NETL (2013) *Cradle-to-Gate Life Cycle Analysis Model for Alternative Sources of CO2*.

NETL (2015) *Cost and Performance Baseline for Fossil Energy Plants Volume 1a: Bituminous Coal and Natural Gas to Electricity Revision 3 (DOE/NETL-2010/1723),*.

Ng, D. K. S., Tan, R. R., Foo, D. C. Y. and El-Halwagi, M. M. (2015) ‘Process System Engineering Tools for Biomass Polygeneration Systems with Carbon Capture and Reuse’, in Ng, D. K. S., Tan, R. R., Foo, D. C. Y., and El-Halwagi, M. M. (eds) *Process Design Strategies for Biomass Conversion Systems*. Chichester, UK: John Wiley & Sons, Ltd, pp. 96–108. doi: 10.1002/9781118699140.

Ng, K. S., Zhang, N. and Sadhukhan, J. (2012a) ‘A graphical CO2 emission treatment intensity assessment for energy and economic analyses of integrated decarbonised production systems’, *Computers & Chemical Engineering*, 45, pp. 1–14. doi: 10.1016/j.compchemeng.2012.04.013.

Ng, K. S., Zhang, N. and Sadhukhan, J. (2012b) ‘Decarbonised coal energy system advancement through CO2 utilisation and polygeneration’, *Clean Technologies and Environmental Policy*, 14(3), pp. 443–451. doi: 10.1007/s10098-011-0437-2.

Ng, K. S., Zhang, N. and Sadhukhan, J. (2013) ‘Techno-economic analysis of polygeneration systems with carbon capture and storage and CO2 reuse', *Chemical Engineering Journal*, 219, pp. 96–108. doi: 10.1016/j.cej.2012.12.082.

Nikolic, V. M., Tasic, G. S., Maksic, A. D., Saponjic, D. P., Miulovic, S. M. and Marceta Kaninski, M. P. (2010) 'Raising efficiency of hydrogen generation from alkaline water electrolysis – Energy saving', *International Journal of Hydrogen Energy*. Elsevier Ltd, 35(22), pp. 12369–12373. doi: 10.1016/j.ijhydene.2010.08.069.

ofgem (2017) *Electricity Market Reform*.

Olah, G. a (2005) 'Beyond oil and gas: the methanol economy.', *Angewandte Chemie (International ed. in English)*, 44(18), pp. 2636–9. doi: 10.1002/anie.200462121.

Olah, G. a, Goeppert, A. and Prakash, G. K. S. (2009) 'Chemical recycling of carbon dioxide to methanol and dimethyl ether: from greenhouse gas to renewable, environmentally carbon neutral fuels and synthetic hydrocarbons.', *The Journal of organic chemistry*, 74(2), pp. 487–98. doi: 10.1021/jo801260f.

Olajire, A. A. (2010) 'CO2 capture and separation technologies for end-of-pipe applications – A review', *Energy*, 35(6), pp. 2610–2628. doi: https://doi.org/10.1016/j.energy.2010.02.030.

Ozbilen, A., Dincer, I. and Rosen, M. a. (2011) 'A comparative life cycle analysis of hydrogen production via thermochemical water splitting using a Cu–Cl cycle', *International Journal of Hydrogen Energy*. Elsevier Ltd, 36(17), pp. 11321–11327. doi: 10.1016/j.ijhydene.2010.12.035.

Pelletier, N., Ardente, F., Brandão, M., De Camillis, C. and Pennington, D. (2015) 'Rationales for and limitations of preferred solutions for multi-functionality problems in LCA: is increased consistency possible?', *International Journal of Life Cycle Assessment*, 20(1), pp. 74–86. doi: 10.1007/s11367-014-0812-4.

Pera-Titus, M. (2014) 'Porous Inorganic Membranes for CO 2 Capture: Present and Prospects', *Chemical Reviews*, 114(2), pp. 1413–1492. doi: 10.1021/cr400237k.

Pérez-Fortes, M., Bocin-Dumitriu, A. and Tzimas, E. (2014) 'CO2 utilization pathways: Techno-economic assessment and market opportunities', *Energy Procedia*. Elsevier B.V., 63(i), pp. 7968–7975. doi: 10.1016/j.egypro.2014.11.834.

Pérez-Fortes, M., Schöneberger, J. C., Boulamanti, A. and Tzimas, E. (2016) 'Methanol synthesis using captured CO2 as raw material: Techno-economic and environmental assessment', *Applied Energy*. Elsevier Ltd, 161, pp. 718–732. doi: 10.1016/j.apenergy.2015.07.067.

Petrescu, L., Bonalumi, D., Valenti, G., Cormos, A. M. and Cormos, C.-C. (2017) 'Life Cycle Assessment for supercritical pulverized coal power plants with post-combustion carbon capture and storage', *Journal of Cleaner Production*, 157, pp. 10–21.

Pipitone, G. and Bolland, O. (2009) 'Power generation with CO2 capture: Technology for CO2 purification', *International Journal of Greenhouse Gas Control*, 3(5), pp. 528–534. doi: https://doi.org/10.1016/j.ijggc.2009.03.001.

Pires, J. C. M., Martins, F. G., Alvim-Ferraz, M. C. M. and Simões, M. (2011) 'Recent developments on carbon capture and storage: An overview', *Chemical Engineering Research and Design*. Institution of Chemical Engineers, 89(9), pp. 1446–1460. doi: 10.1016/j.cherd.2011.01.028.

Pirngruber, G. D. and Leinekugel-le-cocq, D. (2013) 'Design of a Pressure Swing Adsorption Process for Postcombustion CO 2 Capture'.

Reese, M., Marquart, C., Malmali, M., Wagner, K., Buchanan, E., McCormick, A. and Cussler, E. L. (2016) 'Performance of a Small-Scale Haber Process', *Industrial and Engineering*

Chemistry Research, 55(13), pp. 3742–3750. doi: 10.1021/acs.iecr.5b04909.

Sadhukhan, J., Ng, K. S. and Hernandez, E. M. (2014) *Biorefineries and Chemical Processes: Design, Integration and Sustainability Analysis*. Chichester, UK: John Wiley & Sons, Ltd. doi: 10.1002/9781118698129.

Safi, R., Agarwal, R. K. and Banerjee, S. (2016) 'Numerical simulation and optimization of CO 2 utilization for enhanced oil recovery from depleted reservoirs', *Chemical Engineering Science*, 144, pp. 30–38. doi: 10.1016/j.ces.2016.01.021.

Santoyo-Castelazo, E. and Azapagic, A. (2014) 'Sustainability assessment of energy systems: Integrating environmental, economic and social aspects', *Journal of Cleaner Production*. Elsevier Ltd, 80, pp. 119–138. doi: 10.1016/j.jclepro.2014.05.061.

Sayah, A. K. and Sayah, A. K. (2011) 'Wind-hydrogen utilization for methanol production: An economy assessment in Iran', *Renewable and Sustainable Energy Reviews*. Elsevier Ltd, 15(8), pp. 3570–3574. doi: 10.1016/j.rser.2011.05.013.

Schach, M.-O., Schneider, R., Schramm, H. and Repke, J.-U. (2010) 'Techno-Economic Analysis of Postcombustion Processes for the Capture of Carbon Dioxide from Power Plant Flue Gas', *Industrial & Engineering Chemistry Research*, 49(5), pp. 2363–2370. doi: 10.1021/ie900514t.

SCOT (2017) *CO2 utilisation projects*.

Sharma, I., Hoadley, A. F. A., Mahajani, S. M. and Ganesh, A. (2016) 'Multi-objective optimisation of a Rectisol^{TM} process for carbon capture', *Journal of Cleaner Production*, 119, pp. 196–206. doi: https://doi.org/10.1016/j.jclepro.2016.01.078.

Simonen, K. (2014) *Life Cycle Assessment (PocketArquitecture)*. Routledge.

Singh, B., Strømman, A. H. and Hertwich, E. G. (2011) 'Comparative life cycle environmental assessment of CCS technologies', *International Journal of Greenhouse Gas Control*. Elsevier Ltd, 5(4), pp. 911–921. doi: 10.1016/j.ijggc.2011.03.012.

Skorek-Osikowska, A., Janusz-Szymańska, K. and Kotowicz, J. (2012) 'Modeling and analysis of selected carbon dioxide capture methods in IGCC systems', *Energy*, 45(1), pp. 92–100. doi: 10.1016/j.energy.2012.02.002.

Smitkova, M., Janíček, F. and Riccardi, J. (2011) 'Life cycle analysis of processes for hydrogen production', *International Journal of Hydrogen Energy*, 36(13), pp. 7844–7851. doi: 10.1016/j.ijhydene.2011.01.177.

Socolow, R. H.; Desmond, M. J. (2011) *Direct Air Capture of CO2 with Chemicals: A technology Assessment for the APS Panel on Public Affair*.

Srisang, W., Pouryousefi, F., Osei, P. A., Decardi-Nelson, B., Akachuku, A., Tontiwachwuthikul, P. and Idem, R. (2017) 'Evaluation of the heat duty of catalyst-aided amine-based post combustion CO 2 capture', *Chemical Engineering Science*, 170, pp. 48–57. doi: 10.1016/j.ces.2017.01.049.

Stamicarbon (2017) *Urea facts*.

Sternberg, A. and Bardow, A. (2015) 'Power-to-What? – Environmental assessment of energy storage systems', *Energy Environ. Sci.*, pp. 389–400. doi: 10.1039/C4EE03051F.

Stojić, D. L., Marčeta, M. P., Sovilj, S. P. and Miljanić, Š. S. (2003) 'Hydrogen generation from water electrolysis—possibilities of energy saving', *Journal of Power Sources*, 118(1–2), pp. 315–319. doi: 10.1016/S0378-7753(03)00077-6.

Stranddorf, H., Hoffmann, L. and Schmidt, A. (2005) *Impact categories, normalisation and* *weighting in LCA*.

Styring, P. and Jansen, D. (2011) *Carbon Capture and Utilisation in the green economy*. The Centre for Low Carbon Futures 2011.

Suh, S. and Huppes, G. (2005) 'Methods for Life Cycle Inventory of a product', *Journal of Cleaner Production*, 13(7), pp. 687–697. doi: 10.1016/j.jclepro.2003.04.001.

Suleman, F., Dincer, I. and Agelin-Chaab, M. (2015) 'Environmental impact assessment and comparison of some hydrogen production options', *International Journal of Hydrogen Energy*. Elsevier Ltd, 40(21), pp. 6976–6987. doi: 10.1016/j.ijhydene.2015.03.123.

Tang, Q., Shen, Z., Huang, L., He, T., Adidharma, H., Russell, A. G. and Fan, M. (2017) 'Synthesis of methanol from CO 2 hydrogenation promoted by dissociative adsorption of hydrogen on a Ga 3 Ni 5 (221) surface', *Physical Chemistry Chemical Physics*, 19(28), pp. 18539–18555. doi: 10.1039/C7CP03231E.

Tian, H., Siriwardane, R., Simonyi, T. and Poston, J. (2013) 'Natural Ores as Oxygen Carriers in Chemical Looping Combustion', *Energy & Fuels*, 27(8), pp. 4108–4118. doi: 10.1021/ef301486n.

Troy, S., Schreiber, A. and Zapp, P. (2016) 'Life cycle assessment of membrane-based carbon capture and storage', *Clean Technologies and Environmental Policy*. Springer Berlin Heidelberg, 18(6), pp. 1641–1654. doi: 10.1007/s10098-016-1208-x.

Trudewind, C. a., Schreiber, A. and Haumann, D. (2014) 'Photocatalytic methanol and methane production using captured CO2 from coal-fired power plants. Part I – a Life Cycle Assessment', *Journal of Cleaner Production*. Elsevier Ltd, 70, pp. 27–37. doi: 10.1016/j.jclepro.2014.02.014.

Vasudevan, S., Farooq, S., Karimi, I. A., Saeys, M., Quah, M. C. G. and Agrawal, R. (2016) 'Energy penalty estimates for CO2 capture: Comparison between fuel types and capture-combustion modes', *Energy*. Elsevier Ltd, 103, pp. 709–714. doi: 10.1016/j.energy.2016.02.154.

Versteeg, P. and Rubin, E. S. (2011) 'A technical and economic assessment of ammonia-based post-combustion CO2 capture at coal-fired power plants', *International Journal of Greenhouse Gas Control*, 5(6), pp. 1596–1605. doi: 10.1016/j.ijggc.2011.09.006.

van der Voet, E., Reid, Li. J. and Luo, L. (2010) 'Life-cycle assessment of biofuels, convergence and divergence', *Biofuels*, 1(3), pp. 435–449.

Wang, M., Wang, Z., Gong, X. and Guo, Z. (2014) 'The intensification technologies to water electrolysis for hydrogen production - A review', *Renewable and Sustainable Energy Reviews*. Elsevier, 29, pp. 573–588. doi: 10.1016/j.rser.2013.08.090.

Wardenaar, T., Van Ruijven, T., Beltran, A. M., Vad, K., Guinée, J. and Heijungs, R. (2012) 'Differences between LCA for analysis and LCA for policy: A case study on the consequences of allocation choices in bio-energy policies', *International Journal of Life Cycle Assessment*, 17(8), pp. 1059–1067. doi: 10.1007/s11367-012-0431-x.

Wattanaphan, P., Sema, T., Idem, R., Liang, Z. and Tontiwachwuthikul, P. (2013) 'Effects of flue gas composition on carbon steel (1020) corrosion in MEA-based CO2 capture process', *International Journal of Greenhouse Gas Control*. Elsevier Ltd, 19, pp. 340–349. doi: 10.1016/j.ijggc.2013.08.021.

Weimer, T., Berger, R., Hawthorne, C. and Abanades, J. C. (2008) 'Lime enhanced gasification of solid fuels: Examination of a process for simultaneous hydrogen production and CO2 capture', *Fuel*, 87(8–9), pp. 1678–1686. doi: 10.1016/j.fuel.2007.08.023.

Xiang, X., Guo, L., Wu, X., Ma, X. and Xia, Y. (2012) 'Urea formation from carbon dioxide and ammonia at atmospheric pressure', *Environmental Chemistry Letters*, 10(3), pp. 295–300. doi: 10.1007/s10311-012-0366-2.

Xu, G., Liang, F., Yang, Y., Hu, Y., Zhang, K. and Liu, W. (2014) 'An improved CO2 separation and purification system based on cryogenic separation and distillation theory', *Energies*, 7(5), pp. 3484–3502. doi: 10.3390/en7053484.

Xu, G., Yang, Y., Ding, J., Li, S., Liu, W. and Zhang, K. (2013) 'Analysis and optimization of CO2 capture in an existing coal-fired power plant in China', *Energy*. Elsevier Ltd, 58, pp. 117–127. doi: 10.1016/j.energy.2013.04.012.

Yang, C.-J. and Jackson, R. B. (2012) 'China's growing methanol economy and its implications for energy and the environment', *Energy Policy*. Elsevier, 41, pp. 878–884. doi: 10.1016/j.enpol.2011.11.037.

Yang, S., Qian, Y. and Yang, S. (2016) 'Development of a Full CO 2 Capture Process Based on the Rectisol Wash Technology', *Industrial & Engineering Chemistry Research*, 55(21), pp. 6186–6193. doi: 10.1021/acs.iecr.6b00747.

Yoo, B.-Y., Choi, D.-K., Huh, C., Kang, S.-G. and Kim, I.-S. (2013) 'A Feasibility Study on CO2 Marine Transport in South Korea', *Energy Procedia*. Elsevier B.V., 37, pp. 3199–3211. doi: 10.1016/j.egypro.2013.06.207.

Yoo, C.-J., Lee, D.-W., Kim, M.-S., Moon, D. J. and Lee, K.-Y. (2013) 'The synthesis of methanol from CO/CO2/H2 gas over Cu/Ce1−xZrxO2 catalysts', *Journal of Molecular Catalysis A: Chemical*. Elsevier B.V., 378, pp. 255–262. doi: 10.1016/j.molcata.2013.06.023.

Yuan, L. C., Pfotenhauer, J. M. and Qiu, L. M. (2014) 'A preliminary investigation of cryogenic CO2 capture utilizing a reverse Brayton Cycle', in, pp. 1107–1114. doi: 10.1063/1.4860829.

Zeman, F. (2007) 'Energy and Material Balance of CO 2 Capture from Ambient Air', *Environmental Science & Technology*, 41(21), pp. 7558–7563. doi: 10.1021/es070874m.

Zeman, F. (2014) 'Reducing the cost of ca-based direct air capture of CO2', *Environmental Science and Technology*, 48(19), pp. 11730–11735. doi: 10.1021/es502887y.

Zeng, K. and Zhang, D. (2010) 'Recent progress in alkaline water electrolysis for hydrogen production and applications', *Progress in Energy and Combustion Science*. Elsevier Ltd, 36(3), pp. 307–326. doi: 10.1016/j.pecs.2009.11.002.

Zhai, H. and Rubin, E. S. (2013) 'Techno-economic assessment of polymer membrane systems for postcombustion carbon capture at coal-fired power plants.', *Environmental science & technology*, 47(6), pp. 3006–14. doi: 10.1021/es3050604.

Zhang, L., Zhang, Y. and Chen, S. (2012) 'Applied Catalysis A : General catalyst for methanol synthesis from CO 2 hydrogenation', 416, pp. 118–123. doi: 10.1016/j.apcata.2011.12.013.

Zhang, X., Bauer, C., Mutel, C. L. and Volkart, K. (2017) 'Life Cycle Assessment of Power-to-Gas : Approaches , system variations and their environmental implications', *Applied Energy*. Elsevier Ltd, 190, pp. 326–338. doi: 10.1016/j.apenergy.2016.12.098.

Zhang, Y., Cruz, J., Zhang, S., Lou, H. H. and Benson, T. J. (2013) 'Process simulation and optimization of methanol production coupled to tri-reforming process', *International Journal of Hydrogen Energy*. Elsevier Ltd, 38(31), pp. 13617–13630. doi: 10.1016/j.ijhydene.2013.08.009.

Zhou, Q., Koiwanit, J., Piewkhaow, L., Manuilova, a., Chan, C. W., Wilson, M. and Tontiwachwuthikul, P. (2014) 'A Comparative of Life Cycle Assessment of Post-combustion, Pre-combustion and Oxy-fuel CO2 Capture', *Energy Procedia*. Elsevier B.V., 63, pp. 7452–7458. doi: 10.1016/j.egypro.2014.11.782.

Zoannou, K.-S., Sapsford, D. J. and Griffiths, A. J. (2013) ‘Thermal degradation of monoethanolamine and its effect on CO2 capture capacity’, *International Journal of Greenhouse Gas Control*. Elsevier Ltd, 17(x), pp. 423–430. doi: 10.1016/j.ijggc.2013.05.026.

3 Overview of Life Cycle Assessment and Relevant Regulation for Carbon Dioxide Utilisation

The interest in assessing the environmental performance of a system is not a new concept; however, in Rio de Janeiro in 1992 this interest reached a new level. The United Nations Framework Convention on Climate Change was held for the first time (also known as 'Earth Summit'). From this point onwards, efforts have been made towards reaching a sustainable model while questioning what this sustainable model should be. Although the term 'sustainability' is nowadays used in many areas, the term is still often used lightly delivering unmeasurable results (Milicevic 2008; Agol *et al.* 2014; Moldan *et al.* 2012; Heijungs 2013). It is defined by the World Commission on Environment and Development as "development that meets the needs of the present without compromising the ability of future generations to meet their own needs" (Butlin, 1989). One of the problems with defining this term is that although a process might reach what is deemed to be a 'sustainable level'; this level can always be surpassed by increasing quantities and qualities. This leads to a loop where sustainability is always chased. Using such a term can be misleading and thus, is often used for marketing purposes more than for its environmental significance (Heijungs 2013). More recently, there have been efforts to expand the term towards linking society, economy and ecology under one dependant system. Known as the triple bottom line (society-environment-economy), it has gained popularity within the corporate sector thanks to the inclusion of economic prosperity (Glavas & Mish 2014).

This lack of consensus on an assessment method is no different in the area of chemical transformation of CO_2. It should not be seen only as direct result of the complexity of the chemical processes, but as a joint problem from a technological and a sustainability point of view. In the last five years there has been an increased interest in assessing carbon dioxide utilisation from a life cycle assessment perspective (Pérez-Fortes *et al.* 2014; Morales Mora *et al.* 2016; Von der Assen *et al.* 2013a; Cuéllar-Franca & Azapagic 2014). This interest is driven by the necessity to allocate carbon dioxide emissions properly and determine potential environmental benefits of any given CO_2 utilisation process. As it is with other assessment methods, there is no direct methodology or framework to follow, only guidelines. Much of the research is now focused on establishing these guidelines and moving towards a triple bottom line model/outcome. The next sections give an overview of life cycle thinking tools and environmental frameworks applied to carbon dioxide utilisation.

3.1 Life cycle assessment and CO_2 utilisation

Life cycle assessment (LCA) is a method that is regulated by the ISO standards 14040, 14041 and 14044 (ISO, 1998, 2006a, 2006b). These standards define life cycle assessment as a study that describes environmental aspects and potential impacts throughout a product´s life cycle, i.e raw materials, acquisition, production, use and disposal. To perform a life cycle assessment study, an end-product must always be defined. The impacts are divided into categories and assessed based on a set of potentials that are already established. This method has gained attention partly because of its all-round approach to environmental impacts in a supply chain format. It is now used in the private and public sector as a decision-making tool in sustainability packages. Although it is still a relatively new method (in terms of widespread use), the first records of this type of studies date from 1960 (Suh and Huppes, 2005).

Because CO_2 utilisation processes use a flow that was once a waste, there is an appeal in using life cycle assessments to evaluate potential environmental impacts. The first study in literature that connects both areas was published in Von der Assen *et al.* (2013a). It is in this study that the challenges and opportunities of assessing carbon dioxide utilisation using life cycle thinking became apparent. After this study, research in the area has grown largely. In the last three years, the main studies published from this work include: Von der Assen & Bardow (2014); Sternberg & Bardow (2015); Von der Assen *et al.* (2013a); Von der Assen e*t al.* (2014); Azapagic & Cue (2015). Two studies discuss methodology, one is a critical review and two apply the methods described in von der Assen & Bardow (2014) and von der Assen *et al.* (2013b).

Overall, there is still a lack of full studies available; however, this does not necessarily mean that applicable research does not exist. There is a lot of information related to carbon utilisation that can be used in life cycle assessments or sustainability studies; the main problem found was the lack of a standard format to present this information. This is often the norm with these studies, especially at the earlier stages of process development. Having information in different formats complicates inventory collection and assessment. An example of this is literature found for methanol and urea from carbon utilisation and related fields. Nine different research areas provided useful data but were not part of an integrated study (**Table 3.1**).

Table 3.1 Summary of research related to life cycle assessments for CO_2 utilisation, years 1999-2017

Type of study	**Number of related studies**	**Year Published**
Performance studies for CCS^1 (LCA, emissions, techno- economics)	21	2008-2015
Performance studies for CDU^2 (LCA, emissions, techno economics	35	1999-2017
Technical (CCS^1)	30	2006-2014
Technical (CDU^2)	30	2009-2017
CO_2 pipelines and transport	4	2010-2013
Auxiliary units (Compression, dehydration, power plant theory)	7	2009-2015
LCA methods	13	2001-2016
Industrial information	3	2009-2014
3 in 1: technical, environmental and economic studies	2	2002-2006

[1] Carbon capture and storage [2] Carbon dioxide utilisation

As an example, methanol production through catalytic hydrogenation using CO_2 captured from post-combustion capture processes are frequently mentioned (Sternberg & Bardow 2015; von der Assen *et al.* 2013a; von der Assen *et al*. 2014). However, there is no full life cycle assessment report to the author´s knowledge that includes both capture and utilisation in one study.

The next following sections will give an overview of found literature that is relevant to life cycle assessment and CO_2 utilisation. There is an emphasis on production of methanol through catalytic hydrogenation of CO_2 and urea production through hydrogen and CO_2 as these are the case studies for this research.

3.2 Overview of life cycle assessment work for methanol and urea production using CO_2 as feedstock

Overall, few studies bridge sustainability and CO_2 utilisation from a life cycle assessment perspective. Currently one review paper (to our knowledge) compiles life cycle assessment work on carbon utilisation (Cuéllar-Franca & Azapagic 2014). The review studies sixteen papers dedicated to CO_2 transformation processes. Nine out of the sixteen studies are dedicated to diesel production from microalgae while the rest are divided into enhanced oil recovery, production of chemicals, and mineral carbonation. None of these discusses methanol or urea production from CO_2. It is however, a first attempt to collect information under one ‘carbon dioxide utilisation’ sector.

Most recently, a study by Zhang *et al*. (2017) used the guidelines available to present a power to gas life cycle assessment. This is the first full study that considers carbon utilisation specifics and considers them in their assessment. It follows the line of work started by von der Assen *et al.* (2013a) and it applies it to the production of synthetic natural gas (SNG). This study makes emphasis on the impact of allocation rules and is a good example on how carbon utilisation processes could be assessed. While it has a full life cycle assessment, it does not consider either the economic or social aspects of the process. These aspects should be furthered explored in parallel for decision-making to validate the sustainability of the process. However, the inclusion of the term “poly-generation” is a useful concept for carbon utilisation since it analyses multiple processes interconnected as one large process (Ng, Zhang and Sadhukhan, 2012a, 2012b, 2013; Ng *et al.*, 2015). The following section reviews independent studies that link together to create a carbon utilisation scenario for methanol and urea production from CO_2 capture and renewable energy.

Methanol

There is one study conducted that thoroughly assesses the supply chain of photocatalytic methanol and methane using CO_2 captured from coal-fired power plants (Trudewind *et al.* 2014). This study used a system expansion method to compare three systems: A conventional power plant and traditional methanol/methane production, a carbon capture system with six capture options and a carbon utilisation process. Results in this study showed that primary demand and global warming scores were lower for carbon utilisation coupled with an oxy-fuel plant. The benefit of this system was the high CO_2 capture rate of 95 %. However, other impacts were not analysed for this capture method thus further work is still needed to compare the capture processes equally.

There is also a comparison between methanol and methane, where methane production has lower environmental impacts due to the lower energy requirements than for methanol production. However, according to the life cycle assessment methodology for carbon utilisation by Von der Assen *et al.* (2014), two different products can only be compared based on the same end function, regardless of their production route or pathway. Product or process comparison challenges are often encountered, one way to overcome this is by using allocation methods as mentioned in Sadhukhan *et al*. (2014). Allocation is further discussed in **Section 3.3.3**.

Methanol from carbon dioxide is used as an example in several methodological studies of life cycle assessment (LCA) applied to carbon utilisation (Von der Assen *et al.* 2013a; Von der Assen *et al*. 2014; Von der Assen & Bardow 2014). There is also a tutorial review (von der Assen *et al.* 2014) where a system that uses recovered CO_2 is compared to a conventional reference system. The functional units (measurable units of the performance of the product systems) are 1,273 kWh and 1,000 kg of methanol. Electricity is produced from a coal-fired power plant and the CO_2 is captured without specifying the capture process. Production of methanol is through catalytic hydrogenation of CO_2 using electrolysis with wind power as the H_2 source. The study follows a simple comparison of the global warming score of methanol from natural gas and methanol from CO_2.

An energy storage analysis (Sternberg & Bardow 2015) briefly mentions methanol from CO_2 from a different approach; hydrogen storage with hydrocarbon conversion using CO_2. Similar work is done by Von der Assen *et al*. (2014, 2013a), who define carbon sources as: non biogenic point sources, biogenic point sources, and air capture.

Apart from the mentioned studies, most life cycle assessment work that can be applied to carbon utilisation is split into the following categories: capture stage, utilisation and renewable energy. Specifically, no assessment was found in literature that evaluates in detail the complete methanol production route from catalytic hydrogenation of CO_2 process and post-combustion capture with amine-based scrubbing. However, as mentioned previously, there are several studies that bring together process modelling with techno-economic assessments (Pérez-Fortes, Bocin-Dumitriu and Tzimas, 2014; Sadhukhan, Ng and Hernandez, 2014; Pérez-Fortes *et al.*, 2016).

Urea

As it is the case with methanol, there are studies available that focus on certain aspects of urea production through different routes. However, there are few urea life cycle assessment studies that bring all information into one study (**Table 3.2**). Part of the challenge is finding these studies and their relationship with the area of carbon dioxide recovery and transformation, since it is still questionable whether urea can count as a CO_2 utilisation process.

Chapter 6 discusses the potential role of urea production from recovered CO_2 further while the next section focuses on current available information. To the best of the author's knowledge, no full life cycle assessment study assesses the supply chain of urea production as a CO_2 utilisation technology. The best approach seen in literature is finding assessment studies for ammonia production, CO_2 capture and urea production individually and bringing them under one poly-generation study. **Table 3.2** shows a compilation of these studies.

Table 3.2 Compilation of studies related to urea production and CO_2 utilisation

Title of research paper	**Reference**
LCA/carbon accounting studies	
Greenhouse gas emissions from nitrogen fertilizer use in China	(Kahrl *et al.*, 2010)
Life cycle assessment (LCA of different fertilizer product types	(Hasler *et al.*, 2015)
Impact assessment and environmental evaluation of various ammonia production processes	(Bicer *et al.*, 2017)
Life cycle assessment of nuclear-based hydrogen and ammonia production options: a comparative study	(Bicer and Dincer, 2016)
Life cycle impact assessment of ammonia production in Algeria: a comparison with previous studies	(Makhlouf, Serradj and Cheniti, 2015)
Technical studies	
Carbon dioxide utilisation for carbamide production by application of the coupled UCG-urea process	(Kempka, Plötz, *et al.*, 2011)
Urea formation from carbon dioxide and ammonia at atmospheric pressure	(Xiang *et al.*, 2012)
Co- production of power and urea from coal with CO_2 capture: performance assessment	(Bose *et al.*, 2015)
Performance of a small-scale Haber process	(Reese *et al.*, 2016)
Techno-economic studies	
CO_2 utilisation pathways: techno-economic assessment and market opportunities	(Pérez-Fortes, Bocin-Dumitriu and Tzimas, 2014)
Urea synthesis using chemical looping process techno-economic evaluation of a novel plant configuration for a green production	(Edrisi, Mansoori and Dabir, 2016)

From the author’s point of view, there is greater focus on life cycle assessment in ammonia synthesis than in urea production. This is perhaps a reflection on the versatility of ammonia production versus a more traditional urea production route. One of the most recent studies by Bicer *et al.* (2017) focuses on the impact assessment of ammonia production through fifteen routes, of which five are electrolysis routes. Results show that the least carbon intensive process is nuclear electrolysis with 0.48 kg CO_2 eq/kg NH_3 and the highest is coal electrolysis with 13.6 kg CO_2 eq/kg NH_3. The same research group published an earlier study (Bicer and Dincer, 2016) where nuclear based hydrogen and ammonia production routes were assessed. The results are comparable to their latest study where nuclear electrolysis-based ammonia production has lower global warming score than thermochemical based options.

Other researchers around the world are also interested in creating life cycle assessments for ammonia production routes. In Algeria, a ‘cradle to gate’ analysis was done for 1 tonne of ammonia produced by the Haber-Bosch process. Results showed a final global warming score of 1.44 (kg CO_2 eq)/kg NH_3 (Makhlouf, Serradj and Cheniti, 2015). Overall, one full life cycle assessment study was found on urea production (and as part of fertilizer). Hasler *et al.* (2015) reported 1.3 (kg CO_2 eq)/kg of fertilizer with ammonia produced through the Haber-Bosch process.

Life cycle assessment and CO_2 capture

The National Energy Technology Laboratory (NETL) is an American institution that is known for developing detailed life cycle assessments. Amongst its list of published reports, there is a cradle to gate life cycle assessment analysis for alternative sources of carbon dioxide. All processes are US based. The analysis accounts for burdens from Natural CO_2 domes, natural gas processing plants and ammonia production plants (NETL, 2013).

Newer studies are moving away from only post-combustion capture with amines analysis. A study by Troy *et al.* (2016) compares membrane systems for oxy-fuel, pre and post-combustion plant. The functional unit is set at 1 kWh, which is in line with most of carbon capture analyses. Like other studies, only general inputs and inputs are presented, thus complicating replicability. This is more evident in studies where units are not well defined or even specified. There was one study found that compares a direct air capture process to post-combustion capture; the study, by Van der Giesen *et al.* (2017), was the only full life cycle assessment study that addresses direct air capture (DAC). Since most research in the area is either purely theoretical in nature or at pilot scale, the assessment mainly focuses on predicted energy demands. The last study (Van der Giesen *et al.*, 2017) combines technical information found in previous literature and simulation work with the life cycle assessment (LCA) methodology presented in Corsten *et al.* (2013) and von der Assen *et al.* (2013b). It is an example of how technologies with a low technology readiness level (TRL) can be assessed from a life cycle thinking perspective.

There are also several techno-economic studies that address energy penalties of using post-combustion CO_2 capture methods (Schach *et al.*, 2010; Kuramochi *et al.*, 2012; Huang, Rebennack and Zheng, 2013; Zhai and Rubin, 2013; Pérez-Fortes, Bocin-Dumitriu and Tzimas, 2014).

In environmental impact terms, studies such as Veltman *et al.* (2010) focus on specific flows and impacts. Results from this study found that absorption process with monoethanolamine (MEA) increase 10 times the toxic impact on freshwater ecosystems compared to a natural gas combined cycle (NGCC) and a conventional coal fired plant without CO_2 capture (420 MW capacity for all cases). The increase in impacts was attributed to volatilization of monoethanolamine (MEA). The Average solvent loss was reported at 2.8 x 10^6 kg/year for a CO_2 capture efficiency of 90% for the same study. This study does not give an overall assessment of the CO_2 capture method but it does assess the impact of monoethanolamine (MEA) for certain environmental categories. In another study, Zhou *et al*. (2014) describe an increase of 187 % environmental impacts from the use of monoethanolamine for water eco-toxicity compared to a baseline scenario and are associated with trace elements from electricity generation and CO_2 capture unit.

CO_2 capture with monoethanolamine (MEA) also increases eutrophication and acidification impacts, while global warming impacts may be reduced, other air pollutants such as NOx and SOx are emitted in greater quantities (Odeh & Cockerill 2008). The benefit of reducing global warming impacts should be weighed against the other pollutants. According to Zhou *et al.* (2014), global warming can decrease by 80 % if direct CO_2 emissions captured are accounted for and eutrophication increases by 66.5 % due to amine use. Unlike the study by Odeh & Cockerill (2008), acidification reduced by 50 % in a post-combustion capture system according to Zhou *et al.*, (2014). Variation in results can be attributed to different system boundaries and baseline scenarios; further analysis is needed to unify studies or produce comparable outcomes.

Life cycle assessment on methanol/urea/hydrogen production

There are life cycle assessment studies that focus on hydrogen production from water electrolysis using wind power (Ozbilen, Dincer and Rosen, 2011; Smitkova, Janíček and

Riccardi, 2011; Bhandari, Trudewind and Zapp, 2013). Overall results showed that the global warming impact of the electrolyser is small. However, the electrolysers are considered as single unit, therefore lacking detailed information on individual components. Global warming and acidification are the impacts that are often analysed in most hydrogen life cycle assessment studies on electrolysis processes according to Bhandari *et al.* (2013).

Another study that compared five methods of hydrogen production concluded that thermochemical water splitting has the lowest kg CO_2 eq. out of steam reforming of natural gas, coal gasification, water electrolysis through wind and solar electrolysis (Cetinkaya *et al.* 2012). However, the study did not analyse any other impact categories, complicating comparability with other studies. **Table 3.3** shows current research on life cycle assessment studies for hydrogen production.

Table 3.3 Comparative life cycle assessment studies found in literature for hydrogen production with 1 kg H_2 as functional unit

Source	**Hydrogen production route**	**Impacts analysed**
(Cetinkaya *et al.* 2012)	*Natural gas steam reforming* Coal gasification Wind electrolysis PV electrolysis Nuclear Cu-Ci cycle	Global warming
(Smitkova *et al.* 2011)	*Thermo-chemical cycles* Westinghouse cycle Westinghouse cycle Sulphur iodine cycle Coal gasification Coal pyrolysis	Human health, ecosystem quality and resources
(Ozbilen *et al.* 2011)	*Nuclear based Cu-Cl cycle* Nuclear based S-I cycle Nuclear based high temp electrolysis Natural gas steam reforming Biomass based electrolysis Wind based electrolysis Solar based electrolysis Natural gas steam reforming	Global warming, acidification
(Suleman *et al.* 2015)	*Electrolysis* Mercury cell electrolysis Diaphragm cell electrolysis Membrane cell electrolysis Sodium chlorine cycle	Human health, ecosystem quality and resources

3.3 Resources for life cycle assessment construction and its applicability to novel chemical transformation routes

There is no shortage of life cycle assessment (LCA) construction tools. Although all methods have important differences, they all follow the ISO standards 14040, 14041 and 14044 (ISO, 1998, 2006a, 2006b). This requires that all studies have four obligatory sections: Goal and scope, life cycle inventory (LCI), life cycle impact assessment (LCIA) and interpretation (see **Figure 3.1**). The following subsections will describe each part and its relation to CO_2 utilisation.

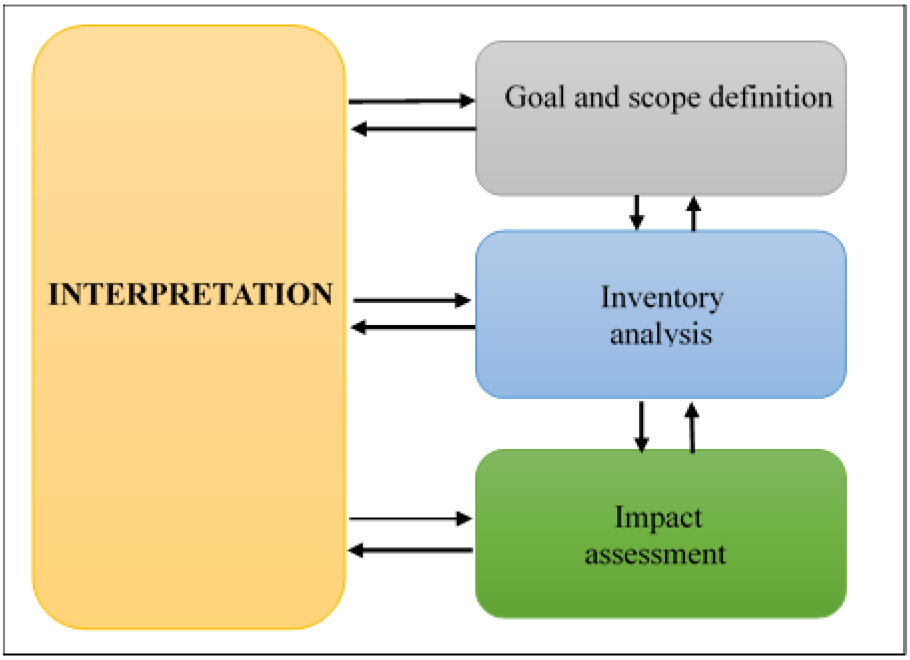


Figure 3.1 Life cycle assessment (LCA) framework based on ISO 14040, 14041 and 14044 (ISO, 1998, 2006a, 2006b)

These assessments handle large databases that require precise order and characterisation. To aid in this, software tools are commonly used specially for assessing impacts. As mentioned previously, one of the main challenges is data collection; after this, any software with the right characterisation tools can be used.

3.3.1 Goal and scope in CO_2 utilisation

Much like with any other product it is the stakeholders, researchers, etc. that set the goal and scope. Perhaps the main difference between a conventional process route and a CO_2 recovery and transformation route is the definition of the functional unit. While in a conventional process the end-product is the functional unit, in CO_2 utilisation is it the CO_2 or the final product? Carbon capture and storage (CCS) research usually uses energy as the end-product (Singh, Strømman and Hertwich, 2011; Kuramochi *et al.*, 2012; Troy, Schreiber and Zapp, 2016), thus CO_2 becomes secondary. When a carbon dioxide utilisation (CDU) process is analysed, the CO_2 is used as feedstock for a product, thus two final products are obtained: utilisation product, and the product before capture. Out of the life cycle assessment (LCA) studies available for utilisation, the functional unit chosen has been both kWh and kg of final product (Von der Assen & Bardow 2014; Assen *et al.* 2016; Von der Assen *et al.* 2013b). Therefore, choosing CO_2 as a functional unit would have little benefit since it is only an intermediate.

Where to set the boundaries?

According to ISO 14040 (ISO, 2006a), a process can either be cradle to grave, cradle to gate, gate to gate, gate to grave or whatever part of the supply chain is to be analysed. The difference is the end-product. Only the same products can be compared but all processes can be studied within certain boundaries. Von der Assen & Bardow (2014) support cradle to gate for carbon dioxide utilisation, if the end-product has the same quality at the gate. There is also the question of what is the sequestration period for carbon dioxide until it is released again? The answer is that for most sequestration (with exceptions such as mineralisation) there is no long-term sequestration at all. Once the product reaches its end of life, the CO_2 will return to the atmosphere. Nevertheless, the benefit comes from utilising CO_2 that would otherwise be emitted without displacing other emissions from a raw material.

3.3.2 Life cycle inventory and its role in CO_2 utilisation technologies

This is one of the most stable parts of the assessment (Suh and Huppes, 2005) as its main aim is data collection. There are several techniques and forms available for life cycle inventories, but the number one priority is to have data to collect. Data availability is the main challenge for CO_2 utilisation/ life cycle assessments and it is studied throughout this work. Life cycle inventory compilation methods include matrix representation of product systems, input-output (IO) and hybrid methods (Suh, 2002).

Two main data collection challenges have been identified for CO_2 utilisation processes: Low technology readiness levels and adapting life cycle assessment methodology to processes. The first challenge is a closed loop. Many processes are at research or even theoretical level; thus, supply chain information is not available. To obtain specific information, processes would need to be operational at large scale, defeating the initial screening purpose. To overcome this, a compromise between available and supplementary information needs to be reached. The research community have approached this challenge by using stoichiometric and simulation data to create life cycle inventories (Cetinkaya, Dincer and Naterer, 2012; Heijungs and Lenzen, 2014; Trudewind, Schreiber and Haumann, 2014; Morales Mora *et al.*, 2016; von der Assen *et al.*, 2016; Zhang *et al.*, 2017). The second challenge has also been mentioned in literature (Burgess and Brennan, 2001; Baumann and Tillman, 2004; Heijungs, Huppes and Guin??e, 2010). Life cycle assessments were initially created to study products and not processes. After its success with product-specific studies, the scope of life cycle thinking has expanded to other areas. Therefore, the data that needs to be collected will be different. **Chapter 4** discusses the proposed methodology to overcome these obstacles when creating and inventory for CO_2 utilisation processes. Information available as well as gaps specific to the study in question are discussed below.

3.3.3 Multifunctionality challenges

Many industrial processes will have more than one final product and are known as multifunctional. Deciding how to assign impacts/burdens/emissions to each product is essential for complying with goals set in life cycle assessments (LCAs). Solving multifunctionality can be a complicated task, especially when there are many by-products and co-products. It is recommended to avoid assessing multifunctional processes whenever possible (ISO, 2006b). However, in carbon utilisation processes multifunctionality issues are often raised. For example, carbon allowances need to be distributed between capture and utilisation industries if these are independent of each other. If, on the other hand, both capture and utilisation are seen as one process, concepts such as CO_2 pinch analysis can be used. The concept of carbon dioxide as an intermediate or utility stream is seen in the novel CO_2 pinch analysis approach. This type of analysis can help with the integration of the CO_2 source and sink (Martinez-Hernandez, Sadhukhan and Campbell, 2013; Ng *et al.*, 2015). Both examples require a different approach to solving multifunctionality. Whilst in the first case a physical or economical partitioning might be applicable, the second one could use a system wide method.

Different processes will have unique characteristics that require a specific solution (Wardenaar *et al.*, 2012). An example of this is when co-products are expressed in different physical quantities (mass, energy, etc.). While the mass allocation method would not be applicable, an economic method would. Although there is no one general solution, finding an approach for carbon utilisation to unify life cycle assessment (LCA) studies is still required. There are three main approaches on how to solve multifunctionality problems according to ISO 14040 (ISO, 2006a):

1. Subdivision of multifunctional processes

This method requires splitting a black-box process into individual processes that can be analysed individually. While this is a practical solution, when supply chains are very large (as they often are), this becomes a time-consuming task. When possible, subdivision should be the first step in allocation procedures according to Wardenaar *et al.* (2012). Allocation is avoided all together with this method. According to the ILCD handbook (European Commission, 2010), for this method to be applicable each individual process should be mono-functional.

2. System expansion (including substitution)

System expansion is based on expanding the product systems to include all co-products. It accounts for all flows or by-products that will enter an additional system. Instead of discarding these flows, they are used to displace economic flows in another system. Thus, the reduction of final impacts is considered for the new process (Von der Assen *et al.* 2013). **Figure 3.2** is an example of system expansion where surplus heat will be used in district heating system. It is also an illustration of foreground/background processes (Baumann and Tillman, 2004). This process is recommended by Von der Assen *et al.* (2013b) for carbon utilisation processes since at least one product will be part of a recycling loop.

The substitution (avoided burden) accounts for the process avoided when producing a co-product. While this method is not directly addressed in ISO 14044 (ISO, 2006b), it has been found in life cycle assessments (Santoyo-Castelazo and Azapagic, 2014). System expansion and avoided burden can often appear like similar methods. One of them adds processes and another one subtracts; but they are still substitution methods (Wardenaar *et al.*, 2012). The main setback for this method are the many assumptions made to determine what process should be avoided.

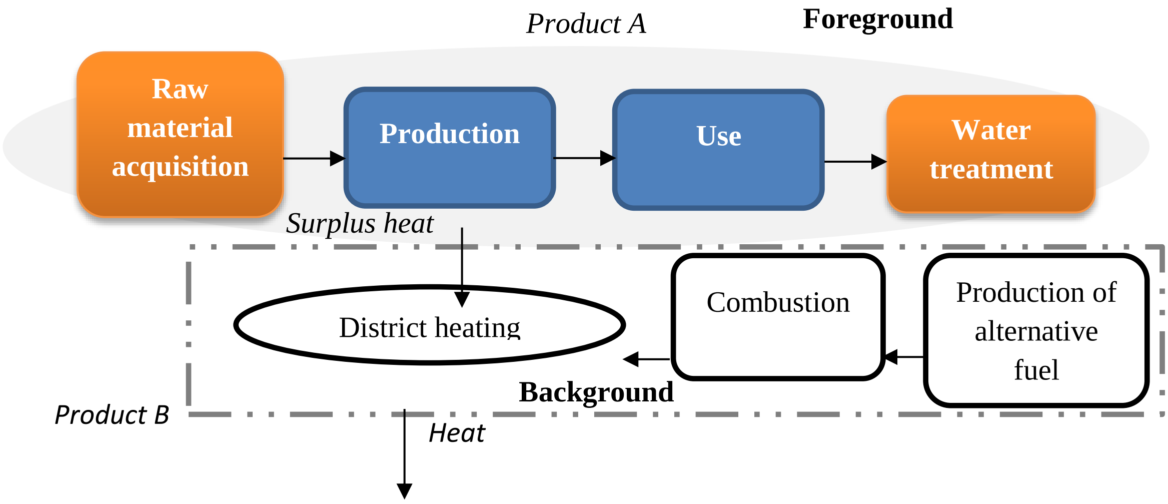


Figure 3.2 System expansion example for a district heating system, adapted from (Baumann and Tillman, 2004)

3. Allocation

While the definition or the role of allocation under ISO is not very well defined or clear; allocation is a common way to a addresses multifunctionality problems (Pelletier *et al.*, 2015).

Allocation gives a value in mass, monetary and/or energetic to by-products that otherwise would be fully assigned to the product. With this method, allocated values are subtracted from a final indicator result; which will only give a result for the product (Baumann and Tillman, 2004).

ISO 14040 (ISO, 2006a) favours physical partitioning as an allocation method. This is one the easiest and most straightforward methods. It only requires identifying a common characteristic between the product and the co-products to allocate. The difficulties arise when products and co-products have different functions (Wardenaar *et al.*, 2012). As an example: in carbon capture, electricity would be the product and CO_2 a waste turned into a non-waste thus functioning as a co-product with its own independent function.

Economical partitioning functions in the same way as physical. It takes the economic value of the product and by-product to allocate instead of taking a physical one. The main disadvantages of this method are the variability of prices in time and economic fluctuations by region (Baumann and Tillman, 2004). Basic guidelines on how to simplify or avoid allocation are shown in **Figure 3.3**.

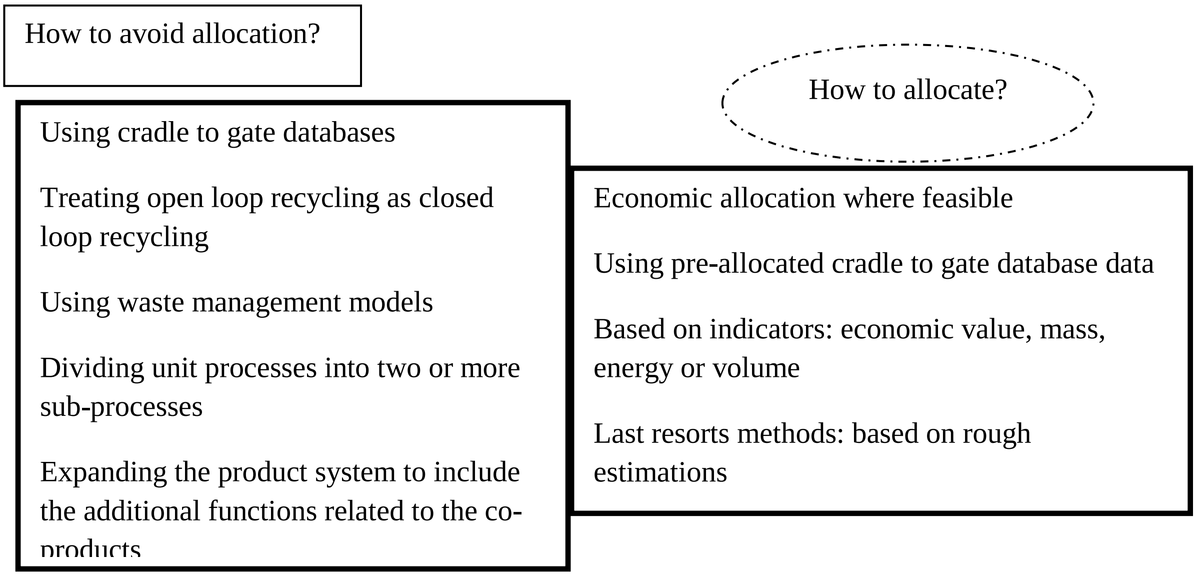


Figure 3.3 Guidelines from Baumann & Tillman (2004) on how to avoid allocation in a system and how to allocate if necessary

Solving multifunctionality issues goes beyond assigning burdens to flows; it also plays an important part in determining the type of assessment. In general, a life cycle assessment (LCA) is consequential or attributional. A consequential study is change-oriented. It quantifies the total impacts associated with changing a process and its effect down and up a supply chain. To study these changes, *system expansion* is said to maybe be the only method for consequential life cycle assessments (Pelletier *et al.*, 2015). On the other hand, attributional studies are descriptive. They attempt to describe all burdens associated to the life cycle of a product. It aims to work in absolute values in any given time. According to Pelletier *et al.* (2015) *substitution* is the most recommend method to allocate attributional studies.

There is a notable interest in the rules to solving multifunctionality problems for carbon utilisation life cycle assessments. Product specific results are often required for studies, thus applying a single evaluation such as system expansion is not always applicable. (Von der Assen *et al.* 2013b; von der Assen *et al.* 2014). In a system where capture is separated from utilisation, other allocation methods should be considered; this is applicable when

CO_2 is captured by one company and utilised by another. Following the ILCD handbook guidelines (European Commission, 2010), more than one method can be applied through one set of analysis if required as long as it is justified in the goal.

As an example, three different methods to solve multifunctionality were tested in Von der Assen *et al.* (2014): system expansion, avoided burden and economic allocation. These methods present an overview on how CO_2 captured can be accounted for within a supply chain and are used in **Chapter 4** for the environmental impact assessment framework. In this case, results showed that economic allocation is best but only in instances when a product specific analysis is required. Avoided burden was the least favourable method since all the environmental credits are assigned to only one product. In a multifunctional process only one product will obtain environmental benefits and the other product will be charged with the rest of impacts (Von der Assen *et al*. 2013b; Von der Assen *et al*. 2014).

Finally, there is also the consideration that allocating itself brings a level of uncertainty. As mentioned above, there is no “one size fits all” solution for all the products, leading to different interpretations. This has a direct effect on its ability to act as a decision-making tool. Allocation uncertainties have been discussed within the life cycle assessment community (Van der Voet *et al.* 2010; Mendoza Beltrán *et al*. 2014; Wardenaar *et al.* 2012). There are several statistical approaches often used to reduce uncertainties levels. These include standardization, sensitivity analysis, peer reviews and scenario modelling. While all options have their applications, scenario modelling is of particular interest in this research. Scenario analyses can be seen as ambiguous as they deal with many processes, allocation methods and designs (Mendoza Beltrán, Guinée and Heijungs, 2014). However, it can also be a tool to describe possible future conditions. By creating a range of scenarios, the influence of inputs and outputs in a system can be analysed (Björklund, 2002). There are still many variables and data gaps to fill in CO_2 utilisation processes, increasing its uncertainty. Creating scenarios can be a way to push a ‘hotspot’ assessment, this approach is discussed further in **Chapters 7** and **8.**

3.3.4 Life cycle impact assessments and its role in CO_2 utilisation systems

Life cycle impact assessment (LCIA) gives a value to the environmental burdens within a system. It is seen as the transformation between the quantities from the inventory to their actual impact. There can be as many impact categories as necessary and is dependent on the study. Many of these categories have been thoroughly studied and have accessible characterisation factors. For this work, the method CML-IA and the ReCiPe (H) model present the categories necessary for evaluation. All eleven of the main impact categories are discussed further below, as well as fossil fuel depletion from ReCiPe (H). **Figure 3.4** explains methodology for life cycle impact assessment according to Guinée *et al.* (2001), while **Figure 3.5** shows mandatory elements according to ISO 14041 (ISO, 1998).

It has been mentioned in literature (von der Assen *et al.*, 2016; Zhang *et al.*, 2017) that global warming and fossil fuel depletion are the impacts to analyse for CO_2 utilisation. A complete life cycle assessment is time consuming, expensive and multidisciplinary. Although this is true, the author believes that all main impacts should at least be addressed with at least a hotspot screening. Neglecting to do this could lead to potential environmental impacts in new areas that would counterbalance the benefit of reusing CO_2 as also mentioned by Azapagic & Cue (2015).

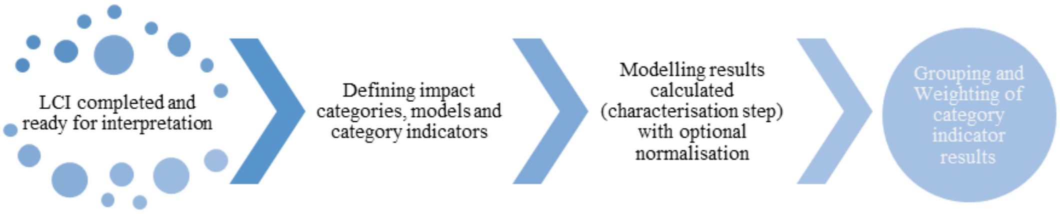


Figure 3.4 Life cycle impact assessment steps based on Guinee *et al.* (2001)

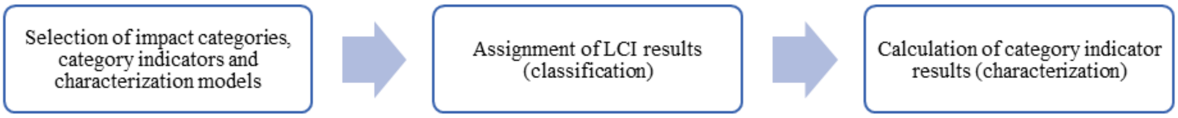


Figure 3.5 Life cycle impact assessment mandatory steps by ISO 14040 (ISO, 2006a)

Global warming

As one of the most studied impacts, climate change is often assessed with the characterisation model global warming potential (GWP) developed by the Intergovernmental Panel on Climate Change (IPCC) in 2001. It is defined as a “simplified index based upon radiative properties that can be used to estimate the potential future impacts of emissions of different gases upon the climate system in a relative sense” (Houghton JT *et al.*, 2001). The baseline characterisation model is set at a 100-year time horizon per kg carbon dioxide equivalent. This time horizon is the most commonly used in regulations. The indicator result is (kg CO_2 eq). In terms of CO_2 utilisation, all life cycle assessment studies and carbon accounting analyses should include this impact. The current aim of a CO_2 utilisation process is to convert CO_2 emissions into a useful chemical feedstock thus potentially averting emission. This conversion is measured by kg of CO_2 captured. Hence, when life cycle assessment is used as a carbon accounting tool, global warming must be measured. Since this is an impact category present in all life cycle assessment studies dedicated to CO_2 utilisation, the results from these studies are discussed throughout this work.

Abiotic depletion

This is an impact that is also discussed as it considers all non-living natural resources including energy (Guinée *et al*. 2001). Its scope is large enough to allow many differences in characterisation methods. Considering CML-IA method, the category indicator uses the ultimate reserves (all geological reserves) and extraction rates as baseline (Schneider *et al.* 2015). It is expressed in kg of minerals and fossil fuel extraction. The characterisation model is the abiotic depletion potential (ADP) per 1 kg Sb equivalent/kg extraction. The unit of indicator result is in (kg Sb eq). Particularly, availability of energy resources and its link with fossil fuels is of great importance in CO_2 utilisation studies. Because of this importance, the fossil fuel depletion factor from ReCiPe (H) model is also frequently used in this area as it excludes mineral extraction from depletion rates. This midpoint fossil depletion indicator result is expressed in (kg oil eq). Both abiotic depletion and fossil fuel depletion impact categories are used in CO_2 utilisation studies.

Fossil depletion factors can be used in CO_2 utilisation to determine the least fossil intensive energy source. In Von der Assen *et al.* (2015), fossil depletion scores range from 0 to 5 kg oil eq./kg H_2 depending on the H_2 source, directly link this value to the minimum fossil depletion of flexible polyurethane in a case study. While for CO_2 sources across Europe, in a study by Assen *et al.* (2016) values range from 0 to 0.46 (kg oil eq)/(kg CO_2 eq avoided) for point sources and 0.16 to 1.08 (kg oil eq) /(kg CO_2 eq avoided) for direct air capture (DAC).

Acidification

Acidification occurs when mainly ammonia (NH_3), sulphur dioxide (SO_2) and nitrogen oxides (NOx) are emitted to the atmosphere as pollutants and are then deposited to the soil causing changes in its PH (Roy *et al.* 2014). A decrease in pH can harm ecosystems, plant and animal species, as well as contributing to crumbling of building materials (Guinée *et al.* 2001; Roy *et al.* 2014). The characterisation factor most used is acidification potential (AP), which is defined as per each acidifying emission to the air in (kg SO_2 eq) as mentioned in the CML-IA method. There are some disadvantages when using this factor as it assumes that H^+ depositions are all within one same geographical zone, not considering the effects on a global scale (Roy *et al.* 2014). Studies by Azevedo *et al.* (2013) and Roy *et al.* (2014) present different methodologies to account for variability and uncertainty in the acidification potential (AP); however, the RAINS10 characterisation model mentioned in Guinée *et al*. (2001) is still used in most studies. Although there is still uncertainty in this factor, there are measurable benefits from monitoring acidification levels. Acid pollution measured in arctic regions has fallen since its industrial peak in the 1960's and 1970's (Kjær *et al.* 2016) driven by legislation and advancements in NOx and SOx removal technologies.

To the best of the author's knowledge there are no specific studies focused on acidification effects of CO_2 utilisation processes and few on carbon capture and storage. The scenarios for carbon and capture storage consider leakage from pipelines and storage sites having the potential to change the PH affecting marine ecosystems and zooplankton in particular (Halsband & Kurihara 2013; Queiros *et al.* 2015). For CO_2 utilisation there are studies that consider acidification as part of life cycle assessment indicators, examples of these are: Aresta & Galatola (1999) where dymethylcarbonate (DMC) production routes are compared, Jaramillo *et al.* (2009) where an enhanced oil recovery process is assessed and Bernard (2009) which consists of a study on the production of microalgae utilising CO_2. There is not as much focus in this impact category as there is in others such as global warming, leaving room for improvement in the assessments for CO_2 utilisation.

Eutrophication

Eutrophication occurs when there is an imbalance in macronutrients in the environment. An increase mainly in nitrogen (N) and phosphorus (P) levels can cause biomass levels to rise in ecosystems and can lead to depressed oxygen levels in water ecosystems (Guinée *et al.* 2001). To measure this impact from a midpoint level, life cycle assessment (LCA) practitioners including environmental product declarations (EPDs) use the characterisation baseline factor presented in CML-IA. This factor measures each eutrophying emission to air, water or soil in Kg PO_4 equivalents/kg emission. Other methods such as ReCiPe (H) can distinguish between marine aquatic and freshwater eutrophication by applying limiting nutrient factors N and P to specific regions. Nonetheless, midpoint impacts are still often calculated using the CML-IA method.

Eutrophication potential is often assessed in carbon capture and storage as part of a full life cycle assessment study. In a power plant with one of either post-combustion, pre-combustion and oxy-fuel carbon capture and storage, levels of NO_2 can reduce with capture; however, an increase in emissions throughout the rest of the carbon capture storage supply chain may not be sufficient to equal net emissions from a plant with no carbon capture (Singh, Strømman & E. Hertwich 2011; Singh, Strømman & E. G. Hertwich 2011; Zapp *et al*. 2012). No study was found that addresses whether CO_2 utilisation routes could lower eutrophication levels compared to a carbon capture and storage process or a conventional production route.

Stratospheric ozone depletion and photochemical oxidation

Stratospheric ozone depletion measures the thinning of the stratospheric ozone layer that allows harmful solar ultraviolet UV-B radiation to penetrate and reach the Earth’s troposphere and surface in larger quantities. The impacts range from human and animal health to damage to ecosystems, materials and biochemical cycles (Guinée *et al.* 2001). Chemicals that contain chlorine and bromine atoms are the main ozone depleting substances since they can slowly destroy ozone molecules by acting as free radical catalysts (Montzka *et al.* 2011). The unit of indicator result is defined as (kg CFC-11 eq) CML-IA. The baseline characterisation factor is ozone depletion potential in the steady state ($ODP_{\text{steady state}}$). Photochemical oxidation measures the increase of precursors of tropospheric ozone: NOx, volatile organic compounds (VOCs) and CO when using a midpoint approach. Tropospheric ozone is hazardous to human health in high concentrations (also known as ‘summer smog’) and can damage vegetation at lower concentrations (Stranddorf, Hoffmann and Schmidt, 2005). The characterisation factor is photochemical ozone creation potential (POCP) with a unit of indicator result of kg ethylene eq, using CML-IA and ReCiPe (H) method. Ethylene is the reference gas as it is one of the strongest ozone precursors of all volatile organic compounds (VOC´s) (Stranddorf, Hoffmann and Schmidt, 2005).

As is the case with other factors, excluding global warming and fossil depletion, there is little to no focus on carbon capture and storage or CO_2 utilisation. Stratospheric ozone depletion and photochemical oxidation impacts are only mentioned as part of integral life cycle assessment studies when referring to carbon capture (Singh, Strømman & E. G. Hertwich 2011; Veltman *et al.* 2010; Koornneef *et al.* 2012). These factors are barely mentioned in other CO_2 utilisation studies (von der Assen *et al.* 2015; Sternberg & Bardow 2015; Assen *et al.* 2016).

Human toxicity

This indicator measures the impact that toxic substances in the environment could have on human health. The characterisation factor by CML-IA for each emission of a toxic substance to water, air, and soil is (kg 1,4-DCB eq). There are other methods such as ReCiPe (H) that have an endpoint and midpoint approaches. Fine particulate matter is another important environmental factor that contributes to human burdens. Exposure to fine particulate matter is linked to lung cancer, reduced life expectancy, chronic respiratory and cardiovascular problems as well as complications during birth (Fantke *et al.*, 2015). The ReCiPe (H) model uses Disability Adjusted Life Years (Dalys) to measure human health damage due to fine particulate matter (diameter less than 10 µm) and non-methane organic compounds (NMVOC) equivalent for midpoint impacts (Goedkoop *et al.* 2009). However, it has been noticed that published studies related to electricity, carbon capture and CO_2 are rarely use an end-point since the method was still at early stages when the studies were published. The human toxicity indicator in life cycle assessments is not a replacement for complete health and safety studies, although it can be used as a pre-screening method for potential high toxicity contributors in the same way that global warming scores are used for detecting carbon hotspots.

Marine aquatic, Freshwater and Terrestrial Ecotoxicity

Ecotoxicity potential covers the effects of toxic substances on different aquatic and terrestrial ecosystems. Its area of protection includes the natural environmental (Stranddorf, Hoffmann and Schmidt, 2005). The characterisation factor used by CML-IA is (kg 1,4-DCB eq) and uses global ecotoxicity as baseline. According to (Stranddorf, Hoffmann and Schmidt, 2005) the number of toxic substances is that large that it cannot fit into defined groups. Overall, the normalisation includes impacts from organotin compounds, metals, organic substances/persistent organic pollutants (POP), and pesticides.

From the literature reviewed, ecotoxicity potentials are only mentioned as part of an integrated life cycle assessment studies. Carbon capture and storage studies include: Singh, Strømman & E. G. Hertwich (2011), Veltman *et al.* (2010), Koornneef *et al.* (2012). For CO_2 utilisation, they are mentioned even less: (Heijungs and Lenzen, 2014; Morales Mora *et al.*, 2016; von der Assen *et al.*, 2016; Zhang *et al.*, 2017). This is no different from the rest of impact categories, where mainly global warming and fossil depletion is assessed in utilisation scenarios.

Table 3.4 lists the characterisation factors and the units of the indicators for CML IA and the ReCiPe method. A full list of factors and units for all available life cycle impact assessment methodologies can be found in Sadhukhan *et al*. (2014).

Table 3.4 Characterisation factors and unit of indicators for CML IA and ReCiPe methods, adapted from Sadhukhan *(et al.* 2014)

Characterisation factors	Unit of indicator
Under CML IA	
Global warming potential	kg CO_2 equivalent
Acidification depletion potential	kg SO_2 equivalent
Eutrophication potential	kg phosphate equivalent
Ozone layer depletion potential	kg CFC-11 equivalent
Abiotic depletion potential, elements	kg Sb equivalent
Abiotic depletion potential, fossil	MJ
Freshwater aquatic ecotoxicity potential	kg DCB equivalent
Human toxicity potential	kg DCB equivalent
Marine aquatic ecotoxicity potential	kg DCB equivalent
Photochemical ozone creation potential	kg ethylene equivalent
Terrestric ecotoxicity potential	kg DCB equivalent
Under ReCiPe	
Climate change	kg CO_2 equivalent
Terrestrial acidification	kg SO_2 equivalent
Freshwater eutrophication potential	kg P equivalent
Ozone depletion potential	kg CFC-11 equivalent
Fossil depletion	kg oil equivalent
Freshwater ecotoxicity	kg DCB equivalent
Ionizing radiation	kg U235 equivalent
Marine ecotoxicity	kg DCB equivalent
Marine eutrophication	kg N equivalent
Metal depletion	kg Fe equivalent
Natural land transformation	m^2
Particulate matter formation	kg PM10 equivalent
Photochemical oxidant formation	kg NMVOC equivalent
Terrestrial ecotoxicity	Kg DCB equivalent
Water depletion	m^3

3.3.5 Interpretation and presentation: CO_2 utilisation

The last section of a life cycle assessment is intended to present life cycle inventory (LCI) or life cycle impact assessment (LCIA) results in a meaningful way. There is an on-going discussion whether results should not be limited to comply with only the goals of study as mentioned in ISO 14040 (ISO, 2006a). By doing this, important information might be missed. A better approach could be to open results to general findings, that can then be up for interpretation (Baumann & Tillman 2004). Some of the tools that are often used to analyse results include: dominance, contribution, Monte Carlo simulations, break-even and decision-making analysis (Simonen, 2014).

As mentioned previously, uncertainties along with data quality are problems to address in life cycle assessments. **Table 3.5** shows the most common uncertainties associated with the introduction stages of the life cycle assessment process that will lead to uncertain results. It is noted that inventory and characterisation phases are the most uncertain. ISO 14040 (ISO, 2006a) recommends to only use data quality assessment tools, but does not standardize the tools. As explained in the allocation section, scenario planning is an option for dealing with CO_2 utilisation process uncertainties.

Table 3.5 Types of uncertainty associated with the introduction phases in LCA. Based on Björklund (2002)

Uncertainty type	**LCA phases**				
	Goal and scope	Inventory	Choice of impact category	Classification	Characterisation
Data inaccuracy		X			X
Data gaps		X			X
Unrepresentative data		X			X
Model uncertainty		X			X
Uncertainty due to choices	X	X	X		X
Spatial variability		X			X
Temporal variability		X			X
Variability between objects/sources		X			X
Epistemological uncertainty	X	X			X
Mistakes	X	X	X	X	X
Estimation of uncertainty		X			X

3.4 Regulatory outlook for CO_2 utilisation and renewables in the UK

Any regulations that include/affect CO_2 utilisation technologies should be considered in any future scenarios. This is also closely linked to renewable energy targets for the UK. These renewable energy targets can allow for the inclusion of CO_2 utilisation technologies as part of the renewable energy agenda in the future. Having a decarbonised grid mix can also lower energy penalties for utilisation scenarios and change the CO_2

sources map. This section explores this further, diving into the current legislation and future challenges of these type of processes in the UK that could affect large-scale deployment.

3.4.1 Carbon capture and storage regulations in the UK

For a while, carbon capture and storage was an important part of the UK's carbon reduction agenda. It was included in the Energy Act created in 2008 and followed the EU CSS Directive Framework. This act introduced guidelines for the safe offshore sequestration of carbon. The UK Electricity Act of 1987 was also amended to include that all new combustion plants over 300MW should include capture facilities. To push carbon capture and storage (CCS) further, the government launched a carbon capture and storage (CCS) commercialisation programme along with the Electricity Market Reform from 2011-2012. In total it allocated £1bn of funding for four commercial scale carbon capture and storage projects (Carbon Capture & Storage Association, 2017). However, in November 2015, an unexpected statement was announced where funding for these projects had been withdrawn (House of Commons and Committee, 2016). Without any future government commitments imminent, the public industry of CCS is on hold for now. This does not mean that there will not be interest from the private sector; however, it is unlikely to see complete funding for large-scale deployment for carbon capture and storage (CCS) in the near future, at least in the UK.

3.4.2 CO_2 utilisation regulations in the UK

Currently, there is no legislation set in place for carbon capture and utilisation, recycling or similar terms. While the government's attention has been drawn to carbon capture and storage (CCS), carbon recycling has presented an opportunity to introduce a new concept to the market. This 'new concept' brings with it new challenges that lack specific regulations. There are research council projects like CO_2 chem and the Centre for Low Carbon Futures that focus on the opportunities of using carbon feedstocks by 2050. These centres push towards including carbon recycling in government policies as well as creating networks through research, private and public sector.

The question is, if there is an open space for new regulations for carbon recycling, what should these be? One of the highly contested issues is the definition of the carbon stream to be used. Is this considered a waste stream, a recycled stream, a feedstock or a utility? How this carbon dioxide is defined will determine allocation rules that will have an impact on environmental burdens and costs of the stream. The Waste Framework Directive (WFD) defines the concept of waste as any substance or object set out in Annex 1 of Directive 91/156/EEC, which the holder discards, intends, or is required to discard (discard includes disposal, recycling and or recovery). Although this concept has been discussed greatly, the basic definition has not changed throughout the years. However, it has been necessary to clarify and explain when a waste is no longer a waste and becomes either a new or a secondary raw material (Environment Agency, 2012).

To turn a carbon dioxide stream from a waste to a non-waste product, it must meet certain criteria for "end of waste" certification (Environment Agency, 2012):

- Waste should be fully recovered or recycled
- Unwanted substances should have been removed from the waste
- Recovered/recycled material should be fully suitable as a replacement for a non-waste material
- The waste should have a certain use after being fully recovered/recycled
- The recovered/recycled material should be used without posing greater risk to the environment and to human health than the non-waste material it replaces
- The waste is converted or transformed into a distinct product

If a carbon dioxide stream was to be considered a by-product, then it would also have to comply with Waste Framework Directive (WFD) regulations. In this case, it would have the same legal status as a product. The Directive also states that if a substance or object was not intentionally produced (residue) it can be considered a non-waste only if:

- Further use of the substance or object is certain
- The substance or object can be used directly without any further processing (other than normal industrial practice)
- The substance or object is produced as an integral part of the production process
- Further use is lawful (complies with all environmental and health protection requirements)

How these regulations would apply to carbon utilisation systems is discussed in **Chapter 8** as part of the general outlook for CO_2 utilisation sustainability.

Overall, including utilisation schemes as a low carbon energy source into the government's agenda could incentivise public and private research of this topic. It would also have the potential to be another technology on the renewable list if it is proven to comply with environmental and health regulations stipulated by Waste Framework Directive (WFD) and other applicable departments.

3.4.3 EU Emissions trading scheme (EU ETS) and its potential role on CO_2 utilisation

The first and biggest carbon-trading scheme was created by the European Commission in 2005. It includes 31 countries and covers 45% of the EU's greenhouse gas emissions (European Commission, 2017b). This scheme works with a 'cap and trade' concept in which there is cap for emissions from a system. This cap is in the form of 'emission allowances' that lower each year to ensure emission reduction targets are met. The trade part allows trading this emission allowances. Each company must have enough allowances each year to pay for their emissions or pay a tax. There is the option to buy more allowances from companies that have extras or from international credits. The allowances are traded through auctioning. To make this system work emission allowances are set every year in a single EU cap. The 2013 cap was set at 2,084,301,854 allowances and decreases each year by a linear factor of 1.74 %. Each allowance is equal to 1 tonne of CO_2 or the equivalent of two more powerful greenhouse gases, perfluorocarbon (PFCs) and nitrous oxide (N_2O). According to the European Commission (2017), having a robust carbon price has proven beneficial. By 2020, emissions will be 21 % lower than in 2005 and with the aim of lowering to 43% by 2030. Participation in the EU emission trading scheme (EU ETS) is mandatory for companies in specific sectors (**Table 3.6**).

Table 3.6 Sector, and gases covered by EU emission trading scheme (EU ETS), adapted from European Commission (2017b)

Industrial Sector	Gases covered
Power and heat generation	Carbon dioxide
Energy intensive industries: Oil refineries, steel works, production of iron, aluminium, metals, cement, lime, glass ceramics, pulp, paper, cardboard, acids and bulk organic chemicals	Carbon dioxide
Commercial aviation	Carbon dioxide
Aluminium production	Nitrous oxide
Nitric, adipic and glyoxylic acid and glyoxal production	Perflourocarbons (PFCs)

Part of the European Commission's efforts to tackling climate change is to support low carbon technologies that can fit into EU emission trading scheme (EU ETS). Programs like NER 300 are designed to fund projects by allocating emission allowances to low carbon initiatives. The name of this project comes from the sale of 300 million allowances to be distributed to new projects. Other initiatives include the European Economic Recovery Programme, Strategic Energy Technology Set and the Global Energy Efficiency and Renewable Energy Fund. These programs support carbon capture and storage and are pushing for recognising it as a legitimate emission reduction technology (European Commission, 2017a). Achieving this would allow carbon capture and storage to be part of the EU emission trading scheme (EU ETS) program. Whilst carbon capture and storage still has support in the EU (excluding the UK that stopped its funding for planned projects), carbon dioxide utilisation is not yet on the political agenda. For it to be considered as part of the trading scheme program it would have to be accepted first as an emission reduction technology. The interest in carbon capture and storage could start to pave the way for technologies with similar characteristics, such as utilisation.

3.4.4 Government and renewables

The UK government has been committed to increasing renewable energy deployment. It is seen as an opportunity to increase energy security whilst meeting carbon reduction targets. By 2020, 20% of the energy demand should be met with renewables. By 2030, it could reach 30-45% as targeted by the Climate Change Committee (CCC). However, this committee does acknowledge that cost reductions and sustainable economic growth are necessary to reach this target (BIS, 2015). As fossil fuel prices become more unstable, the need for alternative energy becomes greater to compensate this instability. So far, the most cost effective plan designed by the government to reach these targets is the Electricity Market Reform (EMR) (BIS, 2015). The EMR is a policy aimed at incentivising low carbon electricity investment through the Energy Act presented in 2013 (ofgem, 2017).

The Department for Business, Innovation & Skills (BIS) set out its own potential roadmap to deliver 234 TWh (eq. of 15%) of renewable energy in 2020 where eight technologies could meet 90% of the necessary generation (**Table 3.7**).

Table 3.7 Renewable energy roadmap for 2020 to deliver 234 TWh (DECC, 2011)

Renewable energy sources	Electricity generation (TWh)
Onshore wind	24 to 32
Offshore wind	33 to 58
Biomass electricity	32 to 50
Marine	1
Biomass heat (non-domestic)	36 to 50
Air source and ground source heat pumps (non-domestic)	16 to 22
Renewable transport	up to 48
Others (including hydro, geothermal, solar and domestic heat)	14
Total	234

Offshore wind

The UK has great offshore wind deployment capacity. It is abundant enough that it could be exported to trading partners, creating new jobs and increasing energy security (BIS, 2015). The UK is part of the 'All Island Approach' agreeing to co-operate on exploiting marine aquatic and wind resources.

There are also uncertainties on whether these targets can be met. Future energy demands, cost of technologies and level of renewable energy deployment contribute to these uncertainties.

Beyond 2020, there is a 2050 goal for carbon budgets but not for renewable energy deployment. However, both are directly linked since carbon emissions cuts cannot be achieved without integrating renewables. The climate change act signed in 2008 commits to a carbon reduction (Including greenhouses gases (GHG)) of at least 80% from 1990 levels in the UK. According to the Climate Change Committee (CCC), up to the third carbon budget, reductions are on target. In 2015 there was a reported 38% carbon emission reduction from 1990 levels. To keep up with the goal, domestic emissions would need to reduce by at least 3% per year. By 2050 no scenario should have unabated coal fired generation (Committe on Climate Change, 2016). According to the optimistic scenario created by BIS (2015), decarbonisation of the grid could reduce up to 16 million tonnes of CO_2 in 2050. This scenario relies on the government's reform of the electricity market, reinforcing the need for low carbon energy policies in the United Kingdom.

3.4.5 Renewable and low carbon energy policy and Brexit

For the last four decades, the UK has collaborated with the EU and operated under EU regulations. By the end of March 2017, the United Kingdom is set to begin negotiations to leave the European Union. After Brexit is complete, the UK will no longer have to comply with the energy targets set under the EU Renewable Energy Directive, which currently are set at 15% from renewable sources by 2020. There is also the uncertainty of what will happen with other schemes, such as EU Emissions Trading Scheme (EU ETS), single market for energy and the EU Industrial Emissions Directive (EU ED). With schemes like EU ED, there was the possibility of 'trading' opportunities if cost of domestic deployment of renewables were to rise for the UK public. (Climate Change Committee (2016) and DECC (2011)).

Other issues such as labour legislations for multi-nationals working in the North Sea will have to be revised. Contracts and restrictions for long-term supply of UK source gas might also be an issue for Brexit. It is also expected that at least initially; EU laws will have to be converted or adapted into UK laws in a complex process (Norton Rose Fulbright 2016).

There are also other issues such as a new independent role in the United Nations Framework Convention on Climate Change (UNFCCC) with new emission targets to set. However, even if EU rules were to apply no longer, the UK is still bound by national and international legislations, including the Climate Change Act from 2008 and the World Trade Organization (WTO) rules. According to the Committe on Climate Change (2016), the UK´s climate goals have not changed and the 2050 target for reducing greenhouse gas emissions is still in place. In order to comply with these commitments, the Committee acknowledges the need to keep EU schemes or replicate them at a national level. These schemes include product and efficiency standards, vehicle and energy efficient product standards, labelling, and the F-gas regulation. Regulations will need to be matched to EU equivalents if carbon targets are to be met.

After Brexit, the UK will have more flexibility to design its own plans for the energy sector since it would no longer be attached to the EU. It also presents an opportunity to strengthen policies if the carbon budgets are to be met. The Committee on Climate Change (2016) agrees that following EU reduction targets would only deliver half of the emission reduction required. This does leave a space for government to close the target gap with internal policies and plans. However, there are also big challenges to overcome if the gap is to be closed. A large portion of the funding for new energy infrastructure came from the EU; the lack of this funding will have an impact on future energy projects if no other funding bodies are found (Norton Rose Fulbright 2016). In only 2015, the European Investment Bank (2017) invested 7.8 billion EUR, where energy projects accounted for 24% of this funding. From 2011 to 2015, the IEB invested over 29 billion EUR in the UK economy, with 28% assigned to the energy sector. To comply with the fifth carbon budget (2015-2030), the power sector will need to contribute with 67% CO_2 reduction (Climate Change Committee 2016).

3.5 Chapter three summary

This Chapter reviews the information available that links sustainability and carbon dioxide utilisation. An overview was made of available literature for methanol and urea production from CO_2. In total, 145 related studies were found. Out of this total, 35 studies are performance specific, whether it is life cycle assessment (LCA), techno-economical or carbon accounting. This highlighted the large range of studies that aim to measure the potential of a CO_2 utilisation process through different indicators. There were few studies found that focused on the methodological aspects of assessing utilisation processes. The most complete assessment was found in Von der Assen *et al.* (2013b), however it focuses only on global warming as an environmental impact indicator. This framework has been the base for more recent studies in the area (Sternberg and Bardow, 2015; Morales Mora *et al.*, 2016; von der Assen *et al.*, 2016; Zhang *et al.*, 2017). This lead to the search on how an environmental or sustainability study with a life cycle thinking approach would vary for if it came from a recovered CO_2 stream.

The standards ISO 14040, 14041 and 14044 (ISO, 1998, 2006a, 2006b) are followed in all studies. From this, four main sections create a life cycle assessment (LCA): Goal and scope, life cycle inventory (LCI), life cycle impact assessment (LCIA) and interpretation. The main difference in goal and scope for a CO_2 utilisation process is the functional unit of choice. The two final products are used as functional units. For the life cycle inventory, the main challenge is data availability. There is a higher reliance on secondary data than for a conventional route that does not rely on recovered carbon dioxide. Specific allocation rules also apply to most CO_2 utilisation scenarios, Assen *et al.* (2016) recommend system expansion. The life cycle impact assessment phase is the most standard, the same impact categories as for conventional processes that do not use recovered carbon dioxide can be applicable. These can include (but are not limited to) climate change, eutrophication, acidification, human toxicity, fossil fuel depletion, stratospheric ozone depletion, abiotic depletion, photochemical oxidation and eco-toxicity. Of these impact categories, climate change and fossil fuel depletion are the most relevant according to Sternberg & Bardow (2015). Lastly, regulations for CO_2 utilisation and renewables in the UK are reviewed. Currently, there is no legislation set in place in the UK. In 2015, the funding for £1bn funding for carbon capture and storage projects in the UK was withdrawn. However, there is still an opportunity to include CO_2 utilisation as part of carbon mitigation agenda incentivising public and private research. There is still a target to meet in 2050, where emissions must reduce by 80% from 1990 levels. At European level, utilisation is not part of the EU Emissions Trading System (ETS) program, as it has not been accepted as an emission reduction technology. There is also the uncertainty of political changes such as Brexit, however it can also present an opportunity to strengthen policies if the carbon budgets are to be met; this could be an opportunity for newer technologies if there is funding for the energy sector.

3.5 Chapter three reference list

Abanades, J. C., Arias, B., Lyngfelt, A., Mattisson, T., Wiley, D. E., Li, H., Ho, M. T., Mangano, E. and Brandani, S. (2015) ‘Emerging CO2 capture systems’, *International Journal of Greenhouse Gas Control*, 40, pp. 126–166. doi: 10.1016/j.ijggc.2015.04.018.

Abbas, Z., Mezher, T. and Abu-Zahra, M. R. M. (2013a) ‘CO2 purification. Part I: Purification requirement review and the selection of impurities deep removal technologies’, *International Journal of Greenhouse Gas Control*. Elsevier Ltd, 16, pp. 324–334. doi: 10.1016/j.ijggc.2013.01.053.

Abbas, Z., Mezher, T. and Abu-Zahra, M. R. M. (2013b) ‘CO2 purification. Part II: Techno-economic evaluation of oxygen and water deep removal processes’, *International Journal of Greenhouse Gas Control*. Elsevier Ltd, 16, pp. 335–341. doi: 10.1016/j.ijggc.2013.01.052.

Abu-Zahra, M. R. M., Schneiders, L. H. J., Niederer, J. P. M., Feron, P. H. M. and Versteeg, G. F. (2007) ‘CO2 capture from power plants’, *International Journal of Greenhouse Gas Control*, 1(1), pp. 37–46. doi: 10.1016/S1750-5836(06)00007-7.

Alie, C., Backham, L., Croiset, E. and Douglas, P. L. (2005) ‘Simulation of CO2 capture using MEA scrubbing: a flowsheet decomposition method’, *Energy Conversion and Management*, 46(3), pp. 475–487. doi: 10.1016/j.enconman.2004.03.003.

Althaus, H., Chudacoff, M., Hischier, R., Jungbluth, N., Osses, M., Primas, A. and Hellweg, S. (2007) ‘Life cycle inventories of chemicals. ecoinvent report No.8, v2.0.’, *Final report ecoinvent data …*, (8), pp. 1–957.

Aresta, M., Dibenedetto, A. and Angelini, A. (2014) ‘Catalysis for the Valorization of Exhaust Carbon: from CO 2 to Chemicals, Materials, and Fuels. Technological Use of CO 2’, *Chemical Reviews*, 114(3), pp. 1709–1742. doi: 10.1021/cr4002758.

Aspelund, A. and Jordal, K. (2007) ‘Gas conditioning—The interface between CO2 capture and transport’, *International Journal of Greenhouse Gas Control*, 1(3), pp. 343–354. doi: 10.1016/S1750-5836(07)00040-0.

von der Assen, N. and Bardow, A. (2014) ‘Life cycle assessment of polyols for polyurethane production using CO2 as feedstock: insights from an industrial case study’, *Green Chemistry*, 16(6), p. 3272. doi: 10.1039/c4gc00513a.

von der Assen, N., Jung, J. and Bardow, A. (2013) ‘Life-cycle assessment of carbon dioxide capture and utilization: avoiding the pitfalls’, *Energy & Environmental Science*, 6(9), p. 2721. doi: 10.1039/c3ee41151f.

von der Assen, N., Müller, L. J., Steingrube, A., Voll, P. and Bardow, A. (2016) ‘Selecting CO2 Sources for CO2 Utilization by Environmental-Merit-Order Curves’, *Environmental Science and Technology*, 50(3), pp. 1093–1101. doi: 10.1021/acs.est.5b03474.

von der Assen, N., Voll, P., Peters, M. and Bardow, A. (2014) ‘Life cycle assessment of CO2 capture and utilization : a tutorial review’, *Chem Soc Rev*, 43, pp. 7982–7994. doi: 10.1039/C3CS60373C.

Azapagic, A. and Cue, R. M. (2015) ‘Carbon capture , storage and utilisation technologies : A critical analysis and comparison of their life cycle environmental impacts’, 9, pp. 82–102.

Baciocchi, R., Storti, G. and Mazzotti, M. (2006) ‘Process design and energy requirements for the capture of carbon dioxide from air’, *Chemical Engineering and Processing: Process Intensification*, 45(12), pp. 1047–1058. doi: 10.1016/j.cep.2006.03.015.

Bansode, A. and Urakawa, A. (2014) ‘Towards full one-pass conversion of carbon dioxide to methanol and methanol-derived products’, *Journal of Catalysis*. Elsevier Inc., 309, pp. 66–70. doi: 10.1016/j.jcat.2013.09.005.

Basavaraja, R. . and Jayanti, S. (2015) ‘Comparative analysis of four gas-fired, carbon capture-enabled power plant layouts’, *Clean Technologies and Environmental Policy*, 17(8), pp. 2143–2156.

Baumann, H. and Tillman, A.-M. (2004) *The Hitch Hiker’s Guide to LCA*. Studentlitteratur.

Bermúdez, J. M., Ferrera-Lorenzo, N., Luque, S., Arenillas, a. and Menéndez, J. a. (2013) ‘New process for producing methanol from coke oven gas by means of CO2 reforming. Comparison with conventional process’, *Fuel Processing Technology*. Elsevier B.V., 115, pp. 215–221. doi: 10.1016/j.fuproc.2013.06.006.

Bernard, O. (2009) ‘Policy Analysis Life-Cycle Assessment of Biodiesel Production from Microalgae’, pp. 6475–6481.

Berstad, D., Anantharaman, R. and Nekså, P. (2013) ‘Low-temperature CO2 capture technologies – Applications and potential’, *International Journal of Refrigeration*, 36(5), pp. 1403–1416. doi: 10.1016/j.ijrefrig.2013.03.017.

Bhandari, R., Trudewind, C. a. and Zapp, P. (2013) ‘Life cycle assessment of hydrogen production via electrolysis – a review’, *Journal of Cleaner Production*. Elsevier Ltd, 85, pp. 151–163. doi: 10.1016/j.jclepro.2013.07.048.

Bhavsar, S. and Veser, G. (2013) ‘Bimetallic Fe–Ni Oxygen Carriers for Chemical Looping Combustion’, *Industrial & Engineering Chemistry Research*, 52(44), pp. 15342–15352. doi: 10.1021/ie400612g.

Bičáková, O. and Straka, P. (2012) ‘Production of hydrogen from renewable resources and its effectiveness’, *International Journal of Hydrogen Energy*. Elsevier Ltd, 37(16), pp. 11563–11578. doi: 10.1016/j.ijhydene.2012.05.047.

Bicer, Y. and Dincer, I. (2016) ‘Life cycle assessment of nuclear-based hydrogen and ammonia production options: A comparative evaluation’, *International Journal of Hydrogen Energy*. Elsevier Ltd, pp. 1–12. doi: 10.1016/j.ijhydene.2017.02.002.

Bicer, Y., Dincer, I., Vezina, G. and Raso, F. (2017) ‘Impact Assessment and Environmental Evaluation of Various Ammonia Production Processes’, *Environmental Management*, 59(5), pp. 842–855. doi: 10.1007/s00267-017-0831-6.

BIS (2015) ‘Industrial Decarbonisation & Energy Efficiency Roadmaps to 2050: Cross Sector Summary’, (March), p. 31.

Björklund, A. E. (2002) ‘Survey of approaches to improve reliability in lca’, *The International Journal of Life Cycle Assessment*, 7(2), pp. 64–72. doi: 10.1007/BF02978849.

Boot-Handford, M. E., Abanades, J. C., Anthony, E. J., Blunt, M. J., Brandani, S., Mac Dowell, N., Fernández, J. R., Ferrari, M.-C., Gross, R., Hallett, J. P., Haszeldine, R. S., Heptonstall, P., Lyngfelt, A., Makuch, Z., Mangano, E., Porter, R. T. J., Pourkashanian, M., Rochelle, G. T., Shah, N., Yao, J. G. and Fennell, P. S. (2014) ‘Carbon capture and storage update’, *Energy & Environmental Science*, 7(1), p. 130. doi: 10.1039/c3ee42350f.

Boretti, A. (2013) ‘Renewable hydrogen to recycle CO2 to methanol’, *International Journal of Hydrogen Energy*. Elsevier Ltd, 38(4), pp. 1806–1812. doi: 10.1016/j.ijhydene.2012.11.097.

Bose, A., Jana, K., Mitra, D. and De, S. (2015) ‘Co-production of power and urea from coal with CO2 capture: Performance assessment’, *Clean Technologies and Environmental Policy*. Springer Berlin Heidelberg, 17(5), pp. 1271–1280. doi: 10.1007/s10098-015-0960-7.

Burgess, A. A. and Brennan, D. J. (2001) ‘Application of life cycle assessment to chemical processes’, 56, pp. 2589–2604.

Butlin, J. (1989) ‘Our common future. By World commission on environment and development. (London, Oxford University Press, 1987, pp.383 £5.95.)’, *Journal of International Development*, 1(2), pp. 284–287. doi: 10.1002/jid.3380010208.

Byrnes, B. H. (1990) ‘Environmental effects of N fertilizer use - An overview’, *Fert.Res.*, 26, pp. 209–215. doi: 10.1007/BF01048758.

Carbon Capture & Storage Association (2017) *CCS Policy and Regulation*.

Cetinkaya, E., Dincer, I. and Naterer, G. F. (2012) ‘Life cycle assessment of various hydrogen production methods’, *International Journal of Hydrogen Energy*. Elsevier Ltd, 37(3), pp. 2071–2080. doi: 10.1016/j.ijhydene.2011.10.064.

Commission, C. E. (2014) *Low carbon fuel standard*.

Committe on Climate Change (2016) *The Climate Change Act and UK regulations*.

Compernolle, T., Welkenhuysen, K., Huisman, K., Piessens, K. and Kort, P. (2017) ‘Off-shore enhanced oil recovery in the North Sea: The impact of price uncertainty on the investment decisions’, *Energy Policy*, 101, pp. 123–137. doi: 10.1016/j.enpol.2016.11.034.

Connect, S. (2014) *Carbon dioxide sequestration by direct mineral carbonation with carbonic acid*.

Corsten, M., Ramírez, A., Shen, L., Koornneef, J. and Faaij, A. (2013) ‘Environmental impact assessment of CCS chains – Lessons learned and limitations from LCA literature’, *International Journal of Greenhouse Gas Control*. Elsevier Ltd, 13, pp. 59–71. doi: 10.1016/j.ijggc.2012.12.003.

CRI (2017) *Reduction of Carbon Emissions*.

Cuéllar-Franca, R. M. and Azapagic, A. (2014) ‘Carbon capture, storage and utilisation technologies: A critical analysis and comparison of their life cycle environmental impacts’, *Journal of CO2 Utilization*, 9, pp. 82–102. doi: 10.1016/j.jcou.2014.12.001.

DECC (2011) ‘UK Renewable Energy Roadmap’, *Carbon*, 5(July), pp. 293–298. doi: 10.1021/es00108a605.

DEFRA (2015) ‘The British Survey of Fertiliser Practice - Fertiliser use on farm for the 2014 crop year’, (April), p. 6.

Department of Energy, N. E. T. L. (2012) *NETL Life Cycle Inventory Data – Unit Process: CO2 Pipeline Construction. U.S.*

Dincer, I. and Acar, C. (2017) ‘Innovation in hydrogen production’, *International Journal of Hydrogen Energy*. Elsevier Ltd, 42(22), pp. 14843–14864. doi: 10.1016/j.ijhydene.2017.04.107.

Dincer, I. and Zamfirescu, C. (2012) ‘Sustainable hydrogen production options and the role of IAHE’, *International Journal of Hydrogen Energy*, 37(21), pp. 16266–16286. doi: 10.1016/j.ijhydene.2012.02.133.

Dufour, J., Serrano, D. P., Gálvez, J. L., González, A., Soria, E. and Fierro, J. L. G. (2012) ‘Life cycle assessment of alternatives for hydrogen production from renewable and fossil sources’, *International Journal of Hydrogen Energy*, 37(2), pp. 1173–1183. doi: 10.1016/j.ijhydene.2011.09.135.

Dumitrache, D. C., Inoan, I. and De Schutter, B. (2014) ‘An analytic model for a isotope separation process by cryogenic distillation’, *Journal of Process Control*, 24(5), pp. 463–474.

doi: 10.1016/j.jprocont.2013.12.005.

Edrisi, A., Mansoori, Z. and Dabir, B. (2016) 'Urea synthesis using chemical looping process - Techno-economic evaluation of a novel plant configuration for a green production', *International Journal of Greenhouse Gas Control*. Elsevier Ltd, 44, pp. 42–51. doi: 10.1016/j.ijggc.2015.10.020.

Environment Agency (2012) 'Guidance on The Legal Definition of Waste and Its Application', (August), p. 69.

Esmaili, P., Dincer, I. and Naterer, G. F. (2015) 'Development and analysis of an integrated photovoltaic system for hydrogen and methanol production', *International Journal of Hydrogen Energy*, 40(34), pp. 11140–11153. doi: 10.1016/j.ijhydene.2015.04.077.

European Commission (2010) *International Reference Life Cycle Data System (ILCD) Handbook -- General guide for Life Cycle Assessment -- Detailed guidance, Constraints*. doi: 10.2788/38479.

European Commission (2017a) *Research and Innovation, technical background*.

European Commission (2017b) *The EU Emissions Trading System (EU ETS)*.

Eurostat (2017) *Greenhouse gas emission statistics*.

Fantke, P., Jolliet, O., Evans, J. S., Apte, J. S., Cohen, A. J., Hänninen, O. O., Hurley, F., Jantunen, M. J., Jerrett, M., Levy, J. I., Loh, M. M., Marshall, J. D., Miller, B. G., Preiss, P., Spadaro, J. V., Tainio, M., Tuomisto, J. T., Weschler, C. J. and McKone, T. E. (2015) 'Health effects of fine particulate matter in life cycle impact assessment: findings from the Basel Guidance Workshop', *The International Journal of Life Cycle Assessment*, 20(2), pp. 276–288. doi: 10.1007/s11367-014-0822-2.

FAO (2015) *World fertilizer trends and outlook to 2018, Food and Agriculture Organization of United Nations*.

Favre, E. (2011) 'Membrane processes and postcombustion carbon dioxide capture: Challenges and prospects', *Chemical Engineering Journal*, 171(3), pp. 782–793. doi: 10.1016/j.cej.2011.01.010.

Van der Giesen, C., Meinrenken, C. J., Kleijn, R., Sprecher, B., Lackner, K. S. and Kramer, G. J. (2017) 'A Life Cycle Assessment Case Study of Coal-Fired Electricity Generation with Humidity Swing Direct Air Capture of CO 2 versus MEA-Based Postcombustion Capture', *Environmental Science & Technology*, 51(2), pp. 1024–1034. doi: 10.1021/acs.est.6b05028.

Global CCS institute (2014) *CO2 pipeline infraestructure*.

Godec, M. L., Kuuskraa, V. A. and Dipietro, P. (2013) 'Opportunities for Using Anthropogenic CO 2 for Enhanced Oil Recovery and CO 2 Storage', *Energy & Fuels*, 27, p. 4183−4189.

Guinée, J. B., Gorrée, M., Heijungs, R., Huppes, G., Kleijn, R., De Koning, A., Van Oers, L., Sleeswijk, A. W., Suh, S. and Udo de Haes, H. A. (2001) *Life Cycle Assessment-An operational guide to the ISO standards Part 2A*.

Haghpanah, R., Majumder, A., Nilam, R., Rajendran, A., Farooq, S., Karimi, I. A. and Amanullah, M. (2013) 'Multiobjective Optimization of a Four-Step Adsorption Process for Postcombustion CO 2 Capture Via Finite Volume Simulation', *Industrial & Engineering Chemistry Research*, 52(11), pp. 4249–4265. doi: 10.1021/ie302658y.

Hasler, K., Broring, S., Omta, S. W. F. and Olf, H.-W. (2015) 'Life cycle assessment (LCA) of different fertilizer product types', *European Journal of Agronomy*, 69, pp. 41–45.

Heijungs, R., Huppes, G. and Guin??e, J. B. (2010) 'Life cycle assessment and sustainability analysis of products, materials and technologies. Toward a scientific framework for sustainability life cycle analysis', *Polymer Degradation and Stability*, 95(3), pp. 422–428. doi: 10.1016/j.polymdegradstab.2009.11.010.

Heijungs, R. and Lenzen, M. (2014) 'Error propagation methods for LCA - A comparison', *International Journal of Life Cycle Assessment*, 19(7), pp. 1445–1461. doi: 10.1007/s11367-014-0751-0.

Ho, M. T., Allinson, G. W. and Wiley, D. E. (2011) 'Comparison of MEA capture cost for low CO2 emissions sources in Australia', *International Journal of Greenhouse Gas Control*. Elsevier Ltd, 5(1), pp. 49–60. doi: 10.1016/j.ijggc.2010.06.004.

Hopkinson, D., Luebke, D., Li, Z. and Chen, S. (2014) 'Solvent Optimization of Conventional Absorption Processes for CO 2 Capture from Postcombustion Flue Gases', *Industrial & Engineering Chemistry Research*, 53(17), pp. 7149–7156. doi: 10.1021/ie403869y.

Houghton JT, Y, D., DJ, G., M, N., PJ, van der L., X, D., K, M. and C, J. (2001) 'Climate Change 2001: The Scientific Basis', *Climate Change 2001: The Scientific Basis*, p. 881. doi: 10.1256/004316502320517344.

House of Commons, E. and C. C. and Committee (2016) *Future of carbon capture and storage in the UK, Second Report of Session 2015–16*.

Huang, Y., Rebennack, S. and Zheng, Q. P. (2013) 'Techno-economic analysis and optimization models for carbon capture and storage: a survey', *Energy Systems*, 4(4), pp. 315–353. doi: 10.1007/s12667-013-0086-0.

IEA Greenhouse Gas R&D Programme (2008) *CO 2 CAPTURE IN THE CEMENT INDUSTRY*.

Im, D., Roh, K., Kim, J., Eom, Y. and Lee, J. H. (2015) 'Economic assessment and optimization of the Selexol process with novel additives', *International Journal of Greenhouse Gas Control*, 42, pp. 109–116. doi: https://doi.org/10.1016/j.ijggc.2015.08.001.

IPCC (2005) *Carbon Dioxide Capture and Storage*.

ISO (1998) *ISO 14041 Environmental Management-Life Cycle Assessment-Goal and Scope Definition and Inventory Analysis*.

ISO (2000) *ISO 14042:2000 Environmental management--Life cycle assessment-Life cycle impact assessment*.

ISO (2006a) *ISO 14040 Environmental Management- Life Cycle Assessment-Principles and Framework*.

ISO (2006b) *ISO 14044 Environmental management--Life Cycle Assessment--Requirements and guidelines*.

Kahrl, F., Li, Y., Su, Y., Tennigkeit, T., Wilkes, A. and Xu, J. (2010) 'Greenhouse gas emissions from nitrogen fertilizer use in China', *Environmental Science and Policy*. Elsevier Ltd, 13(8), pp. 688–694. doi: 10.1016/j.envsci.2010.07.006.

Kapetaki, Z., Brandani, P., Brandani, S. and Ahn, H. (2015) 'Process simulation of a dual-stage Selexol process for 95% carbon capture efficiency at an integrated gasification combined cycle power plant', *International Journal of Greenhouse Gas Control*, 39, pp. 17–26. doi: https://doi.org/10.1016/j.ijggc.2015.04.015.

Kar, S., Sen, R., Goeppert, A. and Prakash, G. K. S. (2018) 'Integrative CO 2 Capture and Hydrogenation to Methanol with Reusable Catalyst and Amine: Toward a Carbon Neutral Methanol Economy', *Journal of the American Chemical Society*, 140(5), pp. 1580–1583. doi: 10.1021/jacs.7b12183.

Karimi, M., Hillestad, M. and Svendsen, H. F. (2011) ‘Capital costs and energy considerations of different alternative stripper configurations for post combustion CO2 capture’, *Chemical Engineering Research and Design*. Institution of Chemical Engineers, 89(8), pp. 1229–1236. doi: 10.1016/j.cherd.2011.03.005.

Keith, D. W., Ha-Duong, M. and Stolaroff, J. K. (2006) ‘Climate strategy with CO2 capture from the air’, *Climatic Change*, 74(1–3), pp. 17–45. doi: 10.1007/s10584-005-9026-x.

Kempka, T., Plotz, M.-L., Schluter, R., Hamman, J., Deowan, S. A. and Azzam, R. (2011) ‘Carbon dioxide utilisation for carbamide production by application of the coupled UCG-urea process’, *Energy procedia*, 4, pp. 2200–2205.

Kempka, T., Plötz, M. L., Schlüter, R., Hamann, J., Deowan, S. A. and Azzam, R. (2011) ‘Carbon dioxide utilisation for carbamide production by application of the coupled UCG-Urea process’, in *Energy Procedia*. doi: 10.1016/j.egypro.2011.02.107.

Kolding, H., Fehrmann, R. and Riisager, A. (2012) ‘CO2 Capture technologies: Current status and new directions using supported ionic liquid phase (SILP) absorbers’, *Science China Chemistry*, 55(8), pp. 1648–1656. doi: 10.1007/s11426-012-4683-x.

Koornneef, J., Spruijt, M., Molag, M., Ramírez, A., Turkenburg, W. and Faaij, A. (2010) ‘Quantitative risk assessment of CO2 transport by pipelines--a review of uncertainties and their impacts.’, *Journal of hazardous materials*, 177(1–3), pp. 12–27. doi: 10.1016/j.jhazmat.2009.11.068.

Kotowicz, J. (2012) ‘Optimisation of the connection of membrane CCS installation with a supercritical coal- fi red power plant’, 38(x), pp. 118–127. doi: 10.1016/j.energy.2011.12.028.

Kuramochi, T., Ramírez, A., Turkenburg, W. and Faaij, A. (2012) ‘Comparative assessment of CO2 capture technologies for carbon-intensive industrial processes’, *Progress in Energy and Combustion Science*. Elsevier Ltd, 38(1), pp. 87–112. doi: 10.1016/j.pecs.2011.05.001.

Labus, K. and Machnikowski, J. (2014) ‘Separation of Carbon Dioxide from Coal Gasi fi cation-Derived Gas by Vacuum Pressure Swing Adsorption’.

Lackner, K. . (2013) ‘Thermodynamics of direct air capture of carbon dioxide’, *Energy*. doi: 10.1016/j.energy.2012.09.012.

Li, C., Yuan, X. and Fujimoto, K. (2014) ‘2014’, *Applied Catalysis A: General*. Elsevier B.V., 469, pp. 306–311. doi: 10.1016/j.apcata.2013.10.010.

Li, J., Zhang, H., Gao, Z., Fu, J., Ao, W. and Dai, J. (2017) ‘CO 2 Capture with Chemical Looping Combustion of Gaseous Fuels: An Overview’, *Energy & Fuels*, 31(4), pp. 3475–3524. doi: 10.1021/acs.energyfuels.6b03204.

Liu, Z., Grande, C. a., Li, P., Yu, J. and Rodrigues, A. E. (2011) ‘Multi-bed Vacuum Pressure Swing Adsorption for carbon dioxide capture from flue gas’, *Separation and Purification Technology*. Elsevier B.V., 81(3), pp. 307–317. doi: 10.1016/j.seppur.2011.07.037.

Liu, Z. and Green, W. H. (2013) ‘Experimental Investigation of Sorbent for Warm CO 2 Capture by Pressure Swing Adsorption’, *Industrial & Engineering Chemistry Research*, 52(28), pp. 9665–9673. doi: 10.1021/ie303534u.

Liu, Z., Wang, L., Kong, X., Li, P., Yu, J. and Rodrigues, A. E. (2012) ‘Onsite CO 2 Capture from Flue Gas by an Adsorption Process in a Coal-Fired Power Plant’, *Industrial & Engineering Chemistry Research*, 51(21), pp. 7355–7363. doi: 10.1021/ie3005308.

López Ortiz, A., Meléndez Zaragoza, M. J. and Collins-Martínez, V. (2016) ‘Hydrogen production research in Mexico: A review’, *International Journal of Hydrogen Energy*, 41(48), pp. 23363–23379. doi: 10.1016/j.ijhydene.2016.07.004.

Makhlouf, A., Serradj, T. and Cheniti, H. (2015) ‘Life cycle impact assessment of ammonia production in Algeria: A comparison with previous studies’, *Environmental Impact Assessment Review*. Elsevier Inc., 50, pp. 35–41. doi: 10.1016/j.eiar.2014.08.003.

Martinez-Hernandez, E., Sadhukhan, J. and Campbell, G. M. (2013) ‘Integration of bioethanol as an in-process material in biorefineries using mass pinch analysis’, *Applied Energy*, 104, pp. 517–526. doi: 10.1016/j.apenergy.2012.11.054.

Mendoza Beltrán, A., Guinée, J. and Heijungs, R. (2014) ‘A statistical approach to deal with uncertainty due to the choice of allocation methods in LCA’, *9th International Conference LCA of Food*, p. 10.

Methanol Institute (2011a) *Methanol Basics*.

Methanol Institute (2011b) *Methanol gasoline blends: Alternative Fuel for Today’s Automobiles and Cleaner Burning Octane for Today’s Oil Refinery*.

Middleton, R. S., Keating, G. N., Viswanathan, H. S., Stauffer, P. H. and Pawar, R. J. (2012) ‘Effects of geologic reservoir uncertainty on CO2 transport and storage infrastructure’, *International Journal of Greenhouse Gas Control*. Elsevier Ltd, 8, pp. 132–142. doi: 10.1016/j.ijggc.2012.02.005.

Middleton, R. S., Kuby, M. J., Wei, R., Keating, G. N. and Pawar, R. J. (2012) ‘A dynamic model for optimally phasing in CO2 capture and storage infrastructure’, *Environmental Modelling & Software*. Elsevier Ltd, 37, pp. 193–205. doi: 10.1016/j.envsoft.2012.04.003.

Morales Mora, M. a., Vergara, C. P., Leiva, M. a., Martínez Delgadillo, S. a. and Rosa-Domínguez, E. R. (2016) ‘Life cycle assessment of carbon capture and utilization from ammonia process in Mexico’, *Journal of Environmental Management*. Elsevier Ltd, 183, pp. 998–1008. doi: 10.1016/j.jenvman.2016.09.048.

Mukherjee, S., Kumar, P., Yang, A. and Fennell, P. (2015) ‘A systematic investigation of the performance of copper-, cobalt-, iron-, manganese- and nickel-based oxygen carriers for chemical looping combustion technology through simulation models’, *Chemical Engineering Science*, 130, pp. 79–91. doi: https://doi.org/10.1016/j.ces.2015.03.009.

Nandy, A., Loha, C., Gu, S., Sarkar, P., Karmakar, M. K. and Chatterjee, P. K. (2016) ‘Present status and overview of Chemical Looping Combustion technology’, *Renewable and Sustainable Energy Reviews*, 59, pp. 597–619. doi: https://doi.org/10.1016/j.rser.2016.01.003.

NETL (2013) *Cradle-to-Gate Life Cycle Analysis Model for Alternative Sources of CO2*.

NETL (2015) *Cost and Performance Baseline for Fossil Energy Plants Volume 1a: Bituminous Coal and Natural Gas to Electricity Revision 3 (DOE/NETL-2010/1723),*.

Ng, D. K. S., Tan, R. R., Foo, D. C. Y. and El-Halwagi, M. M. (2015) ‘Process System Engineering Tools for Biomass Polygeneration Systems with Carbon Capture and Reuse’, in Ng, D. K. S., Tan, R. R., Foo, D. C. Y., and El-Halwagi, M. M. (eds) *Process Design Strategies for Biomass Conversion Systems*. Chichester, UK: John Wiley & Sons, Ltd, pp. 96–108. doi: 10.1002/9781118699140.

Ng, K. S., Zhang, N. and Sadhukhan, J. (2012a) ‘A graphical CO2 emission treatment intensity assessment for energy and economic analyses of integrated decarbonised production systems’, *Computers & Chemical Engineering*, 45, pp. 1–14. doi: 10.1016/j.compchemeng.2012.04.013.

Ng, K. S., Zhang, N. and Sadhukhan, J. (2012b) ‘Decarbonised coal energy system advancement through CO2 utilisation and polygeneration’, *Clean Technologies and Environmental Policy*, 14(3), pp. 443–451. doi: 10.1007/s10098-011-0437-2.

Ng, K. S., Zhang, N. and Sadhukhan, J. (2013) ‘Techno-economic analysis of polygeneration systems with carbon capture and storage and CO2 reuse', *Chemical Engineering Journal*, 219, pp. 96–108. doi: 10.1016/j.cej.2012.12.082.

Nikolic, V. M., Tasic, G. S., Maksic, A. D., Saponjic, D. P., Miulovic, S. M. and Marceta Kaninski, M. P. (2010) 'Raising efficiency of hydrogen generation from alkaline water electrolysis – Energy saving', *International Journal of Hydrogen Energy*. Elsevier Ltd, 35(22), pp. 12369–12373. doi: 10.1016/j.ijhydene.2010.08.069.

ofgem (2017) *Electricity Market Reform*.

Olah, G. a (2005) 'Beyond oil and gas: the methanol economy.', *Angewandte Chemie (International ed. in English)*, 44(18), pp. 2636–9. doi: 10.1002/anie.200462121.

Olah, G. a, Goeppert, A. and Prakash, G. K. S. (2009) 'Chemical recycling of carbon dioxide to methanol and dimethyl ether: from greenhouse gas to renewable, environmentally carbon neutral fuels and synthetic hydrocarbons.', *The Journal of organic chemistry*, 74(2), pp. 487–98. doi: 10.1021/jo801260f.

Olajire, A. A. (2010) 'CO2 capture and separation technologies for end-of-pipe applications – A review', *Energy*, 35(6), pp. 2610–2628. doi: https://doi.org/10.1016/j.energy.2010.02.030.

Ozbilen, A., Dincer, I. and Rosen, M. a. (2011) 'A comparative life cycle analysis of hydrogen production via thermochemical water splitting using a Cu–Cl cycle', *International Journal of Hydrogen Energy*. Elsevier Ltd, 36(17), pp. 11321–11327. doi: 10.1016/j.ijhydene.2010.12.035.

Pelletier, N., Ardente, F., Brandão, M., De Camillis, C. and Pennington, D. (2015) 'Rationales for and limitations of preferred solutions for multi-functionality problems in LCA: is increased consistency possible?', *International Journal of Life Cycle Assessment*, 20(1), pp. 74–86. doi: 10.1007/s11367-014-0812-4.

Pera-Titus, M. (2014) 'Porous Inorganic Membranes for CO 2 Capture: Present and Prospects', *Chemical Reviews*, 114(2), pp. 1413–1492. doi: 10.1021/cr400237k.

Pérez-Fortes, M., Bocin-Dumitriu, A. and Tzimas, E. (2014) 'CO2 utilization pathways: Techno-economic assessment and market opportunities', *Energy Procedia*. Elsevier B.V., 63(i), pp. 7968–7975. doi: 10.1016/j.egypro.2014.11.834.

Pérez-Fortes, M., Schöneberger, J. C., Boulamanti, A. and Tzimas, E. (2016) 'Methanol synthesis using captured CO2 as raw material: Techno-economic and environmental assessment', *Applied Energy*. Elsevier Ltd, 161, pp. 718–732. doi: 10.1016/j.apenergy.2015.07.067.

Petrescu, L., Bonalumi, D., Valenti, G., Cormos, A. M. and Cormos, C.-C. (2017) 'Life Cycle Assessment for supercritical pulverized coal power plants with post-combustion carbon capture and storage', *Journal of Cleaner Production*, 157, pp. 10–21.

Pipitone, G. and Bolland, O. (2009) 'Power generation with CO2 capture: Technology for CO2 purification', *International Journal of Greenhouse Gas Control*, 3(5), pp. 528–534. doi: https://doi.org/10.1016/j.ijggc.2009.03.001.

Pires, J. C. M., Martins, F. G., Alvim-Ferraz, M. C. M. and Simões, M. (2011) 'Recent developments on carbon capture and storage: An overview', *Chemical Engineering Research and Design*. Institution of Chemical Engineers, 89(9), pp. 1446–1460. doi: 10.1016/j.cherd.2011.01.028.

Pirngruber, G. D. and Leinekugel-le-cocq, D. (2013) 'Design of a Pressure Swing Adsorption Process for Postcombustion CO 2 Capture'.

Reese, M., Marquart, C., Malmali, M., Wagner, K., Buchanan, E., McCormick, A. and Cussler, E. L. (2016) 'Performance of a Small-Scale Haber Process', *Industrial and Engineering*

Chemistry Research, 55(13), pp. 3742–3750. doi: 10.1021/acs.iecr.5b04909.

Sadhukhan, J., Ng, K. S. and Hernandez, E. M. (2014) *Biorefineries and Chemical Processes: Design, Integration and Sustainability Analysis*. Chichester, UK: John Wiley & Sons, Ltd. doi: 10.1002/9781118698129.

Safi, R., Agarwal, R. K. and Banerjee, S. (2016) ‘Numerical simulation and optimization of CO 2 utilization for enhanced oil recovery from depleted reservoirs’, *Chemical Engineering Science*, 144, pp. 30–38. doi: 10.1016/j.ces.2016.01.021.

Santoyo-Castelazo, E. and Azapagic, A. (2014) ‘Sustainability assessment of energy systems: Integrating environmental, economic and social aspects’, *Journal of Cleaner Production*. Elsevier Ltd, 80, pp. 119–138. doi: 10.1016/j.jclepro.2014.05.061.

Sayah, A. K. and Sayah, A. K. (2011) ‘Wind-hydrogen utilization for methanol production: An economy assessment in Iran’, *Renewable and Sustainable Energy Reviews*. Elsevier Ltd, 15(8), pp. 3570–3574. doi: 10.1016/j.rser.2011.05.013.

Schach, M.-O., Schneider, R., Schramm, H. and Repke, J.-U. (2010) ‘Techno-Economic Analysis of Postcombustion Processes for the Capture of Carbon Dioxide from Power Plant Flue Gas’, *Industrial & Engineering Chemistry Research*, 49(5), pp. 2363–2370. doi: 10.1021/ie900514t.

SCOT (2017) *CO2 utilisation projects*.

Sharma, I., Hoadley, A. F. A., Mahajani, S. M. and Ganesh, A. (2016) ‘Multi-objective optimisation of a Rectisol^{TM} process for carbon capture’, *Journal of Cleaner Production*, 119, pp. 196–206. doi: https://doi.org/10.1016/j.jclepro.2016.01.078.

Simonen, K. (2014) *Life Cycle Assessment (PocketArquitecture)*. Routledge.

Singh, B., Strømman, A. H. and Hertwich, E. G. (2011) ‘Comparative life cycle environmental assessment of CCS technologies’, *International Journal of Greenhouse Gas Control*. Elsevier Ltd, 5(4), pp. 911–921. doi: 10.1016/j.ijggc.2011.03.012.

Skorek-Osikowska, A., Janusz-Szymańska, K. and Kotowicz, J. (2012) ‘Modeling and analysis of selected carbon dioxide capture methods in IGCC systems’, *Energy*, 45(1), pp. 92–100. doi: 10.1016/j.energy.2012.02.002.

Smitkova, M., Janíček, F. and Riccardi, J. (2011) ‘Life cycle analysis of processes for hydrogen production’, *International Journal of Hydrogen Energy*, 36(13), pp. 7844–7851. doi: 10.1016/j.ijhydene.2011.01.177.

Socolow, R. H.; Desmond, M. J. (2011) *Direct Air Capture of CO2 with Chemicals: A technology Assessment for the APS Panel on Public Affair*.

Srisang, W., Pouryousefi, F., Osei, P. A., Decardi-Nelson, B., Akachuku, A., Tontiwachwuthikul, P. and Idem, R. (2017) ‘Evaluation of the heat duty of catalyst-aided amine-based post combustion CO 2 capture’, *Chemical Engineering Science*, 170, pp. 48–57. doi: 10.1016/j.ces.2017.01.049.

Stamicarbon (2017) *Urea facts*.

Sternberg, A. and Bardow, A. (2015) ‘Power-to-What? – Environmental assessment of energy storage systems’, *Energy Environ. Sci.*, pp. 389–400. doi: 10.1039/C4EE03051F.

Stojić, D. L., Marčeta, M. P., Sovilj, S. P. and Miljanić, Š. S. (2003) ‘Hydrogen generation from water electrolysis—possibilities of energy saving’, *Journal of Power Sources*, 118(1–2), pp. 315–319. doi: 10.1016/S0378-7753(03)00077-6.

Stranddorf, H., Hoffmann, L. and Schmidt, A. (2005) *Impact categories, normalisation and* *weighting in LCA*.

Styring, P. and Jansen, D. (2011) *Carbon Capture and Utilisation in the green economy*. The Centre for Low Carbon Futures 2011.

Suh, S. and Huppes, G. (2005) 'Methods for Life Cycle Inventory of a product', *Journal of Cleaner Production*, 13(7), pp. 687–697. doi: 10.1016/j.jclepro.2003.04.001.

Suleman, F., Dincer, I. and Agelin-Chaab, M. (2015) 'Environmental impact assessment and comparison of some hydrogen production options', *International Journal of Hydrogen Energy*. Elsevier Ltd, 40(21), pp. 6976–6987. doi: 10.1016/j.ijhydene.2015.03.123.

Tang, Q., Shen, Z., Huang, L., He, T., Adidharma, H., Russell, A. G. and Fan, M. (2017) 'Synthesis of methanol from CO 2 hydrogenation promoted by dissociative adsorption of hydrogen on a Ga 3 Ni 5 (221) surface', *Physical Chemistry Chemical Physics*, 19(28), pp. 18539–18555. doi: 10.1039/C7CP03231E.

Tian, H., Siriwardane, R., Simonyi, T. and Poston, J. (2013) 'Natural Ores as Oxygen Carriers in Chemical Looping Combustion', *Energy & Fuels*, 27(8), pp. 4108–4118. doi: 10.1021/ef301486n.

Troy, S., Schreiber, A. and Zapp, P. (2016) 'Life cycle assessment of membrane-based carbon capture and storage', *Clean Technologies and Environmental Policy*. Springer Berlin Heidelberg, 18(6), pp. 1641–1654. doi: 10.1007/s10098-016-1208-x.

Trudewind, C. a., Schreiber, A. and Haumann, D. (2014) 'Photocatalytic methanol and methane production using captured CO2 from coal-fired power plants. Part I – a Life Cycle Assessment', *Journal of Cleaner Production*. Elsevier Ltd, 70, pp. 27–37. doi: 10.1016/j.jclepro.2014.02.014.

Vasudevan, S., Farooq, S., Karimi, I. A., Saeys, M., Quah, M. C. G. and Agrawal, R. (2016) 'Energy penalty estimates for CO2 capture: Comparison between fuel types and capture-combustion modes', *Energy*. Elsevier Ltd, 103, pp. 709–714. doi: 10.1016/j.energy.2016.02.154.

Versteeg, P. and Rubin, E. S. (2011) 'A technical and economic assessment of ammonia-based post-combustion CO2 capture at coal-fired power plants', *International Journal of Greenhouse Gas Control*, 5(6), pp. 1596–1605. doi: 10.1016/j.ijggc.2011.09.006.

van der Voet, E., Reid, Li. J. and Luo, L. (2010) 'Life-cycle assessment of biofuels, convergence and divergence', *Biofuels*, 1(3), pp. 435–449.

Wang, M., Wang, Z., Gong, X. and Guo, Z. (2014) 'The intensification technologies to water electrolysis for hydrogen production - A review', *Renewable and Sustainable Energy Reviews*. Elsevier, 29, pp. 573–588. doi: 10.1016/j.rser.2013.08.090.

Wardenaar, T., Van Ruijven, T., Beltran, A. M., Vad, K., Guinée, J. and Heijungs, R. (2012) 'Differences between LCA for analysis and LCA for policy: A case study on the consequences of allocation choices in bio-energy policies', *International Journal of Life Cycle Assessment*, 17(8), pp. 1059–1067. doi: 10.1007/s11367-012-0431-x.

Wattanaphan, P., Sema, T., Idem, R., Liang, Z. and Tontiwachwuthikul, P. (2013) 'Effects of flue gas composition on carbon steel (1020) corrosion in MEA-based CO2 capture process', *International Journal of Greenhouse Gas Control*. Elsevier Ltd, 19, pp. 340–349. doi: 10.1016/j.ijggc.2013.08.021.

Weimer, T., Berger, R., Hawthorne, C. and Abanades, J. C. (2008) 'Lime enhanced gasification of solid fuels: Examination of a process for simultaneous hydrogen production and CO2 capture', *Fuel*, 87(8–9), pp. 1678–1686. doi: 10.1016/j.fuel.2007.08.023.

Xiang, X., Guo, L., Wu, X., Ma, X. and Xia, Y. (2012) 'Urea formation from carbon dioxide and ammonia at atmospheric pressure', *Environmental Chemistry Letters*, 10(3), pp. 295–300. doi: 10.1007/s10311-012-0366-2.

Xu, G., Liang, F., Yang, Y., Hu, Y., Zhang, K. and Liu, W. (2014) 'An improved CO2 separation and purification system based on cryogenic separation and distillation theory', *Energies*, 7(5), pp. 3484–3502. doi: 10.3390/en7053484.

Xu, G., Yang, Y., Ding, J., Li, S., Liu, W. and Zhang, K. (2013) 'Analysis and optimization of CO2 capture in an existing coal-fired power plant in China', *Energy*. Elsevier Ltd, 58, pp. 117–127. doi: 10.1016/j.energy.2013.04.012.

Yang, C.-J. and Jackson, R. B. (2012) 'China's growing methanol economy and its implications for energy and the environment', *Energy Policy*. Elsevier, 41, pp. 878–884. doi: 10.1016/j.enpol.2011.11.037.

Yang, S., Qian, Y. and Yang, S. (2016) 'Development of a Full CO 2 Capture Process Based on the Rectisol Wash Technology', *Industrial & Engineering Chemistry Research*, 55(21), pp. 6186–6193. doi: 10.1021/acs.iecr.6b00747.

Yoo, B.-Y., Choi, D.-K., Huh, C., Kang, S.-G. and Kim, I.-S. (2013) 'A Feasibility Study on CO2 Marine Transport in South Korea', *Energy Procedia*. Elsevier B.V., 37, pp. 3199–3211. doi: 10.1016/j.egypro.2013.06.207.

Yoo, C.-J., Lee, D.-W., Kim, M.-S., Moon, D. J. and Lee, K.-Y. (2013) 'The synthesis of methanol from CO/CO2/H2 gas over Cu/Ce1−xZrxO2 catalysts', *Journal of Molecular Catalysis A: Chemical*. Elsevier B.V., 378, pp. 255–262. doi: 10.1016/j.molcata.2013.06.023.

Yuan, L. C., Pfotenhauer, J. M. and Qiu, L. M. (2014) 'A preliminary investigation of cryogenic CO2 capture utilizing a reverse Brayton Cycle', in, pp. 1107–1114. doi: 10.1063/1.4860829.

Zeman, F. (2007) 'Energy and Material Balance of CO 2 Capture from Ambient Air', *Environmental Science & Technology*, 41(21), pp. 7558–7563. doi: 10.1021/es070874m.

Zeman, F. (2014) 'Reducing the cost of ca-based direct air capture of CO2', *Environmental Science and Technology*, 48(19), pp. 11730–11735. doi: 10.1021/es502887y.

Zeng, K. and Zhang, D. (2010) 'Recent progress in alkaline water electrolysis for hydrogen production and applications', *Progress in Energy and Combustion Science*. Elsevier Ltd, 36(3), pp. 307–326. doi: 10.1016/j.pecs.2009.11.002.

Zhai, H. and Rubin, E. S. (2013) 'Techno-economic assessment of polymer membrane systems for postcombustion carbon capture at coal-fired power plants.', *Environmental science & technology*, 47(6), pp. 3006–14. doi: 10.1021/es3050604.

Zhang, L., Zhang, Y. and Chen, S. (2012) 'Applied Catalysis A : General catalyst for methanol synthesis from CO 2 hydrogenation', 416, pp. 118–123. doi: 10.1016/j.apcata.2011.12.013.

Zhang, X., Bauer, C., Mutel, C. L. and Volkart, K. (2017) 'Life Cycle Assessment of Power-to-Gas : Approaches , system variations and their environmental implications', *Applied Energy*. Elsevier Ltd, 190, pp. 326–338. doi: 10.1016/j.apenergy.2016.12.098.

Zhang, Y., Cruz, J., Zhang, S., Lou, H. H. and Benson, T. J. (2013) 'Process simulation and optimization of methanol production coupled to tri-reforming process', *International Journal of Hydrogen Energy*. Elsevier Ltd, 38(31), pp. 13617–13630. doi: 10.1016/j.ijhydene.2013.08.009.

Zhou, Q., Koiwanit, J., Piewkhaow, L., Manuilova, a., Chan, C. W., Wilson, M. and Tontiwachwuthikul, P. (2014) 'A Comparative of Life Cycle Assessment of Post-combustion, Pre-combustion and Oxy-fuel CO2 Capture', *Energy Procedia*. Elsevier B.V., 63, pp. 7452–7458. doi: 10.1016/j.egypro.2014.11.782.

Zoannou, K.-S., Sapsford, D. J. and Griffiths, A. J. (2013) ‘Thermal degradation of monoethanolamine and its effect on CO2 capture capacity’, *International Journal of Greenhouse Gas Control*. Elsevier Ltd, 17(x), pp. 423–430. doi: 10.1016/j.ijggc.2013.05.026.

4 Environmental Impact Assessment Framework for CO_2 Utilisation Scenarios

The objective of this work is to present an environmental impact assessment framework that can be applicable specifically to CO_2 utilisation processes. To the best of the author's knowledge, no other study brings all the multidisciplinary aspects related to this subject into one general framework. As mentioned in **Section 3.1** there is a need for guidelines that can unify CO_2 utilisation assessments. To create this framework, the environmental impact assessment was divided into four areas: the design of the CO_2 utilisation process, locational availability of renewable energy, the impact assessment and, lastly, other aspects of CO_2 utilisation. Results from the assessment were used for scenario planning and multi criteria decision analysis (MCDA). The diagram of the general framework is shown in **Figure 4.1**. **Sections 4.2 to 4.7** describe the steps towards creating the guidelines that address the specific issues for carbon dioxide utilisation processes. In **Chapters 5 to 8**, this framework is applied to two CO_2 based chemicals.

4.1 Reasons for developing an environmental impact assessment framework for CO_2 utilisation

The assessment of carbon capture technologies has been of increased interest to researchers since the Intergovernmental Panel on Climate Change (IPCC) presented a special report in 2005 (IPCC, 2005). This report was specific to carbon capture and storage, but it provided capture information that would later be useful for utilisation processes. One of the knowledge gaps described in this report was the lack of guidelines for estimating emissions from CO_2 utilisation processes. From the data reviewed since 1999, at least fifty-four studies have used a form of life cycle assessment both for carbon capture and storage and CO_2 utilisation. Thirteen studies presented different methodologies for carbon accounting and, in total, 203 related studies were found. This highlighted the demand for assessment tools, but also the lack of general guidelines to follow (refer to **Section 3.1** for more detailed information).

The demand for assessment tools in carbon dioxide utilisation stems from two main reasons: carbon emissions management and advancements in carbon recycling, utilisation, and/or sequestration processes. As an example of carbon management, a 52% reduction in coal use caused UK carbon emissions to drop by 5.8%, in 2016. This was the largest drop on record for the UK. Only 37 Mt of CO_2 was emitted from coal compared to 137 Mt CO_2 emitted in 2006 (BEIS, 2017). Drivers for the drop in coal use included carbon taxes, cheaper gas and an increase in renewables (Evans, 2017). Overall carbon management will continue to be required for carbon budgets to be met (refer to **Section 3.3**). There is also an increased interest in areas related to carbon optimisation. Whether it is utilising, minimising or capturing, newer technologies are constantly emerging. Stakeholders increasingly want to see sustainability studies that can help determine the potential of these processes. In general, the aim is to find optimal processes with the least negative impacts.

Previous studies (Trudewind, Schreiber and Haumann, 2014; Sternberg and Bardow, 2015; Troy, Schreiber and Zapp, 2016; Zhang *et al.*, 2017) have used life cycle assessments as assessment tools, following international standards set in place for their development. These standards are ISO 14040, 14041 and 14044 (ISO, 1998, 2006a, 2006b). They detail the principles and guidelines for creating a life cycle assessment and a life cycle inventory for environmental aspects. The standards are open to adapting methodologies within individual phases. However, they do not describe in detail the techniques used to create an assessment, most notably allocation methods. As mentioned in **Section 3.2.3**, carbon allowances need to be separated between capture and utilisation processes. Carbon dioxide is not a final product; thus, multi-functionality issues need to be considered. For these reasons, in this chapter, a specific environmental impact assessment framework is created for carbon utilisation processes, with study cases based in the UK as a reference.

4.2 Overview of the environmental impact assessment framework

The development of this framework is the result of a compilation of methods, extensive research and data. To create this framework, the main aspects that differ in CO_2 utilisation to conventional methods were identified and used as a baseline. These aspects are:

- Allocation of emissions: Who gets the credit for using the CO_2 available?
- CO_2 market: What is the availability of CO_2 sources within a region and how does this affect the production of a CO_2-based product?
- Renewable energy: Availability, security, grid mix and future projections

Whilst these aspects have also been identified by other authors as key factors (von der Assen, Jung and Bardow, 2013), there is no consensus on how these should be weighted in sustainability reports.

The information generated and collected for this work is brought together under one general study to answer issues related to CO_2 utilisation. The core sections include scenario analysis and decision-making analysis. In scenario analysis, the design of the CO_2 utilisation process, locational availability of renewable energy and the impact assessment, along with other aspects of CO_2 utilisation are analysed to create the life cycle assessment. The second core section includes analysing the results from the first section by using multi criteria decision analysis (MCDA). This last section is aggregation work. By obtaining aggregated scores, a comparison between utilisation routes is possible.

This is a fixed framework that gives guidance for the optimiser of a process. The outcomes can be used to indicate where optimisation would result in the greatest benefits if possible – this is done by assessing the process and determining the biggest contributing factors to the outcomes, allowing for the suggestion to attempt to mitigate these. This could be a suggestion to attempt to reduce the quantity of certain chemicals, or to switch to an alternative option that results in a drop in global warming impacts. The benefits of this approach are a quicker and simpler primary screening designed to be fast. It allows for process optimisation to be considered independently and can be ran through the same fixed system as many times as required. The drawbacks of using a fixed system is that it lacks the flexibility of an integrated process which allows for dynamic results compared to a fixed assessment. A flexible system can also allow for the optimisation of interconnections between CO_2 source and CO_2 utilisation such as CO_2 pinch analysis (Ng *et al.*, 2015), with this being an extra advantage over fixed analysis systems where the responsibility for such an analysis may fall on the process optimiser. In this framework we allow for the technology developer, researcher, owner, or engineer who does optimise independently of the screening analysis. Such an approach allows for input from process specialists when considering optimisation and also ensures that the optimised results reflect an achievable reality – whether this be based on empirical, experimental or theoretical model data. The complete framework steps can be seen in **Figure 4.1** and are discussed in detail in the following sections.

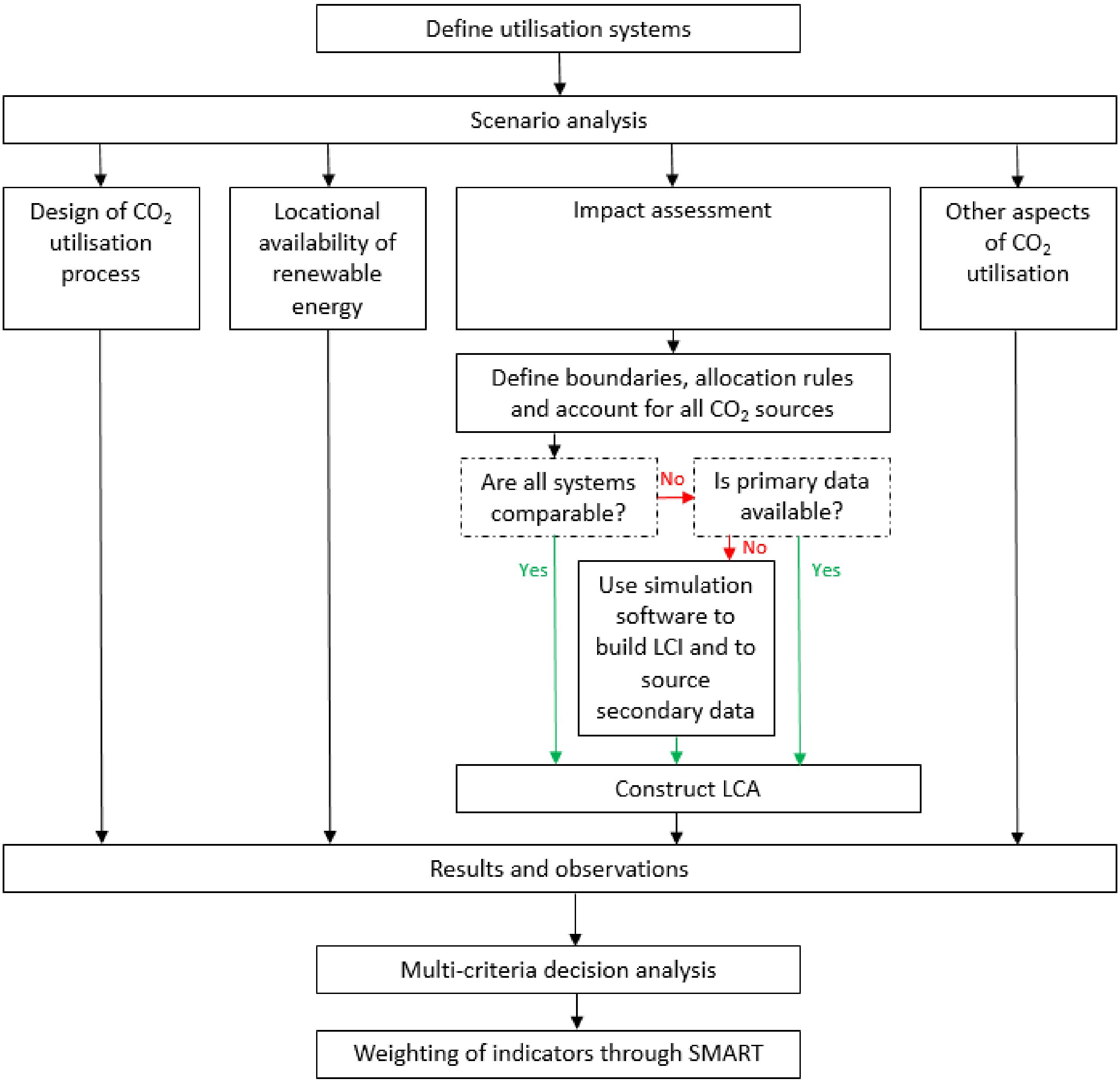


Figure 4.1 Environmental impact assessment framework designed for the chemical transformation of CO_2 for utilisation

4.2.1 Define utilisation system

The systems follow a life cycle assessment (LCA) approach where environmental and interventions are accounted for. **Figure 4.2** shows the boundaries, based on ISO 14040, 14041 and 14044 (ISO, 1998, 2006a, 2006b), that were adapted for a carbon utilisation system. A cradle to gate boundary is set in all cases with a focus on the production process. The supply chain includes raw materials, infrastructure, production, storage and end of life. The use phase is outside of the scope of the study as it is a comparative process-based study. If the product use is the same in both systems, regardless of whether it is from captured CO_2 or is fossil fuel based, the comparison will make no overall difference to the result since it will generate the same impacts. To select the utilisation systems, several questions formed the basis of the initial assessment: What CO_2 chemical transformation processes were more advanced? Is there a market for the product? What is the current research interest in the UK?

Detailed answers to the above questions can be found in **Chapters 5 and 6** where the utilisation systems are selected and assessed. Methanol serves as benchmark for the framework, based on the data availability for this chemical, and urea is assessed because of its production potential and demand in the UK. Alone in 2015, 1 Mt of nitrogen fertilisers were consumed in the UK (Agricultural Industries Confederations, 2016). The search for a less carbon-intensive process for urea production coupled with renewable energy justifies applying sustainability assessment tools.

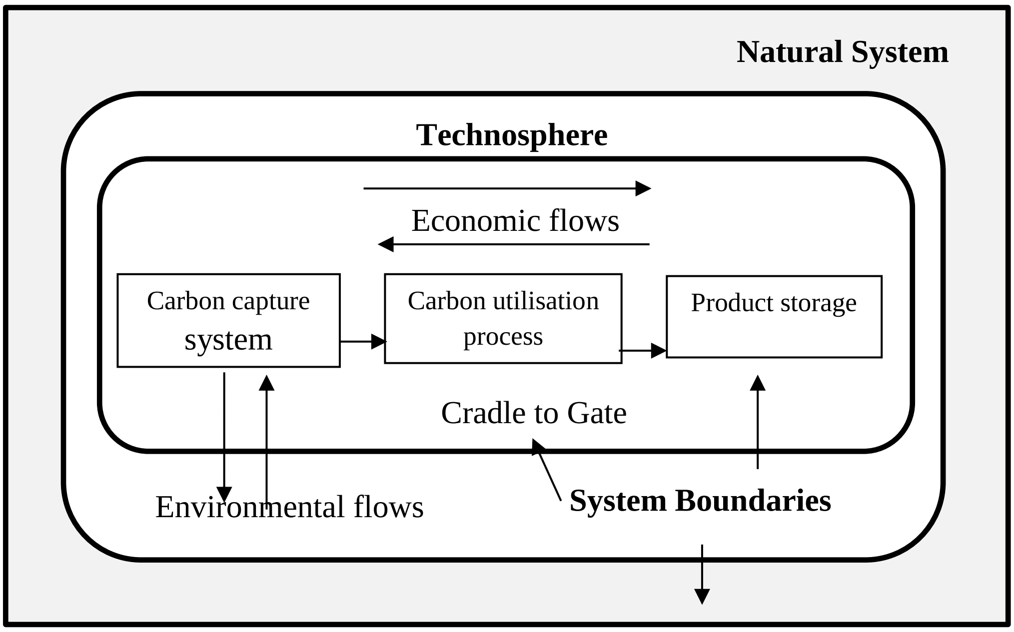


Figure 4.2 Diagram of boundaries for CO_2 utilisation systems based on the ISO standard 14040 (ISO, 2006a)

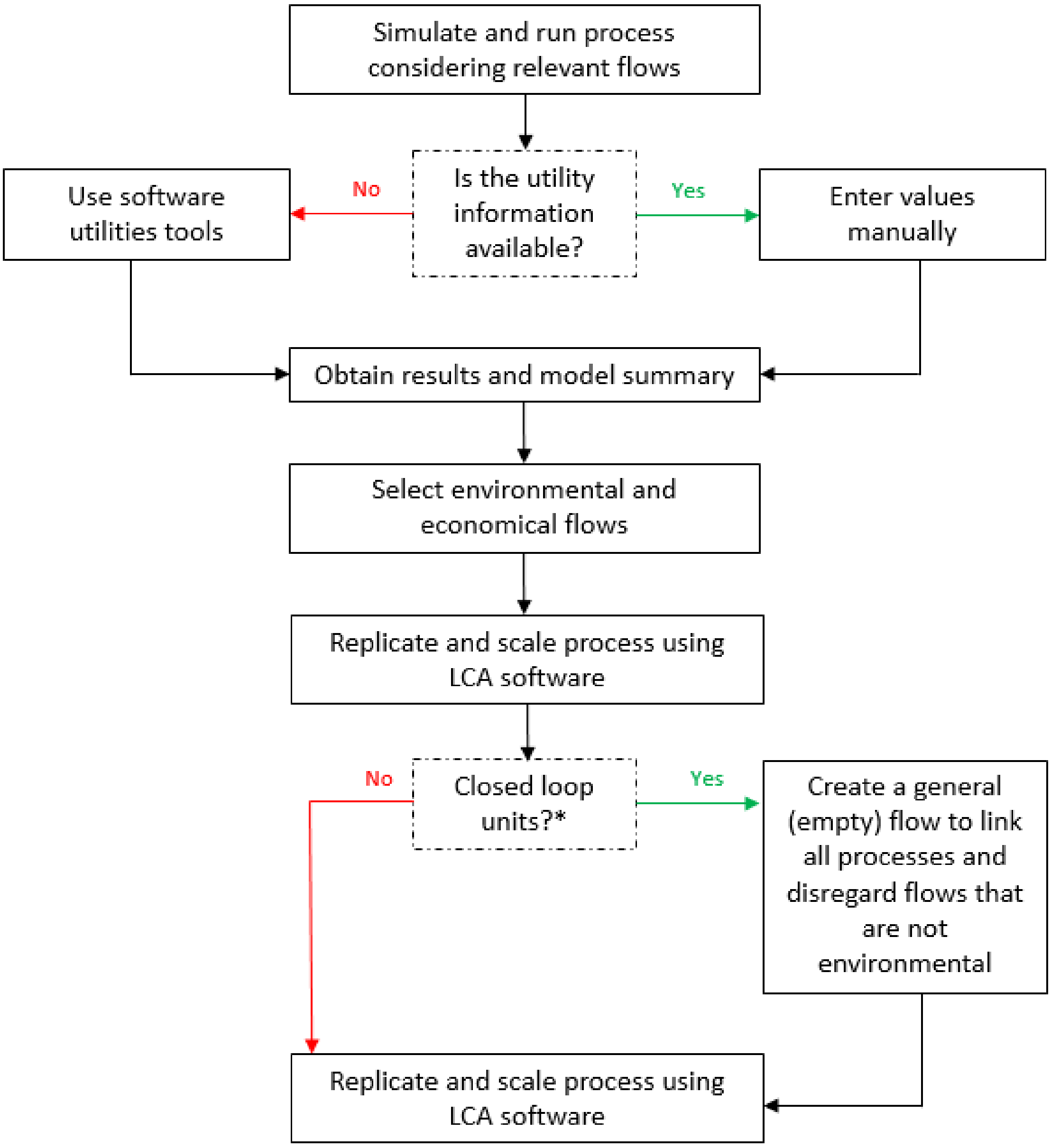
4.2.2 Scenario analysis

Scenarios have been used in organizations since the 1950's. The Department of Defence of the United States used scenario planning to raise awareness of the difficulties of a nuclear war (Coates, 2016). Since then they have become increasingly popular for forming coherent 'stories' when it is difficult to interpret information. As mentioned by Stewart *et al*. (2013) and Coates (2016), there are two main types of scenarios: i) mapping possible outcomes/solutions for situations that could arise within an organization, and ii) discussing the implications of a certain action, such as the inclusion of a new policy.

Carbon utilisation processes are currently directly linked to renewable energy availability within a region. This leads to an uncertain future where grid mixes are susceptible to changes. From technological advances to political decisions, this can reflect in the demand and supply of electricity. Thus, the first type of scenario was used in this work to analyse future outcomes. The uncertainty includes grid mix variability until 2050 for carbon dioxide capture methods and utilisation processes. The four sections: design of the CO_2 utilisation process, locational availability of renewable energy, impact assessment and other aspects of CO_2 utilisation sections are explained in the following sections for the scenarios investigated.

4.3 Design of CO_2 utilisation process

Successful sustainability assessments rely on good data. Primary sources of information will always be favourable to secondary sources. However, a data compromise must be reached for CO_2 utilisation, as there is not much primary data available at present. As research develops so will data availability; in the meantime, alternatives must be created to show preliminary results. The solution presented in this work combines simulations and available inventories as secondary sources, providing the information necessary to fill a life cycle inventory and assess it. Since there are no established standards known to date on how to apply simulations to create a life cycle inventory (LCI), it was necessary to create a general guideline to follow, as shown in **Figure 4.3**. This guideline bridges the gap between process-based modelling and life cycle assessments. This section also ensures that all the necessary information to assess CO_2 utilisation is obtained. Three main parts were identified for this subdivision: the source of CO_2, capture and utilisation.



* Flows within the system that are not connected to the environment

Figure 4.3 Diagram with general guidelines to creating life cycle assessments (LCAs) with simulations for CO_2 utilisation processes

4.3.1 CO_2 source, capture and utilisation

Through extensive research in the area, the following questions were proposed: how would CO_2 be supplied? Would it be biogenic, a point source or from direct air capture? Would the CO_2 concentration be adequate for utilisation, and if it were, does it need extra dehydration steps? This information was obtained from available research and adapted to the proposed scenarios. Refer to **Appendix I** for a summary of initial questions used to describe all four sections of the life cycle assessment.

Capture routes were researched based on information availability, relevance to the utilisation method and place of study. Then, secondary data was collected to simulate in Aspen Plus® version 8.4 to obtain utilities useful for the life cycle inventory. Using simulations was not possible for some capture methods, for example direct air capture (DAC), and instead a black box approach was the best way to estimate a future scenario. All extra units such as compression and removal of impurities are also considered and modelled when possible.

Utilisation routes were also modelled with Aspen Plus® version 8.4 when information was available. Alternatively, utilities were obtained from research available and adapted to fit the scenarios. Secondary data was backed with life cycle inventory databases such as ecoinvent version 3.3 and GaBi ts version 8.7.0.18. Finally, the last step for utilisation was to consider a variety of electricity sources and mixes in different regions. This information was also sourced directly from purchasable life cycle inventory databases.

4.4 Impact assessment

There are sustainability issues with chemical transformation processes. High energy penalties, water consumption and emissions are all environmental aspects associated with the chemical industry and the energy sector (Aresta and Galatola, 1999; Styring and Jansen, 2011; Pérez-Fortes, Bocin-Dumitriu and Tzimas, 2014; Santoyo-Castelazo and Azapagic, 2014; Morales Mora *et al.*, 2016). This is no different for utilisation processes. While the initial aim is to reduce carbon emissions, this benefit could be offset by other environmental impacts (Azapagic and Cue, 2015). the capture stage in particular involves high energy penalties (Abu-Zahra *et al.*, 2007; Ramirez and Uu, 2013). There are several suggestions made throughout this work to counterbalance these penalties; these recommendations are presented in the following chapters.

Studies in this area agree that the major environmental impacts associated with CO_2 utilisation are fossil fuel depletion and climate change (Von der Assen & Bardow 2014; Assen *et al*. 2016; Sternberg & Bardow 2015). The expectation is that by utilising captured carbon dioxide these impacts could be lowered when compared to non-CO_2 based production routes. However, these two are not the only environmental impacts that can be assessed. Efforts should be made to identify and assess other environmental impacts at least at an initial screening level.

Table 4.1 shows potential aspects and impacts of the CO_2 based products used as case studies. The environmental aspects are stated in the international standard 14001 (ISO, 2015), which suggests considering environmental aspects from:

- emissions to air
- releases to water
- releases to land
- use of raw materials and natural resources
- energy
- generation of waste
- use of space

A qualitative assessment of each environmental aspect along the supply was made, considering known impacts from other studies and life cycle inventories (LCI) for both conventional and CO_2 utilisation routes for methanol and urea as well as the initial process design specifications of the urea production facilities.

Raw material (Extraction, transportation): The life cycle inventories of the materials and chemicals needed for capture and CO_2 utilisation were used to determine potential environmental aspects from extraction and transportation. The list of inventories is shown in **Table 4.2**. From this, the main environmental aspects are: air and water emissions, use of materials, resources and energy, generation of waste and land use.

Infrastructure: Both case studies follow the infrastructure module (chemical plants, organics) from ecoinvent 3.3. This module considers land use, buildings and facilities including dismantling. The three main environmental aspects available are land use, use of materials/energy and generation of waste.

Production and end of life: The report “cost and performance baseline for fossil energy plants” by NETL (2015) was used for the capture stage of both case studies. The environmental aspects found based on this report were: air and water emissions, use of materials, resources and energy, generation of waste, and hazardous waste.

For urea synthesis, the life cycle inventory profile *urea, as N, at regional storehouse for Europe* from ecoinvent 3.3 was used. The environmental aspects sourced from this inventory are: air emissions, emissions to water, use of materials, resources and energy and generation of waste. For methanol synthesis, including hydrogen production, the design and simulation work of Van-Dal & Bouallou (2013) and Pérez-Fortes *et al.* (2014) was used as a reference for methanol, and communications by ITM Power Limited (2016) for hydrogen production. The environmental aspects sourced are: use of materials, resources and energy, emissions to air and water and generation of waste.

Storage: For both case studies, the cut-off boundaries were set at gate with no further information available for storage. Although there are storage plans for urea these were still not defined at the time of this assessment.

The associated impacts and evaluation factors are obtained from the CML-IA and ReCiPe (H) methods for life cycle assessments. This work follows the life cycle assessment framework established in the international standard 14040 (ISO, 2006a). Life cycle assessment is a sustainability tool used to assess inputs and outputs and to identify potential environmental impacts in a supply chain throughout its life cycle (ISO, 2006a). It is often used to compare products within cradle-grave, cradle-gate and gate-gate boundaries (Baumann & Tillman 2004). The international standard establishes the guidelines for performing life cycle assessment studies. The norm specifies the framework and its four main sections: goal and scope, inventory analysis, impact assessment and interpretation (**Section 3.2**). This norm was taken only as a base and was modified as required. It is not the aim of this study to repeat a methodology that is established, but to adapt it to new conditions while still following the general standardised guidelines. One of these changes is the use of a subtraction method for allocation, which is not mentioned in the norm. By using this method, CO_2 emissions avoided or generated can be assigned to different parts of the supply chain as required.

Table 4.1 Potential environmental aspects and impacts of case study CO_2 based products

Environmental aspects and impacts			Supply chain stages				
Environmental aspects	Associated impacts	Evaluation factors	Raw material (extraction, transportation)	Infrastructure	Production	Product Storage	End of life
Emissions to air	Climate change, ozone depletion, Photo-oxidant formation	Global warming, particulate matter, photochemical oxidation	x		x		x
Emissions to water	Water pollution	Eutrophication, nitrification, ecotoxicity	x		x		x
Emissions to land, land use	Land pollution, change of use	Abiotic depletion, ecotoxicity	x	x			
Use of materials/natural resources/energy	Water and energy consumption, fossil and materials depletion	Fossil depletion, abiotic depletion	x	x	x		x
Generation of waste	Land pollution, odours, recycling	Human and ecotoxicity	x	x	x		x
Hazardous waste	Human health implication, ecotoxicity	Human toxicity and ecotoxicity		x	x		x

Using this methodology as a basis, the goal and scope describes the intended application, reasons for study, system boundaries, functional unit and allocation. In this work, the functional unit is set at:

- 1 kg of product from the CO_2 utilisation production route
- 1.43 kWh of electricity / kg of methanol produced (when coal fired power stations are used as CO_2 supply)
- 0.8 kWh of electricity / kg of urea produced (when coal fired power stations are used as CO_2 supply)

Since the aim of the study was to evaluate chemical transformation routes with the same end-product, a cradle to gate approach was used for all scenarios in this chapter. Other goal and scope variables are defined accordingly to each scenario in **Chapter 5 and 6**.

The inventory analysis included all input and output flows that intervene within the system, including utilities, natural resources and emissions. The data for these interventions was obtained from the design of the CO_2 utilisation process mentioned previously as the direct source for the life cycle inventory. Indirect emissions (or 'background data') were obtained from purchasable databases. **Table 4.2** lists the database names selected for each flow in both cases studies. The approach used considers all processes to be linear, using a matrix inversion method for process-based modelling. This technique has been documented by authors such as Suh & Huppes 2005; Heijungs 1994; Islam *et al*. 2016. Other methods, such as Input-Output (IO) analysis and integrated hybrid, have also gained popularity in environmental studies; however, there is still a lack of economic data available in this research area to apply these methods. The first method estimates the indirect inputs in the LCA process system by using the economic input-output analysis; the second combines two base processes such as input analysis with process-based modelling to develop a more robust methodology (Koh *et al.*, 2013).

Following the $n \times n$ matrix inversion method mentioned in Heijungs *et al.* (2013), the life cycle inventory per commodity output can be calculated by the system:

$$\tilde{A}\tilde{\boldsymbol{x}} = \tilde{\boldsymbol{y}}$$

Equation 4.1

Where:

Ã= $|a_{ij}|$ inputs or outputs of a commodity i of process j for a certain process duration

$\tilde{x}$ = Vector for process operation time (also known as 'occurrence' or 'scaling factor')

$\tilde{y}$ = Commodity net output of the system

This is equal to:

$$\text{Total commodity delivered} = \text{amount produced} - \text{amount used}$$

Once the commodities were calculated, they were used to assess environmental impacts in the next life cycle assessment phase. Certain inputs, such as infrastructure, required a general method and were calculated separately with individual formulas.

Table 4.2 Names of the inventory database used for methanol and urea cases studies

Inventory database		
CO_2 capture: alternative inventories		
Country	**Name of input**	**Database**
EU-27	Process water	thinkstep 8.7.0.18
EU-27	Triethylene glycol	PlasticsEurope
EU-27	Municipal waste treatment (mix)	thinkstep 8.7.0.18
EU-27	Municipal solid waste on landfill	thinkstep 8.7.0.18
Germany	Calcium hydroxide (dry, slaked lime)	thinkstep 8.7.0.18
Germany	Activated carbon	thinkstep 8.7.0.18
Germany	Limestone flour ($CaCO_3$)	thinkstep 8.7.0.18
Great Britain	Electricity from hard coal	thinkstep 8.7.0.18
Great Britain	Ammonia (NH_3)	thinkstep 8.7.0.18
Great Britain	Process steam from natural gas 85%	thinkstep 8.7.0.18
Great Britain	Electricity grid mix	thinkstep 8.7.0.18
Great Britain	Ethylene oxide (EO) via air	thinkstep 8.7.0.18
Utilisation systems including hydrogen production: alternative inventories		
Country	**Name of input**	**Database**
EU-27	Process water	thinkstep 8.7.0.18
Europe	Chemical factory construction, organics	ecoinvent 3.3
Europe	Market for natural gas, high pressure	ecoinvent 3.3
Europe	Carbon tetrachloride production	ecoinvent 3.3

Country	Name of input	Database
Europe	Aluminium oxide, at plant	ecoinvent 3.3
Europe	Copper oxide, at plant	ecoinvent 3.3
Europe	Molybdenum, at regional storage	ecoinvent 3.3
Europe	Zinc, primary, at regional storage	ecoinvent 3.3
Europe	Market for waste graphical paper	ecoinvent 3.3
Europe without Switzerland	Market for waste graphical paper	ecoinvent 3.3
Global	Market for barite	ecoinvent 3.3
Global	Market for calcium chloride	ecoinvent 3.3
Global	Market for carbon tetrachloride	ecoinvent 3.3
Global	Market for sludge, NaCl electrolysis	ecoinvent 3.3
Global	Soda ash, light, crystaline, heptahydrate to generic market for neutralising agent	ecoinvent 3.3
Global	Market for sodium chloride, powder	ecoinvent 3.3
Global	Market for sulfuric acid	ecoinvent 3.3
Global	Market for hazardous waste, for undeground deposit	ecoinvent 3.3
Global	Market for asbestos, crysolite type	ecoinvent 3.3
Global	Market for mercury	ecoinvent 3.3
Global	Market for spent activated carbon with mercury	ecoinvent 3.3
Global	Nickel, 99.5 %, at plant	ecoinvent 3.3
Global	Synthetic gas, production mix, at plant	ecoinvent 3.3
Global	Natural gas, production onshore	ecoinvent 3.3
Global	Market for sodium hydroxide, without water, in 50% solution state	ecoinvent 3.3
Great Britain	Market for electricity, medium voltage	ecoinvent 3.3
Great Britain	Market for hydrochloric acid, without water, in 30% solution state	ecoinvent 3.3
Global	Market, for solvent, organic	ecoinvent 3.3
Europe	Market group for heavy fuel oil	ecoinvent 3.3
Great Britain	Treatment of municipal solid waste, incineration	ecoinvent 3.3
Europe	Market for urea, as N	ecoinvent 3.3
Europe	Market group for heat, district or industrial, natural gas	ecoinvent 3.3
Great Britain	Electricity from hard coal	thinkstep 8.7.0.18
Great Britain	Electricity grid mix	thinkstep 8.7.0.18
Great Britain	Electricity from wind power	thinkstep 8.7.0.18
Great Britain	Isopropanol	thinkstep 8.7.0.18
Global	Compressed air 7 bar (low power consumption)	thinkstep 8.7.0.18
EU-27	Tap water	thinkstep 8.7.0.18

4.4.1 Infrastructure

For all scenarios, infrastructure inputs were calculated based on the ecoinvent unit: *chemicals, organics, at plant*. All comparison scenarios use ecoinvent version 3.3 values, as there was a need to continue using this standardised unit when no primary data was available. New models were scaled by adapting the infrastructure from Heijungs *et al.* (2010).

The calculation for one chemical plant unit is as follows:

$$\frac{50{,}000\ t}{year} \times 50\ years = 1\ chemical\ plant\ (unit)$$

One chemical plant unit is hence equivalent to a plant with an output of 50,000 tonnes of product annually, with a life span of 50 years. Thus, one chemical plant unit is the equivalent amount of infrastructure needed to produce 2.5 million tonnes of product. For 1 kg of product, the following relationship is established:

$$1\ kg\ \ of\ product\ requires\ 4\ x\ 10^{-10}\ \ units\ of\ chemical\ plant$$

To calculate the total amount of infrastructure, the following equation can be used:

$$\left(\frac{Annual\ plant\ production\left(\frac{t}{yr}\right) \times lifespan(yr)}{2.5\ million\left(\frac{t}{unit}\right)}\right) = units\ of\ chemical\ plant$$

4.4.2 Life cycle impact assessment (LCIA)

The next step was to assess the environmental impacts obtained from the life cycle inventory. Several methods can be used for life cycle impact assessment (LCIA) (see **Section 3.2.4**). The method selected for this work was the one presented by Guinee *et al.* (2002), referred to as CML-IA. This method is often used in published work and is thus useful for comparing results. The exception is the fossil fuel depletion factor, which is not part of CML-IA impact categories. The ReCiPe (H) method was used instead to calculate this midpoint impact. This factor is assessed along with the CML-IA guidelines as a primary indicator.

CML-IA has a midpoint approach and evaluates eleven impacts: climate change, stratospheric ozone depletion, photochemical oxidation, acidification, nitrification, human-toxicity, ecotoxicity, abiotic depletion, particulate matter and sequestration of

CO_2. For more information on these indicators and impacts, refer to **Section 3.2.4**. The GaBi ts version 8.7.0.18 platform was used to calculate these impacts, with the inventory previously obtained.

The matrix representation of a product system was also used to calculate environmental interventions. Following results from **Equation. 4.1** by Heijungs *et al.* (2013)**:**

$$\widetilde{\boldsymbol{M}} = \widetilde{\boldsymbol{B}}\,\widetilde{\boldsymbol{A}}^{-1}\widetilde{\boldsymbol{k}}$$

Equation 4.2

Where:

$\widetilde{M}$ = Direct and indirect environmental intervention matrix

$\tilde{B} = |b_{ij}|$, i are natural resources or emissions consumed or emitted by process j in a given time

$\tilde{A} = |a_{ij}|$, inputs or outputs of a commodity i of process j for a certain process duration

$\tilde{k}$ = Vector for functional unit of the system

The results are generated with these tools and are not aggregated in any form, as this complicates interpretation. To avoid this, net impacts for a carbon utilisation supply chain were calculated considering the following stages:

- Power supply
- Water supply
- Material extraction and transportation
- CO_2 source impacts
- Transportation of CO_2 stream
- Waste management
- Process emissions

The net impacts were equal to the sum of all the stages. All stages fell within scope 1, 2 and 3 for greenhouse gases (GHG) (see **Figure 4.4**). Scope 1 includes all direct greenhouse gas emissions, scope 2 considers all purchased electricity and scope 3 refers to other emissions produced from operations of an organization and outsourced processes

(Koh *et al.*, 2013). **Table 4.3** shows environmental aspects/impacts for carbon utilisation according to their scope.

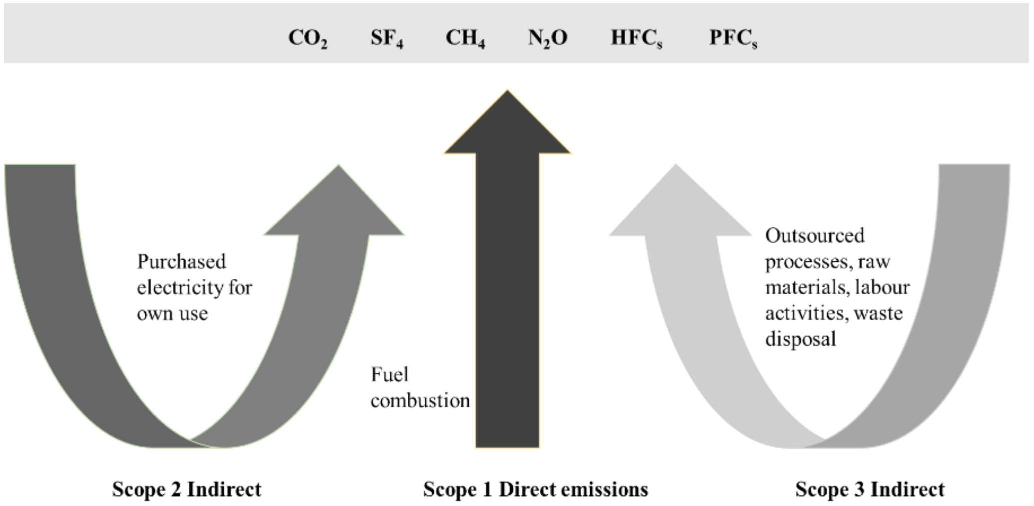


Figure 4.4 Visual aid of scope 1, 2 and 3 emissions (Koh *et al.*, 2013)

Table 4.3 Greenhouse gas emissions sources, scope 1, 2 and 3 areas for CO_2 utilisation processes

Sources of greenhouse gas emissions by scope for CO_2 utilisation processes		
Scope 1	Scope 2	Scope 3
Combustion of fossil fuels for capture stage, dehydration of CO_2 and utilisation process	Purchased electricity for utilisation process if plant is not on a power generating site or has individual renewable power input	Waste disposal from capture and utilisation, including solvents and refrigerants
Process emissions from chemical transformation of CO_2	Purchased electricity for additional transportation of CO_2 streams	Production and/or extraction of raw materials for capture and utilisation process
Fugitive emissions from chemical transformation of CO_2		Transportation and distribution up and down the supply chain
Mobile combustion from the operation of vehicles on site for capture, utilisation and emissions from storing the final product		Labour activities: Commuting, business travel, logistics, etc.

The results obtained from the assessment were used for the interpretation phase. This section is included in scenario planning for the final analysis (**Chapter 8**). Scenario planning and decision-making allowed all sections to come under one general framework with a measurable outcome. Within interpretation, it was also necessary to measure the robustness of the study. Quality analysis is traditionally done by a third independent party or by the same life cycle analyst. In this work, uncertainty and sensitivity analysis were both considered by the author.

4.4.3 Uncertainty in the assessment of CO_2 utilisation processes

All life cycle assessment-based studies suffer from uncertainty problems. Although the international standards 14040 and 14044 (ISO, 2006a, 2006b) acknowledge this, they do not favour any type of data quality analysis. Methods can either be statistical or expert based (Guo and Murphy, 2012). There are sampling methods such as Monte Carlo that have been used for more than 10 years to address these issues (Heijungs and Lenzen, 2014). This type of method works best with smaller inventories, as they require less iterations. The Intergovernmental Panel on Climate Change (IPCC) 2006 guidelines also recommend using Monte Carlo to estimate life cycle inventory uncertainties. According to Sadhukhan *et al.* (2014), other methods include dominance analysis, contribution analysis and testing the robustness of the results.

Dominance analysis shows the activities with the highest values of a specific environmental impact. It is a hot spot analysis that allows easy interpretation of the results. Contribution analysis_identifies the chemicals that cause higher environmental impacts within the life cycle of a product or process. Like dominance analysis, it is also a hot spot method. This analysis can help to replace pollutants with less intensive chemicals and help to reduce emissions from its source. To test the robustness of results, scenario analysis, sensitivity analysis and monte carlo simulations can be used.

Dominance analysis has been added to this work in the form of a bar graph for each environmental characterisation. It has been applied to both methanol and urea case studies. A comparative analysis between impacts is also included as part of the interpretation. This last study compares the relative contributions of each environmental impact for each case scenario for both methanol and urea synthesis.

To test the robustness of the results, all three options mentioned by Sadhukhan *et al.* (2014) are considered in this work. Sensitivity analysis is described in the section below (**4.4.4**) and scenario analysis is described in **Section 4.6**.

Lastly, because of the small size of the input and output matrix created for CO_2 utilisation, all studies were run through a Monte Carlo simulation with a ± 10 variance in all inputs/outputs with 2,000 random points calculated to test the feasibility of using this method when stoichiometric inputs are used. Since the results cannot go below stoichiometric values, to show the sensitivity of the impact categories an indexed value graph was used instead. This method measures the inefficiencies from 100% to 200% above stoichiometric when the main inputs are varied.

4.4.4 Sensitivity measured with solving multifunctionality

Sensitivity studies are required, in order to analyse the influence of variable factors, such as allocation or multifunctionality of a process. The importance of allocation rules is stressed in **Section 3.2.3**, where using a different method to solve multifunctionality leads to a different interpretation. In this work, sensitivity analyses were run for all global warming scenarios using most applicable allocation types.

The system expansion method was used as benchmark for all calculations. (More information on this method and allocation for carbon dioxide utilisation is given in **Chapter 3**). Both avoided burden and economic allocation were used to compare results. The formulas were adapted from Von der Assen *et al.* (2014) and are as follows:

System expansion

1. $GW_{utilsation} = \sum PPU_{CO_2\,outputs} + \sum UP_{CO_2\,outputs} + \sum RP_{CO_2\,outputs}$

2. $GW_{conventional} = \sum PPC_{CO_2\,outputs} + \sum CP_{CO_2\,outputs}$

Equations 4.3

Avoided burden

3. $GW_{utilsation,\ primary\,product}$

$$= \left(\sum PPU_{CO_2\,outputs} + \sum UP_{CO_2\,outputs} + \sum RP_{CO_2\,outputs}\right) - \sum PPC_{CO_2\,outputs}$$

4. $GW_{electricity,\ \ secondary\ product} = \sum PPC_{CO_2\ outputs}$

5. $GW_{electricity,\ \ primary\ \ product}$

$$= \left(\sum PPU_{CO_2\ outputs} + \sum UP_{CO_2\ outputs} + \sum RP_{CO_2\ outputs}\right) - \sum CP_{CO_2\ outputs}$$

6. $GW_{utilsation,\ \ secondary\ product} = \sum CP_{CO_2\ outputs}$

Equations 4.4

Economic allocation

7. $GW_{electricity} = \sum PPU_{CO_2\ outputs} * Electricity\ revenues$
8. $GW_{CO_2 feedstock} = PPU_{\ CO_2\ feedstock} * \ CO_{2\ feedstock}\ revenues$
9. $GW_{product} = PPU_{\ CO_2\ feedstock} + \sum UP_{CO_2\ outputs} + \sum RP_{CO_2\ outputs}$

Where:

$GW\ = Global\ warming$

$PPU_{CO_2\ outputs}\ = CO_2\ emissions\ from\ power\ plant\ with\ \ carbon\ capture$

$UP_{CO_2\ outputs}\ = CO_2\ emissions\ from\ carbon\ dioxide\ utilisation\ plant$

$RP_{CO_2\ outputs}\ = CO_2\ emissions\ from\ renewable\ energy\ production$

$PPC_{CO_2\ outputs}\ = CO_2\ emissions\ from\ power\ plant\ without\ carbon\ capture$

$CP_{CO_2\ outputs}\ = CO_2\ emissions\ from\ conventional\ chemical\ production\ route$

$CP_{CO_2\ feedstock}\ = Total\ \ CO_2\ emissions\ from\ capture$

Equations 4.5

4.5 Locational availability of renewable energy and other aspects of CO_2 utilisation

4.5.1 Locational availability of renewable energy

Carbon dioxide utilisation and renewable energy issues are deeply intertwined (Sayah and Sayah, 2011; Styring and Jansen, 2011; Boretti, 2013; Matzen, 2016). Where will the energy to power the production of CO_2-based products come from? This leads to supply and demand issues that needs to be addressed. A way to assess this is by investigating the potential of different energy mixes. To determine this, a compilation of electricity resource data was collected for EU countries. This information was used to create scenarios based on baseline cases for methanol and urea synthesis. This also included the mapping of CO_2 related sources:

- CO_2 availability by source in Europe
- Industry and electricity generation sites by CO_2 emission rates in Europe
- Industry and electricity generation sites with < 0.2 Mt emissions in Europe
- Industry and electricity generation sites with < 0.2 Mt emissions in the UK by commercial sector

Data was obtained from European Commission reports (Database, 2014) and mapped using Microsoft Office software. Specific information for the UK was also collected. This included power stations by region, fuel source, emissions and installed capacity. The data was sourced from the newest Digest of UK Energy Statistics (BEIS, 2016a) and considered all renewable energy in the United Kingdom.

Auxiliary information such as CO_2 pipelines and land availability in a specified region were only assessed for the scenarios selected. To date, there is little public data available for CO_2 pipelines. The most reliable sources are studies by the IEA Greenhouse Gas R&D Programme and the National Energy Technology Laboratory (based in the U.S). However, due to its high uncertainty and undisclosed information, this data was only used for general assumptions.

4.5.2 Electricity outlook

The need for an adequate energy source for CO_2 use in the synthesis of chemicals and fuels has been mentioned in the literature (Styring and Jansen, 2011; von der Assen *et al.*, 2015; Schakel *et al.*, 2016; Aresta, Dibenedetto and Dutta, 2017). In particular when reforming CO_2 to fuels without a renewable energy source, these utilisation systems are limited (Olah, Goeppert and Prakash, 2009; Aresta, Dibenedetto and Dutta, 2017). Therefore, it is suggested that a framework aimed at carbon dioxide utilisation should also consider energy outlooks in its assessment. In this work, that energy source is electricity.

The grid mix of a region is constantly changing. In the UK, during the 1920's, 99 % of the fuel input for electricity generation came from coal. By 2015, coal supplied 27 % of the total fuel input (BEIS, 2016a). This change can be tracked from the 50's, when hydro power was introduced to the grid, followed by natural gas and renewables. Nuclear has also had a contribution to the mix; in the late 1990s, nuclear power plants produced 25% of the annual electricity generated in the UK (Singh and Ashcroft, 2017). Currently, the grid is a lot more mixed than it has ever been. All forecasts up to 2050 (BEIS, 2017) point towards higher mixes and less dependency on fossil fuels. However, these forecasts are very sensitive not only to scientific development but also political development. As an example, during 2016, a wave of political instability arrived in the UK and to an extent, worldwide. This lead to higher levels of uncertainty in the energy sector as it was unclear what environmental policies would be supported (see **Section 3.3.5**).

To analyse the potential of a carbon utilisation product, it is necessary to include electricity scenarios that could reflect the probable grid mixes of a region under certain conditions and timeframes. These have been included in the interpretation phase of this study; an example can be seen in **Chapter 7**.

The scenarios are created using future mixes provided by the National Grid (2017) and BEIS (2017). These include grid mixes for the years 2015, 2025 and 2050. The projected electricity impacts are used instead of the baseline scenario to calculate overall impacts for each case study in a specific year. All calculations are run for both methanol and urea case studies.

4.5.3 Utilities

Costing rates of electricity and gas were calculated either by using simulation software or manually, depending on the process. The quarterly energy prices presented by the Department for Business, Energy & Industrial Strategy (BEIS) were used when electricity was required from the UK grid (BEIS, 2016b). All similar scenarios used the values found in prices of fuels purchased by non-domestic consumers in the UK (including the Climate Change Levy). For purpose of this study, a medium consumer (2000-19,999 MWh) was used with an average electricity price of all 4th quarters of 2016. Process and cooling water costs were obtained from EU databases (European Comission, 2017).

The steps to calculate overall utility costs are as follows:

- Summation of individual utilities for each stage under each scenario
- Substitution of energy values for energy costs
- Total sum of costs per scenario in £/kg of product

The levelised cost of electricity (LCOE), based on the discounted cash flow method, was used for wind power energy costs. Levelised cost of electricity (LCOE) is used as a life cycle thinking technique for electricity costs. Levelised costs follow the general equation (Cartelle Barros *et al.*, 2016):

$$LCOE = \frac{TLCC}{TLEP}$$

Equation 4.6

where:

$LCOE \ = levelised\ cost\ of\ electricity$

$TLCC \ = total\ life\ cycle\ clost$

$TLEP \ = total\ lifetime\ energy\ production$

4.5.4 Market for CO_2 utilisation product

Recycling carbon dioxide and providing a useful product are the pillars that sustain carbon dioxide utilisation. While most research efforts are towards determining environmental impacts, it is also important to address the opportunities of such a product in the current market. To qualitatively assess this, the following aspects were considered:

- Current supply of product from conventional production route in the UK and in the EU
- Current demand of product from conventional production route in the UK and in the EU
- Imports and exports of product in the UK
- Retail price of product in the UK
- Industry outlook for supply and demand in the UK

These aspects are also considered for the interpretation phase as seen in **Section 7.4.**

4.5.5 Human health

The human toxicity impact category by CML-IA was selected to measure human health toxicity. There are many frameworks available from a health & safety perspective that deal with human health management, OHSA1800 being a common standard in America for occupational health and safety, with its British Standard equivalent in the UK. However, from a life cycle assessment (LCA) point of view, human toxicity potential (midpoint) or DALY (Disability Adjusted Life Years, endpoint), where one Daly equals one year of life lost, are the characterisation factors to use. The units used to assess whether a carbon utilisation process will have more or less human toxicity scores than the conventional chemical process was kg 1,4-DCB eq. To calculate net human health impacts, the following formulas were used (**Equation 4.7** and **Equation 4.8**):

$$\begin{aligned}\mathrm{HT}_{\text{Carbon utilisation process}} &= \mathrm{HT}_{\text{Power supply}} + \mathrm{HT}_{\text{Water supply}} + \mathrm{HT}_{\text{Materials}} + \mathrm{HT}_{\mathrm{CO_2}\text{ source}} \\ &+ \mathrm{HT}_{\text{transportation}} + \mathrm{HT}_{\text{waste management}}\end{aligned}$$

Equation 4.7

HT avoided for carbon utilisation was then calculated by:

$$\mathrm{HT}_{\text{avoided(carbon utilisation)}} = \mathrm{HT}_{\text{Conventional process}} - \mathrm{HT}_{\text{carbon utilisation process}}$$

Equation 4.8

Where HT represents human toxicology

The ReCiPe (H) model was also used to measure human health damage due to fine particulate matter (diameter less than 10 µm). Although there are some limitations to assessing this impact as mentioned in **Section 3.3.4**, the health concerns related to this impact are high and thus it is important to at least report the results with available models such as ReCiPe (H).

4.5.6 Main impact categories of CO_2 utilisation

The main impacts considered in this section are those that will affect current and future generations. A similar approach has been seen in Perdan & Azapagic (2011) and Santoyo-Castelazo & Azapagic (2014).

In this work, climate change and depletion of fossil fuel reserves are both considered to be main impacts. Climate change is an issue for multiple generations, where climate predictions are very uncertain. The characterisation factor used is the global warming potential (GWP_{100}), as specified in **Section 3.2.4**. Depletion of fossil fuel reserves are calculated by using the characterisation factor from ReCiPe (H). The use of these characterisation factors has been applied to similar work done by von der Assen & Bardow (2014) and Sternberg & Bardow (2015) and Santoyo-Castelazo & Azapagic (2014). Net impacts were calculated by applying the same formula used for human toxicity scores. This is illustrated in **Equation 4.9** and **Equation 4.10** for the example of fossil depletion. More information on these factors is available in **Section 3.2.4**.

$$\begin{aligned}\mathrm{FD}_{\text{Carbon utilisation process}} \\ = \mathrm{FD}_{\text{Power supply}} + \mathrm{FD}_{\text{Water supply}} + \mathrm{FD}_{\text{Materials}} + \mathrm{FD}_{\text{CO2 source}} \\ + \mathrm{FD}_{\text{transportation}} + \mathrm{FD}_{\text{waste management}}\end{aligned}$$

Equation 4.9

$$\mathrm{FD}_{\text{avoided(carbon utilisation)}} = \mathrm{FD}_{\text{Conventional process}} - \mathrm{FD}_{\text{carbon utilisation process}}$$

Equation 4.10

Where:

Where FD represents fossil depletion

4.6 Scenario analysis and Multi criteria decision analysis

As mentioned in **Chapter 3**, multi-functionality problems are part of carbon dioxide utilisation processes. While allocation aims to address these issues, there is still a high level of uncertainty. Overall, environmental based decisions are uncertain by nature. These require information from many areas, from natural to social, physical, political, economic, etc. There are many environmental tools available to address these areas; however, its implementation is still limited. According to Huang *et al.* (2011), these limitations can be divided into three main issues: emerging risks, different assessment approaches and information available to stakeholders with a high level of uncertainty. These limitations can either be caused by internal or external factors. External uncertainty comes from not knowing the consequences from a present or future environmental change. Internal uncertainty arises from imprecise information and internal decision making issues (Durbach and Stewart, 2012). Because of the many methods available to assess this variance, authors often do not differentiate between internal or external uncertainty. This can be a problem, as finding a suitable method to carry out the study is challenging.

There is also the task of finding a sustainability development tool that can deal with its multidisciplinary nature as well as its uncertainty. Amongst the tools available, multi criteria decision analysis (MCDA) is a popular choice (Ribeiro, Ferreira and Araújo, 2013). This tool has been used for integrated sustainability studies and is widely accepted within the area (Wang *et al.*, 2009; Huang, Keisler and Linkov, 2011; Niekamp *et al.*, 2015; Vo *et al.*, 2016).

Multi criteria decision analysis (MCDA) is a tool for evaluating several possible routes, decision or alternatives. It is a flexible method that allows information to be judged, ranked or sorted in a chosen order (Durbach and Stewart, 2012). An example can be ranking from 'bad' to 'good', 'high' to 'low', or through a number scale. It can also be used when information and data is multidisciplinary, with conflictive objectives, socio-economic systems or with high levels of uncertainty. This type of analysis will generally consist of an *m* x *n* matrix, where *m* is the alternatives to be evaluated and *n* is the criteria (Wang *et al.*, 2009).

To the author's knowledge, there are not yet any carbon dioxide utilisation studies coupled with MCDA. However, it is not uncommon to see this type of analysis in the energy sector (Maxim, 2014; Santoyo-Castelazo and Azapagic, 2014; Klein and Whalley, 2015; Vo *et al.*, 2016). These types of sustainability assessments often focus on electricity technologies. In these studies, electricity-generating technologies can be ranked by using aggregated indicators. Studies of renewable technologies are of particular interest, as the uncertainties of the optimal mix can compare to uncertainties in carbon dioxide utilisation. In a review study by Wang *et al.* (2009) the decision making process is divided into four sections:

1. Criteria selection: select the criteria and normalize the original data.
2. Criteria weighting: determine the weights that will show the importance of the criteria in the decision-making process.
3. Evaluation: rank the alternatives with criteria weights using a multi criteria decision analysis (MCDA) method.
4. Final treatment and aggregation: order the ranking of alternatives and compare against other multi criteria decision analysis methods (MCDA).

Weighting methods are generally classified into equal weighting and rank-order weights. As mentioned by Wang *et al.* (2009), equal weights is the most common method used in sustainability-based decision making. It is the simplest method since it requires the least input without assigning priorities to criteria. M. Dawes & Corrigan (1974) argued that this method produces almost as good results as the other weighting methods. When the rank-order method is applied, this either can be through subjective or objective weighting. With subjective weighting, the decision-makers can assign priorities to the criteria (Niekamp *et al.*, 2015). With the objective method, the weights are obtained through mathematical methods using the initial data (Wang *et al.*, 2009).

There are many potential ways to conduct multi criteria decision analysis (MCDA). There are even several ways of classifying these, depending on the author. Wang *et al.* (2009) classify them into elementary, unique synthesizing criteria and outranking categories. Durbach & Stewart (2012) classify them into probabilities, decision weights, explicit risk measures, fuzzy numbers and scenarios. A more recent study by (Niekamp *et al.,* 2015) classify them into multi-attribute value theory (MAVT), analytical hierarchy process (AHP) and outranking models.

With multi attribute value theory (MAVT) the units are converted to a same scale or value, to allow for comparison between results. Each criterion is compared and scored against the others, on a scale from 0 to 1 for performance (Niekamp *et al.*, 2015). According to Wang *et al.* (2009) and Niekamp *et al.* (2015) the weighted sum method (WSM), which is a MAVT method, is the most commonly used in energy studies and is also the simplest. Next, analytical hierarchy process (AHP) is a method where relative judgements of the scoring are made by the decision maker. These are non-numerical scores such as better than" "less important than" that are translated into numerical values between 0 and 1 (Niekamp *et al.*, 2015). Lastly, outranking models are used to determine which options outperform others without needing all options to be comparable (Wang *et al.*, 2009).

As mentioned in Niekamp *et al.* (2015), all methods can also include fuzzy set approaches. These approaches are useful when the weights and scores are better described quantitatively than qualitatively. The values can be represented through fuzzy numbers and transformed to quantitative values. Examples of fuzzy set theory being used to evaluate sustainability indicators include work by Pask *et al.* (2017), Cornelissen *et al.* (2001) and Chhipi-Shrestha *et al.* (2017)

Based on the classification by Durbach & Stewart (2012) and Niekamp *et al.* (2015), the decision making applied in this work was based on a scenario approach and multi attribute value theory (MAVT).

Decision analysis based on scenarios

While for CO_2 utilisation processes there is internal and external uncertainty, the interpretation of the life cycle assessment results is limited by external factors. Aspects such as renewable energy availability play a key role in its sustainability performance;

this aspect is classified as an external factor. To deal with this type of uncertainty, Durbach & Stewart (2012) recommend decision analysis based on scenarios. With this method, possible future outcomes can be constructed if they are consistent and coherent. This method is traditionally more quantitative than qualitative; however, efforts have been made to add decision making steps to it (Wang *et al.*, 2009). Evaluating these scenarios and presenting alternatives can add a multi-decision aspect, thus combining scenario planning and multi criteria decision analysis (MCDA) (Durbach and Stewart, 2012; Stewart, French and Rios, 2013).

The reasoning behind selecting this approach to create a conceptual framework for decision analysis can be summarised as:

1. It is practical to comprehend for decision makers, compared to other measures that are operationally difficult.
2. It is particularly useful when dealing with external uncertainties, since possible outcomes can be described.
3. With scenario modelling, a formal quantitative modelling can be avoided and is favoured by an informal but informed judgement. This is particularly useful for this work since it operates at screening level. The goal is to generate initial discussions on process alternatives for further analysis when the processes are at higher technological readiness levels (TRLs).
4. The weighted sum method (WSM) was selected to present a general score, as it is the method most used across energy systems (Wang *et al.*, 2009). This will facilitate the comparison of results when life cycle assessment studies in CO_2 utilisation are more commonplace.

As future work, and as the interest to assess the performance of CO_2 based processes increases, the expectation is to expand the environmental impact assessment to a sustainability framework where fuzzy numbers can be applied to the greater range of impacts (both qualitative and quantitative).

Building from the study by Stewart *et al.* (2013), scenarios and multi criteria decision analysis (MCDA) are represented in this work, as shown in the example in **Table 4.4**.

Table 4.4 Example of scenarios for decision analysis based on Stewart *et al.* (2013)

Alternatives	**Scenarios for decision analysis**			
	Scenario S_1		**Scenario S_2**	
	Criteria C1	Criteria C2	Criteria C1	Criteria C2
a1	X	X	Y	Y
a2	Y	X	X	X
a3	X	Y	Y	Y

Here, for every scenario (S) there are certain criteria (c), and for every criterion there is an alternative (a). This method follows a similar approach presented by Goodwin and Wright, later replicated by Stewart *et al.* (2013).

By using this method, it is easier to spot the relationships between each scenario. As an example, for alternative a1, the outcome will not change from criteria to criteria but will from scenario to scenario, whereas in a2 and a3, scenario 1 and 2 have opposing outcomes. For this work, alternatives refer to the capture method and utilisation process, while scenarios include potential grid mixes for the UK until 2050. Criteria refers to impacts assessed. **Table 4.5** shows the scenario matrix for urea production as an example.

The conceptual framework created for scenario analysis (interpretation phase) follows these basic steps:

1. Define matrix for scenario: here alternatives are evaluated against certain criteria under certain scenarios.
2. Define criteria: these include all quantitative indicators selected for this framework. A summary of these is presented in **Table 4.6** where 20 indicators are selected to form an environmental impact assessment framework, 15 of which are quantitative.
3. Weighting of results: an equal weighting multi attribute value theory (MVAT) approach is used for ranking all indicators as the primary decision-making tool. A second weighting is arranged for comparison, based on the indicators selected for CO_2 utilisation, using the simple multi attribute ranking technique known also referred to as SMART.

The simple multi attribute rating technique (SMART) method is a linear model that adds the performance scores of each criterion and, in this work, scenarios with a weighted value (DTU Transport Compendium Series part 2, 2014). Ten specific questions and values for each criterion were developed for the ranking criteria through private communications and informal meetings with the decision-makers. In this instance these decision-makers consisted of the research group involved in the case studies. While this approach has limitations, since stakeholder participation is not feasible at this stage, it is a way to demonstrate the applicability of this framework to future studies, with increased data availability and increased stakeholder engagement. The main steps taken to use the simple multi attribute rating technique (SMART) in this framework, to provide decision support, are:

- Identification of criteria: ten questions tailored to CO_2 utilisation are used to rank each indicator from 0-100.
- Give values for each criterion: the criterion is ranked from 0-100 in intervals of 25. The highest value is assigned to the impacts with highest relevance to CO_2 utilisation. 0 = no relevance, 25 = little relevance, 50 = relevant, 100 = very relevant.
- Calculation of weighted average: the weights are normalised to sum 1.
- Final ranking: The scenarios are ranked based on the weighted results.

Table 4.5 Matrix for scenario planning and decision-making: urea example

Ammonia production		**CO_2 supply for urea production**								
		Post-combustion capture plant			**Direct air capture**			**Haber-Bosch process**		
		Grid mix variables			Grid mix variables			Grid mix variables		
Process	Energy source	2015	2025	2050	2015	2025	2050	2015	2025	2050
Water electrolysis	Hydrogen production connected to grid	▨	▨	▨	▨	▨	▨			
	Hydrogen production connected to wind power	▨	▨	▨	▨	▨	▨			
NaCl electrolysis	Hydrogen production connected to grid	▨	▨	▨	▨	▨	▨			
	Hydrogen production connected to wind power	▨	▨	▨	▨	▨	▨			
Steam reforming	Natural gas							▨	▨	▨

Table 4.6 Summary of indicators for environmental impact assessment of CO_2 utilisation processes

Indicators for environmental impact assessment		
Aspect	Characterisation factor	Unit of indicator
Energy requirements	1. Extra energy for capture	kWh/kg CO_2 captured
	2. Energy penalties for utilisation	kWh/kg utilisation product
	3. Renewable energy consumption	kWh $_{\text{renewables}}$/kg utilisation product
	4. Total energy consumption	kWh/kg final product
Potential for CO_2 savings	5. Net CO_2 avoided	(kg CO_2)/kg product
CO_2 use in utilisation process	6. Net CO_2 utilised	(kg CO_2)/kg product
CO_2 capture	7. Capture efficiency	Percentage %
Global warming	8. Global warming potential (GWP_{100})	(kg CO_2 eq)/kg product
Eutrophication	9. Eutrophication potential (EP)	(kg PO_4 eq)/kg product
Acidification	10. Acidification potential (AP)	(kg SO_2 eq)/kg product
Ozone layer depletion	11. Ozone depletion potential ($ODP_{\text{steady state}}$)	(kg CFC-11 eq)/kg product
Photochemical oxidation	12. Photochemical ozone creation potential (POCP)	(kg ethylene eq)/kg product
Land aspects	13-15. Ecotoxicity potential (MAETP, TAETP, $FAETP_{\text{inf.}}$)	(kg 1,4-DCB eq)/kg product
Human health aspects	16. Human toxicity potential (HTP)	(kg 1,4-DCB eq)/kg product
	17. Particulate matter formation (PMF)	(kg PM_{10} eq)/kg product
Intergenerational aspects	18. Fossil depletion potential (FDP)	(kg oil eq)/kg product
	19. Abiotic depletion potential (ADP)	(kg Sb eq)/kg product
Energy costs	20. Cost of utilities	£/ /kg product

4.7 Chapter four summary

This chapter discusses the environmental impact assessment framework created for the CO_2 utilisation processes under review as worked examples. The application of this framework is seen in **Chapters 5 to 8**. The main guidelines created to perform a life cycle assessment for a CO_2 utilisation process are divided into four main sections: the design of the CO_2 utilisation process, locational availability of renewable energy, the impact assessment and other aspects of CO_2 utilisation.

Design of the CO_2 utilisation process: this focuses on determining CO_2 sources and capture and utilisation methods. This section collects data from process simulations, literature and the private sector to create a life cycle inventory.

Impact Assessment: indicators are determined, based on specific aspects in CO_2 utilisation, and assessed using life cycle assessment methodology. Specific allocation rules are applied. All scenarios work under system expansion assumptions. Sensitivity and uncertainty analysis are carried out for study cases.

Locational availability of renewable energy and other impacts: CO_2 availability is mapped for optimising CO_2 potential. To assess the energy outlook until 2050, all results are calculated for all impacts in each year, with the specific electricity grid mix. Other areas assessed include utility prices, human health, market for utilisation products and main impacts.

As a last step, the framework considers a decision step, using multi criteria decision analysis (MCDA) and scenarios. With this approach, scenarios are ranked in line with issues of CO_2-based processes and through an equal ranks method, for comparison. The issues are determined through the simple multi attribute rating technique **(**SMART) method. The outcome is a conceptual framework that can be replicated for other carbon dioxide utilisation assessments.

4.8 Chapter four reference list

Abu-Zahra, M. R. M., Schneiders, L. H. J., Niederer, J. P. M., Feron, P. H. M. and Versteeg, G. F. (2007) ‘CO2 capture from power plants’, *International Journal of Greenhouse Gas Control*, 1(1), pp. 37–46. doi: 10.1016/S1750-5836(06)00007-7.

Agricultural Industries Confederations (2016) *Fertiliser Statitics 2016*.

Aresta, M., Dibenedetto, A. and Dutta, A. (2017) ‘Energy issues in the utilization of CO2 in the synthesis of chemicals: The case of the direct carboxylation of alcohols to dialkyl-carbonates’, *Catalysis Today*, 281, pp. 345–351. doi: 10.1016/j.cattod.2016.02.046.

Aresta, M. and Galatola, M. (1999) ‘Life cycle analysis applied to the assessment of the environmental impact of alternative synthetic processes. The dimethylcarbonate case: part 1’, *Journal of Cleaner Production*, 7(3), pp. 181–193. doi: 10.1016/S0959-6526(98)00074-2.

von der Assen, N. and Bardow, A. (2014) ‘Life cycle assessment of polyols for polyurethane production using CO2 as feedstock: insights from an industrial case study’, *Green Chemistry*, 16(6), p. 3272. doi: 10.1039/c4gc00513a.

von der Assen, N., Jung, J. and Bardow, A. (2013) ‘Life-cycle assessment of carbon dioxide capture and utilization: avoiding the pitfalls’, *Energy & Environmental Science*, 6(9), p. 2721. doi: 10.1039/c3ee41151f.

von der Assen, N., Müller, L. J., Steingrube, A., Voll, P. and Bardow, A. (2016) ‘Selecting CO2 Sources for CO2 Utilization by Environmental-Merit-Order Curves’, *Environmental Science and Technology*, 50(3), pp. 1093–1101. doi: 10.1021/acs.est.5b03474.

von der Assen, N., Sternberg, A., Kätelhön, A. and Bardow, A. (2015) ‘Environmental potential of carbon dioxide utilization in the polyurethane supply chain’, *Faraday Discuss*. doi: 10.1039/C5FD00067J.

von der Assen, N., Voll, P., Peters, M. and Bardow, A. (2014) ‘Life cycle assessment of CO2 capture and utilization : a tutorial review’, *Chem Soc Rev*, 43, pp. 7982–7994. doi: 10.1039/C3CS60373C.

Azapagic, A. and Cue, R. M. (2015) ‘Carbon capture , storage and utilisation technologies : A critical analysis and comparison of their life cycle environmental impacts’, 9, pp. 82–102.

BEIS (2016a) *Digest of United Kingdom Energy Statistics (DUKES) 2016*.

BEIS (2016b) *Electricity generation costs*.

BEIS (2017) *UPDATED ENERGY AND EMISSIONS PROJECTIONS 2016*.

Boretti, A. (2013) ‘Renewable hydrogen to recycle CO2 to methanol’, *International Journal of Hydrogen Energy*. Elsevier Ltd, 38(4), pp. 1806–1812. doi: 10.1016/j.ijhydene.2012.11.097.

Cartelle Barros, J. J., Lara Coira, M., de la Cruz López, M. P. and del Caño Gochi, A. (2016) ‘Probabilistic life-cycle cost analysis for renewable and non-renewable power plants’, *Energy*, 112, pp. 774–787. doi: 10.1016/j.energy.2016.06.098.

Chhipi-Shrestha, G., Hewage, K. and Sadiq, R. (2017) ‘Selecting Sustainability Indicators for Small to Medium Sized Urban Water Systems Using Fuzzy-ELECTRE’, *Water Environment Research*, 89(3), pp. 238–249. doi: 10.2175/106143016X14798353399494.

Coates, J. F. (2016) ‘Scenario planning’, *Technological Forecasting & Social Change*, pp. 99–102.

Cornelissen, A. M. ., van den Berg, J., Koops, W. ., Grossman, M. and Udo, H. M. . (2001) ‘Assessment of the contribution of sustainability indicators to sustainable development: a novel approach using fuzzy set theory’, *Agriculture, Ecosystems & Environment*, 86(2), pp. 173–185. doi: 10.1016/S0167-8809(00)00272-3.

Database, E.-P. (2014) *CO2 emission data*.

DTU Transport Compendium Series part 2 (2014) *Multi Criteria decision analysis for use in transport decision making*.

Durbach, I. N. and Stewart, T. J. (2012) ‘Modeling uncertainty in multi-criteria decision analysis’, *European Journal of Operational Research*. Elsevier B.V., 223(1), pp. 1–14. doi: 10.1016/j.ejor.2012.04.038.

European Comission (2017) *Critical Raw Materials*.

Evans, S. (2017) *Analysis: UK carbon emissions fell 6% in 2016 after record drop in coal use, Carbon Brief*.

Guinée, J. B., Gorrée, M., Heijungs, R., Huppes, G., Kleijn, R., De Koning, A., Van Oers, L., Sleeswijk, A. W., Suh, S. and Udo de Haes, H. A. (2001) *Life Cycle Assessment-An operational guide to the ISO standards Part 2A*.

Guo, M. and Murphy, R. J. (2012) ‘Science of the Total Environment LCA data quality : Sensitivity and uncertainty analysis’, *Science of the Total Environment, The*. Elsevier B.V., 435–436, pp. 230–243. doi: 10.1016/j.scitotenv.2012.07.006.

Heijungs, R., Huppes, G. and Guin??e, J. B. (2010) ‘Life cycle assessment and sustainability analysis of products, materials and technologies. Toward a scientific framework for sustainability life cycle analysis’, *Polymer Degradation and Stability*, 95(3), pp. 422–428. doi: 10.1016/j.polymdegradstab.2009.11.010.

Heijungs, R. and Lenzen, M. (2014) ‘Error propagation methods for LCA - A comparison’, *International Journal of Life Cycle Assessment*, 19(7), pp. 1445–1461. doi: 10.1007/s11367-014-0751-0.

Heijungs, R., Settanni, E. and Guin??e, J. (2013) ‘Toward a computational structure for life cycle sustainability analysis: Unifying LCA and LCC’, *International Journal of Life Cycle Assessment*, 18(9), pp. 1722–1733. doi: 10.1007/s11367-012-0461-4.

Huang, I. B., Keisler, J. and Linkov, I. (2011) ‘Multi-criteria decision analysis in environmental sciences: Ten years of applications and trends’, *Science of the Total Environment*. Elsevier B.V., 409(19), pp. 3578–3594. doi: 10.1016/j.scitotenv.2011.06.022.

IPCC (2005) *Carbon Dioxide Capture and Storage*.

ISO (1998) *ISO 14041 Environmental Management-Life Cycle Assessment-Goal and Scope Definition and Inventory Analysis*.

ISO (2006a) *ISO 14040 Environmental Management- Life Cycle Assessment-Principles and Framework*.

ISO (2006b) *ISO 14044 Environmental management--Life Cycle Assessment--Requirements and guidelines*.

ISO (2015) *ISO 14001 Environmental Management Systems*.

ITM Power Limited (2016) ‘Personal communication’.

Klein, S. J. W. and Whalley, S. (2015) ‘Comparing the sustainability of U.S. electricity options through multi-criteria decision analysis’, *Energy Policy*. Elsevier, 79, pp. 127–149. doi:

10.1016/j.enpol.2015.01.007.

Koh, S. C. L., Genovese, A., Acquaye, A. a., Barratt, P., Rana, N., Kuylenstierna, J. and Gibbs, D. (2013) ‘Decarbonising product supply chains: design and development of an integrated evidence-based decision support system – the supply chain environmental analysis tool (SCEnAT)’, *International Journal of Production Research*, 51(7), pp. 2092–2109. doi: 10.1080/00207543.2012.705042.

M. Dawes, R. and Corrigan, B. (1974) *Linear Models in Decision Making, Psychological Bulletin*. doi: 10.1037/h0037613.

Matzen, M. (2016) ‘Methanol and dimethyl ether from renewable hydrogen and carbon dioxide : Alternative fuels production and life-cycle assessment’, 139, pp. 1068–1077. doi: 10.1016/j.jclepro.2016.08.163.

Maxim, A. (2014) ‘Sustainability assessment of electricity generation technologies using weighted multi-criteria decision analysis’, *Energy Policy*. Elsevier, 65, pp. 284–297. doi: 10.1016/j.enpol.2013.09.059.

Morales Mora, M. a., Vergara, C. P., Leiva, M. a., Martínez Delgadillo, S. a. and Rosa-Domínguez, E. R. (2016) ‘Life cycle assessment of carbon capture and utilization from ammonia process in Mexico’, *Journal of Environmental Management*. Elsevier Ltd, 183, pp. 998–1008. doi: 10.1016/j.jenvman.2016.09.048.

National Grid (2017) ‘Future Energy Scenarios (FES)’, (July).

NETL (2015) *Cost and Performance Baseline for Fossil Energy Plants Volume 1a: Bituminous Coal and Natural Gas to Electricity Revision 3 (DOE/NETL-2010/1723),*.

Ng, D. K. S., Tan, R. R., Foo, D. C. Y. and El-Halwagi, M. M. (2015) ‘Process System Engineering Tools for Biomass Polygeneration Systems with Carbon Capture and Reuse’, in Ng, D. K. S., Tan, R. R., Foo, D. C. Y., and El-Halwagi, M. M. (eds) *Process Design Strategies for Biomass Conversion Systems*. Chichester, UK: John Wiley & Sons, Ltd, pp. 96–108. doi: 10.1002/9781118699140.

Niekamp, S., Bharadwaj, U. R., Sadhukhan, J. and Chryssanthopoulos, M. K. (2015) ‘A multi-criteria decision support framework for sustainable asset management and challenges in its application’, *Journal of Industrial and Production Engineering*. Taylor & Francis, 32(1), pp. 44–57. doi: 10.1080/21681015.2014.1000401.

Olah, G. a, Goeppert, A. and Prakash, G. K. S. (2009) ‘Chemical recycling of carbon dioxide to methanol and dimethyl ether: from greenhouse gas to renewable, environmentally carbon neutral fuels and synthetic hydrocarbons.’, *The Journal of organic chemistry*, 74(2), pp. 487–98. doi: 10.1021/jo801260f.

Pask, F., Lake, P., Yang, A., Tokos, H. and Sadhukhan, J. (2017) ‘Sustainability indicators for industrial ovens and assessment using Fuzzy set theory and Monte Carlo simulation’, *Journal of Cleaner Production*, 140, pp. 1217–1225. doi: https://doi.org/10.1016/j.jclepro.2016.10.038.

Perdan, S. and Azapagic, A. (2011) ‘Carbon trading: Current schemes and future developments’, *Energy Policy*. Elsevier, 39(10), pp. 6040–6054. doi: 10.1016/j.enpol.2011.07.003.

Pérez-Fortes, M., Bocin-Dumitriu, A. and Tzimas, E. (2014) ‘CO2 utilization pathways: Techno-economic assessment and market opportunities’, *Energy Procedia*. Elsevier B.V., 63(i), pp. 7968–7975. doi: 10.1016/j.egypro.2014.11.834.

Ramirez, A. and Uu, W. S. (2013) ‘power plants with carbon capture and storage – A sustainability assessment’, (November 2009), pp. 1–111.

Ribeiro, F., Ferreira, P. and Araújo, M. (2013) 'Evaluating future scenarios for the power generation sector using a Multi-Criteria Decision Analysis (MCDA) tool: The Portuguese case', *Energy*. Elsevier Ltd, 52, pp. 126–136. doi: 10.1016/j.energy.2012.12.036.

Sadhukhan, J., Ng, K. S. and Hernandez, E. M. (2014) *Biorefineries and Chemical Processes: Design, Integration and Sustainability Analysis*. Chichester, UK: John Wiley & Sons, Ltd. doi: 10.1002/9781118698129.

Santoyo-Castelazo, E. and Azapagic, A. (2014) 'Sustainability assessment of energy systems: Integrating environmental, economic and social aspects', *Journal of Cleaner Production*. Elsevier Ltd, 80, pp. 119–138. doi: 10.1016/j.jclepro.2014.05.061.

Sayah, A. K. and Sayah, A. K. (2011) 'Wind-hydrogen utilization for methanol production: An economy assessment in Iran', *Renewable and Sustainable Energy Reviews*. Elsevier Ltd, 15(8), pp. 3570–3574. doi: 10.1016/j.rser.2011.05.013.

Schakel, W., Oreggioni, G., Singh, B., Strømman, A. and Ramírez, A. (2016) 'Assessing the techno-environmental performance of CO2 utilization via dry reforming of methane for the production of dimethyl ether', *Journal of CO2 Utilization*, 16, pp. 138–149. doi: 10.1016/j.jcou.2016.06.005.

Singh, R. and Ashcroft, S. (2017) *Special Feature-Nuclear capacity in the UK*.

Sternberg, A. and Bardow, A. (2015) 'Power-to-What? – Environmental assessment of energy storage systems', *Energy Environ. Sci.*, pp. 389–400. doi: 10.1039/C4EE03051F.

Stewart, T. J., French, S. and Rios, J. (2013) 'Integrating multicriteria decision analysis and scenario planning-Review and extension', *Omega (United Kingdom)*. Elsevier, 41(4), pp. 679–688. doi: 10.1016/j.omega.2012.09.003.

Styring, P. and Jansen, D. (2011) *Carbon Capture and Utilisation in the green economy*. The Centre for Low Carbon Futures 2011.

Troy, S., Schreiber, A. and Zapp, P. (2016) 'Life cycle assessment of membrane-based carbon capture and storage', *Clean Technologies and Environmental Policy*. Springer Berlin Heidelberg, 18(6), pp. 1641–1654. doi: 10.1007/s10098-016-1208-x.

Trudewind, C. a., Schreiber, A. and Haumann, D. (2014) 'Photocatalytic methanol and methane production using captured CO2 from coal power plants. Part II – Well-to-Wheel analysis on fuels for passenger transportation services', *Journal of Cleaner Production*. Elsevier Ltd, 70, pp. 38–49. doi: 10.1016/j.jclepro.2014.02.024.

Van-Dal, É. S. and Bouallou, C. (2013) 'Design and simulation of a methanol production plant from CO2 hydrogenation', *Journal of Cleaner Production*. Elsevier Ltd, 57, pp. 38–45. doi: 10.1016/j.jclepro.2013.06.008.

Vo, T. T. Q., Xia, A., Rogan, F., Wall, D. M. and Murphy, J. D. (2016) 'Sustainability assessment of large-scale storage technologies for surplus electricity using group multi-criteria decision analysis', *Clean Technologies and Environmental Policy*. Springer Berlin Heidelberg, pp. 1–15. doi: 10.1007/s10098-016-1250-8.

Wang, J. J., Jing, Y. Y., Zhang, C. F. and Zhao, J. H. (2009) 'Review on multi-criteria decision analysis aid in sustainable energy decision-making', *Renewable and Sustainable Energy Reviews*, 13(9), pp. 2263–2278. doi: 10.1016/j.rser.2009.06.021.

Zhang, X., Bauer, C., Mutel, C. L. and Volkart, K. (2017) 'Life Cycle Assessment of Power-to-Gas : Approaches , system variations and their environmental implications', *Applied Energy*. Elsevier Ltd, 190, pp. 326–338. doi: 10.1016/j.apenergy.2016.12.098.

5 Environmental Assessment of Methanol Production Coupling CO_2 Utilisation and Hydrogen Production from Renewable Energy

This chapter applies the framework presented in **Chapter 4** to a theoretical carbon dioxide utilisation process. This assessment allowed for testing of the feasibility of the framework, its benefits, challenges and applicability. This chapter is a pre-evaluation of the environmental impact assessment framework to use in **Chapter 6** for a utilisation process that is under development by the University of Sheffield. The process under assessment includes the capture of CO_2 to synthesise methanol powered by renewable wind energy. The functional unit is set at 1 kg CH_3OH of final product and 1.43 kWh of electricity generated for the grid. This chapter addresses the technical and environmental aspects of the framework.

5.1 CO_2 utilisation system

The demand for methanol is high, with close to 200,000 tons/day used as a chemical feedstock and as a transport fuel (Methanol Institute, 2017). It is an industry that generates $55 billion per year and spans throughout the world. Its ability to be produced from different feedstocks including CO_2, make it a process that can be adapted to utilise CO_2 emissions as a feedstock. As discussed in **Section 2.2.1**, methanol in the CO_2 utilisation industry is one of the most well documented processes. The level of information available for CH_3OH synthesis with CO_2 makes it a suitable process for determining an environmental impact assessment framework that can be then expanded to other utilisation processes.

This works presents the environmental impacts of scenarios for methanol production using carbon capture. **Figure 5.1** depicts the carbon flows for the main scenario under study. A comparative assessment is made between a non-carbon dioxide utilisation (non-CO_2 utilisation) process and CO_2 utilisation routes. Results are used to identify hotspots throughout the production stage and suggest improvement opportunities. Through a set of indicators, the potential of CO_2 utilisation processes as a carbon neutral or carbon avoidance process can be determined. Three main scenarios are evaluated and summarised below, each with independent variables: CO_2 chemical transformation with non-biogenic point source capture, CO_2 chemical transformation with direct air capture and methanol synthesis from conventional methods.

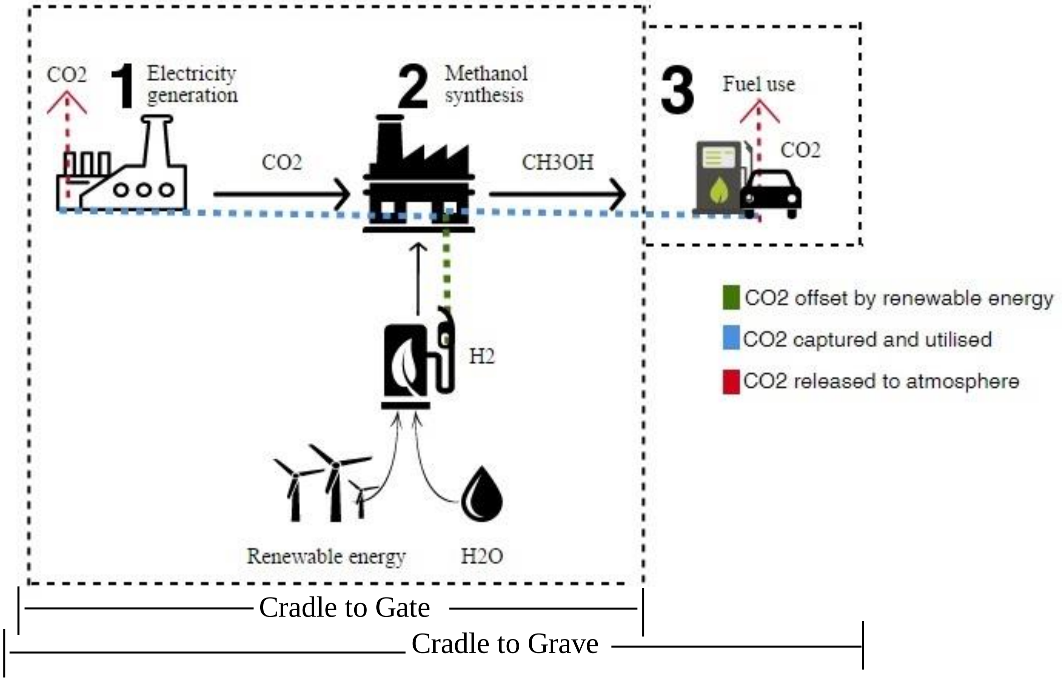


Figure 5.1 Diagram of carbon dioxide flow in methanol production process (baseline case)

Non-biogenic point source capture

CO_2 is supplied from a subcritical 550 MW PC (pulverised coal) plant with post-combustion capture. The capture method is through absorption using amines. After capture, the wet CO_2 is dehydrated using glycol and then compressed for transport. The power station absorbs energy requirements by providing the necessary power for the capture process. Methanol is then produced through catalytic hydrogenation of CO_2 where the main inputs are H_2 and captured CO_2. Hydrogen can be obtained through steam reforming of natural gas or water electrolysis, for this case study, water electrolysis is used as the chosen production process. Both renewable energy and fossil fuels were assessed for powering the utilisation process.

Direct air capture

CO_2 is directly captured from air. To capture CO_2, an absorption column with sodium hydroxide solution is considered as detailed in **Section 2.1.1**. CO_2 is then compressed and used as a feedstock for methanol production using the same utilisation processes as mentioned previously for non-biogenic point source capture.

Conventional methods

To compare a CO_2 utilisation process with a conventional process, methanol is produced through the steam reforming process of natural gas and syngas (generated from biomass). Energy is supplied with fossil fuels and a UK based electricity grid mix. **Figure 5.2** shows the comparison system of both production routes, the process units all fall within the same boundary.

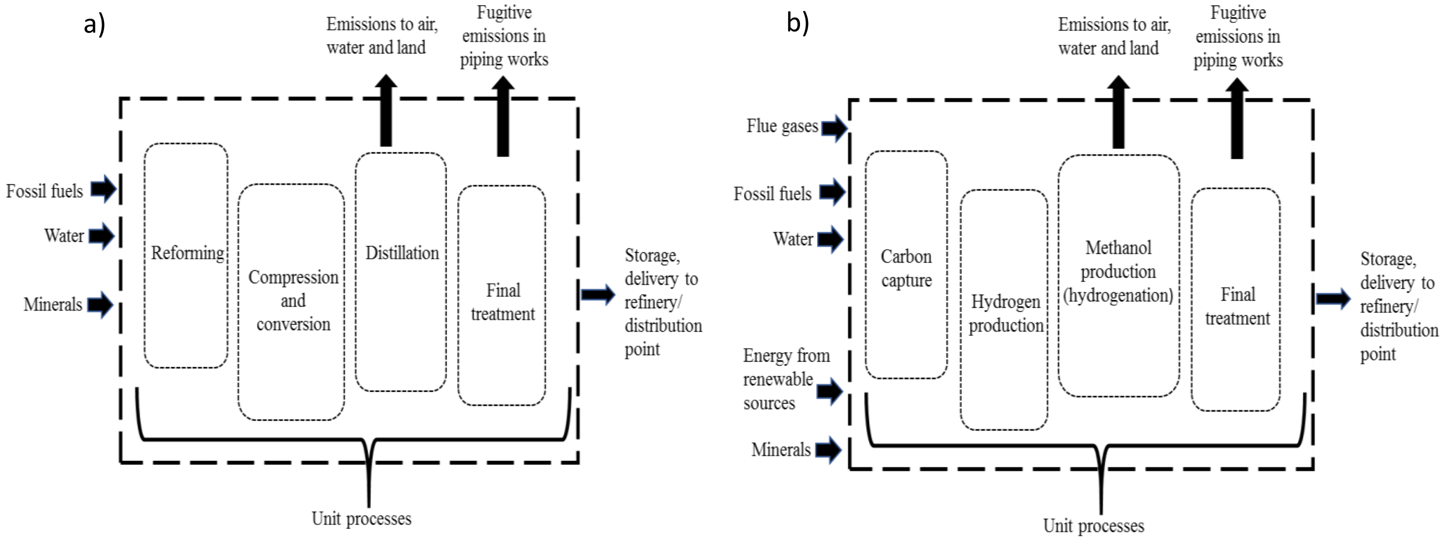


Figure 5.2 a) System product, CH_3OH from SMR (steam methane reforming), b) CH_3OH from catalytic hydrogenation of CO_2 using renewable H_2

5.1.1 Process description and boundaries

The functional unit is defined as ´the production of 1 kg of methanol and 1.43 kWh of electricity generated for the grid’. Authors within carbon capture research typically opt for a functional unit of 1 kWh (Singh, Strømman and Hertwich, 2011; Corsten *et al.*, 2013; Volkart, Bauer and Boulet, 2013). However, an important difference between carbon capture and storage (CCS) and CO_2 utilisation is the conversion of CO_2 to different products instead of storage. It has been suggested by Von der Assen *et al.* (2013) and

Sternberg & Bardow (2015) that using energy production and final product as functional unit is a fairer comparison. The assumptions in **Table 5.1** were made for all cases:

Table 5.1 General methanol plant specifications

Plant specifications	Unit
Methanol total production	1,000 kg/day (no losses)
Functional unit	1 kg of product
Operational hours	8,000 hours/year

There are three main supply chain stages throughout the process: electricity generation, CO_2 capture and methanol synthesis. **Figure 5.3** shows the mass balance calculations for the utilisation assuming 100% efficiency; production is set for up to 1,000 kg of CH_3OH and scaled to 1 kg for life cycle assessment (LCA) comparison. It is assumed that methanol production using CO_2 would have similar infrastructure requirements as conventional routes, therefore only a general comparative analysis is made. Materials and chemicals production include extraction, manufacture and all related transportation. The operational phase includes utilities use (energy and water) for every stage of the manufacturing process and fuel for transportation. The last stage considers waste collection and waste management processes. Demolition is outside the study boundaries. The overall assessment has a ‘cradle to gate’ approach. Distribution, use and end of life of methanol is beyond the scope of this study (refer to **Section 3.2.1** for more information). **Figure 5.4** shows the boundaries for each main production stage; stage three shows the process variables chosen for methanol synthesis.

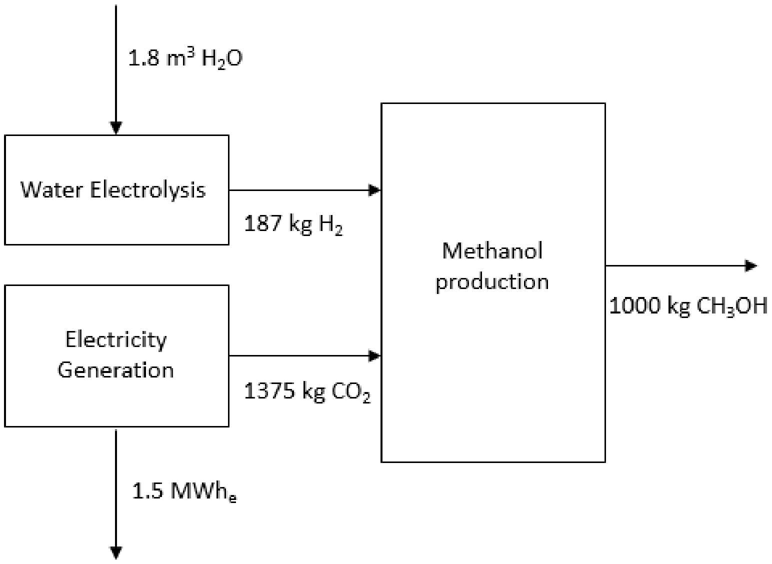
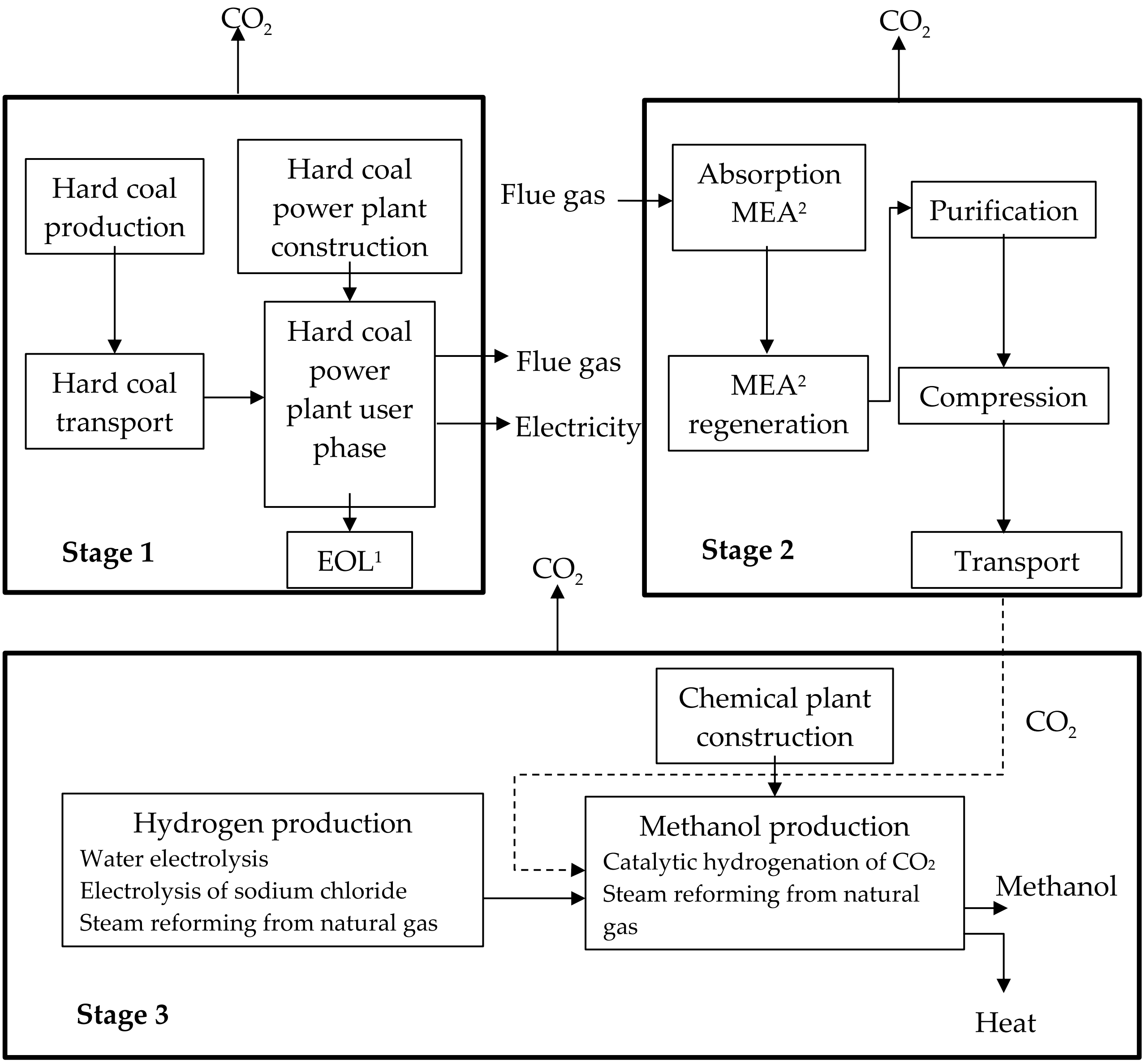


Figure 5.3 Mass balance diagram for minimum inputs required for methanol production from captured CO_2, total CH_3OH production of 1000 kg, 100% conversion



[1]End of life [2] monoethanolamine

Figure 5.4 Cradle to gate boundaries for the environmental impact assesment of methanol production from CO_2 capture and hydrogen from renewable energy

5.2 Life cycle inventory (LCI)

The life cycle (LCI) inventory includes economic and environmental interventions scaled down to produce 1 kg of methanol. Overall, the process was divided into three main categories: CO_2 source, CH_3OH synthesis and H_2 production. The following sections describe the process and create the inventory for these three categories.

CO_2 supply

For fixed-point scenarios, CO_2 was obtained from a post-combustion capture process. Three different power plants ranging from a net power output of 550 MW to 630 MW were considered as the flue gas source. While CO_2 can be sourced from many other industrial processes, foreground data was most available for post-combustion capture. The performance for the power plants with/without capture is shown in **Table 5.2**. The inventory was taken from DOE/NETL–2015/1723 (NETL, 2015). The flue gas is used as feedstock for the capture stage; therefore, all background information is based on kWh production rate. The auxiliary power is covered by increasing the boiler size and generator/turbine in the pulverised coal (PC) plants. Background information was taken from ecoinvent 3.3 and adapted to represent UK conditions where possible. As an example, the process selected to model electricity from hard coal has a database from Great Britain.

Table 5.2 Summary of power plant performance indicators for a subcritical and supercritical pulverised coal plant and a natural gas combined cycle plant. (Data obtained from DOE/NETL-2015/1723)

Performance Indicators	**Results by type of power plant**		
	Subcritical, PC[1]	Supercritical, PC[1]	NGCC[2]
Net power output (MWe)			
without capture	550	550	630
with capture	550	550	550
Net plant HHV Efficiency (%)			
without capture	39	40.7	51.5
without capture	31	32.5	45.7
Capture efficiency for power plant with carbon capture (%)	90	90	90
CO_2 separation	Amines	Amines	Selexol
Auxiliary power (MWe)			
without capture	31	30	11
with capture	94	91	42
Process water discharge (lpm)			
without capture	4,304	4,009	2,252
with capture	7,268	6,863	3782
Raw water withdrawal (lpm)			
without capture	20,960	19,320	10,020
with capture	31,960	29,840	15,230
CO_2 emissions (kg/MWh_{net})			
without capture	807	733	356
with capture	101	97	40

[1] Pulverised coal power plant [2] Natural gas combined cycle power plant

The capture process includes an absorption and regeneration unit, dehydration and CO_2 compression. A diagram of a conventional capture unit with absorption and regeneration columns is shown in **Figure 5.5.** In this process flue gases go through the absorption column filled with monoethanolamine (MEA); off gases exit through the top of the column and the CO_2 rich solvent stream passes to the regeneration column. Through thermal regeneration, a wet CO_2 stream exits through the top of the column and the CO_2 depleted solvent is returned to the column with monoethanolamine (MEA) top up to account for losses. This process is currently the most used CO_2 capture method (refer to **Section 2.1.2** for more information).

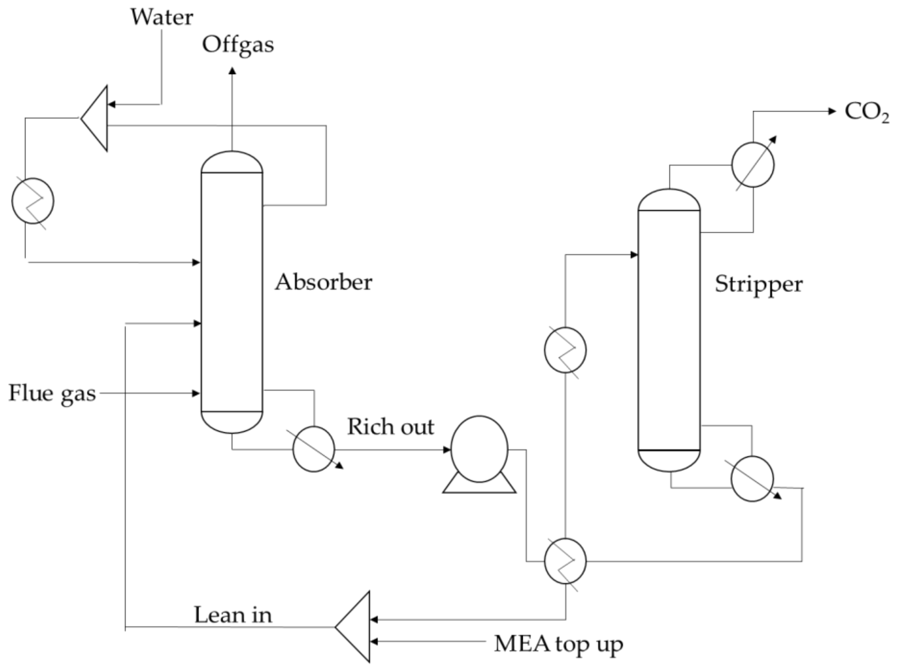


Figure 5.5 Schematic diagram of CO_2 capture unit for post-combustion capture using absorption with monoethanolamine (MEA), based on Abu-Zahra *et al.* (2007)

The compressor used in the inventory by DOE/NETL –2015/1723 (NETL, 2015) is centrifugal with 8 stages of discharge pressure. Between stage 4 and 5, there is a dehydration unit that uses triethylene glycol (TEG) as the absorbent. This dehydration unit reduces moisture in the CO_2 stream to 300 ppmv. **Figure 5.6** shows a conventional dehydration unit with triethylene glycol as the solvent. As with capture, the process is divided into absorption and regeneration; where dry CO_2 is obtained at the top of the absorption column and H_2O loaded triethylene glycol (TEG) is regenerated into lean triethylene glycol (TEG) for recycling. The basics of this process are described in Abbas *et al.* (2013).

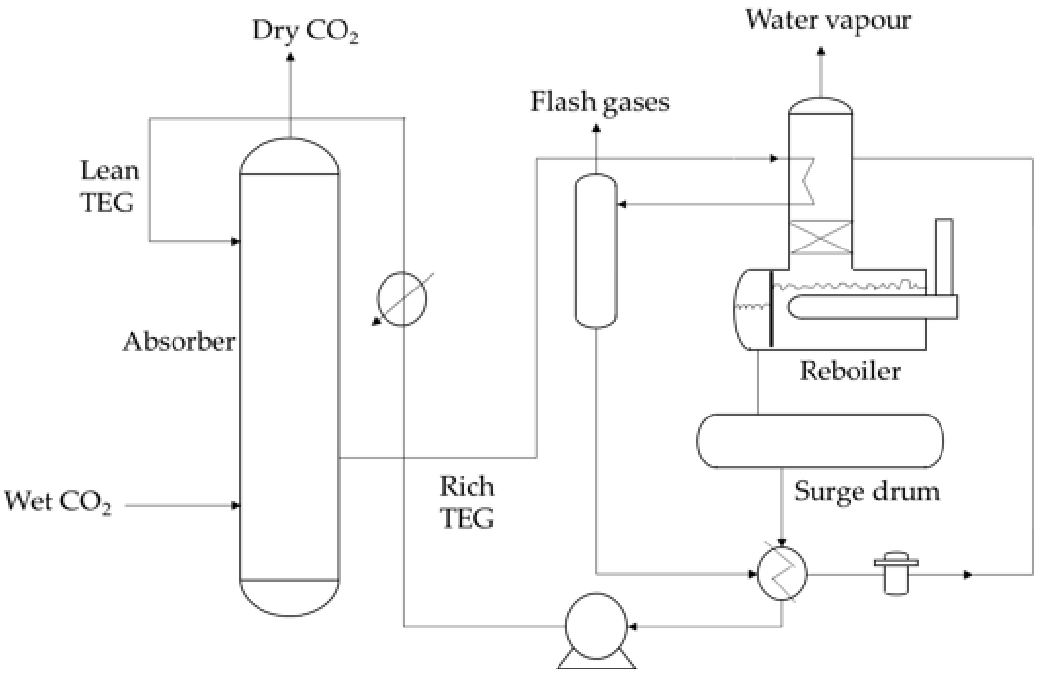


Figure 5.6 Schematic of dehydration unit using triethylene glycol (TEG) for wet CO_2 from post-combustion capture plant, based on Abbas *et al.* (2013)

Water for CO_2 capture

The parameters from **Table 5.2** were used to calculate water use in the capture stage. Taking the values for the subcritical PC (pulverised coal) plant, the raw water withdrawal was set at 31 m^3/min. This value equates to 0.004 m^3/kWh. This rate considers an internal recycle of 4.9 m^3/min (NETL, 2015). For process water, 0.0009 m^3 are discharged for every kWh generated. Datasets from the life cycle assessment (LCA) software GaBi ts version 8.7.0.18 were used for background emission (EU-27, process water, underground and municipal wastewater treatment).

Consumables

The main consumables for the CO_2 capture process under study are shown in **Table 5.3**. These values are taken from the inventory DOE/NETL –2015/1723 (NETL, 2015), and represent the inputs needed to capture 1,000 kg of CO_2. Since the solvent used in the database was undisclosed, monoethanolamine (MEA) from the NETL (2013) report was used as a replacement.

Table 5.3 Consumables for post-combustion capture unit with 90% capture based on NETL (2015) & NETL (2013)

Consumables	**Value** (considering 1,000 kg of CO_2 captured per 1,100 kWh generated)
Limestone (kg)	54.0
Hydrated lime (kg)	11.0
Activated carbon (kg)	0.4.0
Triethylene glycol (kg)	36.0
SCR catalyst (m^3)	4×10^{-5}
Ammonia (kg)	1.6
Monoethanolamine (kg)	1.4
Thermal reclaimer unit waste (kg)	0.2

Direct air capture

Direct air capture (DAC) was another CO_2 supply alternative considered in this study. This industry has been growing in recent years; companies such as Carbon Engineering and Skytree (Carbon Engineering, 2017; Skytree, 2017) are working on commercializing small to medium CO_2 capture units. Carbon Engineering is planning to deploy full scale, commercialising air to fuels facilities after 2019. Skytree is expected to implement their re-capture process at the International Space Station in 2017. While this technology expands, there are questions on how it will affect overall life cycle emissions in a scenario that relies on carbon dioxide utilisation processes. Although direct emissions will reduce, indirect might not. Currently, there are no public inventories available for this type of capture units; nevertheless, there is research available that provides energy performance data. This information can be used to determine potential carbon savings. Thus, for this work it was decided to only use energy use as a first assessment to compare between CO_2 capture from fixed point and CO_2 capture from air and analyse carbon flows in CO_2 utilisation scenarios. The relevant sensitivity analysis was made to account for uneven inventories between alternatives. A summary of the power required to capture 1 tonne of CO_2 according to different sources using direct air capture (DAC) from older to newer research and is shown in **Table 5.4**.

Table 5.4 Summary of energy penalties for a direct air capture system using thermal reformation and humidity swing processes found in literature. Scaled to 1 tonne of CO_2 capture

Energy consumption (GJ/tCO_2)	Direct air capture processes found in literature				
	DAC[1] thermal reformation using NaOH				HS-DAC[2]
	(Zeman, 2014)	(Baciocchi, Storti and Mazzotti, 2006)	(Socolow, R. H.; Desmond, 2011)	(Zeman, 2014)	(Van der Giesen *et al.*, 2017)
Electricity	2.8	1.8	1.8	1.7	1.4
Thermal	7.2	8.8	8.1	6.7	0.0

[1] Direct air capture [2] Humidity-swing direct air capture

The processes selected are thermal reformation with sodium hydroxide as solvent and HS-DAC (standard climate 20°C, 30% relative humidity) as a newer process**. Section 2.1.1** has more information on these methods.

The baseline scenario considers direct air capture (DAC) with thermal regeneration using sodium hydroxide as sorbent and is based on the work by Zeman (2014) which is based on a report published by the American Physical Society (Socolow *et al.*, 2011). In a best-case scenario, the thermal energy carbon emissions are negligible, as the system would re-capture any CO_2 emitted. However, the upstream impacts do not disappear, and should be accounted for.

H_2 supply

In the case study (baseline scenario), hydrogen is supplied through water electrolysis. To produce 1,000 kg of CH_3OH requires a minimum of 187.5 kg of H_2 from 1,687.5 kg of H_2O (as seen in **Equation 5.1**).

$$1{,}687.5\ kg\ H_2O \ \rightarrow 187.5\ kg\ H_2\ +\ 1{,}500\ kg\ O_2$$

Equation 5.1

As an alternative and for the sensitivity analysis included later in this chapter, the chlor-alkali databases by ecoinvent version 3.3 are also used. For the latter, three different cells designs are used as shown in **Figure 5.7**. All data for hydrogen production from chlor-alkali production was obtained from ecoinvent version 3.3 databases (Althaus *et al.*, 2007). Energy consumption values were adapted for renewable energy and fossil fuel-based scenarios in the UK. Hydrogen and methanol production are within one industrial site to simplify the model (by eliminating transportation between sites). Waste management includes the recycling of surplus heat and water as utilities for the process.

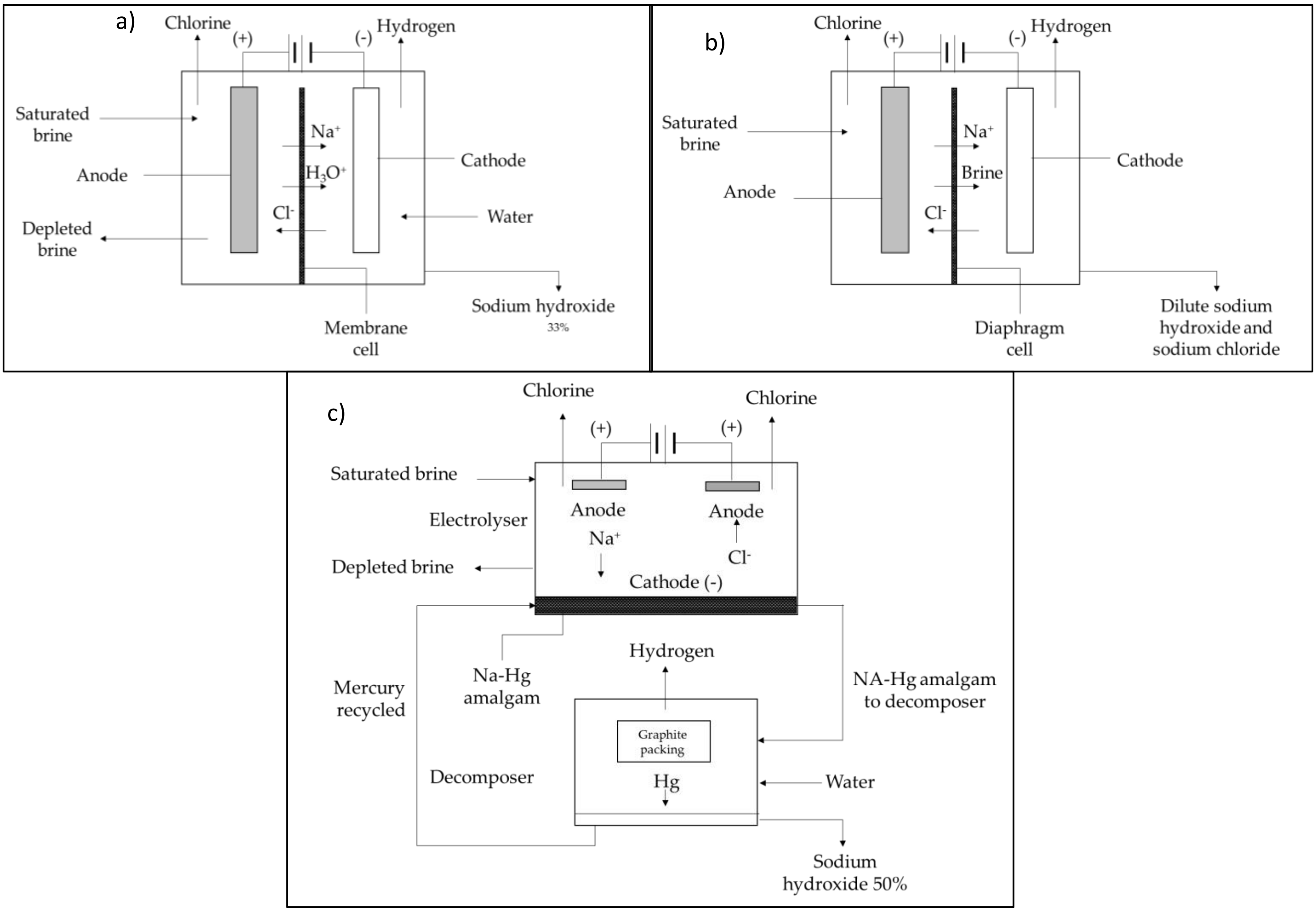


Figure 5.7 schematic diagram of chlor alkali electrolyser with three different membranes. a) Membrane cell, b) Diaphragm cell, c) Mercury cell, based on ecoinvent 3.3 chemicals database (Althaus *et al.*, 2007)

To obtain background data and environmental impacts a commercially available software is used (GaBi ts version 8.7.0.18) for all stages of the model. Great Britain (GB) databases are used when possible to obtain local scenarios. If Great Britain (GB) values are not available, then EU or global data is used. As a last resource and if the energy mix cannot be adapted a value from Germany (DE) is taken as it has there is often more data available than other for other European countries (see **Appendix II** for full models). This information is used to identify carbon hotspots in **Section 5.3**.

Methanol synthesis

The last production stage in a cradle to gate scenario is the production phase and, in this case, the synthesis of methanol. For this stage, a catalytic hydrogenation of captured CO_2 process has been selected to produce methanol. CH_3OH synthesis follows the next **Equation 5.2** with a ΔH = -11.9 kcal/mol (Boretti, 2013):

$$1.357\ kgCO_2 + 0.1875\ KgH_2 = 1\ kgCH_3OH + 0.5625\ kgH_2O$$

Equation 5.2

1 tonne of methanol will require **1.4 tonnes of CO_2** and **0.18 tonnes of H_2**. Methanol synthesis consists of a reactor and a distillation column; H_2 and CO_2 are mixed and then compressed before entering the reactor as seen in the diagram from **Figure 5.8**. The main process parameters are shown in **Table 5.5**.

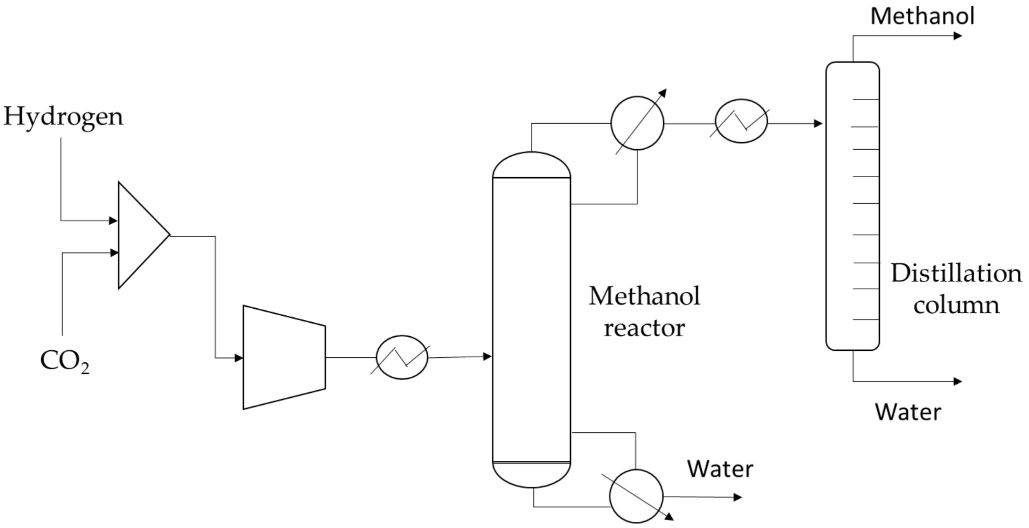


Figure 5.8 Schematic diagram of methanol production through catalytic hydrogenation of CO_2 using H_2 from renewables and captured CO_2 as feedstock material, based on Abu-Zahra *et al.* (2007)

Table 5.5 Process parameters per tonne of CH_3OH from catalytic hydrogenation of CO_2 using water electrolysis for hydrogen production, based on Boretti (2013)

Parameter	**Value**
Reaction temperature (°C)	260.0
Pressure (bar)	83.0
Water (m^3)	1.5
Energy (GJ)	
H_2 production	45.6
Compression	10.0
Distillation	1.7
Reaction heat	-1.5
Total	56.7

Refer to **Section 2.2.1** for more information on this process. Since a basic stoichiometric analysis was considered in this stage, the only chemical feedstocks included are hydrogen and CO_2. The impact of catalyst use has not been assessed due to the lack of specific databases. However, in **Chapter 2** there is general information on catalyst use. Uncertainty and sensitivity analyses have been run to account for cut-off data in each production stage. The full boundaries of the main commodities for methanol production are shown in **Figure 5.9**. The cradle to gate assessment finishes after methanol is distilled and is ready for storage and then distribution.

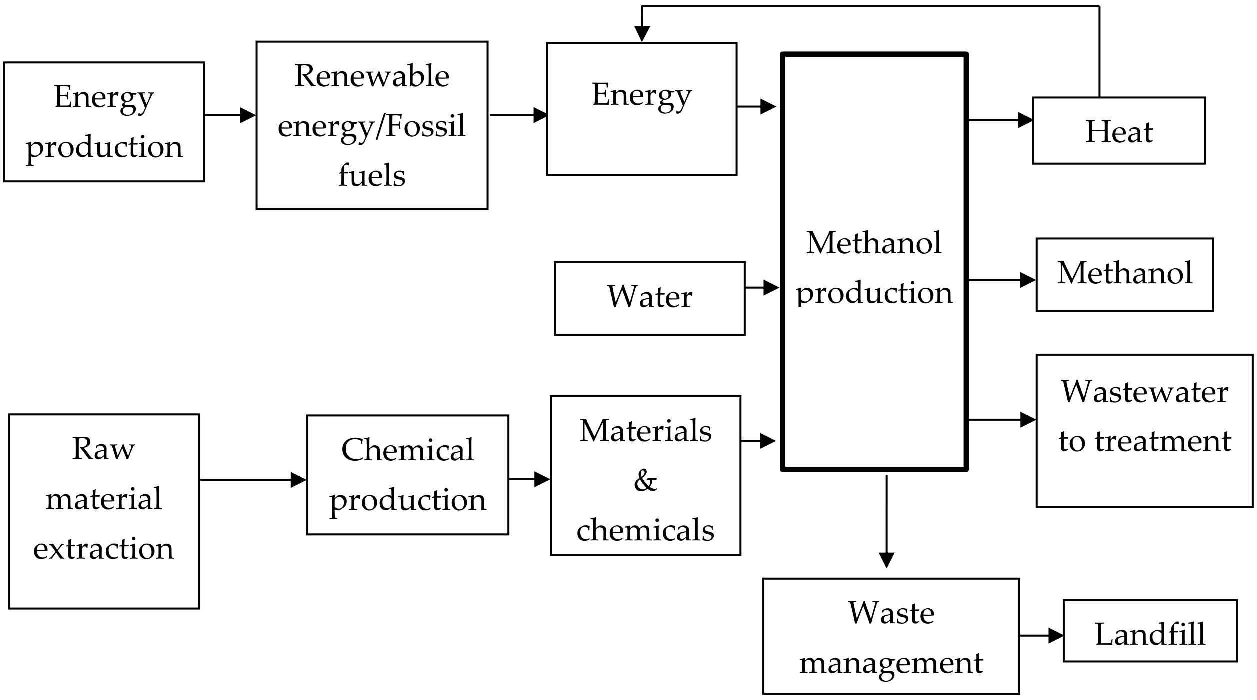


Figure 5.9 Boundaries for methanol production

Infrastructure and transport

It is assumed that CO_2 is transported through a pipeline to the chemical production site. The transportation of all other materials is included as background data. The formula provided by ecoinvent version 3.3 for infrastructure was used to calculate the impact of the installation of the utilisation plant. This is only a theoretical value and can only serve for general comparison purposes with other literature-based datasets. Following the method described in **Section 4.4.1**, for 20 years and 333 t/year of CH_3OH produced, the chemical plant unit is 1.5×10^{-7} per kg of product.

5.2.1 General inventory

In this section, all the inputs and outputs for methanol production are brought together under one study. For this, a general commodity matrix (**Table 5.6**) scaled to 1,000 kg of CH_3OH was created following the method established in Heijungs *et al*. (2013). This method allows identifying how a commodity intervenes throughout the supply chain, thus simplifying the creation of a life cycle inventory (LCI). All negative values indicate the use of a commodity, while positive values indicate the generation of a commodity. Scaling to a final production of 1 kg of CH_3OH, the main commodities are 0.2 kg of H_2 and 1.4 kg of CO_2.

Table 5.6 Commodities matrix for methanol production (1,000 kg/day), baseline scenario

	Commodities									
Inputs	Hydrogen (kg)		Water (kg)		CO_2 (kg)		Electricity (MJ)		Methanol (kg)	
	Consumed	Generated	Consumed	Generated	Consumed	Generated	Consumed	Generated	Consumed	Generated
Methanol unit (pieces)	0	0	0	0	0	0	0	0	0	1
Energy (GJ)	46	0	0	0	5	0	0	62	10	0
Hydrogen (kg)	0	187	0	0	0	0	0	0	187	0
Water (kg)	1,687	0	0	4,817	1,630	0	0	0	1,500	0
Carbon dioxide (kg)	0	0	0	0	0	1,375	0	0	1,375	0

The data presented in the commodity matrix is used as the baseline study (or case study); this is the main process and route of interest. With this inventory, hotspots can be detected and addressed. However, other alternatives needed to be presented to compare its performance indicators (presented in **Section 4.7**). A conventional methanol route was used for a comparative study. Alternative databases are also used for each main input for sensitivity and uncertainty analyses (**Figure 5.10**). The variables data is shown in the following sections.

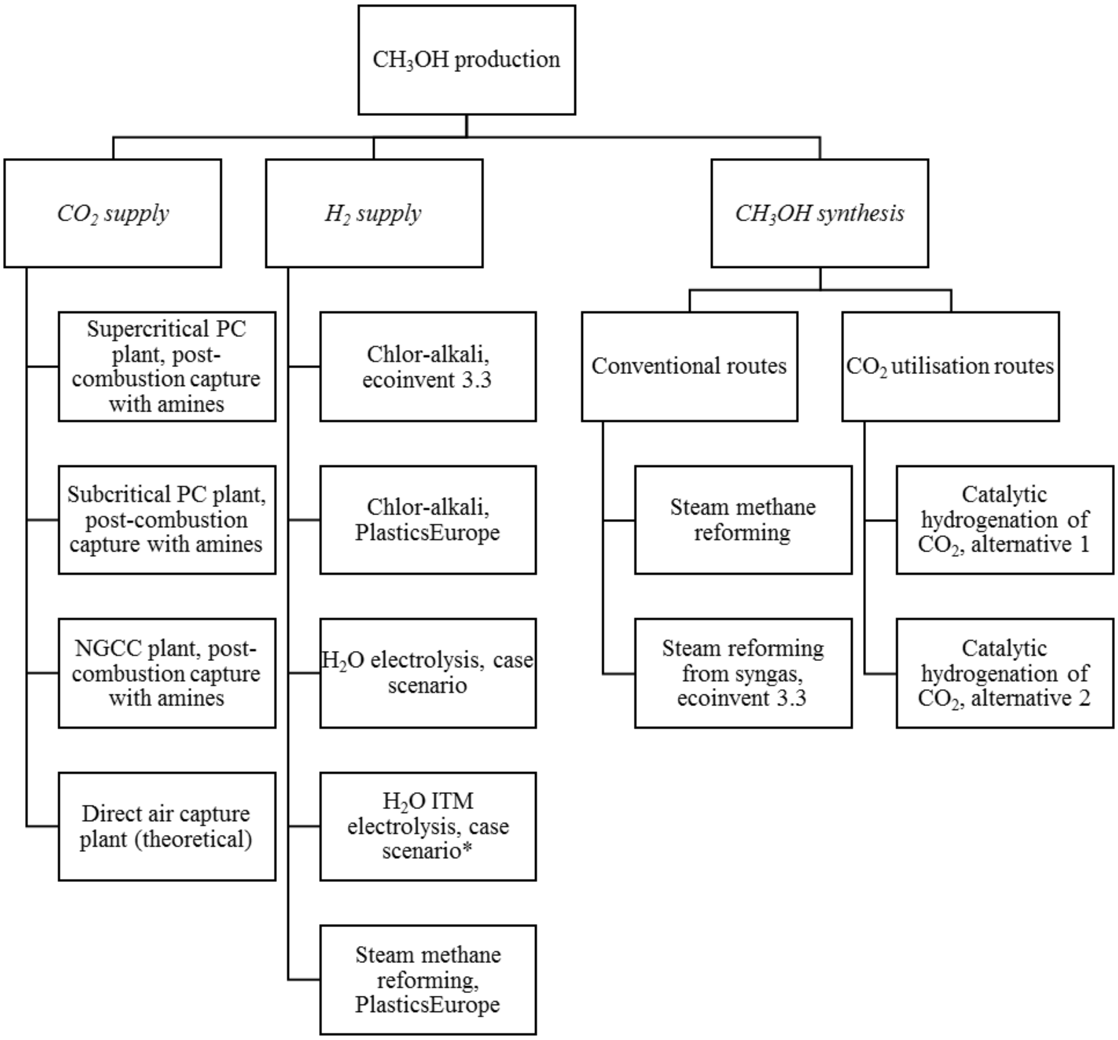


Figure 5.10 Database variables for sensitivity analysis for the life cycle impact assessment (LCIA). H_2 and CO_2 supply for methanol production

CO_2 capture: alternative inventories

For this work, CO_2 is either supplied from a post-combustion capture process, or a direct air capture scenario. For the first case, three different power plants are used as the CO_2 source (process parameters shown in **Table 5.2**). The capture process is the same for all post-combustion capture cases. For the second process, the utilisation process uses a theoretical direct air capture (DAC) with only energy considered as a commodity (based on the work by Zeman (2014)). **Table 5.7** shows inputs for each CO_2 supply alternative.

Table 5.7 Inputs for CO_2 supply. 1) Post-combustion carbon capture, from a subcritical PC (pulverised coal) power plant 2) Post-combustion carbon capture plant, from a supercritical PC (pulverised coal) power plant 3) Post-combustion for a carbon capture plant, natural gas combined cycle (NGCC) power plant 4) Theoretical direct air

Inputs	**Process alternatives (scaled to 1.4 kg CO_2)**			
	CO_2^1	CO_2^2	CO_2^3	CO_2^4
Energy (MJ)	0.6	0.6	0.2	3.8
Ammonia (kg)	1.9×10^{-3}	1.9×10^{-3}	1.8×10^{-3}	0.0
Activated carbon (kg)	0.4×10^{-3}	0.3×10^{-3}	0.0	0.0
Calcium carbonate (kg)	0.1	0.1	0.0	0.0
Monoethanolamine, (kg)	1.9×10^{-3}	1.9×10^{-3}	1.9×10^{-3}	0.0
Water (kg)	3.3	3.2	4.3	0.0
Triethylene glycol (kg)	4.4×10^{-3}	4.5×10^{-2}	2.0×10^{-7}	0.0
Hydrated lime (kg)	1.4×10^{-2}	1.4×10^{-2}	0.0	0.0
Makeup water and waste treatment (kg)	1.6×10^{-3}	1.6×10^{-3}	0.2×10^{-2}	0.0
Waste in reclaimer (kg)	0.2×10^{-3}	0.2×10^{-3}	0.1×10^{-3}	0.0

H_2 production: alternative inventories

Water electrolysis, chlor-alkali electrolysis and H_2 from natural gas were the three alternatives with inventories. The baseline scenario uses theoretical values based on Boretti (2013). Chlor-alkali electrolysis used ecoinvent version 3.3 and PlasticsEurope databases. Chlor-alkali databases include sodium chloride with membrane, diaphragm and mercury cell. The last alternative is H_2 from natural gas as the conventional route. There is an extra H_2 production process (ITM power limited electrolyser) added for comparison and it is used as the main variable in **Chapter 6.** The inputs for each H_2 supply alternative are shown in **Table 5.8**. Renewable energy (wind, solar and hydro) and fossil fuels are also evaluated for the supply stage and are discussed in **Section 2.4.3**.

Table 5.8 H_2 supply inputs. 1) case scenario, theoretical values based on Boretti (2013) 2) ITM electrolyser 3), 4), 5) diaphragm, membrane and mercury cell, chlor-alkali electrolysis by ecoinvent 3.3 6) chlor-alkali electrolysis PlasticsEurope 7) steam methane reforming (SMR) by PlasticsEurope

Inputs	**Process alternatives (scaled to 0.2 kg of H_2)**						
	H_2 (kg)[1]	H_2 (kg)[2]	H_2 (kg)[3]	H_2 (kg)[4]	H_2 (kg)[5]	H_2 (kg)[6]	H_2 (kg)[7]
Energy (MJ)	46	44	24	20	24	2 x 10^{-2}	1
Water (kg)	2	5	539	187	187	1 x 10^{-2}	1
Sodium chloride, powder (kg)	0	0	3	3	3	0	0
Soda ash, powder (kg)	0	0	2 x 10^{-2}	2 x 10^{-2}	2 x 10^{-2}	0	0
Barite (kg)	0	0	7 x 10^{-3}	7 x 10^{-3}	7 x 10^{-3}	0	0
Calcium chloride (kg)	0	0	4 x 10^{-2}	3 x 10^{-2}	3 x 10^{-2}	0	0
Hydrochloric acid, 30% in water (kg)	0	0	4 x 10^{-2}	4 x 10^{-2}	4 x 10^{-2}	0	0
Sulphite (kg)	0	0	2 x 10^{-4}	2 x 10^{-4}	2 x 10^{-4}	0	0
Sodium hydroxide, 50% solution state (kg)	0	0	4 x 10^{-3}	7 x 10^{-2}	1 x 10^{-2}	0	0
Asbestos, crysotile type, (kg)	0	0	4 x 10^{-4}	0	0	0	0
chemical plant, organics (unit)	0	0	7 x 10^{-10}	7 x 10^{-10}	7 x 10^{-10}	0	0
Sludge, NaCl electrolysis (kg)	0	0	3 x 10^{-2}	3 x 10^{-2}	3 x 10^{-2}	3 x 10^{-3}	0
Spent activated carbon with mercury [waste]	0	0	0	0	5 x 10^{-5}	0	0
disposal, hazardous waste, 0% water, to underground deposit (kg)	0	0	2 x 10^{-4}	0	0	10 x 10^{-5}	0
Mercury, liquid (kg)	0	0	0	0	1 x 10^{-5}	0	0
Sulfuric acid (kg)	0	0	2 x 10^{-2}	2 x 10^{-2}	2 x 10^{-2}	0	0

CH_3OH synthesis: alternative inventories

The assessment includes two main methanol production routes: the conventional process using CH_4 and a CO_2 utilisation process. The conventional routes are taken from ecoinvent version 3.3 and adapted to UK conditions (energy and water), these include CH_3OH from fossil fuel based H_2 and CH_3OH from syngas. For the CO_2 utilisation route, a stoichiometric balance is used for the main commodities (**Table 5.6**) and is used as the main case study. **Table 5.9** shows the input values for each database.

Table 5.9 Inputs for CH_3OH production according to process alternatives

Inputs	**Process alternatives (scaled to 1 kg of CH_3OH)**		
	CH_3OH^1	CH_3OH^2	CH_3OH^3
Electricity (MJ)	10	26×10^{-2}	96×10^{-2}
Water (kg)	15×10^{-2}	85×10^{-2}	85×10^{-2}
Hydrogen (kg)	19×10^{-2}	0	0
Carbon dioxide (kg)	14×10^{-2}	0	0
Natural gas, production onshore (Nm^3)	0	43×10^{-2}	0
Natural gas, high pressure at consumer (kg)	0	9	0
Syngas (kg)	0	0	8
Nickel, 99.5% (MJ)	0	2×10^{-5}	2×10^{-5}
Aluminium oxide (kg)	0	24×10^{-5}	24×10^{-5}
Copper oxide (kg)	0	9×10^{-5}	9×10^{-5}
Molybdenum (kg)	0	1×10^{-5}	1×10^{-5}
Zinc (kg)	0	3×10^{-5}	3×10^{-5}
Chemical plants, organics (unit)	1×10^{-7}	4×10^{-11}	4×10^{-11}
Wastewater treatment (m^3)	0	53×10^{-4}	53×10^{-4}

[1] Case scenario based on stoichiometric calculations, catalytic hydrogenation of CO_2 [2] H_2 from steam methane reforming (SMR) by ecoinvent 3.3 [3] CH_3OH with syngas, ecoinvent 3.3

The commercial database flows used for the inventories in this chapter are summarised in **Table 5.10**.

Table 5.10 Flows from commercial database used for the methanol case study inventory

Inventory database		
CO_2 capture		
Country	**Name of input**	**Database**
EU-27	Process water	thinkstep 8.7.0.18
EU-27	Triethylene glycol	PlasticsEurope
EU-27	Municipal waste treatment (mix)	thinkstep 8.7.0.18
EU-27	Municipal solid waste on landfill	thinkstep 8.7.0.18
Germany	Calcium hydroxide (dry, slaked lime)	thinkstep 8.7.0.18
Germany	Activated carbon	thinkstep 8.7.0.18
Germany	Limestone flour ($CaCO_3$)	thinkstep 8.7.0.18
Great Britain	Electricity from hard coal	thinkstep 8.7.0.18
Great Britain	Ammonia (NH_3)	thinkstep 8.7.0.18
Great Britain	Process steam from natural gas 85%	thinkstep 8.7.0.18
Great Britain	Electricity grid mix	thinkstep 8.7.0.18
Great Britain	Ethylene oxide (EO) via air	thinkstep 8.7.0.18
Utilisation systems including hydrogen production		
Country	**Name of input**	**Database**
EU-27	Process water	thinkstep 8.7.0.18
Europe	Chemical factory construction, organics	ecoinvent 3.3
Europe	Market for natural gas, high pressure	ecoinvent 3.3
Europe	Sulfite production	ecoinvent 3.3
Europe	Carbon tetrachloride production	ecoinvent 3.3
Europe	Aluminium oxide, at plant	ecoinvent 3.3
Europe	Copper oxide, at plant	ecoinvent 3.3
Europe	Molybdenum, at regional storage	ecoinvent 3.3
Europe	Zinc, primary, at regional storage	ecoinvent 3.3
Europe	Market for waste graphical paper	ecoinvent 3.3
Europe without Switzerland	Market for waste graphical paper	ecoinvent 3.3
Global	Market for barite	ecoinvent 3.3
Global	Market for calcium chloride	ecoinvent 3.3
Global	Market for carbon tetrachloride	ecoinvent 3.3
Global	Market for sludge, NaCl electrolysis	ecoinvent 3.3
Global	Soda ash, light, crystaline, heptahydrate to generic market for neutralising agent	ecoinvent 3.3
Global	Market for sodium chloride, powder	ecoinvent 3.3
Global	Market for sulfuric acid	ecoinvent 3.3

Country	Name of input	Database
Global	Market for hazardous waste, for undeground deposit	ecoinvent 3.3
Global	Market for asbestos, crysolite type	ecoinvent 3.3
Global	Market for mercury	ecoinvent 3.3
Global	Market for spent activated carbon with mercury	ecoinvent 3.3
Global	Nickel, 99.5 %, at plant	ecoinvent 3.3
Global	Synthetic gas, production mix, at plant	ecoinvent 3.3
Global	Natural gas, production onshore	ecoinvent 3.3
Global	Market for sodium hydroxide, without water, in 50% solution state	ecoinvent 3.3
Great Britain	Electricity from hard coal	thinkstep 8.7.0.18
Great Britain	Electricity grid mix	thinkstep 8.7.0.18
Great Britain	Electricity from wind power	thinkstep 8.7.0.18
Great Britain	Market for electricity, medium voltage	ecoinvent 3.3
Great Britain	Market for hydrochloric acid, without water, in 30% solution state	ecoinvent 3.3

Data quality matrix

All the inventories were assessed according to the data quality matrix shown in **Appendix III**. Results show that almost all scenarios have a medium quality score (**Table 5.11**). By using secondary sources, there is a compromise between geographical correlation, databases within date and available data to assess. Data availability is a challenge for processes such as carbon dioxide utilisation. There must be a trade-off between using commercial and public databases to fill life cycle inventories. As can be seen in the table, the process that has the highest quality index is the ITM power limited electrolyser; all information from this process is primary, thus the index is higher. However, a high-quality index does not equal a complete inventory; it only guarantees that the inputs/outputs are reliable for assessing.

Table 5.11 Quality indicators for the inventories for methanol synthesis, 1 kg product

Process	**Scores for each quality indicator (scale 1 to 5)**				
	Source reliability	Database within date	Geographical correlation	Technical similarities	Overall score
Case study: methanol synthesis	2	3	1	1	3
Case study: CO_2 capture	2	1	3	1	3
Case study: hydrogen production	2	3	1	1	3
Methanol: H_2 from SMR[1] (ecoinvent 3.3)	2	3	3	1	3
Methanol: Syngas (ecoinvent 3.3)	2	3	3	1	3
H_2: Electrolyser, membrane cell (ecoinvent 3.3)	2	3	3	3	3
H_2: Electrolyser, mercury cell (ecoinvent 3.3)	2	3	3	3	3
H_2: Electrolyser, diaphragm (ecoinvent 3.3)	2	3	3	3	3
H_2: Electrolyser, average technology (PlasticsEurope)	2	3	3	3	3
H_2: Electrolyser, (ITM power limited proposal)	1	1	1	1	1

[1] Steam methane reforming

5.3 Impact assessment

In this section, the inventory is assessed using a life cycle assessment (LCA) approach to determine the environmental burdens of producing methanol with captured CO_2. The life cycle impact assessment (LCIA) phases includes carbon accounting and other environmental impacts (such as acidification, eutrophication, fossil fuel depletion, etc.). The results were analysed, and various conditions were considered to investigate sensitivity and uncertainty (i.e. the robustness of the results). More information on the environmental assessment method in **Section 4.4**.

5.3.1 Carbon accounting

Overall, there is an assessment for five main scenarios; each scenario has alternative processes as seen in **Section 5.2.1**. The first assessment step was to calculate direct and indirect carbon emissions for each case. An initial screening of the utilisation potential is made by determining direct carbon emissions; however, the addition of indirect emissions determines the overall life cycle carbon dioxide utilisation potential.

Since allocation from electricity generation is a necessary step, carbon capture emissions must be accounted first. **Figure 5.11** shows the results from calculating direct and indirect emissions of 1,000 kg of CO_2 captured from a subcritical PC (pulverised coal) power plant (process specifications on **Table 5.2** and **Table 5.3**). In this scenario, the extra energy required for capture is calculated from converting auxiliary power MWe (**Table 5.2**) to additional kWh needed/ kWh generated. A total of 1,111 kg CO_2 are required to capture 90% 1,000 kg of CO_2 and deliver at the same time 1,100 kWh to the grid. Further calculations are shown in **Appendix IV**.

Background data is then used to calculate indirect emissions from electricity generated. The GaBi ts database version 8.7.0.18 used was *GB: electricity from hard coal* where 0.882 kg CO_2 life cycle emissions are generated per kWh of electricity delivered to the grid. Indirect emissions for kWh generated are calculated as:

$$kg\ CO_2 emissons\ background\ data - kg\ CO_2\ direct\ emissions \\ - kg\ CO_2\ captured = kg\ CO_2 indirect\ emissions$$

As a last step, the indirect emissions of carbon capture are also accounted for. For every 1,000 kg of CO_2 captured, 95 kg of CO_2 are emitted as indirect carbon capture emissions. This includes all non-energy extra inputs required for only the capture stage (refer to **Table 5.3 column 1** for input values).

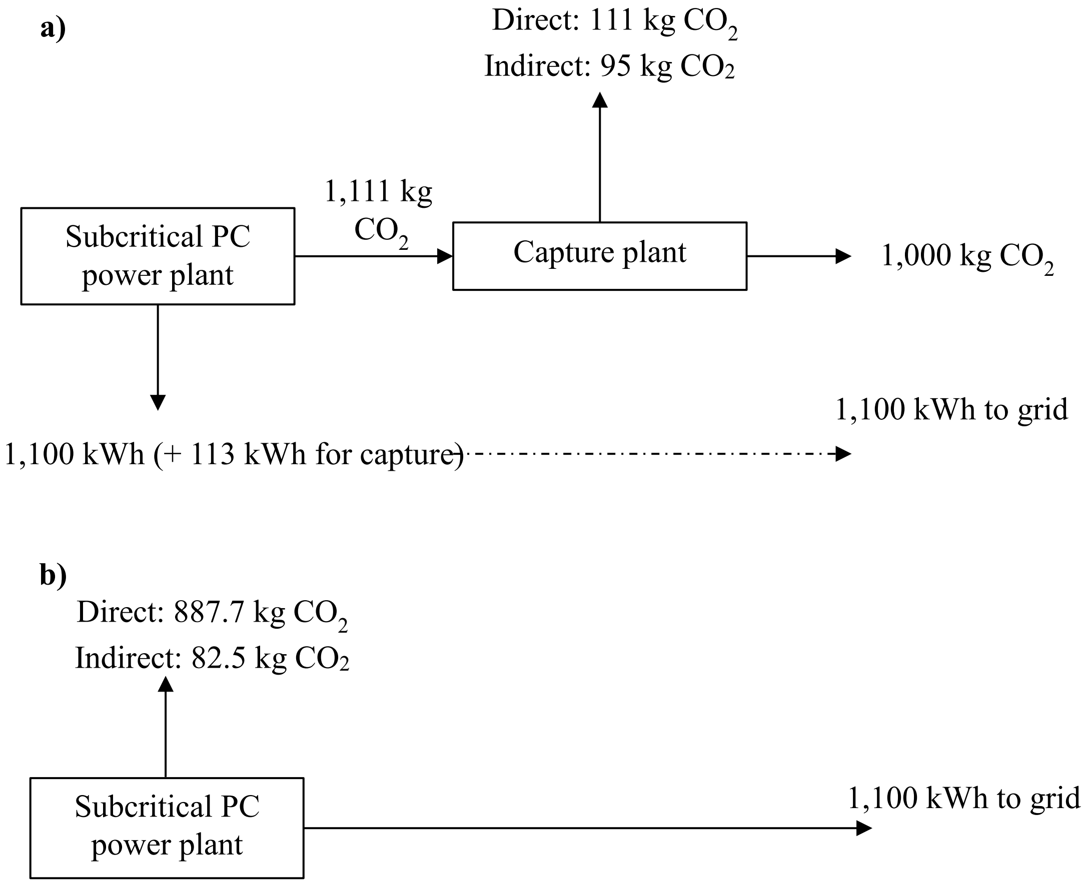


Figure 5.11 Direct and indirect CO_2 emission balance for a) Subcritical PC (pulverised coal) power plant with capture b) Subcritical PC (pulverised coal) plant without capture (baseline scenario)

While the main scenario studied used the pulverised coal (PC) subcritical power plant a comparison was made to other technologies. **Figure 5.12** compares emission results from two other power plants with the main scenario, these plants are a supercritical pulverised coal plant (PC) and natural gas combined cycle plant (NGCC). Results show that as the efficiency of the plant increases, more electricity needs to be generated to capture the same amount of CO_2. The higher the efficiency, the higher the surplus in electricity. Selecting the pulverised coal (PC) subcritical power plant allowed to calculate the lowest carbon dioxide utilisation potential; from this, a range from worst to best case can be achieved. There is also the issue of comparability, other important life cycle assessments on this topic use this type of power plant as basis (von der Assen *et al.*, 2014). As mentioned previously, **Appendix IV** includes all the information for carbon accounting of all three post-combustion capture options.

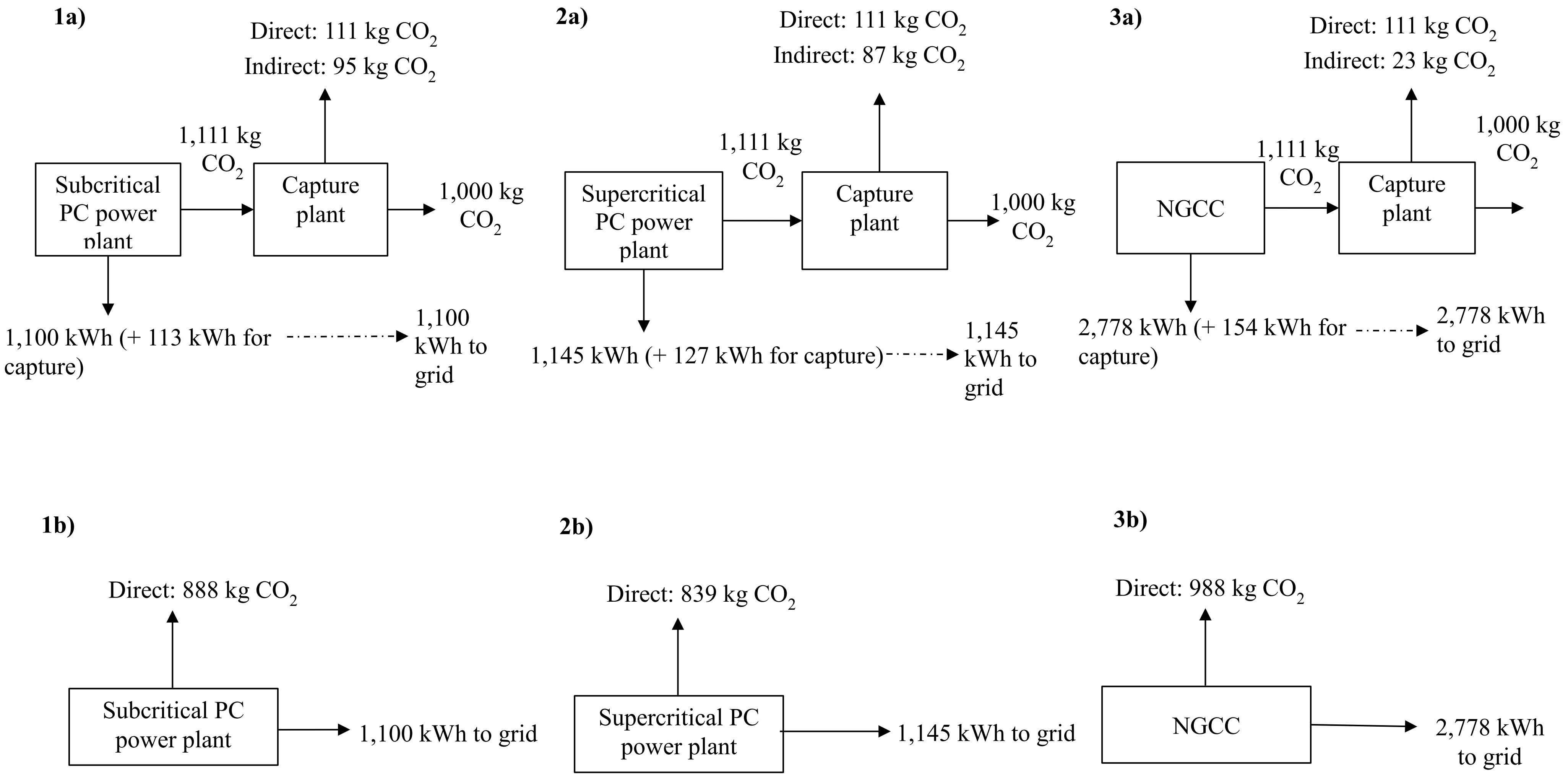


Figure 5.12 Carbon dioxide emissions from post-combustion plants and electricity generation. Capture rate set at 1000 kg CO_2 1a) subcritical power plant 550 MW with capture 1b) subcritical PC (pulverised coal) power plant no carbon capture 2a) supercritical PC (pulverised coal) power plant 550 MW with capture 2b) supercritical PC (pulverised coal) power plant 550MW no capture 3a) natural gas combined cycle (NGCC) power plant 559 MW with capture 3b) natural gas combined cycle (NGCC) power plant 559 MW no capture

Case 1a) in **Figure 5.12** is scaled to capture 1.375 kg of CO_2 necessary to produce 1 kg of CH_3OH. The parameters for these capture conditions are summarised in **Table 5.12**. The parameters shown were adjusted to fit the capture requirements of this case study.

Table 5.12 Parameters for capturing 1.375 kg of CO_2 from a subcritical PC (pulverised coal) power plant with a post-combustion capture unit, data based on NETL (2015)

Parameters	Value
Power plant performance	
Net power output (MWe)	550.0
Capacity factor (%)	85.0
Net electricity output for power plant (kWh)	11,220,000.0
Capture conditions	
Capture rate (%)	90.0
Electricity output from the coal fired power plant scaled to fit the capture rate (kWh)	1.5
CO_2 capture (kg)	1.4
Total CO_2 emitted (kg)	0.1
Energy for capture	
Auxiliary power for capture (MWe)	63.0
Net auxiliary electricity for capture (kWh)	0.2

With the value of the parameters adjusted and the carbon balance calculated, the five scenarios were defined as follow:

Scenario 1: Case study for 1 kg of CH_3OH, CO_2 utilisation process connected to the grid, CO_2 capture from post-combustion capture

This scenario considers H_2 produced from water electrolysis (**Table 5.8 column 1**) and connected to the UK grid. As mentioned above, CO_2 supply is from a subcritical pulverised coal (PC) power plant with post-combustion capture (**Table 5.7 column 1**). Transportation for the final product is out of the scope; however, transportation of CO_2 through a pipeline for 500 km is within the process boundary. The comparison for system expansion is power generation plus methanol production with natural gas (Scenario 3). **Figure 5.12** shows the carbon balance results for this system.

Scenario 2: Case study for 1 kg of CH_3OH, CO_2 utilisation process connected to wind power, CO_2 capture from post-combustion capture

This scenario considers H_2 produced from water electrolysis (**Table 5.8 column 1**) and connected to wind power (using *GaBi ts: GB, electricity from wind power ts, technology mix*). All other conditions are identical to Scenario 1. The comparison for system expansion is power generation plus methanol production with natural gas (scenario 3). **Figure 5.13** shows the carbon balance results for this case study.

Scenario 3: Baseline scenario for 1 kg of CH_3OH from natural gas

This scenario considers methanol produced through the conventional route of using natural gas to produce syngas for conversion to methanol. There is no renewable energy used in this case study. No transport of intermediate products or final product is included. The comparison for system expansion is electricity generated from a subcritical PC (pulverised coal) power plant plus methanol synthesis. **Figure 5.13** to **Figure 5.16** use Scenario 3 as the comparison model.

Scenario 4: Case study for 1 kg of CH_3OH, CO_2 utilisation process connected to the electricity grid, CO_2 capture from direct air capture (DAC)

This scenario considers H_2 produced from water electrolysis (**Table 5.8 column 1**) and powered by the UK electricity grid. CO_2 is supplied from a theoretical direct air capture system (**Table 5.7 column 4**). Transportation for the final product is out of the scope; however, transportation of CO_2 through a pipeline for 500 km is within the process boundary. The comparison for system expansion is power generation plus methanol production with natural gas (Scenario 3). **Figure 5.8** shows the carbon balance results for this case.

Scenario5: Case study for 1 kg of CH_3OH, CO_2 utilisation process connected to wind power, CO_2 capture from direct air capture (DAC)

This scenario considers H_2 produced from water electrolysis (**Table 5.8 column 1**) powered by wind power (using *GaBi ts: GB, electricity from wind power TS, technology* *mix*). All other conditions are identical to Scenario 4. The comparison for system expansion is power generation plus methanol production with natural gas (Scenario 3). **Figure 5.9** shows the carbon balance results for this case.

For the next step, all net life cycle CO_2 emissions for each scenario are calculated using the method established in **Section 4.4.3**. Where:

CO_2 power supply = all carbon emissions and fossil associated with the production, distribution and use of electricity and thermal energy throughout the system

CO_2 water supply = all emissions associated with the extraction, distribution and use of water throughout the system

CO_2 materials supply = all emissions associated with the extraction/production, distribution and use of materials and chemicals throughout the system

CO_2 source = all emissions associated with the supply of carbon dioxide as feedstock for utilisation processes

CO_2 transportation = all emissions associated with the use of transportation throughout the system

CO_2 waste = all emissions associated with reuse, recycling and disposal activities

The emissions results are shown in **Table 5.13** and **Table 5.14**, where for a second analysis, only energy values are calculated as inputs. The comparison between both results is used as a sensitivity analysis. Results show that only the CO_2 utilisation scenarios that use renewable energy have the potential to be carbon neutral or at least avoid some carbon emissions. Whether there is any carbon avoidance or not, it relies on the energy penalties from the synthesis process and the hydrogen requirements. The highest carbon avoidance was found to be 0.1 kg CO_2 avoided per kg CH_3OH produced (Scenario 2). However, this gain disappears when only energy emissions are accounted for, where a conservative scenario would be neutral emissions at best. Although the carbon avoidance is low, there is potential for improving the system by decarbonising the entire methanol synthesis process (i.e. including H_2 compression) and optimising the process. **Table 5.15** and **Table 5.16** show carbon avoided results for both analysis: all inputs assessed and only energy inputs analysed respectively.

Table 5.13 Sum of net life cycle CO_2 emissions for all cases studies, per 1 kg of methanol, following method from section 4.4.3

Process	kg of CO_2 emitted per process						
	Total sum	Power supply	Water supply	Material	Source	Transportation	Waste
1) Methanol synthesis, electricity from grid mix	**8.5**	8.2	6.0 x 10^{-3}	0.0	0.2	1.8 x 10^{-3}	0.0
2) Methanol synthesis, electricity from wind power	**1.8**	1.6	6.0 x 10^{-3}	0.0	0.2	1.8 x 10^{-3}	0.0
3) Methanol synthesis from natural gas	**1.9**	1.3	0.0	0.6	0	0.0	0.0
4) Methanol synthesis, electricity from grid mix, CO_2 from DAC[1]	**8.8**	8.2	6.0 x 10^{-3}	0.0	0.5	0.0	0.0
5) Methanol synthesis, electricity from wind power, CO_2 from DAC[1]	**2.1**	1.6	6.0 x 10^{-3}	0.0	0.5	0.0	0.0

[1] Direct Air Capture

Table 5.14 Sum of net life cycle CO_2 emissions for all case studies per 1 kg methanol, sensitivity analysis with only power emissions analysed, following method from Section 4.4.3

Process	kg of CO_2 emitted (from power emissions)						
	Total sum	Power supply	Water supply	Material	Source	Transportation	Waste
1) Methanol synthesis, electricity from grid mix	**8.3**	8.2	0.0	0.0	0.1	0.0	0.0
2) Methanol synthesis, electricity from wind power	**1.7**	1.6	0.0	0.0	0.1	0.0	0.0
3) Methanol synthesis from natural gas	**1.6**	1.3	0.0	0.3	0.0	0.0	0.0
4) Methanol synthesis, electricity from grid mix, CO_2 from DAC[1]	**8.7**	8.2	0.0	0.0	0.5	0.0	0.0
5) Methanol synthesis, electricity from wind power, CO_2 from DAC[1]	**2.0**	1.6	0.0	0.0	0.5	0.0	0.0

[1] Direct Air Capture

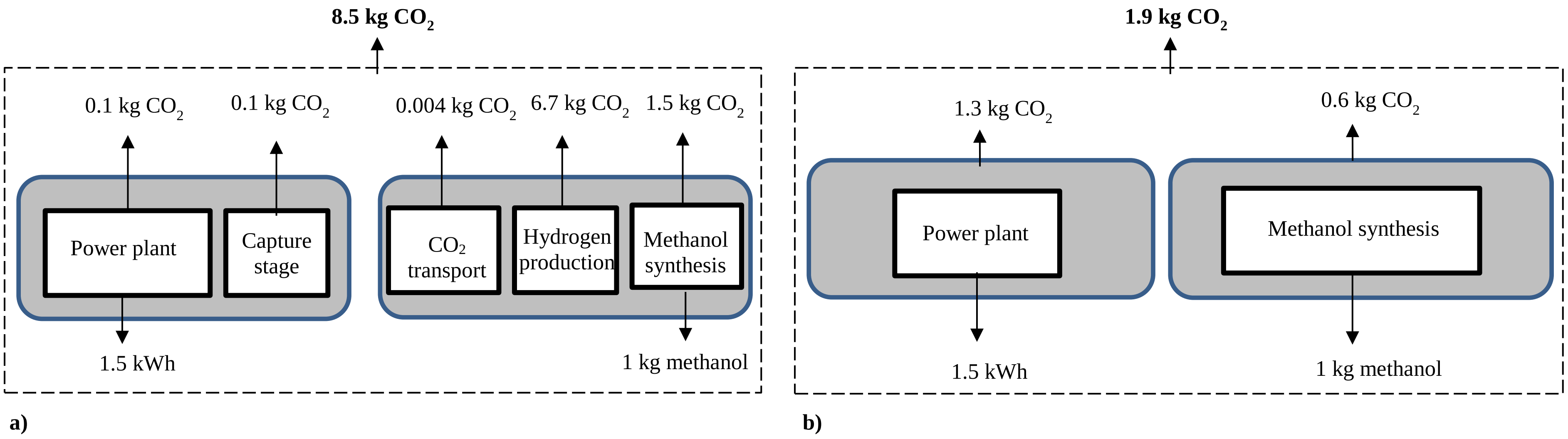
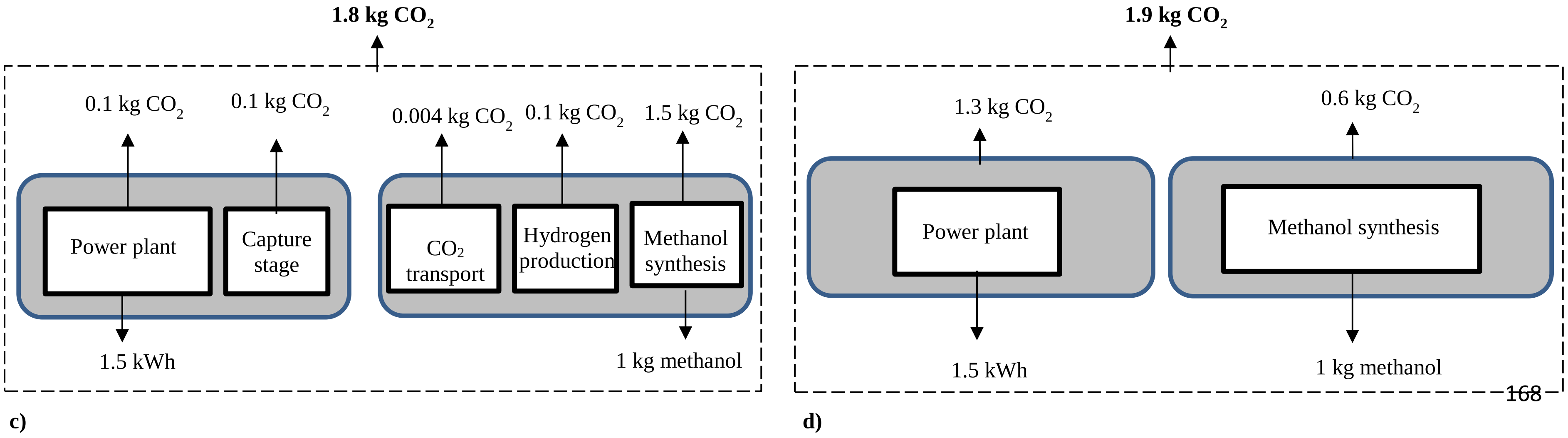


Figure 5.13 a) Total life cycle CO_2 emissions for scenario 1, compared to b) Total life cycle CO_2 emissions for scenario 3, system expansion

Figure 5.14 c) Total life cycle CO_2 emissions for scenario 2, compared to d) Total life cycle CO_2 emissions for scenario 3, system expansion



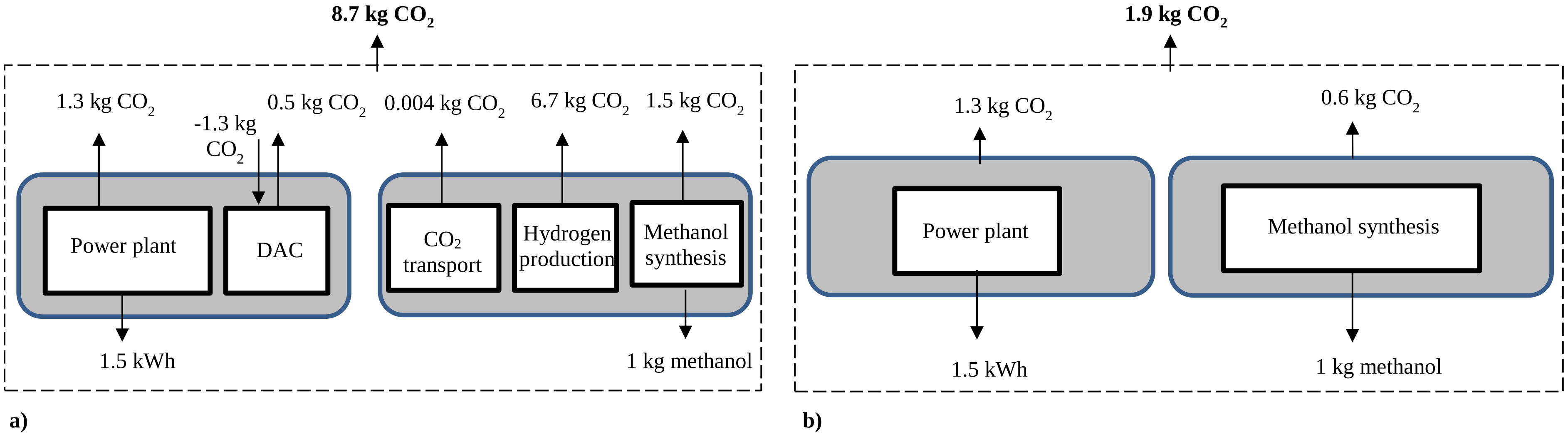


Figure 5.15 a) Total life cycle CO$_2$ emissions for scenario 4, compared to b) total life cycle CO$_2$ emissions for scenario 3, system expansion

Figure 5.16 c) Total life cycle CO$_2$ emissions for scenario 5, compared to d) Total life cycle CO$_2$ emissions for scenario 3, system expansion

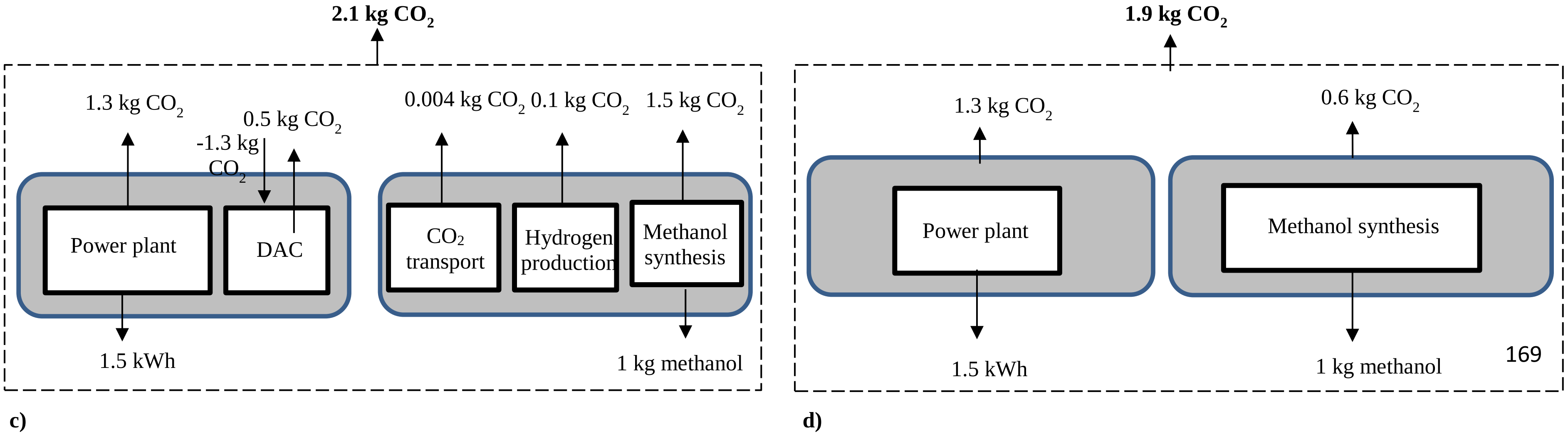


Table 5.15 Net avoided CO_2 per 1 kg of CH_3OH produced

Scenarios	Avoided and emitted emissions (kg)			
	kg net CO_2 avoided cdu	kg net CO_2 generated cdu	kg CO_2 emitted non-cdu	kg CO_2 emitted cdu
1	**0.0**	7.1	1.9	9.0
2	**0.1**	0.0	1.9	2.0
3	**0.0**	0.0	1.9	N/A
4	**0.0**	7.3	1.9	9.0
5	**0.1**	0.0	1.9	2.0

Table 5.16 Net avoided CO_2 with sensitivity analysis, only energy emissions analysed, per 1 kg of CH_3OH produced

Scenarios	Avoided and emitted emissions (kg)			
	kg net CO_2 avoided	kg net CO_2 generated cdu	kg CO_2emitted non-cdu	kg CO_2 emitted cdu
1	**0.0**	6.7	1.7	8.0
2	**0.0**	3.0×10^{-2}	1.7	2.0
3	**0.0**	0.0	1.7	N/A
4	**0.0**	7.0	1.7	9.0
5	**0.0**	0.4	1.7	2.0

The results can also be displayed according to production phases; this is a useful tool to determine carbon hotspots throughout the process. **Figure 5.17** shows the net life cycle CO_2 emissions from CO_2 capture, hydrogen production, electricity generation and methanol synthesis. From this, it is seen that producing hydrogen from water electrolysis whilst using electricity from the current grid mix to power it is unsustainable. This is in line with observations from other studies such as Styring & Jansen (2011), Wang *et al.* (2014) and Pérez-Fortes *et al.* (2014).

The application of the framework leads to the expected outcomes in this worked example. This fits with the intention of completing a "proof of concept" case study while generating information that can be discussed, analysed and weighed. The guidelines on how to apply system expansion and carbon accounting can be used for other CO_2 utilisation systems that will have different environmental impacts as results, as shown in the urea working example in **Chapter 6**.

In this analysis, not using a renewable source of energy for a process that uses recovered CO_2 and transforms it will quadruple CO_2 emissions when compared to the reference case of CH_3OH from natural gas. H_2 must be generated from a renewable source if, at the very least, neutral carbon avoidance is to be achieved. There is also no major improvement from using post-combustion for capture and using direct air capture. Although theoretically -1 kg of CO_2 captured from air equals 1 kg CO_2 avoided, it is the indirect emissions that reduce net carbon avoidance.

As of now, indirect emissions from energy supply are five times greater for a direct air capture (DAC) (theoretical and conservative values) process than for the post-combustion capture process evaluated in this work. Overall, methanol production from natural gas is not as carbon intensive as the CO_2 utilisation route, however; the added electricity generated with CO_2 utilisation favours the overall carbon balance as this offset further emissions by producing power. This presents a potential case for utilisation if electricity would still have to be generated regardless of capturing carbon or not.

The carbon balance for all four CO_2 utilisation scenarios also shows that the difference between CO_2 emitted from a CO_2 utilisation and a conventional process is very low in some scenarios, i.e. Scenario 2. This is in part due to the allocation method where by using system expansion a power plant (without capture) with the same generating power as the power plant with capture is added to the conventional process. System expansion makes the processes comparable and easier to assess. The drawback is that by having low differences between total outputs using system expansion, there is a potential for overstating the CO_2 emissions benefits. The results may "overlap" (thus suggesting no reduction or an increase of CO_2 emissions for the CO_2 utilisation plant) if any significant deviation from the mean may be found.

To determine the sensitivity of all CO_2 outputs, a normalised distribution curve was created using 2,000 iterations with a standard deviation from the mean of ± 100% for all four system expansion comparisons. The results in **Table 5.17** show that for most cases there is no significative difference up to the 1st standard deviation (68 % chance that it falls within that range) and in some cases up the 2nd (95 % chance that it falls within that range). However, methanol synthesis in the CO_2 utilisation scenarios is the most variable due to the electricity required to compress H_2 before conversion to methanol. This output can be made less variable by using a decarbonised energy source.

To determine the standard error of the mean, the following **Equation 5.3** was used:

$$\sigma_{\bar{x}} = \frac{\sigma}{\sqrt{n}}$$

Equation 5.3

Where

σ is the standard deviation of the population

n is the size of the sample

This standard error was then used to calculate confidence limits in the mean value, 95% confidence limits were calculated as shown in the **Equations 5.4 and 5.5**:

$$Upper\ 95\ \%\ limit\ = \bar{x} + (SE\ \times 1.96)$$

Equation 5.4

$$Lower\ 95\ \%\ limit\ = \bar{x}\ + (SE\ \times 1.96)$$

Equation 5.5

Where

$\bar{x}$ is equal to the sample mean

SE is equal to the standard error for the sample mean

1.96 is the 0.975 quantile of the normal distribution

The results for each scenario are shown in **Table 5.18**. The upper confidence limit of the CO_2 utilisation processes was compared to the lower confidence limit of the conventional process to determine whether the difference in the two reported values is statistically different. **Table 5.19** shows that the standard error of the mean suggests that you can be reasonable confident in the results reported, for most CO_2 outputs the upper and lower don’t overlap or deviate significantly from the reported results. Out of all scenarios, Scenario 2 has the least clear result where a second decimal place is needed to see the difference (therefore the process is no worse than the conventional and could be improved by using renewable electricity for the methanol process).

Table 5.17 Showing standard deviations for methanol scenarios applying system expansion

Scenario	**Input**	**kg CO_2 emitted**						
		Mean	**Standard deviation**	**68% min**	**68% max**	**95% min**	**95% max**	**99.7% max**
1	Power plant with CO_2 capture	0.3	0.2	0.1	0.4	0.0	0.6	0.7
	CO_2 transport	4.0 x 10^{-3}	2.0 x 10^{-3}	2.0 x 10^{-3}	6.0 x 10^{-3}	0.000	9.0 x 10^{-3}	1.1 x 10^{-2}
	H_2 generation	6.5	3.8	2.8	10.3	0.0	14.1	17.9
	Methanol synthesis, CO_2 utilisation	1.5	0.9	0.6	2.4	0.0	3.3	4.1
	Power plant without CO_2 capture	1.3	0.8	0.6	2.1	0.0	2.9	3.7
	Methanol synthesis, conventional	0.6	0.4	0.3	1.0	0.0	0.7	1.7
2	Power plant with CO_2 capture	0.3	0.2	0.1	0.4	0.0	0.6	0.7
	CO_2 transport	4.0 x 10^{-3}	2.0 x 10^{-3}	2.0 x 10^{-3}	6.0 x 10^{-3}	0.000	9.0 x 10^{-3}	1.1 x 10^{-2}
	H_2 generation	0.1	0.0	0.0	0.1	0.0	0.1	0.2
	Methanol synthesis, CO_2 utilisation	1.5	0.9	0.6	2.4	0.0	3.3	4.1
	Power plant without CO_2 capture	1.3	0.8	0.6	2.1	0.0	2.9	3.7
	Methanol synthesis, conventional	0.6	0.4	0.3	1.0	0.0	0.7	1.7
4	Power plant with CO_2 capture	0.5	0.3	0.2	0.8	0.0	1.1	1.4
	CO_2 transport	4.0 x 10^{-3}	2.0 x 10^{-3}	2.0 x 10^{-3}	6.0 x 10^{-3}	0.000	9.0 x 10^{-3}	1.1 x 10^{-2}
	H_2 generation	6.5	3.8	2.8	10.3	0.0	14.1	17.9
	Methanol synthesis, CO_2 utilisation	1.5	0.9	0.6	2.4	0.0	3.3	4.1
	Power plant without CO_2 capture	1.3	0.8	0.6	2.1	0.0	2.9	3.7
	Methanol synthesis, conventional	0.6	0.4	0.3	1.0	0.0	0.7	1.7
5	Power plant with CO_2 capture	0.5	0.3	0.2	0.8	0.0	1.0	1.3
	CO_2 transport	4.0 x 10^{-3}	2.0 x 10^{-3}	2.0 x 10^{-3}	6.0 x 10^{-3}	0.000	9.0 x 10^{-3}	1.1 x 10^{-2}
	H_2 generation	0.1	0.0	0.0	0.1	0.0	0.1	0.2
	Methanol synthesis, CO_2 utilisation	1.5	0.9	0.6	2.4	0.0	3.3	4.1
	Power plant without CO_2 capture	1.3	0.8	0.6	2.1	0.0	2.9	3.7
	Methanol synthesis, conventional	0.6	0.4	0.3	1.0	0.0	0.7	1.7

Table 5.18 Showing standard error from the mean for methanol scenarios applying system expansion

Scenario	Input	kg CO_2 emitted			
		Standard error	95% confidence interval	Upper limit	Lower limit
1	Power plant with CO_2 capture	3.0 x 10^{-3}	7.0 x10^{-3}	0.3	0.3
	CO_2 transport	5.0 x 10^{-5}	5.0 x 10^{-5}	4.0 x10^{-3}	4.0 x10^{-3}
	H_2 generation	8.4 x 10^{-2}	0.2	6.7	6.4
	Methanol synthesis, CO_2 utilisation	1.9 x 10^{-2}	3.8 x 10^{-2}	1.6	1.5
	Power plant without CO_2 capture	1.7 x 10^{-2}	3.3 x 10^{-2}	1.4	1.3
	Methanol synthesis, conventional	1.4 x 10^{-2}	3.7 x 10^{-2}	0.6	0.6
2	Power plant with CO_2 capture	3.4 x10^{-3}	7.0 x10^{-3}	0.3	0.3
	CO_2 transport	5.2 x 10^{-5}	1.0 x 10^{-4}	4.0 x10^{-3}	4.0 x10^{-3}
	H_2 generation	1.0 x 10^{-3}	2.0 x10^{-3}	7.1 x 10^{-2}	6.8 x 10^{-2}
	Methanol synthesis, CO_2 utilisation	1.9 x 10^{-2}	3.8 x10^{-3}	1.6	1.5
	Power plant without CO_2 capture	1.7 x 10^{-2}	3.4 x10^{-3}	1.3	1.3
	Methanol synthesis, conventional	1.4 x 10^{-2}	2.7 x 10^{-2}	0.6	0.6
4	Power plant with CO_2 capture	6.0 x 10^{-3}	1.3 x 10^{-2}	0.5	0.5
	CO_2 transport	5.2 x 10^{-5}	1.0 x 10^{-4}	4.0 x10^{-3}	4.0 x10^{-3}
	H_2 generation	8.4 x 10^{-2}	0.2	6.7	6.4
	Methanol synthesis, CO_2 utilisation	1.9 x 10^{-2}	3.8 x10^{-2}	1.6	1.5
	Power plant without CO_2 capture	1.7 x 10^{-2}	3.4 x10^{-2}	1.4	1.3
	Methanol synthesis, conventional	1.4 x 10^{-2}	2.7 x10^{-2}	0.6	0.6
5	Power plant with CO_2 capture	6.0 x 10^{-3}	1.2 x10^{-2}	0.5	0.5
	CO_2 transport	5.2 x 10^{-5}	1.0 x 10^{-4}	4.0 x10^{-3}	4.0 x10^{-3}
	H_2 generation	1.0 x 10^{-3}	2.0 x10^{-3}	0.1	0.1
	Methanol synthesis, CO_2 utilisation	1.9 x 10^{-2}	3.8 x10^{-2}	1.6	1.5
	Power plant without CO_2 capture	1.7 x 10^{-2}	3.4 x10^{-2}	1.4	1.3
	Methanol synthesis, conventional	1.4 x 10^{-2}	2.7 x10^{-2}	0.6	0.6

Table 5.19 Scenario comparison for upper and lower kg CO_2 emissions for methanol scenarios applying system expansion

Process description	Scenario			
	1	2	4	5
Upper value, CO_2 utilisation process (kg CO_2)	8.5	1.9	8.8	2.1
Lower value, Conventional process (kg CO_2)	1.9	1.9	1.9	1.9

The final step in carbon accounting is to calculate the overall contributions of emissions from greenhouse gases to global warming. For this, the method chosen was CML-IA that uses the characterisation factor of global warming potential over 100 years (GWP_{100}). The same allocation rules also apply to global warming scores as with direct CO_2 emissions, thus the use of system expansion approach. **Table 5.20** shows the contribution percentage of the major greenhouses gases (excluding water vapour) to the total CO_2 equivalent (eq) result of each CO_2 utilisation scenarios.

Table 5.20 Showing contribution of greenhouse gases to the global warming score for CO_2 based methanol

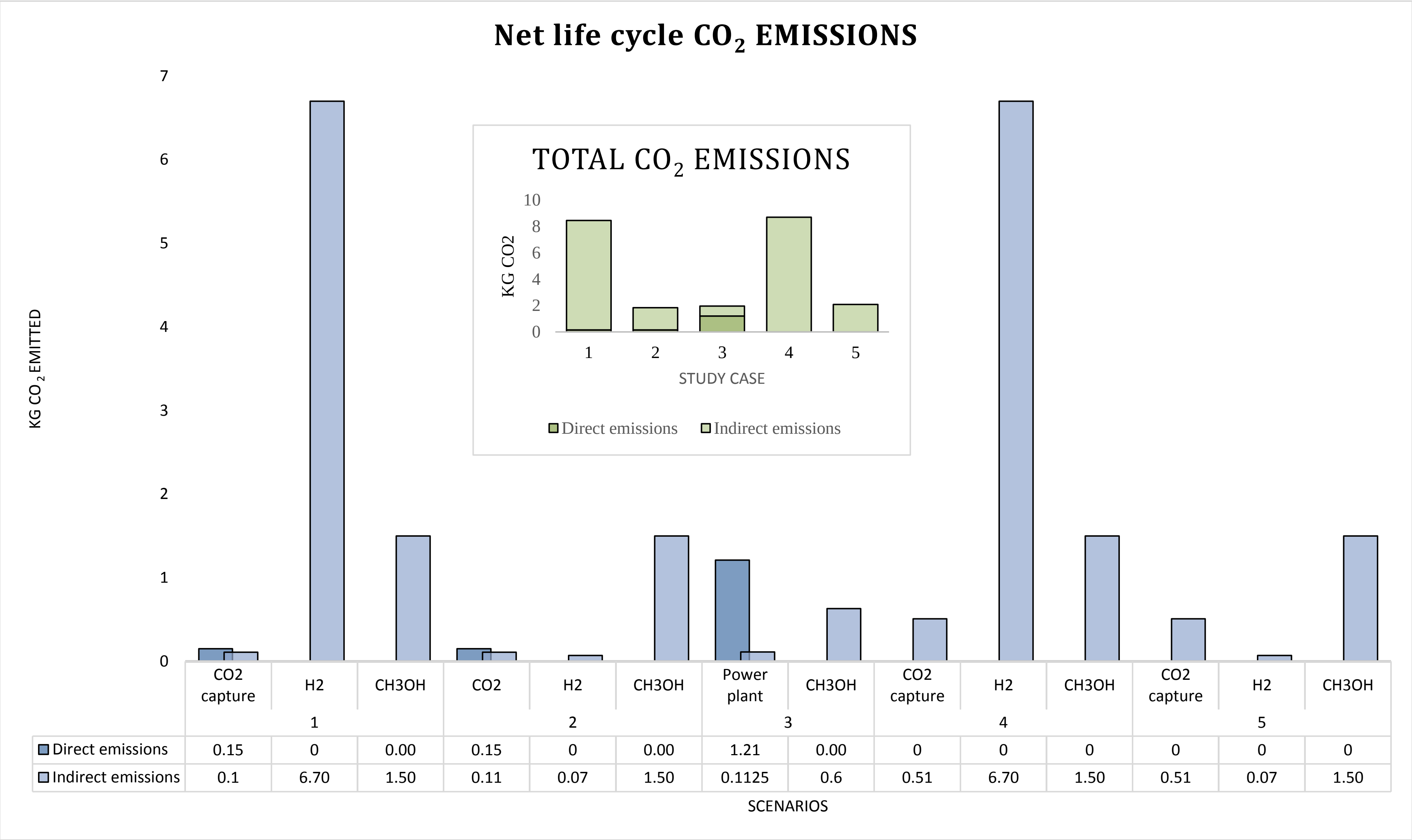
Greenhouse gases	**Contribution to CO_2 eq in scenarios (%)**			
	1	**2**	**4**	**5**
Carbon dioxide (CO_2)	93	88	93	89
Methane (CH_4)	7	11	7	10
Nitrous oxide (N_2O)	1	1	1	1
Sulphur hexaflouride (SF_6)	5×10^{-5}	0	10×10^{-9}	4×10^{-8}

Overall, carbon dioxide emissions contribute 88 to 93% of total emissions to the global warming potential. It is followed by methane (CH_4) emissions and nitrous oxide (N_2O) in third place.

80 % of methane and nitrous oxide emissions in Scenario 1 and 4 are caused by the use of electricity from a grid mix that consists of 40% electricity from natural gas. The rest of the emissions for these scenarios are linked to the capture stage and its power requirements. Of other stressors that contribute to greenhouse emissions is the use of triethylene glycol for post-combustion capture (linked to sulphur hexafluoride emissions).

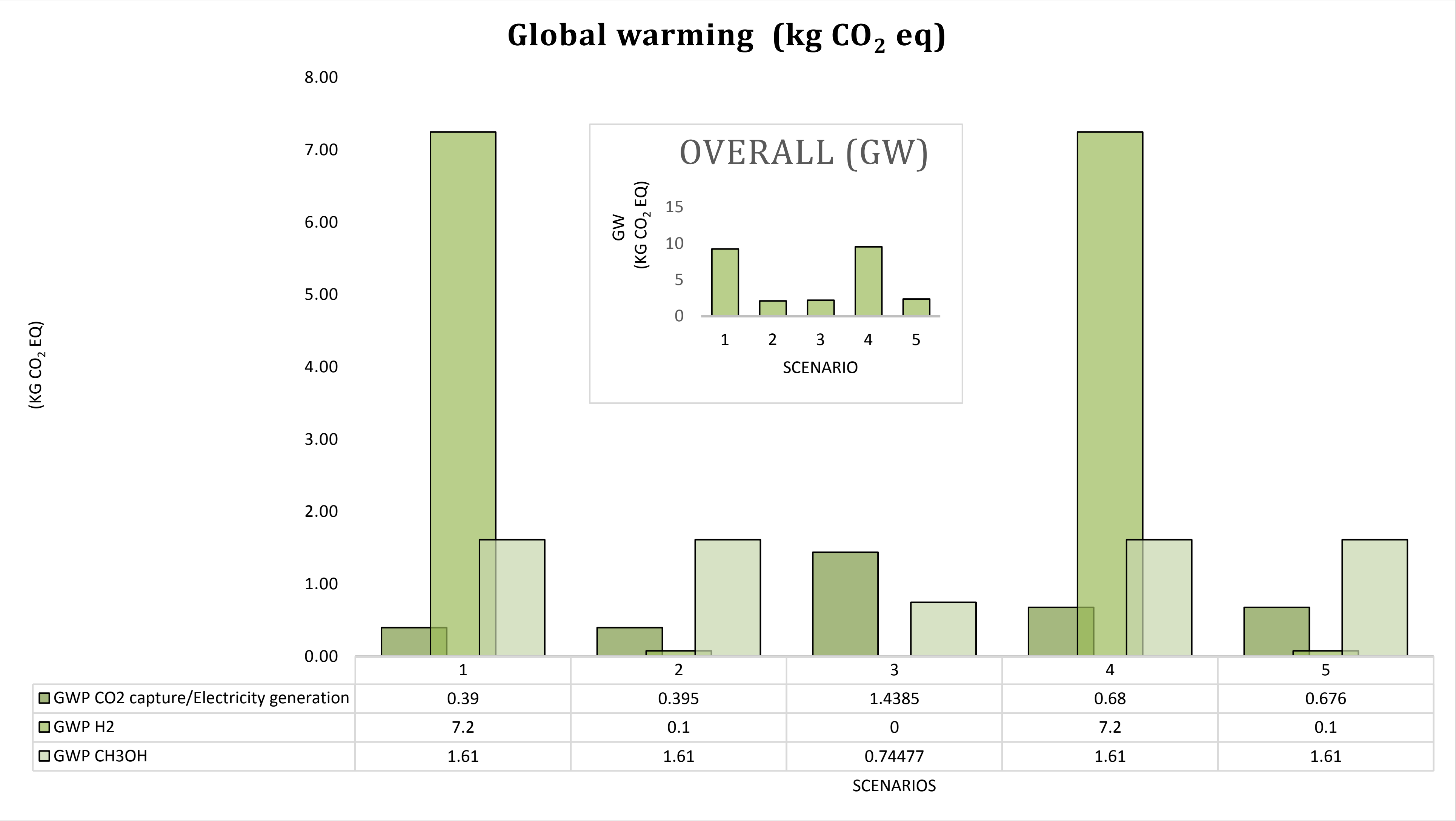
For Scenario 2 and 5, over 98 % of the methane and nitrous oxide emissions are linked to the use of electricity supplied by the grid mix. The higher emissions compared to Scenario 2 and 5 can be accounted for the extra energy requirements for the direct air capture process. Sulphur hexafluoride is also emitted in the capture stage because of triethylene glycol and monoethanolamine in smaller quantities.

Figure 5.18 shows the global warming results comparison between all scenarios (including the conventional Scenario, number 3) with a final product of 1 kg of CH_3OH. Results show the same trends as with kg of carbon dioxide emitted and no major emission shifts. The high percentage of carbon dioxide emissions in the CO_2 utilisation scenarios highlight the need for carbon avoidance/mitigation for the CO_2 based products to be environmentally feasible. For the full life cycle impact assessment (LCIA) results refer to **Appendix V**.



	CO2 capture	H2	CH3OH	CO2	H2	CH3OH	Power plant	CH3OH	CO2 capture	H2	CH3OH	CO2 capture	H2	CH3OH
	1			2			3		4			5		
▨ Direct emissions	0.15	0	0.00	0.15	0	0.00	1.21	0.00	0	0	0	0	0	0
▨ Indirect emissions	0.1	6.70	1.50	0.11	0.07	1.50	0.1125	0.6	0.51	6.70	1.50	0.51	0.07	1.50

Figure 5.17 Net life cycle CO_2 emissions generated per functional unit (1 kg of methanol ready for storage and use). Scenarios 1 to 5 with up to 3 main stages each: CO_2 capture, H_2 production, methanol production. 1) Case scenario of 1 kg methanol, electricity grid mix, with post-combustion carbon capture 2) Case scenario 1 kg methanol, wind power, with post-combustion carbon capture 3) Baseline scenario methanol from natural gas 4) 1 kg of methanol-DAC (direct air capture), H_2-electricity grid mix 5) 1 kg of methanol DAC (direct air capture), H_2-wind power



	1	2	3	4	5
▨ GWP CO2 capture/Electricity generation	0.39	0.395	1.4385	0.68	0.676
🟩 GWP H2	7.2	0.1	0	7.2	0.1
☐ GWP CH3OH	1.61	1.61	0.74477	1.61	1.61

Figure 5.18 Global warming (GW) scores per functional unit (1 kg of methanol ready for storage and use). Scenarios 1 to 5 with up to 3 main stages each: CO$_2$ capture, H$_2$ production, methanol production. 1) Case scenario of 1 kg methanol, electricity grid mix, with post-combustion carbon capture 2) Case scenario 1 kg methanol, wind power, with post-combustion carbon capture 3) Baseline scenario methanol from natural gas 4) 1 kg of methanol-DAC (direct air capture), H$_2$- electricity grid mix 5) 1 kg of methanol-DAC (direct air capture), H$_2$-wind power

5.3.2 Other environmental impacts

Nine other environmental impacts were also assessed as part of the life cycle impact assessment (LCIA). While CO_2 emissions and related impacts are priority in utilisation scenarios, not analysing the rest of the impacts can lead to overestimating the utilisation potential. Some of these impacts are acidification, stratospheric ozone depletion, eutrophication and fossil fuel depletion. CML-IA characterisation factors were used for all impacts except fossil fuel depletion. This last one uses the characterisation factor used in the ReCIPe (H) method with the indicator result in kg oil eq. Results are scaled to fit the functional units of 1 kg of methanol per 1.5 kWh of electricity produced. **Figure 5.18** to **Figure 5.27** show the results for each impact category and for each scenario. There is also a final graph shown in **Figure 5.28** where a comparative analysis between all scenarios for each impact category is made. Results show that methanol synthesis from natural gas has a higher impact values for five categories when compared to the utilisation Scenario 2 (renewable energy dependant). Overall, Scenario 2 has favourable results in most categories except for acidification, photochemical oxidation and terrestrial ecotoxicity. The following sections give a brief description of the results for each impact category.

Fossil fuel depletion

This impact category is one of the most important to study in utilisation scenarios. Ultimately, the aim of the processes under study is to displace primary fossil resources for usable CO_2 emissions. It might also be that although global warming scores might not reduce, the fossil depletion rate would, thus creating a positive impact on fossil reserves. In these scenarios, results show the same trends between global warming and fossil depletion. To lessen the fossil fuel depletion impacts in methanol production from captured CO_2, the synthesis stage needs to achieve lower energy penalties or be sourced from decarbonised electricity. With the current process (Scenario 1), methanol synthesis has 2.4 times higher fossil depletion rates than methanol from natural gas (**Figure 5.19**). However, by obtaining H_2 from water electrolysis and wind power, the fossil depletion rates lower by 44 times compared to methanol from natural gas. In general, the main hotspot that should be controlled in this utilisation route is methanol synthesis.

Eutrophication

Eutrophication potential results show lower impacts when renewables are used in utilisation scenarios (**Figure 5.24**). Higher values, as seen in Scenario 3, are associated with greater nitrogen dioxide emissions from using natural gas for methanol production. High nitrogen oxide emissions are also linked to higher electricity demand (such as Scenario 1 and 4).

Acidification

In all CO_2 utilisation scenarios, there is a higher acidification potential than with methanol from natural gas (**Figure 5.26**). This is attributed to the capture process higher energy consumption. Scenario 1 and 4 have the highest acidification scores at 0.00162 and 0.00167 (kg SO_2 eq) respectively; where the electricity from the grid required to produce H_2 emits the most SO_2. Other high SO_2 emissions are linked to the capture by post-combustion, specifically the use of triethylene glycol as CO_2 dehydrator. Finding alternatives to this solvent and lowering the energy penalty is an option to equal the results of methanol from natural gas.

Stratospheric ozone depletion and abiotic depletion

Methanol from natural gas has the highest stratospheric ozone depletion scores in all five scenarios (**Figure 5.27**). This is attributed to the reliance on natural gas for methanol synthesis, methane being the largest contributor to a higher impact potential of l. For resource depletion, the results do not follow the same impact trends. The scenarios that use wind power quadruplicate the abiotic depletion scores compared to using electricity from the grid. According to (Greening and Azapagic, 2013), the manufacturing stage of wind power turbines (life cycle assessment for micro wind turbines) with the use of molybdenum, accounts for 99% of the depletion potential impacts. Other renewable energy sources should be analysed and consider as alternatives to wind power.

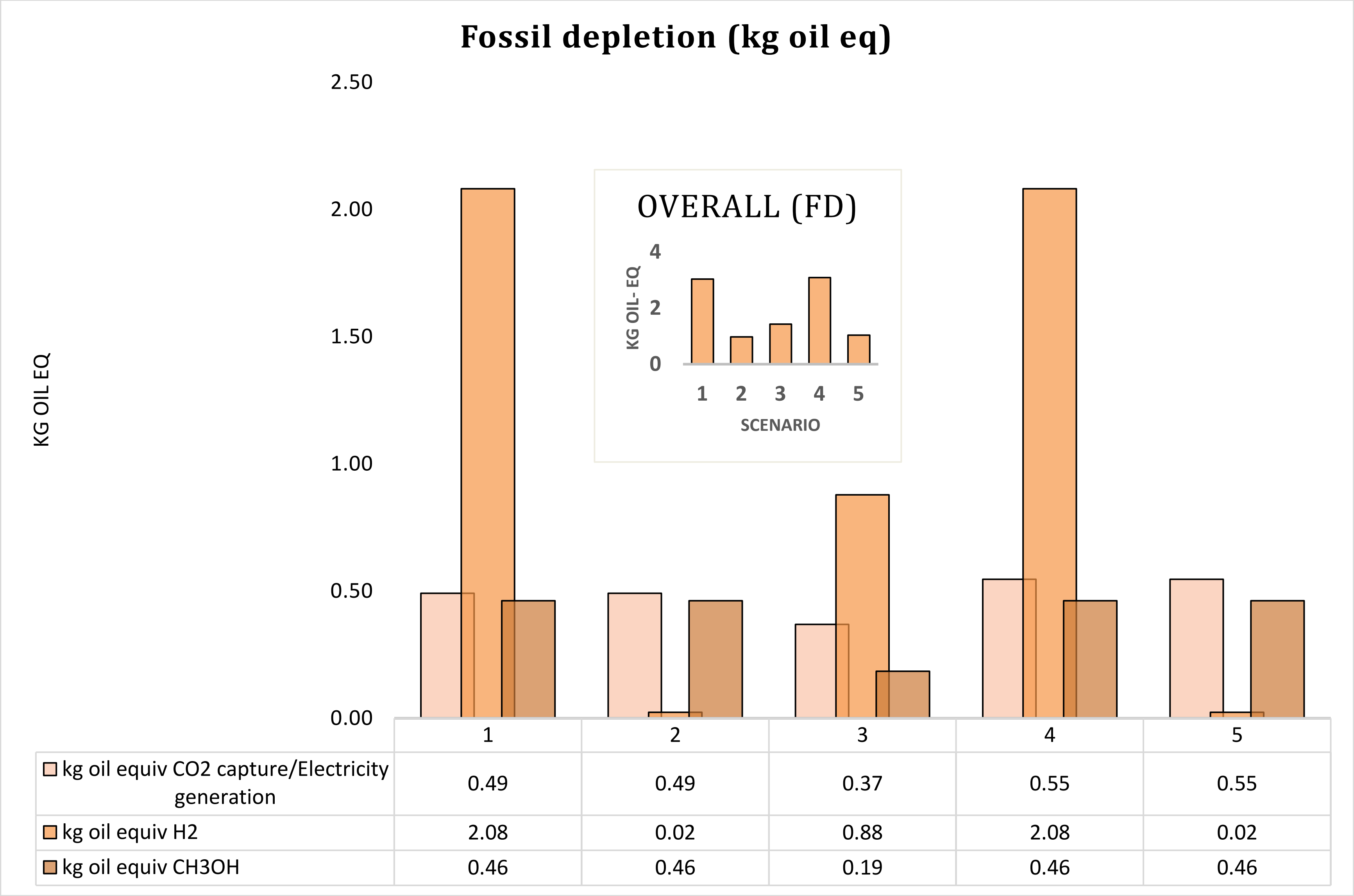
Photochemical oxidation

Results (**Figure 5.21**) show higher non-methane organic volatile compounds (NMOVC) emissions for the CO_2 utilisation scenarios connected to the grid (1 and 4). As is the case with most of the other impact categories, using fossil-based energy is not only directly linked to carbon emissions but also to most of the compounds that contribute to environmental impacts. Overall, Scenario 3 shows a decrease of 13% when compared to Scenario 2. Although the environmental performance improves when H_2 is obtained from a renewable source; the energy penalty to synthesise CH_3OH is still elevated enough to increase photochemical oxidation scores compared to the conventional process.

Marine aquatic, freshwater and terrestrial ecotoxicity

The indicator result used for all ecotoxicity impacts is (kg 1,4-DCB eq). Results show a variation in each impact category. For marine aquatic and terrestrial ecotoxicity (refer to **Figure 5.23**) the high-energy penalties from methanol through catalytic hydrogenation of CO_2 have the highest potential impact results; while carbon dioxide utilisation scenarios with renewables are closer to the values from the conventional process. As mentioned in the other categories, the utilisation process would need to lower its energy footprint in all process stages to compete with conventional methanol production routes. Whilst marine aquatic and terrestrial ecotoxicity do not favour utilisation routes, freshwater ecotoxicity has a positive result. Because of methane requirements for methanol production, freshwater ecotoxicity score increases from 0.005 (kg 1,4-DCB eq) in Scenario 2 to 0.083 (kg 1,4-DCB eq) in Scenario 3.

Figure 5.24 shows the results for these impacts.



	1	2	3	4	5
▢ kg oil equiv CO2 capture/Electricity generation	0.49	0.49	0.37	0.55	0.55
▢ kg oil equiv H2	2.08	0.02	0.88	2.08	0.02
▢ kg oil equiv CH3OH	0.46	0.46	0.19	0.46	0.46

Figure 5.19 Fossil depletion (FD) per functional unit (1 kg of urea ready for use phase). Scenarios 1 to 5 with up to 3 main stages each: CO_2 capture, H_2 production, methanol production. 1) Case scenario of 1 kg methanol, electricity grid mix, with post-combustion carbon capture 2) Case scenario 1 kg methanol, wind power, with post-combustion carbon capture 3) Baseline scenario methanol from natural gas 4) 1 kg of methanol-DAC (direct air capture), H_2- electricity grid mix 5) 1 kg of methanol-DAC (direct air capture), H_2-wind power

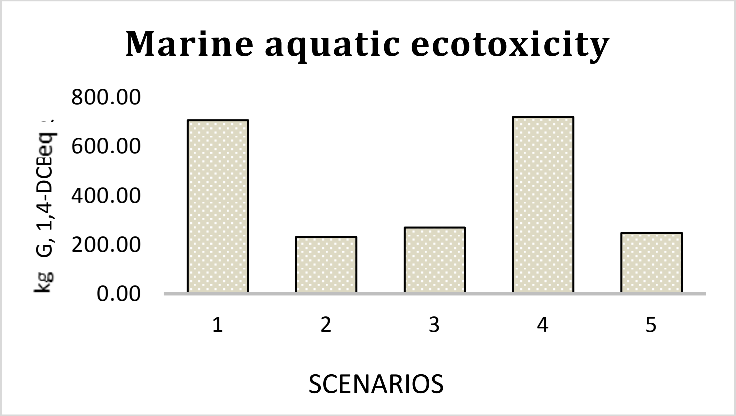


Figure 5.20 Marine aquatic ecotoxicity scores for all scenarios with system expansion, 1 kg of methanol and 1.5 kWh as end products

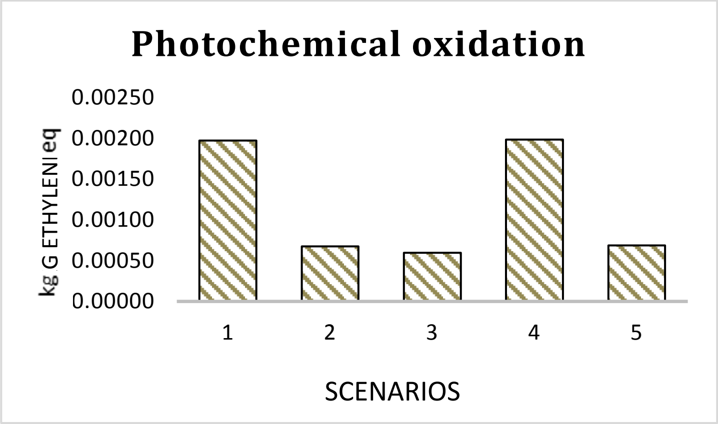


Figure 5.21 Photochemical oxidation scores for all scenarios with system expansion, 1 kg of methanol and 1.5 kWh as end products

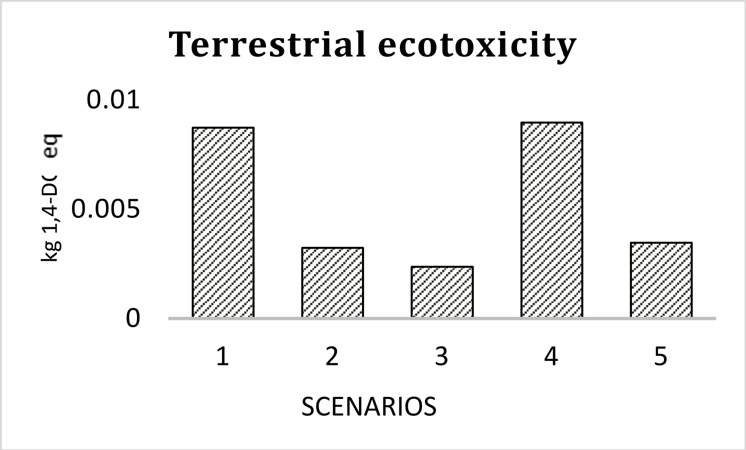


Figure 5.22 Terrestrial ecotoxicity scores for all scenarios with system expansion, 1 kg of methanol and 1.5 kWh as end products.

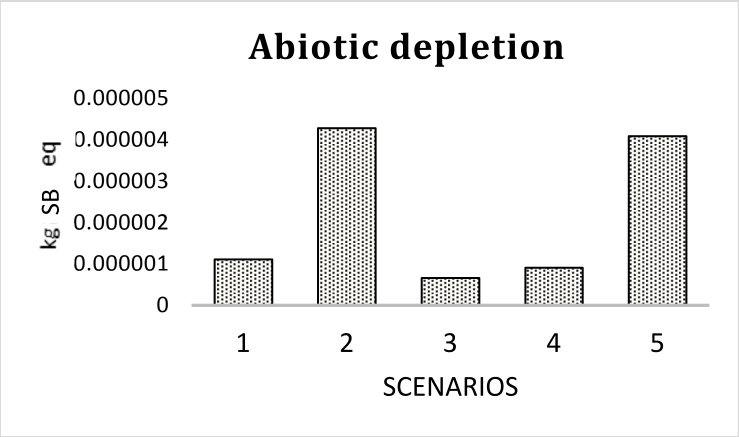


Figure 5.23 Abiotic depletion scores for all scenarios with system expansion, 1 kg of methanol and 1.5 kWh as end products

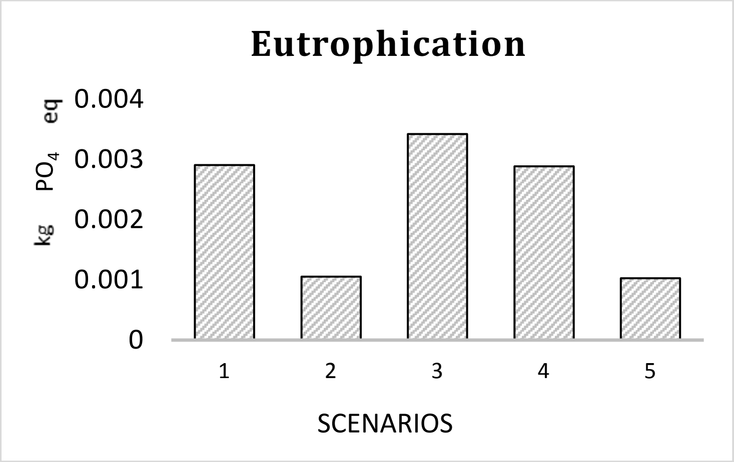


Figure 5.24 Eutrophication scores for all scenarios with system expansion, 1 kg of methanol and 1.5 kWh as end products

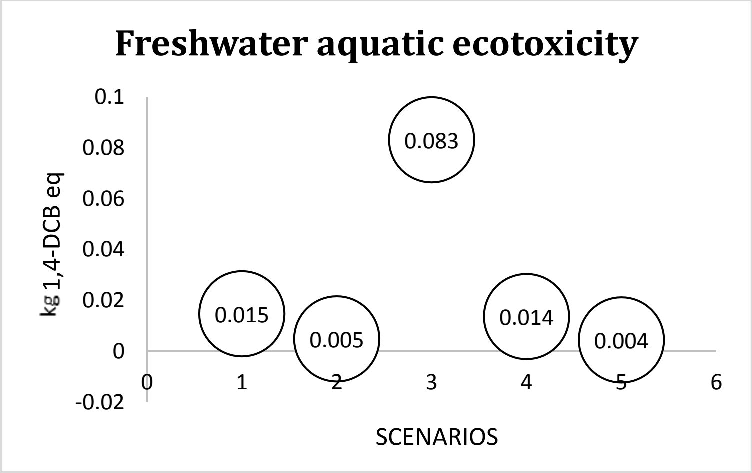


Figure 5.25 Freshwater aquatic ecotoxicity scores for all scenarios with system expansion, 1 kg of methanol and 1.5 kWh as end products

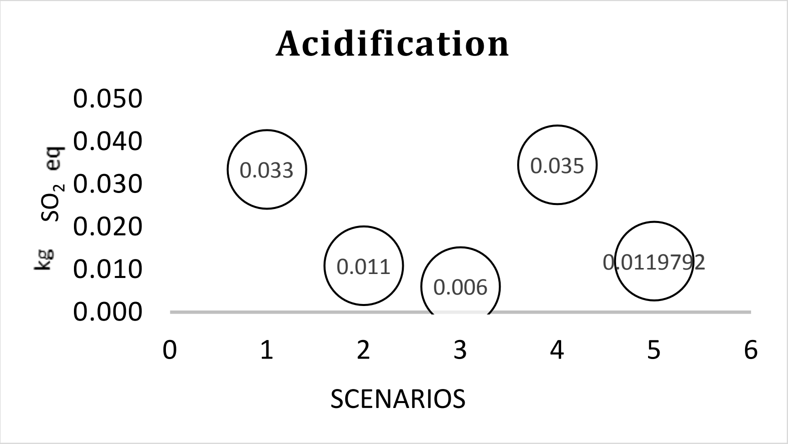


Figure 5.26 Acidification scores for all scenarios with system expansion, 1 kg of methanol and 1.5 kWh as end-product

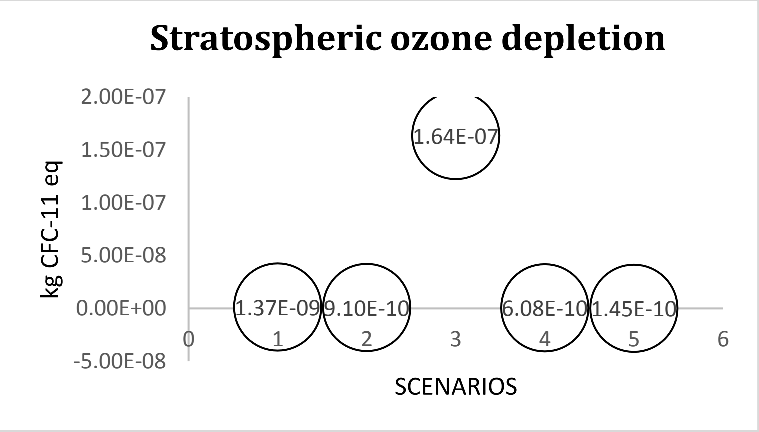


Figure 5.27 Stratospheric ozone depletion scores for all scenarios with system expansion, 1 kg of methanol and 1.5 kWh as end-products

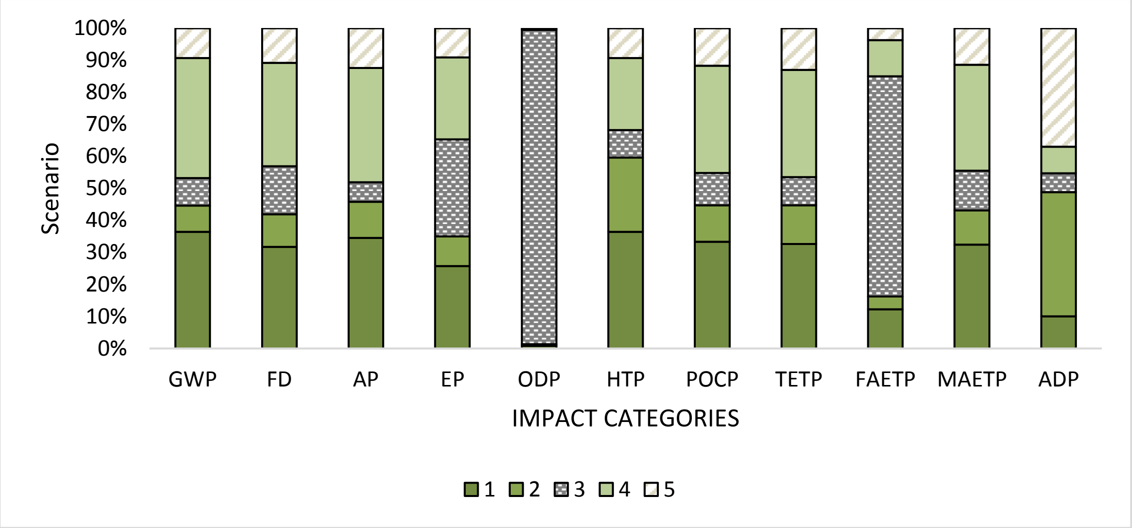


Figure 5.28 Comparative analysis of each scenario per impact category, based on results shown in Figure 17-26

5.4 Sensitivity and uncertainty analysis

This section analyses the outcome reliability with chosen databases for these case studies. The methanol study case is a model based on a collection of sources, thus its uncertainty will be greater than a study with primary data. However, the results from this study are very useful for determining the best ways to analyse said processes. **Chapter 6** uses the knowledge obtained from this chapter and applies it to another utilisation product using primary data. Hence, sensitivity and uncertainty techniques are explained directly in the application chapter (**Section 6.4**) and only a summary of the results is shown in this section.

The first sensitivity test compared between allocation scenarios and results for CO_2 emissions. **Table 5.21** and **Figure 5.29** show the total emissions per functional unit for each scenario and each main allocation rule. In line with other studies (von der Assen *et al.*, 2014, 2016), the avoided burden method shifts all burdens to one part of the process instead of distributing them. There is a case for economic allocation, where results are the most similar to system expansion. However, this requires that captured CO_2 should have an economic value, which is subject to the purity of the CO_2 stream and the market for it. This leaves system expansion as the most feasible option for allocation of CO_2 utilisation emissions. By using this method, both conventional and CO_2 utilisation processes have the same functional units and are assessed evenly.

Table 5.21 Net kg CO_2 emissions for each main scenario with allocation by different methods. Scaled to 1 kg of methanol as final product, with 1.5 kWh generated from a coal-fired power plant.

Allocation method		**Net kg CO_2 emissions per scenario**			
		1	**2**	**4**	**5**
System expansion	Utilisation	8.5	1.8	8.7	2.1
	Conventional	1.9	1.9	1.9	1.9
Avoided burden	Utilisation, primary product	7.1	0.5	7.4	0.8
	Electricity, secondary product	1.3	1.3	1.3	1.3
	Electricity, primary product	7.1	0.5	7.4	0.8
	Utilisation, secondary product	0.6	0.6	0.6	0.6
Economic allocation	Electricity	0.1	0.1	0.2	0.2
	CO_2 feedstock	0.7	0.7	0.7	0.7
	Methanol	8.9	2.3	8.9	2.3

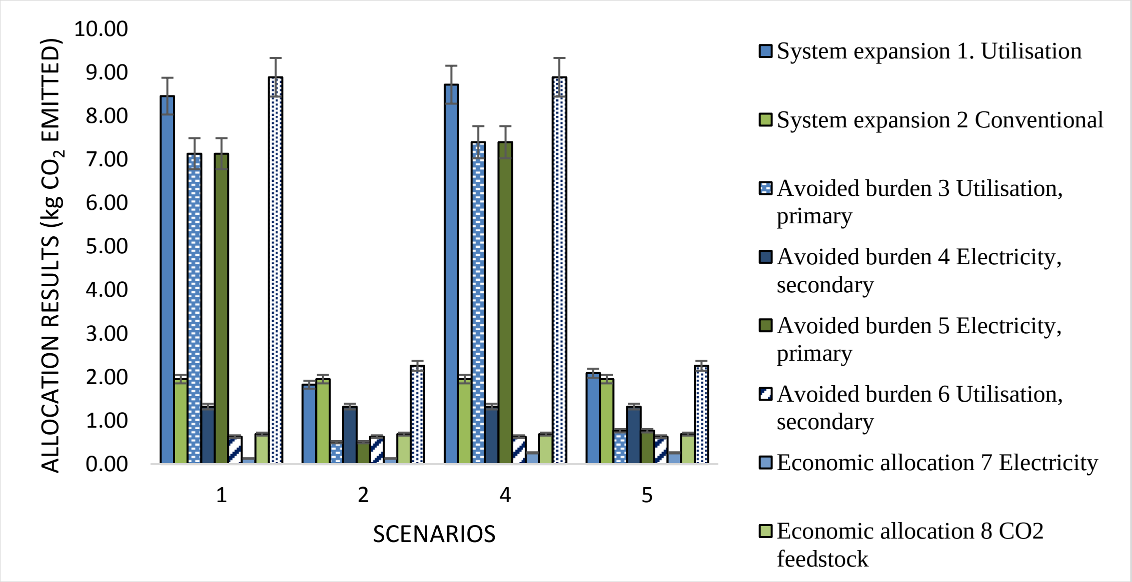


Figure 5.29 Net kg CO_2 emissions for each main scenario with allocation by different methods. Scaled to 1 kg of methanol as final product, with 1.5 kWh generated from a subcritical PC (pulverised coal) fired power plant.

As mentioned in **Section 5.1.1**, for every 1.3 kg of CO_2 captured needed to produce 1 kg of CH_3OH, 1.5 kWh are also delivered to the grid. These values assume that the power plant is a supercritical PC (pulverised coal) and has been taken as base case for this work. However, PC (pulverised coal) plants have been shutting down in recent years (National Grid, 2016); thus a comparison from three different types of power plant was made to measure the impacts of changing the type of power plant (**Table 5.22**). Results in **Figure 5.30** show similar emissions for all three cases: subcritical PC (pulverised coal), supercritical PC (pulverised coal) and natural gas combined cycle (NGCC). Although carbon emissions rise by 8% from a natural gas combined cycle (NGCC) plant compared to a subcritical PC (pulverised coal), electricity to the grid more than doubles (2.5x increase) from natural gas combined cycle (NGCC) plants. This means that as we move towards a more efficient and less carbon intensive electricity generation process, more electricity needs to be generated to obtain the same amount of CO_2 capture rate. The role of CO_2 sources is discussed further in **Chapter 2**.

Table 5.22 Sensitivity analysis for capture variables in each scenario. Results include system expansion method and are set to the production of 1 kg of CH_3OH.

Scenarios	**kg CO_2 emitted with CO_2 capture from different sources**			
	Subcritical PC[1] post - combustion capture (1.5 kWh to grid)	Supercritical PC[1] post - combustion capture (1.6 kWh to grid)	NGCC[2] post - combustion capture (3.8 kWh to grid)	DAC[3]
1	8.5	8.5	8.7	N/A
2	1.8	1.9	2.0	N/A
3	1.9	1.9	2.2	N/A
4	N/A	N/A	N/A	8.9
5	N/A	N/A	N/A	2.1

[1] Pulverised coal [2]Natural gas combined cycle [3]Direct air capture

Several databases were collected from these sources to complete the life cycle inventory (LCI). While not all of them were used in the case study, this information was useful to compare results between similar scenarios. Seven different hydrogen sources were compared against three methanol production routes and two carbon sources. **Figure 5.30** shows the global warming scores of all scenarios with each alternative as a sensitivity test. Results showed that all chlor-alkali databases have lower global warming scores than the case scenario and the scenario with data from an external company (ITM Power Limited electrolyser) when connected to grid. However, the processes from commercial databases are not adapted to run on renewables; hence, Scenario 2 and 4 still have overall lower global warming scores than any other scenario assessed using system expansion. The graph also shows closer results between a theoretical case study and one with information from the stakeholder. This reinforces the usefulness of carrying out a first life cycle assessment (LCA) pre-screen for a CO_2 utilisation process with theoretical data.

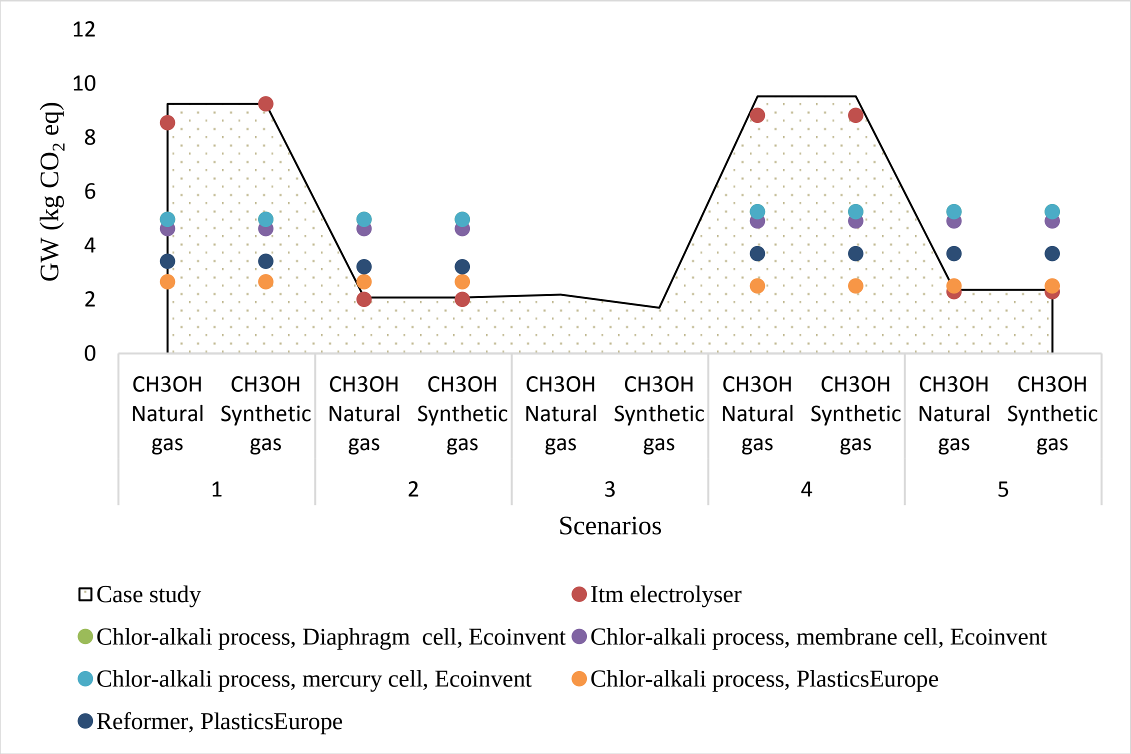


Figure 5.30 Global warming (GW) scores for all scenarios with different hydrogen database sources compared to two methanol production routes. The database used for methanol from natural gas and methanol from synthetic gas was obtained from ecoinvent 3.3. Functional unit of kg CO_2 equivalent per 1 kg of CH_3OH produced and 1.5 kWh to grid.

Lastly, the uncertainty of net kg CO_2 emitted by the production of 1 kg of methanol was calculated with a graphical distribution (**Figure 5.31)**. The variance is set at ± 10% standard deviation scale considering all inputs for Scenario 1 and 2000 random data points. Results show a symmetrical distribution where the probability of occurrence is 8% for 8.5 kg of CO_2 emissions (net Scenario 1). Overall, 68 % of the outputs fall within the range of 8.2 kg to 8.7 kg CO_2 emitted per 1 kg of methanol produced (**Figure 5.32**).

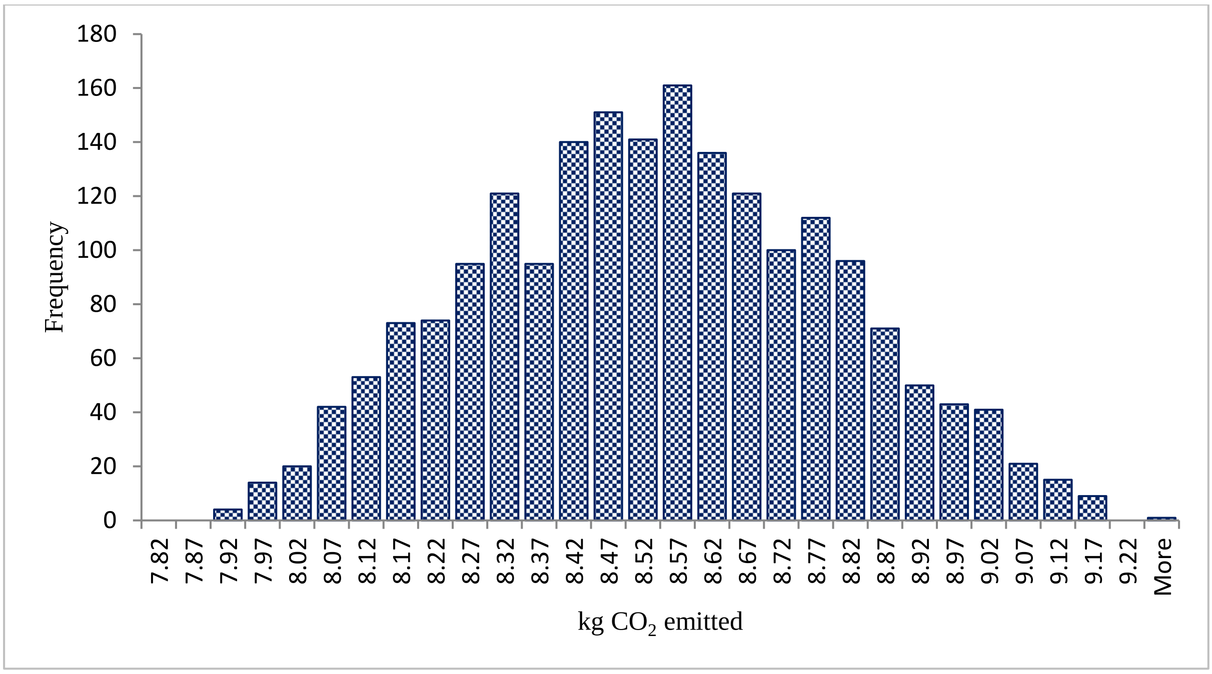


Figure 5.31 Uncertainty analysis of kg CO_2 emissions to produce 1 kg of methanol and 1.5 kWh to the grid, using system expansion. Scenario 1 conditions. ± 10% standard deviation scale, 2,000 points calculated.

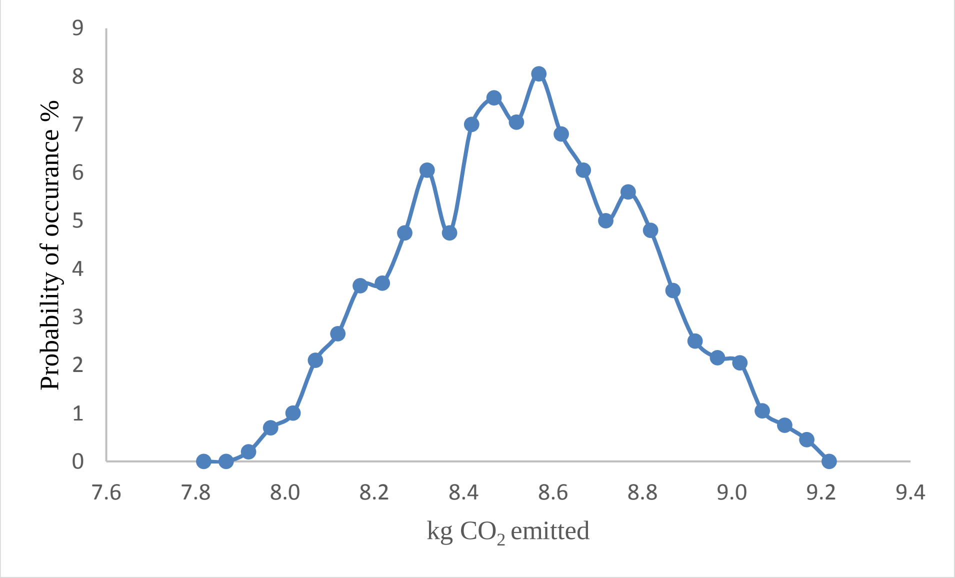


Figure 5.32 Probability distribution against the kg CO_2 emissions necessary to produce 1 kg of methanol and deliver 1.5 kWh to the grid, using system expansion. Scenario 1 conditions. ± 10% standard deviation scale, 2000 points calculated.

Since this worked example considers stoichiometric values for CO_2 and H_2, measuring the sensitivity of the impact categories using normal distribution curves does not return useful values for interpretation. By considering standard deviation half of the results will be below the stoichiometric minimum (as this was used as the mean value) resulting in nonsensical inputs for the production of methanol. Whilst such a sensitivity analysis may still be mathematically valid (i.e. the varying of the inputs to impossibly low levels will still provide values for each impact factor giving an idea on impact category sensitivity to the varied parameter) it was decided to take an approach in which only feasible results were attained. An example of using the normalised distribution curve for varying the capture stage has been included to demonstrate how this method would be utilised (**Figure 5.33**).

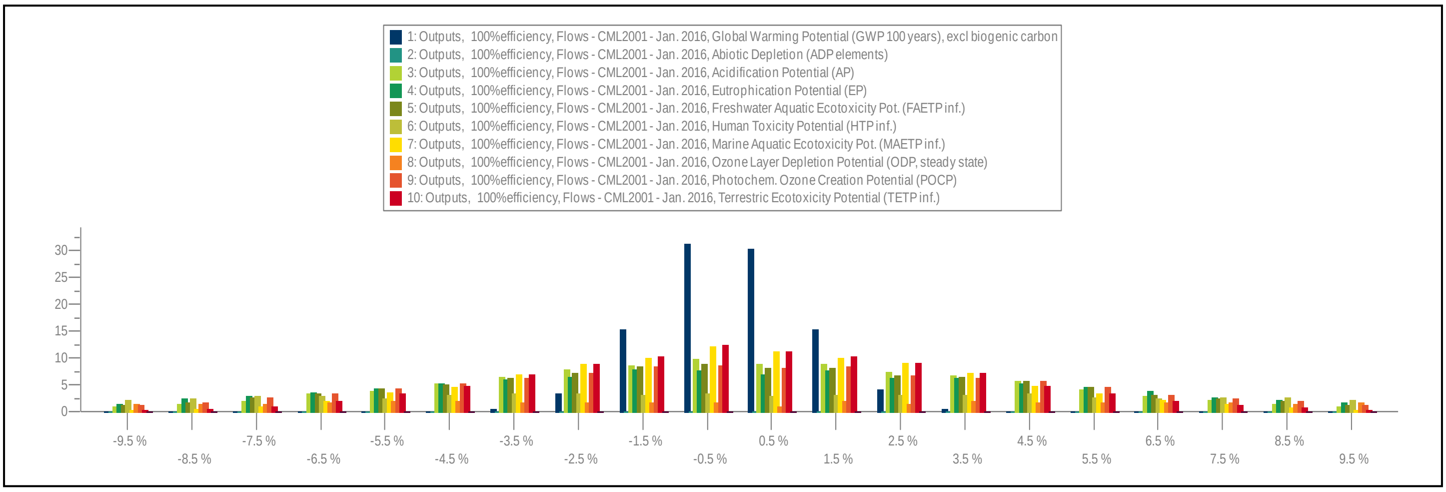


Figure 5.33 Environmental impacts probability distributions with respect to standard deviations from their mean value

Instead it was decided to investigate sensitivity by simulating effective inefficiencies in relation to the stoichiometric values of chosen parameters. 10% of the stoichiometric value was added leading from 100 % (stoichiometric) to 200% (stoichiometric + 100 % additional value).

The simulations were ran using GaBi ts version 8.7.0.18 where the main independent input parameters were varied (CO_2, H_2 and electricity for H_2 production) ten times to cover the 100% - 200% stoichiometric range for all four CO_2 utilisation scenarios. This gave 11 data points which were used to analyse sensitivity. To compare the sensitivity of the impact categories, the following formula (**Equation 5.6**) was used:

$$\frac{Environmental\ impacts\ of\ each\ \%\ increase}{Environmental\ impact\ at\ 100\ \%} = indexed\ value$$

Equation 5.6

Thus, creating a relative scale that allows to compare the sensitivity of each impact. The greater the variance of the index value from the initial indexed value of 1 (the stoichiometric baseline), the more sensitive the impact category. The indexed sensitivity graph for each main output under each CO_2 of the utilisation scenarios is shown from **Figures 5.34 to 5.36**. By plotting each of the index trends for each impact category in a scenario, conclusions can be drawn on the sensitivity of each category.

When the CO_2 parameter is varied, global warming is one of the least sensitive categories to change, this is expected since it relies on a 90% CO_2 capture process. This is the opposite when H_2 and electricity for H_2 is varied in Scenario 1 and 4. Global warming is more sensitive in scenarios that rely on a carbonised electricity grid mix than those that rely on wind power.

Abiotic depletion is a sensitive category for those scenarios where wind power is used, this is expected and is in line with the results shown in **Section 5.3.2**, where it is stated that the manufacturing stage of wind turbines has high abiotic depletion impacts. Ozone depletion is the most sensitive impact category for the scenarios that rely on post-combustion capture when the CO_2 is varied. However, this impact is still very small compared to the other impact categories even with a 200 % increase on the CO_2 required for MeOH synthesis. In general, it is the use of triethylene glycol that contributes the most to ozone depletion impacts in the capture stage.

Comparing the distribution graph shown in **Figure 5.33** to the indexed value graph for Scenario 1 (CO_2) varied (**Figure 5.34**), a similar sensitivity is obtained. While both approaches can be used, the indexed value graph can be used for clearer interpretation as it eliminates results that require inputs below stoichiometric quantities.

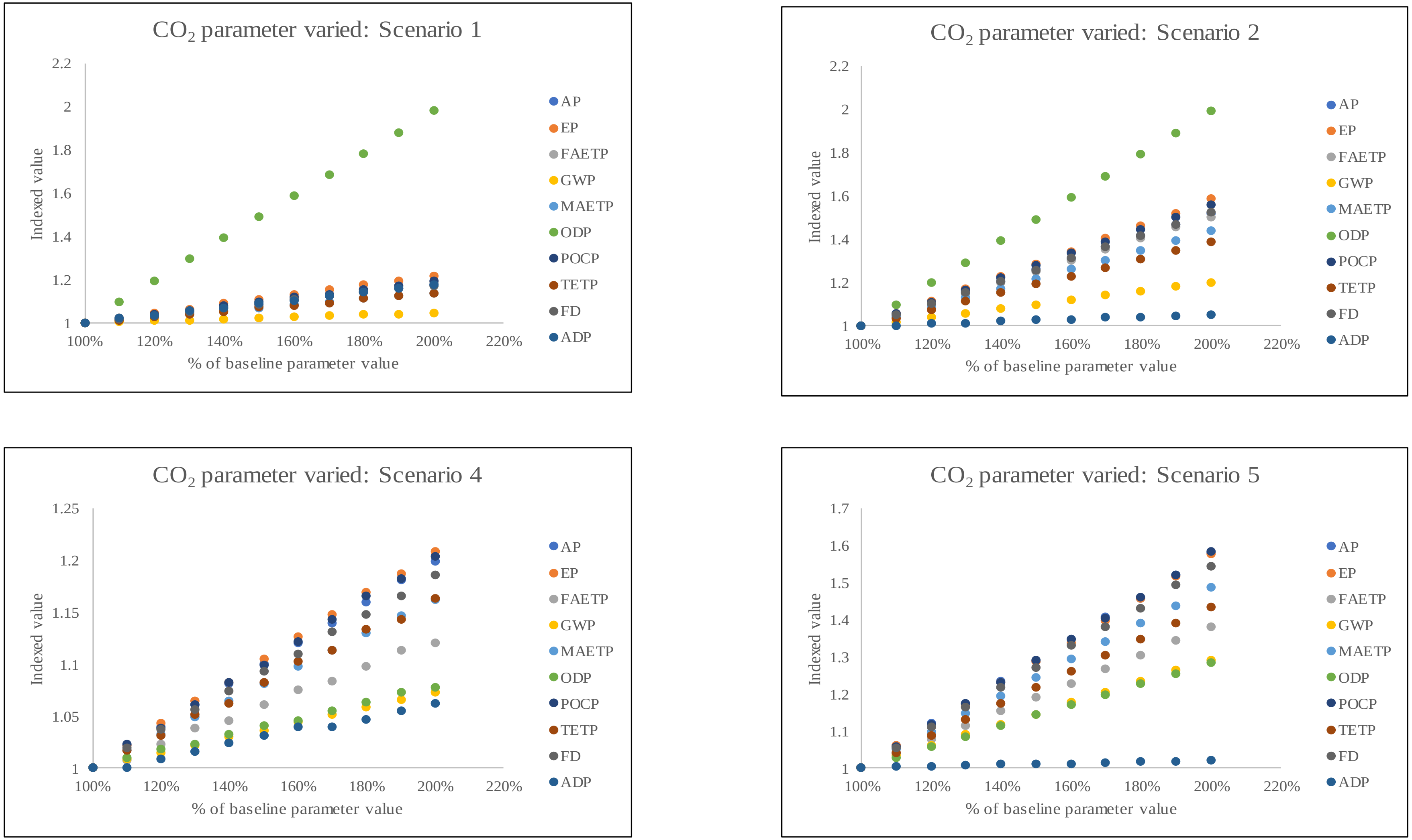


Figure 5.34 Sensitivity indexed graphs for the variation of the CO$_2$ parameter for CO$_2$ based methanol scenarios using system expansion

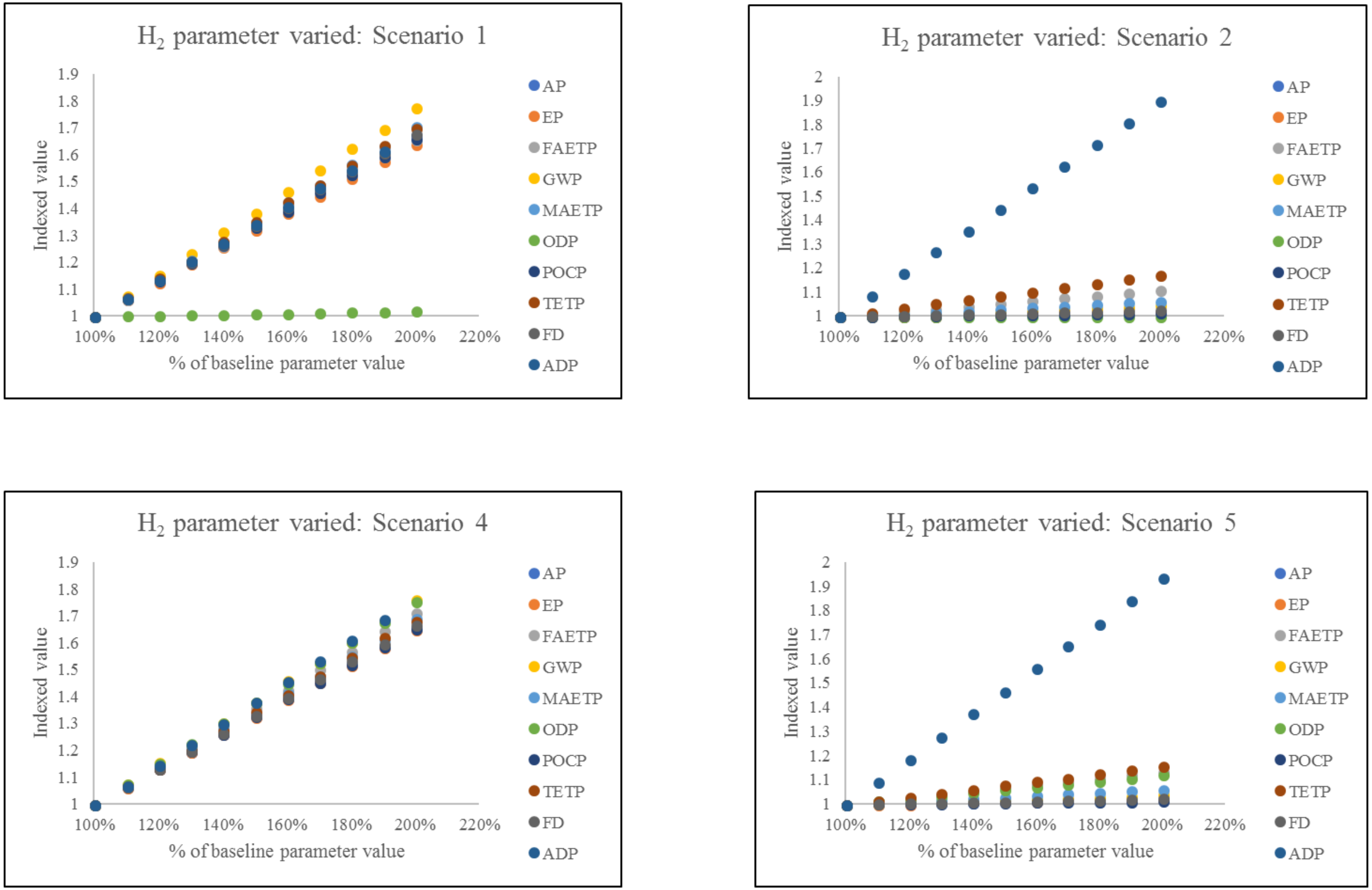


Figure 5.35 Sensitivity indexed graphs for the variation of the NH_3 parameter for CO_2 based methanol scenarios using system expansion

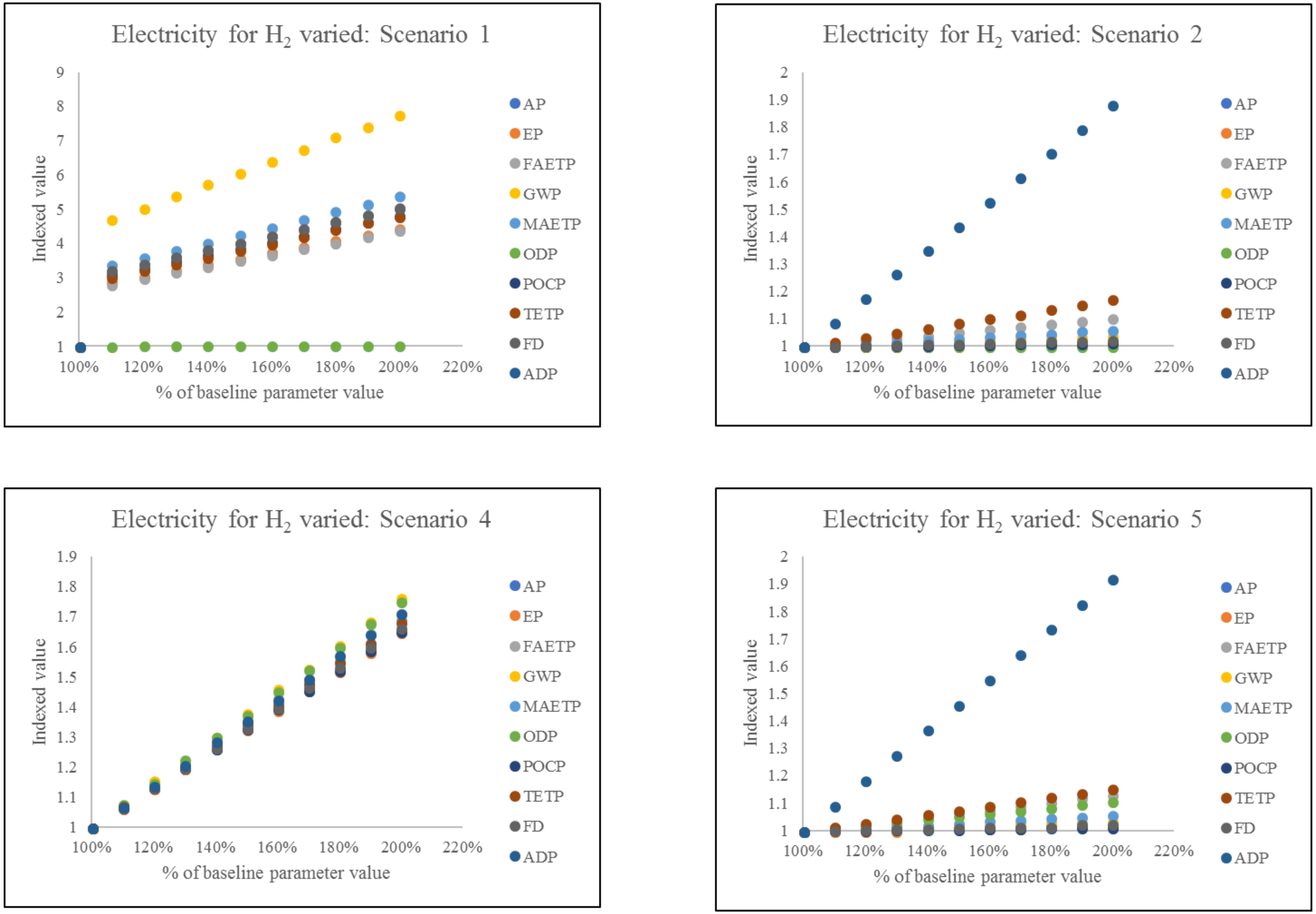


Figure 5.36 Sensitivity indexed graphs for the variation of the electricity required for H_2 production parameter for CO_2 based urea scenarios using system expansion

5.5 Chapter five summary

This chapter tested the first two steps of the framework presented in **Chapter 4**. The framework can be assessed by using datasets commercially available and a range of published sources. For this, a life cycle inventory (LCI) was created to produce 1 kg of CH_3OH from catalytic hydrogenation of CO_2 and the generation of 1.5 kWh from a subcritical PC (pulverised coal) power plant (550MWe) with a post-combustion capture unit. Methanol synthesis included CO_2 supplied from the capture plant and from a theoretical direct air capture unit (DAC). H_2 was produced from water electrolysis. H_2 production emissions were calculated for both renewables and fossil fuels based. The main inputs for a final production of 1 kg of CH_3OH were 0.2 kg H_2, 1.4 kg of CO_2, and 10.2 MJ of energy for methanol synthesis; 46 MJ of electricity and 1.7 kg H_2O for water electrolysis.

After the inventory was completed, ten impact categories were assessed. Results showed a carbon avoidance potential of 0.1 kg CO_2/kg CH_3OH when methanol is produced through catalytic hydrogenation of CO_2 with renewable H_2 compared to methanol from natural gas. However, this value decreases to 0 if a sensitivity test is done only considering electricity. This emphasises the need to lower overall energy penalties through the CO_2 utilisation supply chain if carbon emissions are to be avoided. Unsurprisingly, results show that the worst scenarios occur when the electricity grid only powers the CO_2 utilisation process. In Scenario 1, 7.1 kg CO_2/kg CH_3OH are added compared to methanol from natural gas (1.9 kg CO_2/kg CH_3OH). For the two last Scenarios (4 and 5) results did not show advantages from capturing CO_2 from direct air capture (DAC) or capturing it from post-combustion capture process. While there is a direct CO_2 reduction when using a direct air capture system, this reduction is not enough to balance indirect emissions from energy consumption (0.5 kg CO_2 emitted/1.4 kg CO_2 captured). Other category impacts show similar trends as with carbon avoidance. Fossil fuel depletion, eutrophication and ecotoxicity have lower impacts in utilisation scenarios when renewables are used. Acidification, photochemical oxidation and abiotic depletion impacts are higher in utilisation cases because of SO_2 emissions and manufacturing of wind turbines. Sensitivity and uncertainty analysis corroborated the results from the assessment. Increasing power plant efficiency, reducing capture energy penalties and using renewables for utilisation can have better environmental performance as a utilisation scenario than methanol from natural gas.

5.6 Chapter five reference list

Abbas, Z., Mezher, T. and Abu-Zahra, M. R. M. (2013) 'CO2 purification. Part I: Purification requirement review and the selection of impurities deep removal technologies', *International Journal of Greenhouse Gas Control*. Elsevier Ltd, 16, pp. 324–334. doi: 10.1016/j.ijggc.2013.01.053.

Abu-Zahra, M. R. M., Niederer, J. P. M., Feron, P. H. M. and Versteeg, G. F. (2007) 'CO2 capture from power plants', *International Journal of Greenhouse Gas Control*, 1(2), pp. 135–142. doi: 10.1016/S1750-5836(07)00032-1.

Althaus, H., Chudacoff, M., Hischier, R., Jungbluth, N., Osses, M., Primas, A. and Hellweg, S. (2007) 'Life cycle inventories of chemicals. ecoinvent report No.8, v2.0.', *Final report ecoinvent data …*, (8), pp. 1–957.

von der Assen, N., Jung, J. and Bardow, A. (2013) 'Life-cycle assessment of carbon dioxide capture and utilization: avoiding the pitfalls', *Energy & Environmental Science*, 6(9), p. 2721. doi: 10.1039/c3ee41151f.

von der Assen, N., Müller, L. J., Steingrube, A., Voll, P. and Bardow, A. (2016) 'Selecting CO2 Sources for CO2 Utilization by Environmental-Merit-Order Curves', *Environmental Science and Technology*, 50(3), pp. 1093–1101. doi: 10.1021/acs.est.5b03474.

von der Assen, N., Voll, P., Peters, M. and Bardow, A. (2014) 'Life cycle assessment of CO2 capture and utilization : a tutorial review', *Chem Soc Rev*, 43, pp. 7982–7994. doi: 10.1039/C3CS60373C.

Baciocchi, R., Storti, G. and Mazzotti, M. (2006) 'Process design and energy requirements for the capture of carbon dioxide from air', *Chemical Engineering and Processing: Process Intensification*, 45(12), pp. 1047–1058. doi: 10.1016/j.cep.2006.03.015.

Boretti, A. (2013) 'Renewable hydrogen to recycle CO2 to methanol', *International Journal of Hydrogen Energy*. Elsevier Ltd, 38(4), pp. 1806–1812. doi: 10.1016/j.ijhydene.2012.11.097.

Carbon Engineering (2017) *Direct Air Capture*.

Corsten, M., Ramírez, A., Shen, L., Koornneef, J. and Faaij, A. (2013) 'Environmental impact assessment of CCS chains – Lessons learned and limitations from LCA literature', *International Journal of Greenhouse Gas Control*. Elsevier Ltd, 13, pp. 59–71. doi: 10.1016/j.ijggc.2012.12.003.

Van der Giesen, C., Meinrenken, C. J., Kleijn, R., Sprecher, B., Lackner, K. S. and Kramer, G. J. (2017) 'A Life Cycle Assessment Case Study of Coal-Fired Electricity Generation with Humidity Swing Direct Air Capture of CO 2 versus MEA-Based Postcombustion Capture', *Environmental Science & Technology*, 51(2), pp. 1024–1034. doi: 10.1021/acs.est.6b05028.

Greening, B. and Azapagic, A. (2013) 'Environmental impacts of micro-wind turbines and their potential to contribute to UK climate change targets', *Energy*, 59, pp. 454–466.

Heijungs, R., Settanni, E. and Guin??e, J. (2013) ‘Toward a computational structure for life cycle sustainability analysis: Unifying LCA and LCC’, *International Journal of Life Cycle Assessment*, 18(9), pp. 1722–1733. doi: 10.1007/s11367-012-0461-4.

Methanol Institute (2017) *The Methanol Industry*.

National Grid (2016) ‘Future Energy Scenarios 2016’, (July), pp. 1–194.

NETL (2013) *Cradle-to-Gate Life Cycle Analysis Model for Alternative Sources of CO2*.

NETL (2015) *Cost and Performance Baseline for Fossil Energy Plants Volume 1a: Bituminous Coal and Natural Gas to Electricity Revision 3 (DOE/NETL-2010/1723),*.

Pérez-Fortes, M., Bocin-Dumitriu, A. and Tzimas, E. (2014) ‘CO2 utilization pathways: Techno-economic assessment and market opportunities’, *Energy Procedia*. Elsevier B.V., 63(i), pp. 7968–7975. doi: 10.1016/j.egypro.2014.11.834.

Singh, B., Strømman, A. H. and Hertwich, E. G. (2011) ‘Comparative life cycle environmental assessment of CCS technologies’, *International Journal of Greenhouse Gas Control*. Elsevier Ltd, 5(4), pp. 911–921. doi: 10.1016/j.ijggc.2011.03.012.

Skytree (2017) *Energy conversion*.

Socolow, R. H.; Desmond, M. J. (2011) *Direct Air Capture of CO2 with Chemicals: A technology Assessment for the APS Panel on Public Affair*.

Socolow, R., Desmond, M., Aines, R., Blackstock, J., Bolland, O., Kaarsberg, T., Lewis, N., Mazzotti, M., Pfeffer, A., Sawyer, K., Siirola, J., Smit, B. and Wilcox, J. (2011) ‘Direct Air Capture of CO 2 with Chemicals Panel on Public Affairs’, *American Physical Society - Panel on Public Affairs*, p. 100.

Sternberg, A. and Bardow, A. (2015) ‘Power-to-What? – Environmental assessment of energy storage systems’, *Energy Environ. Sci.*, pp. 389–400. doi: 10.1039/C4EE03051F.

Styring, P. and Jansen, D. (2011) *Carbon Capture and Utilisation in the green economy*. The Centre for Low Carbon Futures 2011.

Volkart, K., Bauer, C. and Boulet, C. (2013) ‘Life cycle assessment of carbon capture and storage in power generation and industry in Europe’, *International Journal of Greenhouse Gas Control*. Elsevier Ltd, 16, pp. 91–106. doi: 10.1016/j.ijggc.2013.03.003.

Wang, M., Wang, Z., Gong, X. and Guo, Z. (2014) ‘The intensification technologies to water electrolysis for hydrogen production - A review’, *Renewable and Sustainable Energy Reviews*. Elsevier, 29, pp. 573–588. doi: 10.1016/j.rser.2013.08.090.

Zeman, F. (2014) ‘Reducing the cost of ca-based direct air capture of CO2’, *Environmental Science and Technology*, 48(19), pp. 11730–11735. doi: 10.1021/es502887y.

6 Environmental Assessment of Urea Production Coupling CO_2 Utilisation and Hydrogen Production from Renewable Energy

This chapter follows the framework presented in Chapter 4, with the aim of assessing a carbon dioxide utilisation process. The case study analysed in this chapter is the minimum production of 250 kg/day of urea to use as fertilizer as required by the stakeholder. The process included the potential use of captured CO_2 as feedstock as well as the alternative use of energy sources. To compare between processes, the functional unit was set as 1 kg of urea and 0.8 kWh of electricity generated as stated in **Section 4.4**. These CO_2 utilisation specifications made it a suitable case study to assess the feasibility of the framework presented in this work. The author is responsible for all assessment work and to its knowledge, there is no other similar work done on this case.

6.1 CO_2 utilisation system

Urea synthesis is a well-known process that relies on the synthesis of NH_3 and the utilisation of CO_2. It is also the production process that uses the most carbon dioxide commercially (Xiang *et al.*, 2012). With 190 million tons of urea produced each year worldwide, it is the most produced chemical in the world. Its high demand is directly link to fertilizer use; with over 80% of urea being used as nitrogen based fertilizer (Stamicarbon, 2017). Although this process is efficient and well understood, there are also significant environmental impacts associated to its production. These include emissions to air, into water and fugitive emissions (data set from ecoinvent version 3.3). Overall, the process is energy intensive with a high fossil-fuel depletion rate (**Table 6.14** for input-output data for conventional urea production). From a carbon dioxide utilisation point of view, there is a possibility of producing carbon neutral urea with captured carbon dioxide. As seen in **Figure 6.1**, ammonia can be produced using renewable energy (theoretically reducing fossil depletion rates) and carbon dioxide can be supplied from several capture sources. The urea is used as fertiliser and the CO_2 utilised is released to the atmosphere after the transformation process in the soil. Per kg of urea applied, 1.57 kilograms of CO_2 are returned to the atmosphere (Althaus *et al.*, 2007). However, an environmental assessment is still required to determine the benefits and/or drawbacks of this process.

This work presents the assessment of a urea production process through a set of indicators to determine its potential as a CO_2 utilisation. The design of the urea plant began in 2014 and remains an ongoing project. Currently the process is at lab scale, with a pilot plant projected to be installed by 2018. This study ran in parallel with the initial design stages to determine carbon hotspots and environmental burdens throughout its supply chain.

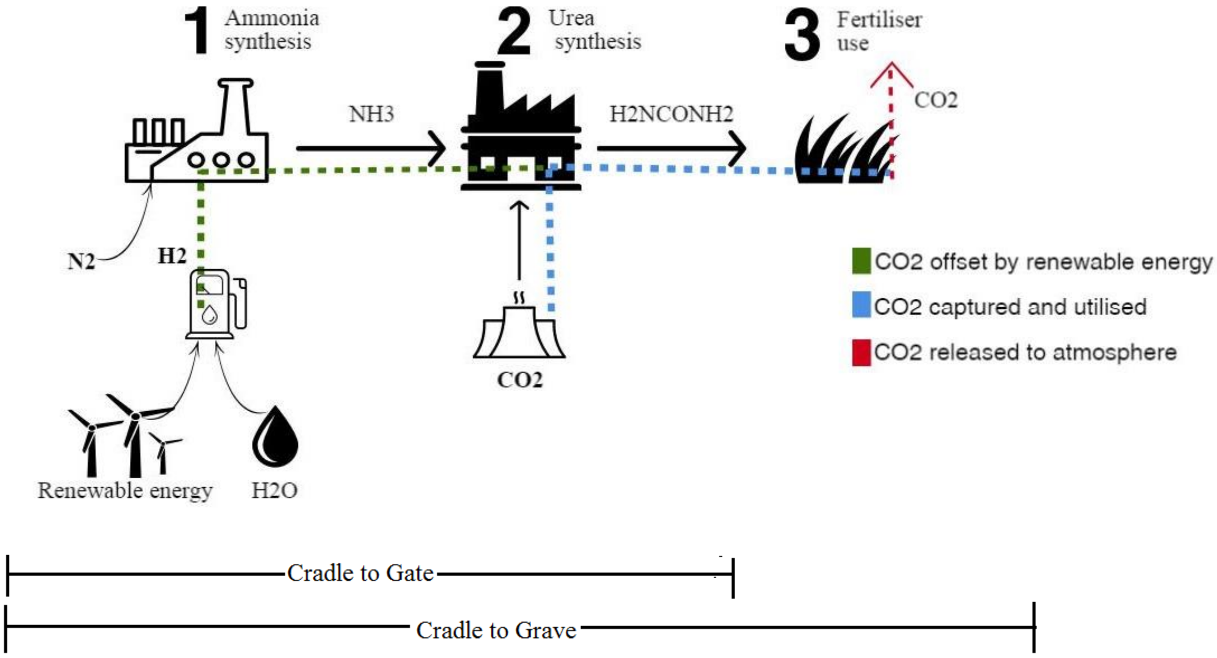


Figure 6.1 Diagram of carbon dioxide flow in urea production process (baseline case)

6.1.1 Process description and boundaries

The UK based chemical production facility is designed to produce a minimum of 250 kg/day of urea. All operations are on site with only CO_2 transportation required as raw material but considered outside the boundary of this study. The final product is stored in a tank and then distributed directly to the land for application. Ammonia is produced using H_2 from a PEM electrolyser and N_2 from a pressure swing absorption unit (PSA). The electrolyser designed by an external company (ITM Power Limited), delivers 33 kg H_2/day and whilst using 55 kWh electricity/day. Electrolyser information was obtained from private communications from ITM Power Limited (2016). Ammonia is then fed into a reactor along with CO_2 to produce urea. A specific capture process to supply CO_2 was not specified, thus several scenarios for different potential sources were analysed. Boundaries for the life cycle assessment study include urea production, ammonia synthesis and CO_2 sourcing (**Figure 6.2**). A plant lifetime of 20 years is considered with a replacement of the PEM electrolyser every 4 years. Urea is only required for seeding season, approximately 4 months; as a result, storage is necessary for the remaining part of the year (Styring, 2016). Storage conditions for 'off-season' months are beyond the scope of this project and are part of the proposed future work. Operational hours are set at 24/7 year-round with this being defined by the research team responsible for the process design (Styring, 2016). Without an indication on maintenance schedules for the small-scale plant it is difficult to assess the viability of this, and so this assumption is upheld to give an indication of a maximum annual output, this falls in line with other studies that have considered a 24/7 operation schedule such as Soltanieh *et al.* (2012) and Galindo Cifre & Badr (2007). It is assumed that should the technology reach a higher TRL a suitable amount of redundancy will be included in the design to allow for continuous operation at the desired annual output. **Figure 6.7** shows the mass balance calculations for the minimum amount of inputs required to produce 250 kg/day urea (assuming 100% conversion).

To be able to compare between scenarios, a functional unit of 1 kg of urea is used. The minimum urea production rate set by the stakeholder was 250 kg/day (**Table 6.1** shows summarised general specifications). However, the initial simulated process is set at the maximum production rate of 325 kg/day. Thus, maximum value is taken for all calculations to allow for unknown losses throughout the process. Process information was obtained from Owen (2016).

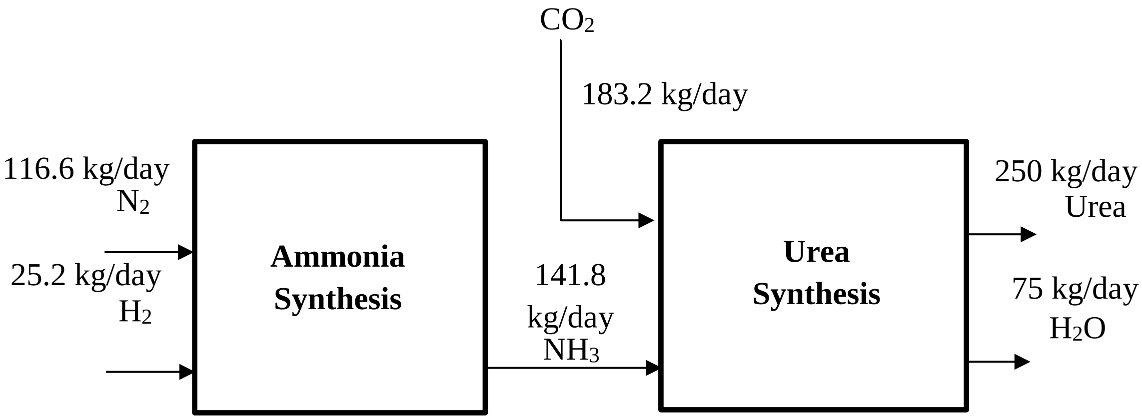


Figure 6.2 Mass balance diagram for minimum inputs required for ammonia and urea synthesis, total urea production of 250 kg/day, 100% conversion

Table 6.1 General urea pilot plant specifications

Specifications for urea pilot plant	Value
Urea total production (kg/day no losses)	325
Functional unit (kg of product)	1
Plant lifetime (years)	20
Electrolyser replacement (years)	4

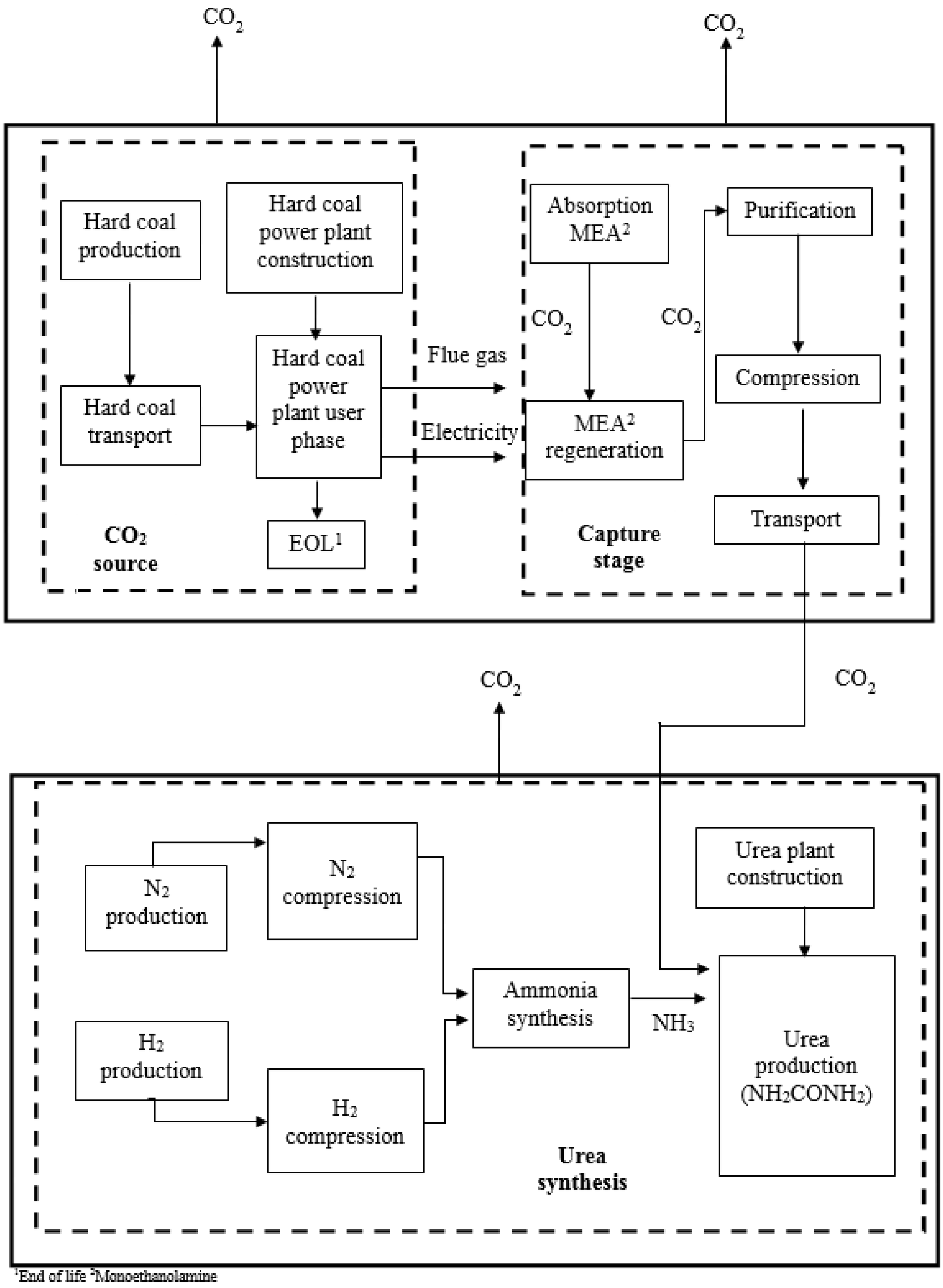


Figure 6.3 Cradle to gate boundaries for the environmental impact assessment of urea production from CO_2 capture and ammonia from renewable energy

One of the objectives of this assessment was to determine the optimal process conditions that correspond with the lowest environmental burdens. Thus, analysing several scenarios to produce urea from CO_2 provided a clearer picture of CO_2 contributions. The variables considered for the scenarios were hydrogen production, CO_2 source and/or urea production (refer to **Table 6.2**). These variables are crucial to CO_2 utilisation, thus considered in this assessment.

Table 6.2 Scenario variables for analysing urea production from carbon utilisation and conventional processes

Product	**Production route alternatives**		
	Alternative 1	Alternative 2	Alternative 3
Hydrogen	Water electrolysis (by ITM Power limited)	NaCl electrolysis	Steam reforming from natural gas/heavy fuel
Carbon dioxide	Post-combustion capture plant	Direct air capture	Ammonia through Haber-Bosch
Ammonia	Hydrogen production connected to grid	Hydrogen production connected to wind power	Steam reforming of natural gas

6.1.2 Data collection

Stakeholders and process modelling provided foreground information. The urea plant design was created using Aspen Plus® simulations version 8.4. The supporting research team created all designs and plans as part of a four-year project (Owen, 2016). This includes ammonia and urea production units. ITM Power Limited provided the electrolyser; their performance data was taken as inputs for this inventory. A blueprint of the electrolyser was provided as a personal communication (ITM Power Limited, 2016). The company provided electricity and water consumption rates for this electrolyser.

During the timeline of this study, on site construction and end of life data were not available: therefore, ecoinvent version 3.3 databases were used to predict potential impacts. For fair comparison, all scenarios for urea production use ecoinvent version 3.3 for construction. Dismantling was considered outside the boundaries and not included in this study. The urea plant scenarios used the same inventories used for CO_2 capture in **Chapter 5**. GaBi ts version 8.7.0.18, ecoinvent version 3.3 and PlasticsEurope databases provided background information for all scenarios.

Cut-off data

As it is often the case with technologies with low technology readiness levels (TRLs), there is little foreground information for carbon dioxide utilisation processes. This complicates comparability between both types of processes assessed. To account for these differences, a sensitivity analysis was run for the main commodity under study: energy. Inputs were also assessed qualitatively if direct comparison was not possible. This sensitivity analysis was not necessary when comparing the same process route since data availability was similar for all processes.

6.2 Life cycle inventory (LCI)

The life cycle inventory (LCI) included all input-output interventions to produce 1 kg of urea. Four main processes form the inventory: hydrogen production, ammonia synthesis, carbon dioxide supply and urea production. The following sections describe these main processes with a general commodities matrix shown in **Table 6.10**.

Hydrogen

The electrolyser designed by ITM Power Limited (PEM electrolysis) can produce the 25.2 kg/day of hydrogen required for ammonia synthesis. The electrolyser has a production range from 25-37 kg/day of hydrogen. An average production of 33 kg H_2/day with a conversion rate of 76.4% was considered to meet the target production of 250 kg urea/day. The total power supply for the electrolysis plant was set at 90 kW per 33 kg H_2/day, 24 hours of operation. 60 kW were specifically required for water electrolysis. The plant included a water purifier system with a 2/3 rejection rate. To produce 13 L/h of required deionised water, 40 L/h of tap water were theoretically necessary. The water supplied based on 24-hour operations, totals 960 kg/day. Other processes within the plant would use the water rejected from the purifier system to reduce utilities (ITM Power Limited, 2016). The water purifying system also includes small quantities of glycol that fall within the cut off data; ITM Power Limited did not report these values. The electrolyser by ITM Power Limited was adapted to either use renewable energy or electricity from the grid. **Table 6.3** shows a summary of electrolyser specifications.

Table 6.3 Summary of electrolyser specifications to supply H_2 for ammonia production

Electrolyser specifications (per day)	Value
Hydrogen production (kg)	33
Total electricity consumption (kW)	90
Electrolysis (kW)	60
Water purifying system (kW)	30
Total water consumption (kg)	960
Recycle stream (kg)	640
Operational hours (hr)	24
Glycol	Trace

Ammonia

The synthesis of ammonia from nitrogen and hydrogen has the following reversible reaction (**Equation 6.1**)

$$N_2 + 3H_2 \leftrightarrow 2NH_3$$

Equation 6.1

ΔH_{298k}= -45.7 kJ mol

Whilst hydrogen production was part of the integrated plant, nitrogen supply was outsourced to other equipment. Until the end of this study, plans for N_2 supply were not decided. The most likely source discussed was N_2 from a rented pressure swing absorption (PSA) unit. **Table 6.4** shows possible pressure swing absorption (PSA) systems that are compatible for this project. Overall, the daily production of NH_3 with a conversion rate of 100% was set at 185.3 kg. This equates to 152.3 kg/day of N_2 and 33 kg/day of H_2 based on a 3:1 molar ratio.

Table 6.4 Pressure swing absorption (PSA) unit options for nitrogen supply in ammonia synthesis

Unit	Capacity	Nitrogen purity
PRISM nitrogen PSA generators	2,600 Nm^3/hr	95-99.99%
IATT onsite nitrogen generators	0.5-10,000 Nm^3/hr	Up to 99.99%
NGP PSA nitrogen generator	Not specified	95-99.99%
Nitrogen generators UK: PSA Nitrogen generators	1-1,000 Nm^3/hr	99% - 99.99%

The catalyst considered for this process is the commonly used promoted magnetite. KATALCO $_{JM}$ 35 series catalyst (Owen, 2016). Reaction pressure was set at 200 bar and feed temperature at 360 C. **Figure 6.4** shows a process flow diagram for the synthesis of ammonia. The simulation results for ammonia synthesis are shown in Owen (2016). **Table 6.5** presents the utilities calculated for this process. Electricity from the grid for compression was the only other input required. To the author´s knowledge, at this design stage, there are no direct emissions reported from this process.

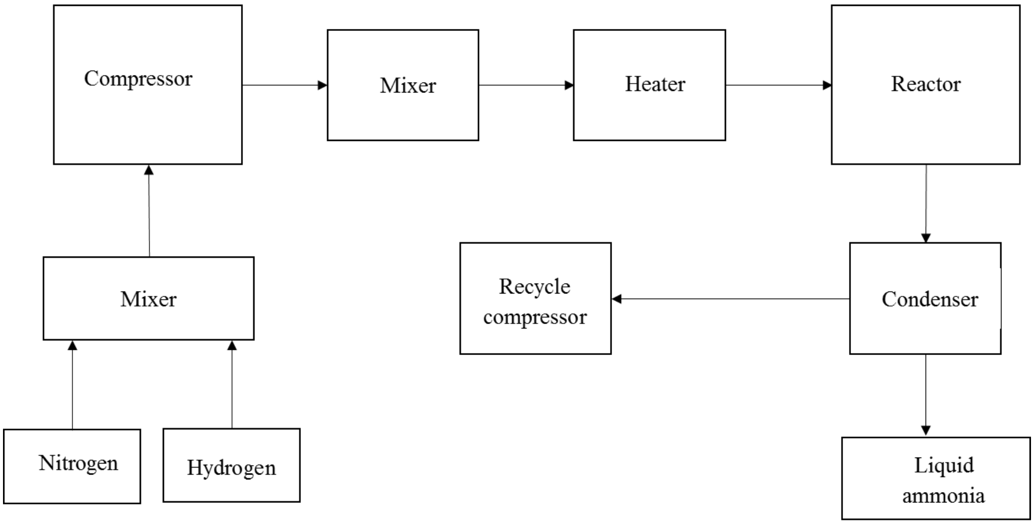


Figure 6.4 Block diagram of ammonia synthesis for baseline case

Table 6.5 Operating conditions and utilities for NH_3 synthesis (scaled to a production of 185.3 kg/day, 100% conversion

Operating parameters for NH_3 synthesis	Value
NH_3 production (kg/day)	185.3
NH_3 production (kg/hr)	7.7
Total heating duty (kW)	11.7
Total cooling duty (kW)	12.0
Total duty (kWh/Kg NH_3)	3.0
Electricity (kW)	11.8
Electricity (kWh/kg NH_3)	2.0

Urea

Urea is synthesised by the reaction of ammonia and carbon dioxide at high temperatures and pressures. The first reversible reaction is the production of ammonium carbamate (**Equation 6.1**). The ammonium carbamate then decomposes to urea (**Equation 6.2)**. The overall process is shown in **Equation 6.3**. The process is exothermic.

$$2NH_3 + CO_2 \leftrightarrow H_2NCOONH_4$$

Equation 6.2

Forward reaction $\Delta H = -117\ kjmol^{-1}$

$$H_2NCOONH_4 \leftrightarrow NH_2NCONH_2 + H_2O$$

Equation 6.3

Forward reaction $\Delta H = +15.5\ kjmol^{-1}$

$$2NH_3 + CO_2 \leftrightarrow H_2NCONH_2 + H_2O$$

Equation 6.4

The highest ammonia production output was used to simulate urea production. 185.3 kilograms of gaseous ammonia at a high pressure (200 bar) were bubbled to a reactor along with 238 kilograms of carbon dioxide. In this simulated scenario, there are no losses throughout the process. This equalled to a total urea production of 325 kg per day. However, the final product requirement is still set at 250 kg of urea per day as specified by the stakeholders.

Heat integration and heat recovery are not included at this initial design stage. It is assumed that all energy needs will be provided by the electricity grid mix. Future iterations of the design are expected to include heat integration. One example as discussed in the personal communication (Owen, 2016) is given as “the cooling effect of the depressurisation of ammonia from 200 bar to atmospheric pressure may be utilised for the cooling of the carbamate formation reaction”. **Figure 6.5** shows a revised mass balance of the overall process.

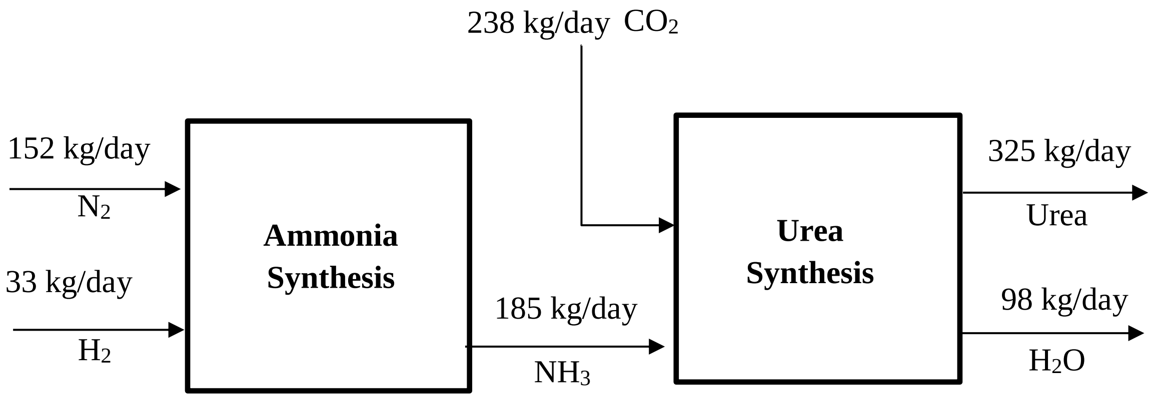


Figure 6.5 Revised mass balance for a maximum urea production of 325 kg/day

The urea synthesis process has three main sections: carbamate formation, filtration, and urea production (as shown in **Figure 6.6**).

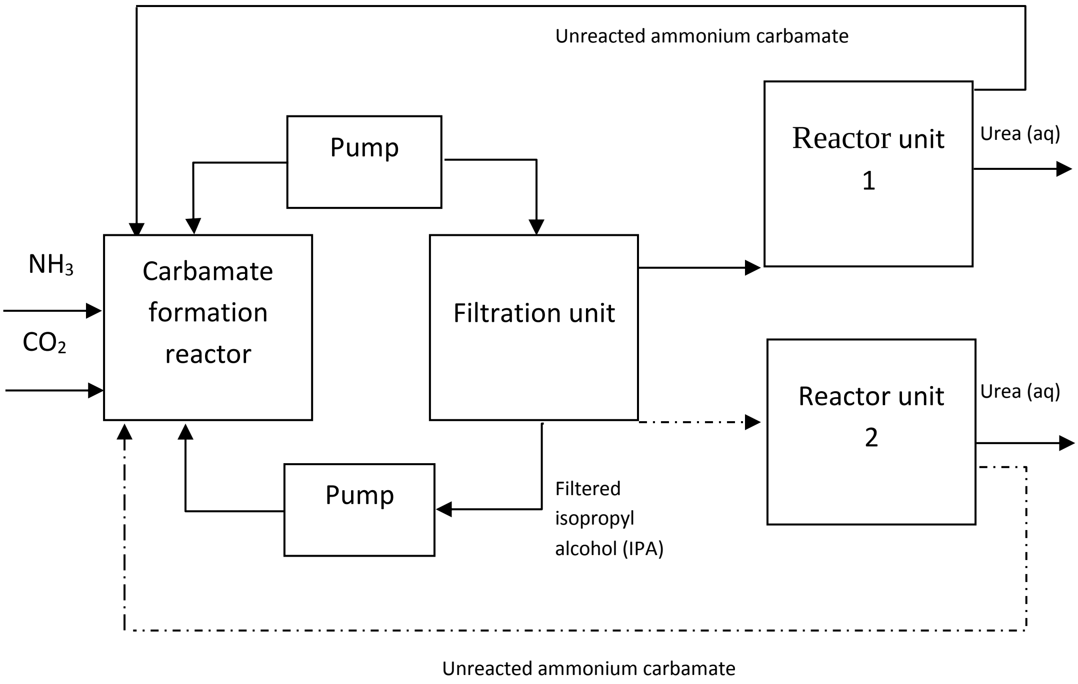


Figure 6.6 Process flow diagram for urea production unit

The carbamate formation reactor required 786 kg/hr (or 1,000 L/hr) of isopropyl alcohol (IPA) as solvent to produce ammonium carbamate. According to the initial pilot tests performed by the researchers leading this project, no more than 1% of solvent was lost per hour. At this stage, it was not possible to quantify the exact top up value; therefore, a sensitivity analysis up to 2% top up was run. In terms of CO_2 emissions, from 0 to 1% top up there is an increase of 1.21 kg CO_2 per kg of urea produced. From 0 to 2% there is an increase of 2.43 kg CO_2 per 1 kg of urea. The scenarios considered work with no solvent losses for baseline calculations. Refer to **Table 6.6** for a summary of top up values for 0%, 1% and 2% solvent losses. The reactor was set at 0°C with a conversion of 97%. The suspension then went through a filtration unit where filtered isopropyl alcohol (IPA) and all unconverted compounds return to the carbamate reactor. Ammonium carbamate passed to a reactor heated at 170°C to produce urea through decomposition. A high mass to volume ratio (0.98g/cm^3) was required to obtain high urea yields with a conversion of 38%. After the reaction, the remaining ammonium carbamate decomposes in the same reactor at 80 °C, with 100% conversion after an hour. There is then urea separation from water and gaseous ammonium carbamate that was recycled through a heated pipeline. To simplify the continuous urea formation process, there are three separate reactors for filtration and reaction units. One reactor for filtration and two for urea formation/decomposition that will alternate in operation. General process specifications are summarised in **Table 6.7**. The flow rate ratio selected was 2:1 of NH_3:CO_2 as this matched recycle gas ratios due to the stoichiometric breakdown of ammonium carbamate. **Table 6.7** also specifies heating duties.

Table 6.6 Summary of Isopropyl alcohol (IPA) top up values for urea synthesis (from 0 top up, to 2%)

Isopropyl alcohol (IPA) top up conditions	**Top up fraction (%)**		
	0	**1**	**2**
Top up (L/hr)	0	10	20
Top up IPA per FU[1] (L/325 kg urea/day)	0	240	480
IPA top up per year (L IPA/year)	0	87,600	175,200
IPA total consumption (L IPA/20 years)	24,000	1,776,000	3,528,000
IPA consumption/kg urea (L IPA/kg urea)	1×10^{-2}	1	2
IPA consumption/FU[1] (L IPA/325 kg urea)	3	243	483

[1] Functional unit

Table 6.7 Process specifications for urea production section

Streams/Scenarios/Duty	**Process specifications for urea production**	
	Value	Notes
Urea (kg/day)	325	Assuming 100% conversion
Urea (kg/hr)	14	
Urea (kg/s)	4×10^{-3}	
IPA[1] (kg/hr)	786	Assuming no losses as baseline
Water (kg/day)	97	
Scenario 1 (kWh/kg)	1.5	
Reactor Heating (kW)	7	
Decomposer Heating (kW)	14	
Total (kW)	21	

[1] Isopropyl alcohol

Additional utilities included electricity from the grid to power the heating jacket. **Table 6.10** presents all urea interventions in matrix based form as established in Heijungs *et al.* (2013). Negative values refer to inputs and positive values to outputs. For CO_2 supply, there was no specific source considered in the initial stages of the project. Therefore, the process allowed assessment flexibility from different CO_2 supply sources. The post-combustion capture plant used in **Chapter 5** is also used here as the main scenario. The direct air capture model is also from **Chapter 5**. Inputs were adapted to a production rate of 238 kg CO_2/day.

Infrastructure and transport

All processes were within one site; thus, there were no major transport requirements besides CO_2. The transportation of CO_2 is assumed to be through pipelines, with this being outside of the study boundaries. For the direct air capture unit, there is an assumption that the facilities are on the same industrial site as the utilisation plant. Since urea generates next to the point of use, there was also no need for extra transportation. The total urea production for an operational lifetime of 20 years is 1,825,000 kg, equivalent to 250 kg/day. Following the method stated in **Section 4.4.1**, this was equal to 5.47×10^{-7} chemical plant units per kg of product.

6.2.1 General inventory

In this stage, all the information obtained for urea production is collected under one inventory. **Table 6.8** shows the intervention matrix for the basic commodities needed to produce urea. Following the method by Heijungs *et al.* (2013) withdrawals from other systems show as negative values. Positive values represent outputs from the system. As an example, in column one; 960 kg of water and 2160 kW are needed to produce 33 kg of hydrogen. This table also shows the dependency of one commodity on another, thus serving as a tool to avoid counting double interventions. Scaling to the functional unit of 1 kg of final product, the main commodity inputs are 0.570 kg NH_3, 1.47 kWh electricity, 2.95 kg H_2O and 0.73 kg of CO_2.

Table 6.8 Commodities matrix table for urea production (325 kg/day)

Inputs	**Commodities**													
	Hydrogen (kg)		Nitrogen (kg)		Water (kg)		CO_2 (kg)		Electricity (MJ)		Ammonia (kg)		Urea (kg)	
	Consumed	Generated	Consumed	Generated	Consumed	Generated	Consumed	Generated	Consumed	Generated	Consumed	Generated	Consumed	Generated
Ammonia (pieces)	0	0	0	0	0	0	0	0	0	0	0	185	185	0
Urea unit (pieces)	0	0	0	0	0	0	0	0	0	0	0	0	0	1
Energy (MW)	8	0	0	0	0	0	0	0	0	0	9×10^{-1}	0	0	5×10^{-1}
Hydrogen (kg)	0	33	0	0	0	0	0	0	0	0	33	0	0	0
Nitrogen (kg)	0	0	0	153	0	0	0	0	0	0	0	153	0	0
Water (kg)	0	960	0	0	0	960	0	0	0	0	0	0	0	960
Carbon dioxide (kg)	0	0	0	0	0	0	0	232	0	0	0	0	238	0

The main comparison of scenarios was between a conventional urea process and the CO_2 utilisation case scenario. However, for sensitivity tests, other process alternatives were also run in the life cycle impact assessment (LCIA). The process alternatives to compare each commodity were split into three main areas: hydrogen production, ammonia synthesis and urea synthesis.

Hydrogen production alternatives

There was a comparison between two hydrogen production routes and the CO_2 utilisation case study. The first was brine electrolysis with four alternative configurations and the second was steam reforming of natural gas.

Two different data sets were used for both production routes to improve the data quality index. The ecoinvent version 3.3 database and the Eco-profile from PlasticsEurope was used for three-chlorine electrolysis process. The GaBi ts database version 8.7.0.18 and the Eco-profile from PlasticsEurope for was used for the steam-reforming process that uses either natural gas or heavy fuel oil to produce H_2. The summary of inputs for all hydrogen production options is shown in **Table 6.9**. The scale is set to 0.102 kg of H_2 per 1 kg of urea produced.

Ammonia production alternatives

Three methods of ammonia synthesis are analysed in this work. These are:

- NH_3 from Haber-Bosch using hydrogen produced by water electrolysis (study case)
- NH_3 from Haber-Bosch using hydrogen from steam methane reforming (SMR)
- Ammonia from partial oxidation of heavy fuel oil

The comparison of production routes was undertaken using ecoinvent version 3.3 and PlasticsEurope. The scale was set at 0.570 kg of NH_3 per 1 kg of urea produced. **Table 6.10** summarises the inputs for ammonia scenarios.

Carbon dioxide process alternatives

Three scenarios for carbon dioxide supply for urea generation are included. A conventional steam reforming process, a hypothetical direct air capture system and a post-combustion capture plant. In a steam reforming process, 733 kg of CO_2 are required to produce 1 tonne of urea. Ammonia synthesis produces carbon dioxide; this process-derived carbon dioxide is then available for utilisation in urea synthesis. Thus, the emissions associated were allocated to ammonia production in this scenario. For direct air capture and post-combustion capture, the processes used in **Chapter 5** were also considered for this section. The ecoinvent version 3.3 database was used for the steam methane reforming (SMR) process. **Table 6.13** shows all major inputs for each variable.

Urea production: process variables

Urea is synthesised through a carbon dioxide utilisation route or through a conventional process. The first process is the proposed ammonia production method. The second process is the conventional urea production process using ecoinvent version 3.3 database for the inventory. Refer to **Table 6.14** for the inventory of both options.

Electricity supply variables

Two main electricity inventories were used to represent the effect of different supply mixes for hydrogen production. Information obtained from the GaBi ts version 8.7.0.18 database version 8.7.0.18 was adapted to the UK conditions when possible. The variables included an electricity standard grid mix and electricity from wind power. The scale was set at 1 kg of hydrogen produced from the ITM Power Limited electrolyser.

The assessment focuses on two processes: a CO_2 utilisation option and conventional route for urea production. **Table 6.9** to **Table 6.12** show the final inventory for each alternative.

Table 6.9 1) ITM Power Limited electrolyser, 2), 3) and 4) Diaphragm, membrane and mercury cell, chlor-alkali electrolysis by ecoinvent 3.3, 5) Chlor-alkali electrolysis by PlasticsEurope, 6) Steam methane reforming (SMR) by PlasticsEurope

Inputs	**Process alternatives (scaled to 0.1 kg of H_2)**					
	H_2 (kg)^1	H_2 (kg)^2	H_2 (kg)^3	H_2 (kg)^4	H_2 (kg)^5	H_2 (kg)^6
Energy (MJ)	-24	13	11	13	0.01	-0.5
Water (kg)	3	293	102	102	6 x 10^{-3}	0.5
Sodium chloride, powder (kg)	0	2	2	2	0	0
Soda ash, powder (kg)	0	1 x 10^{-2}	1 x 10^{-2}	1 x 10^{-2}	0	0
Barite (kg)	0	4 x 10^{-3}	4 x 10^{-3}	4 x 10^{-3}	0	0
Calcium chloride (kg)	0	2 x 10^{-2}	2 x 10^{-2}	2 x 10^{-2}	0	0
Hydrochloric acid, 30% in water (kg)	0	2 x 10^{-2}	2 x 10^{-2}	2 x 10^{-2}	0	0
Sulphite (kg)	0	1 x 10^{-4}	1 x 10^{-4}	1 x 10^{-4}	0	0
Sodium hydroxide, 50% solution state (kg)	0	2 x 10^{-3}	4 x 10^{-2}	6 x 10^{-3}	0	0
Asbestos, crysotile type, (kg)	0	2 x 10^{-4}	0	0	0	0
chemical plant, organics (unit)	0	4 x 10^{-10}	4 x 10^{-10}	4 x 10^{-10}	0	0
Sludge, NaCl electrolysis (kg)	0	1 x 10^{-2}	1 x 10^{-2}	1 x 10^{-2}	1 x 10^{-3}	0
Spent activated carbon with mercury [waste] (kg)	0	0	0	3 x 10^{-4}	0	0
disposal, hazardous waste, 0% water, to underground deposit (kg)	0	1 x 10^{-4}	0	0	5 x 10^{-5}	0
Mercury, liquid (kg)	0	0	0	7 x 10^{-6}	0	0
Sulfuric acid (kg)	0	9 x 10^{-3}	9 x 10^{-3}	9 x 10^{-3}	0	0

Table 6.10 inputs for ammonia production. 1) Process under study 2) Ammonia with hydrogen from steam methane reforming (SMR) 3) Ammonia from partial oxidation of heavy fuel oil

Inputs	**Process alternatives (scaled to 0.6 kg of NH_3)**		
	NH_3^1	NH_3^2	NH_3^3
Energy (MJ)	18.0	0.1	0.4
Hydrogen (kg)	0.1	0.0	0.0
Nitrogen (kg)	0.5	0.0	0.0
Nickel, 99.5 % (kg)	0.0	2.0 x 10^{-4}	0.0
Solvents, organic, unspecified (kg)	0.0	1.7 x 10^{-5}	1.7 x 10^{-5}
Heavy fuel oil (2.5% wt) (kg)	0.0	0.1	0.5
Natural gas, high pressure (m^3)	0.0	0.3	0.0
Water (kg)	0.0	80.3	80.3
Chemical plants, organics (unit)	0.0	2.3 x 10^{-10}	2.3 x 10^{-10}
Municipal solid waste (kg)	0.0	1.0 x 10^{-4}	1.0 x 10^{-4}

Table 6.11 Inputs for CO_2 supply. 1) CO_2 from ammonia production/conventional urea process 2) Theoretical direct air capture (DAC) 3) Carbon capture from post-combustion capture unit

Inputs	**Process alternatives (scaled to 0.7 kg of CO_2)**		
	CO_2^1	CO_2^2	CO_2^3
Electricity (MJ)	0.0	2.0	0.1
Ammonia (kg)	0.5	0.0	1.0 x 10^{-3}
Activated carbon (kg)	0.0	0.0	2.3 x 10^{-4}
Calcium carbonate (kg)	0.0	0.0	4.0 x 10^{-2}
Monoethanolamine MEA (kg)	0.0	0.0	1.0 x 10^{-3}
Water (kg)	0.0	0.0	2.9
Triethylene glycol (kg)	0.0	0.0	2.9 x 10^{-2}
Hydrated lime (kg)	0.0	0.0	7.3 x 10^{-3}
Process water discharge (kg)	0.0	0.0	0.7
Waste in reclaimer (kg)	0.0	0.0	8.6 x 10^{-4}

Table 6.12 Inputs for urea production. 1) Urea from process under study 2) Urea from conventional method/ammonia

Inputs	Process alternatives (scaled to 1 kg/day of urea production)	
	CH_3N_2O[1]	CH_3N_2O[2]
Electricity (MJ)	5.3	1.1
Water (kg)	10.6	285.5
Carbon dioxide (kg)	0.7	0.0
Ammonia (kg)	0.6	1.2
Thermal energy, natural gas (MJ)	0.0	8.0
Isopropanol (kg)	1.0×10^{-2}	0.0
Chemical plants, organics (unit)	0.0	8.70×10^{-10}

The commercial database flows used for the inventories in this chapter are summarised in **Table 6.13**.

Table 6.13 Flows from commercial database used for the urea case study inventory

Inventory database		
CO_2 capture: alternative inventories		
Country	**Name of input**	**Database**
EU-27	Process water	thinkstep 8.7.0.18
EU-27	Triethylene glycol	PlasticsEurope
EU-27	Municipal waste treatment (mix)	thinkstep 8.7.0.18
EU-27	Municipal solid waste on landfill	thinkstep 8.7.0.18
Germany	Calcium hydroxide (dry, slaked lime)	thinkstep 8.7.0.18
Germany	Activated carbon	thinkstep 8.7.0.18
Germany	Limestone flour ($CaCO_3$)	thinkstep 8.7.0.18
Great Britain	Electricity from hard coal	thinkstep 8.7.0.18
Great Britain	Ammonia (NH_3)	thinkstep 8.7.0.18
Great Britain	Process steam from natural gas 85%	thinkstep 8.7.0.18
Great Britain	Electricity grid mix	thinkstep 8.7.0.18
Great Britain	Ethylene oxide (EO) via air	thinkstep 8.7.0.18
Utilisation systems including hydrogen production: alternative inventories		
Country	**Name of input**	**Database**
EU-27	Process water	thinkstep 8.7.0.18
Europe	Chemical factory construction, organics	ecoinvent 3.3
Europe	Market for natural gas, high pressure	ecoinvent 3.3
Europe	Sulfite production	ecoinvent 3.3
Europe	Carbon tetrachloride production	ecoinvent 3.3
Europe	Market for waste graphical paper	ecoinvent 3.3

Country	Name of input	Database
Europe without Switzerland	Market for waste graphical paper	ecoinvent 3.3
Global	Market for barite	ecoinvent 3.3
Global	Market for calcium chloride	ecoinvent 3.3
Global	Market for carbon tetrachloride	ecoinvent 3.3
Global	Market for sludge, NaCl electrolysis	ecoinvent 3.3
Global	Soda ash, light, crystaline, heptahydrate to generic market for neutralising agent	ecoinvent 3.3
Global	Market for sodium chloride, powder	ecoinvent 3.3
Global	Market for sulfuric acid	ecoinvent 3.3
Global	Market for hazardous waste, for underground deposit	ecoinvent 3.3
Global	Market for asbestos, crysolite type	ecoinvent 3.3
Global	Market for mercury	ecoinvent 3.3
Global	Market for spent activated carbon with mercury	ecoinvent 3.3
Global	Natural gas, production onshore	ecoinvent 3.3
Global	Market for sodium hydroxide, without water, in 50% solution state	ecoinvent 3.3
Great Britain	Market for electricity, medium voltage	ecoinvent 3.3
Great Britain	Market for hydrochloric acid, without water, in 30% solution state	ecoinvent 3.3
Global	Nickel, 99.5 %, at plant	ecoinvent 3.3
Global	Market, for solvent, organic	ecoinvent 3.3
Europe	Market group for heavy fuel oil	ecoinvent 3.3
Great Britain	Treatment of municipal solid waste, incineration	ecoinvent 3.3
Europe	Market for urea, as N	ecoinvent 3.3
Europe	Market group for heat, district or industrial, natural gas	ecoinvent 3.3
Great Britain	Electricity from hard coal	thinkstep 8.7.0.18
Great Britain	Electricity grid mix	thinkstep 8.7.0.18
Great Britain	Electricity from wind power	thinkstep 8.7.0.18
Great Britain	Isopropanol	thinkstep 8.7.0.18
Global	Compressed air 7 bar (low power consumption)	thinkstep 8.7.0.18
EU-27	Tap water	thinkstep 8.7.0.18

Data quality matrix

The inventories are assessed according to the quality matrix also used in **Section 5.2.1**. Any set of information that did not have a minimum score of three was not considered for this study. As seen in **Table 6.14**, geographical correlation trended towards lower scores. Life cycle assessment (LCA) databases are not always up to date; the processes that are not as well understood or established are more likely to change resulting in inaccuracies in the database. In this study, ammonia is a process that has not changed much throughout the years, thus an older inventory is acceptably accurate. Updated values were added where possible (such as updating to reflect the current electricity grid mix) to bring the life cycle inventory (LCI) up to date.

Table 6.14 Quality indicators for the inventory of the case study: urea synthesis, 1 kg produced

Process	**Scores for each quality indicator (scale 1 to 5)**				
	Source reliability	Database within date	Geographical correlation	Technical similarities	Overall score
Case study: ammonia synthesis	1	1	1	1	1
Case study: urea synthesis	1	1	1	1	1
Case study: hydrogen production	1	1	1	1	1
Ammonia: SMR[1] (ecoinvent 3.3)	2	1	3	1	3
Ammonia: PO[2] (ecoinvent 3.3)	2	1	3	1	3
H_2: Electrolyser, membrane cell (ecoinvent 3.3)	2	1	3	3	3
H_2: Electrolyser, mercury cell (ecoinvent 3.3)	2	1	3	3	3
H_2: Electrolyser, diaphragm (ecoinvent 3.3)	2	1	3	3	3
H_2: Electrolyser, average technology (PlasticsEurope)	2	1	3	3	3
Urea: Hydrogen SMR[1] (ecoinvent 3.3)	2	1	3	1	3

[1] Steam methane reforming [2] Partial oxidation

6.3 Impact assessment

The design of the CO_2 utilisation process concludes with the life cycle inventory (LCI) required to complete the environmental assessment. The following section now focuses on analysing the data from said inventory. This assessment includes carbon accounting for CO_2 utilisation, fossil fuel depletion, other environmental impacts and allocation sensitivity analysis. Refer to **Section 4.4** for more information on the methods used.

6.3.1 Carbon accounting for carbon dioxide utilisation processes

This case study assessed five main scenarios; **Section 6.2.1** previously discussed the alternatives for each case. A general carbon balance for each scenario to account for direct and indirect carbon emissions of each process using system expansion to allocate was created (refer to **Section 4.4.4** for more information on the method). **Figure 6.8** to **Figure 6.11** show the carbon balance results for each case study.

To account for the capture stage emissions, the results from **Section 5.3.1** were used in Scenarios 1, 2, 4 and 5. These results are summarised in **Table 6.15**, where kg of carbon dioxide emitted per tonne of CO_2 captured for three power plant alternatives was calculated. While direct emissions from capture are the same for all plants (90% capture rate for CO_2), the electricity generated varies from plant to plant. The subcritical plant has the lowest efficiency with 1,100 kWh generated for the grid with 1,000 kg of urea produced. The same CO_2 capture rate for a natural gas combined cycle (NGCC) power plant lead to higher efficiencies, electricity generation doubles from a subcritical PC (pulverised coal), with the same kg of CO_2 emissions. For this study, subcritical pulverised coal (550 MWe) was used as the baseline scenario. Thus, results include a worst post-combustion capture scenario, with the knowledge that extra electricity can be generated with other types of power plants. Values were calculated to produce 1 tonne of CO_2 and scaled down to the 0.73 kg CO_2 required for 1 kg of urea produced.

Table 6.15 Direct carbon emissions for the capture of 1 tonne of CO_2 compared to carbon emissions in a power plant without CO_2 capture

Plant process	**Power output and CO_2 emissions**		
	Electricity generated (kWh)	With capture (kg CO_2)	Without capture (kg CO_2)
Subcritical PC[1]	1,100	111	887
Supercritical PC[1]	1,145	111	839
NGCC[2]	2,777	111	988

[1] Pulverised coal [2] Natural gas combined cycle

Figure 6.7 shows the carbon balance for direct and indirect carbon emissions comparing the power plant with and without a capture stage for 1 tonne of CO_2. The additional power required for a post-combustion capture plant is added to the electricity for final consumption, thus ensuring equal functional units in all cases.

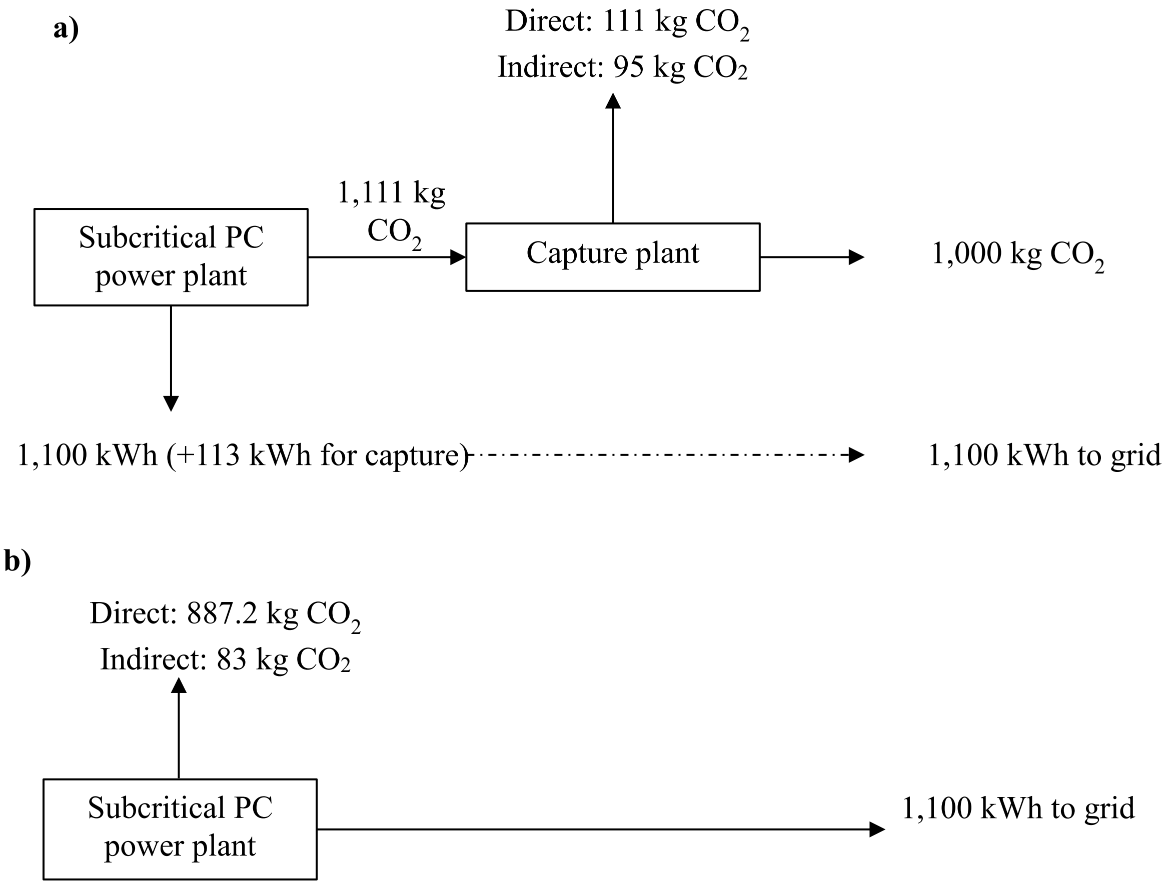


Figure 6.7 Direct and Indirect CO_2 emission balance for a) subcritical PC (pulverised coal) power plant with capture b) subcritical PC (pulverised coal) plant without capture (baseline scenarios)

Scaling down to 0.73 kg of CO_2 and using the baseline scenario of a subcritical PC (pulverised coal) plant: 0.081 kg of direct CO_2 are emitted per 0.73 kg captured CO_2; compared to 0.64 kg direct CO_2 emitted from a plant without capture (0.803 kWh output for both + 0.09 kWh extra for capture). With this carbon balance for capture, the urea scenarios were analysed as follows:

Scenario 1: Case study for 1 kg of urea-grid mix

Where H_2 is produced from water electrolysis (provided by ITM Power Limited) and connected to the UK electricity grid (**Table 6.9 column 1**). CO_2 is captured from a fixed-point source; no transportation is required for the final product and there are no direct emissions from urea production. The comparison for system expansion is power generation, plus urea production through steam methane reforming (SMR). **Figure 6.8** shows the results for the carbon balance.

Scenario 2: Case study for 1 kg of urea-wind power

The conditions are identical to Scenario 1, except for hydrogen production. Where H_2 is produced from water electrolysis (provided by ITM Power Limited), but the electricity required is now provided by wind power. See **Figure 6.9** for carbon balance results.

Scenario 3: Baseline scenario for 1 kg of urea-ammonia

Urea production from ammonia, generated with H_2 from steam methane reforming (SMR) (**Table 6.9 column 2**). No transport of intermediate products or final product is included. CO_2 is a by-product of ammonia production used for urea synthesis. (0.73 kg CO_2 from direct ammonia emissions required to feed into urea production, per 1 kg of final product). Electricity generation from a subcritical PC (pulverised coal) power plant is included in the system expansion model. The carbon balance of this baseline scenario compares emissions between utilisation and conventional processes. **Figure 6.8b** uses this model for carbon accounting.

Scenario 4: Case study for 1 kg of urea-grid mix, CO_2 from direct air capture (DAC)

This scenario covers an example where CO_2 is supplied from a hypothetical direct air capture (DAC) process (**Table 6.11 column 2**). Hydrogen is produced from water electrolysis (provided by ITM Power Limited) and is connected to the UK grid for electricity provision. No transportation is required and there are no direct emissions from urea production. Scenario 3 is used a comparative process. See **Figure 6.10** for the carbon balance.

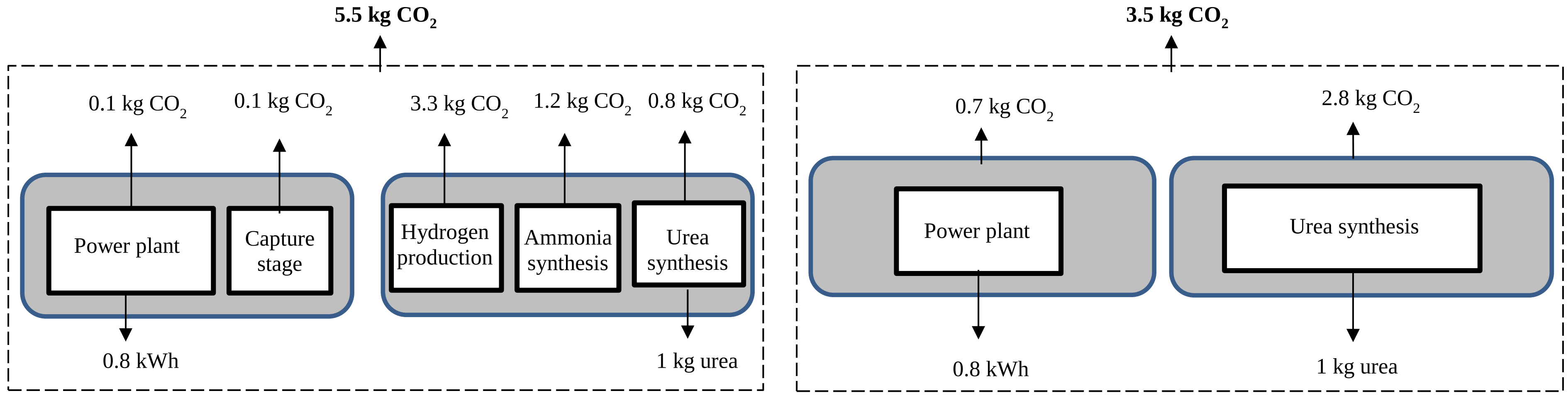
Scenario 5: Case study for 1 kg of urea-wind power, CO_2 from direct air capture (DAC)

The conditions are identical to those described in scenario 4, except for hydrogen production. In this scenario, hydrogen is produced from water electrolysis (provided by ITM Power Limited) connected to an electricity supply powered by wind turbines, instead of the grid. Refer to **Figure 6.11** for the carbon balance.

The requirements described in **Section 4.4.2** to calculate the net life cycle CO_2 emissions for all utilisation scenarios are used in this case study. **Table 6.16** shows the results for all available inputs and outputs. As a sensitivity test, a second calculation was run with only energy inputs, disregarding other flows. In this second run, total energy related CO_2 emissions and direct emissions were added from hydrogen, nitrogen and ammonia production. As seen in **Table 6.17**, the difference is minimal and does not represent any major overall changes. The maximum swing in total carbon avoided is seen in Scenario 2. Total carbon avoided is calculated by subtracting kg of CO_2 emitted by a utilisation process from the kg of CO_2 emitted by the non-utilisation option (as discussed in **Section 4.6.5**).

Figure 6.12 shows net life cycle kg of CO_2 emitted for each scenario, where results are broken down by main production phases. Results show that to avoid carbon emissions, renewable energy for hydrogen production is necessary. There is the potential to avoid up to 37% of CO_2 emissions with the utilisation route (Scenario 2), compared to urea with hydrogen from steam methane reforming (SMR). This relies on producing ammonia from a decarbonised source. If the current UK electricity grid mix were to be used to produce hydrogen with the suggested technology in this study (Scenario 1), overall CO_2 emissions would rise by 57% while 61% of net kg CO_2 emissions are generated from hydrogen production, making it the most carbon intensive process. These extra burdens are associated with scope 2 emissions from purchased electricity for water electrolysis.

Results also show that life cycle carbon emissions do not change significantly between scenarios with different CO_2 sources. Case studies with direct air capture have no direct emissions, but high indirect emissions. Indirect emissions are attributed to high energy penalties associated with direct air capture processes. Eliminating 0.3 kg of indirect energy emissions per 1 kg of urea could create a zero-emission scenario for CO_2 capture. Otherwise, there is no net carbon avoided benefit from using direct air capture over post-combustion capture in this case study. Finally, there is the potential to avoid 1.3 kg of CO_2 emissions with the proposed process compared to urea synthesis with hydrogen from steam methane reforming (SMR).



a) **b)**

Figure 6.8 a) total life cycle CO_2 emissions for scenario 1, compared to b) total life cycle CO_2 emissions for scenario 3, system expansion

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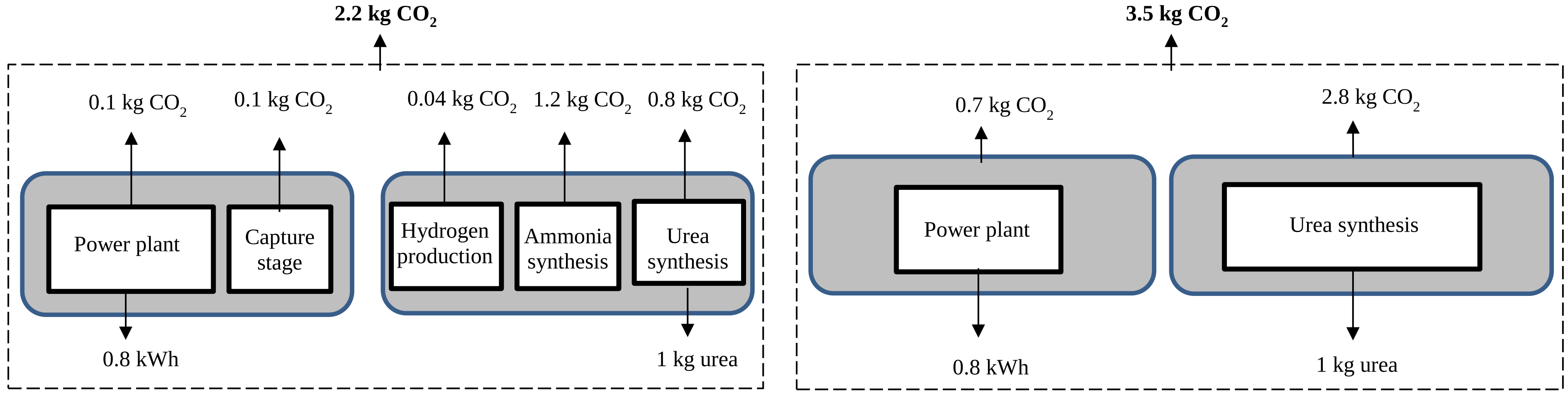


c) **d)**

Figure 6.9 c) total life cycle CO_2 emissions for scenario 2, compared to d) total life cycle CO_2 emissions for scenario 3, system expansion

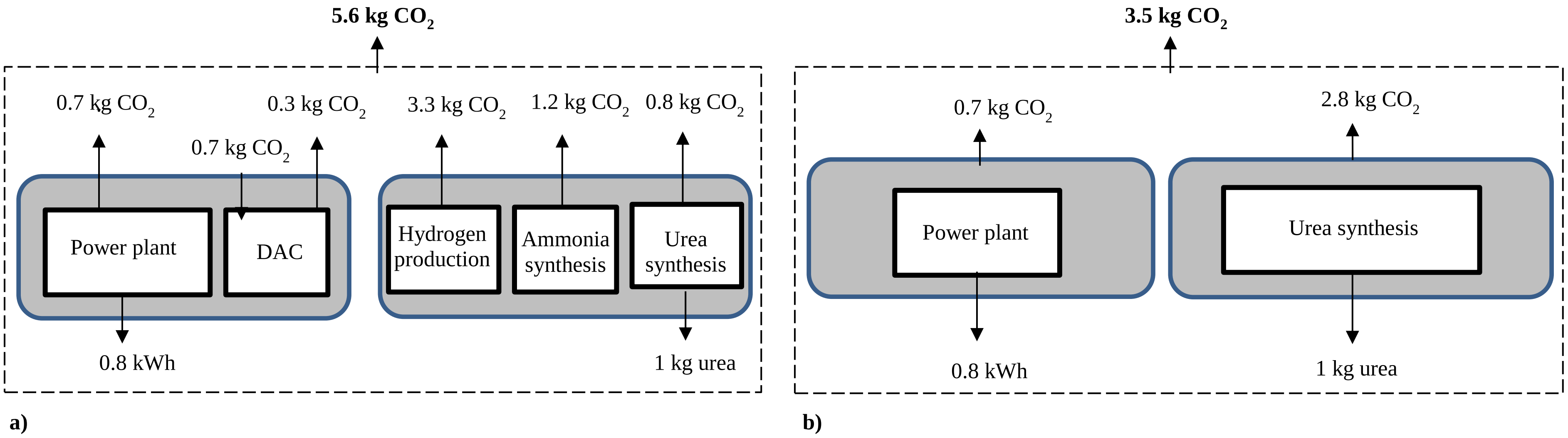


Figure 6.10 a) total life cycle CO_2 emissions for scenario 4, compared to b) total life cycle CO_2 emissions for scenario 3, system expansion

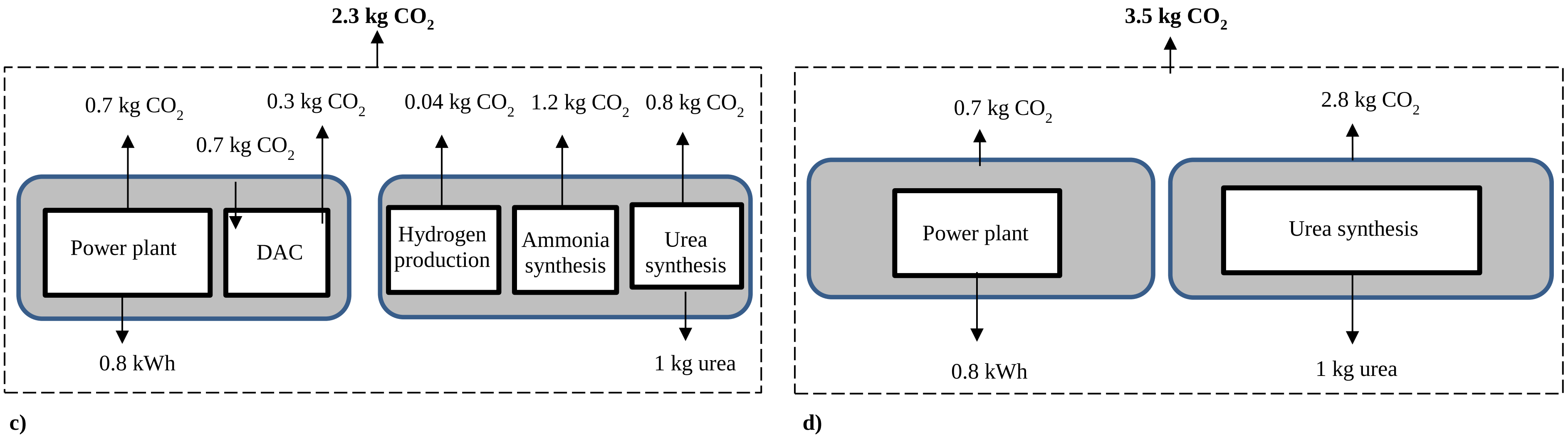


Figure 6.11 c) total life cycle CO_2 emissions for scenario 5, compared to d) total life cycle CO_2 emissions for scenario 3, system expansion

Table 6.16 Sum of net life cycle CO_2 emissions for all case studies, per 1 kg of urea produced, following the method stated in Section 4.4.2

Process	**kg of CO_2 emitted per process**						
	Total sum	Power supply	Water supply	Material	Source	Transportation	Waste
1) Urea synthesis, electricity from grid mix	**5.5**	5.3	5.5×10^{-4}	1.7×10^{-2}	0.1	0.0	0.0
2) Urea synthesis, electricity from wind power	**2.2**	2.0	5.5×10^{-4}	1.7×10^{-2}	0.1	0.0	0.0
3) Urea synthesis from ammonia from steam methane reforming	**2.8**	0.8	0.0	1.9	0.0	0.0	1.1×10^{-4}
4) Urea synthesis, electricity from grid mix, CO_2 from DAC[1]	**5.6**	5.3	5.5×10^{-4}	1.7×10^{-2}	0.3	0.0	0.0
5) Urea synthesis, electricity from wind power, CO_2 from DAC[1]	**2.3**	2.0	5.5×10^{-4}	1.7×10^{-2}	0.3	0.0	0.0

[1] Direct air capture

Table 6.17 Sum of net life cycle CO_2 emissions for all case studies per 1 kg of urea produced, sensitivity analysis with only power emissions considered, following the method stated in Section 4.4.2

Process	**kg of CO_2 emitted (from power emissions)**						
	Total sum	Power supply	Water supply	Material	Source	Transportation	Waste
1) Urea synthesis, electricity from grid mix	**5.4**	5.3	5.0 x 10^{-4}	2.0 x 10^{-2}	5.0 x 10^{-2}	0.0	0.0
2) Urea synthesis, electricity from wind power	**2.1**	2.0	5.0 x 10^{-4}	2.0 x 10^{-2}	5.0 x 10^{-2}	0.0	0.0
3) Urea synthesis from ammonia from steam methane reforming	**2.8**	0.8	0.0	2.0	0.0	0.0	1.0 x 10^{-4}
4) Urea synthesis, electricity from grid mix, CO_2 from DAC[1]	**5.6**	5.3	5.0 x 10^{-4}	2.0 x 10^{-2}	0.3	0.0	0.0
5) Urea synthesis, electricity from wind power, CO_2 from DAC[1]	**2.3**	2.0	5.0 x 10^{-4}	2.0 x 10^{-2}	0.3	0.0	0.0

[1] Direct air capture

Table 6.18 Net avoided CO_2 per 1 kg of urea produced

Scenarios	**Avoided and emitted CO_2 emissions (kg)**			
	kg net CO_2 avoided	kg net CO_2 generated cdu	kg CO_2 emitted non-cdu	kg CO_2 emitted cdu
1	**0.0**	1.9	3.5	5.0
2	**1.3**	0.0	3.5	2.0
3	**0.0**	0.0	3.5	N/A
4	**0.0**	2.1	3.5	6.0
5	**0.0**	1.2	3.5	2.0

Table 6.19 Net avoided CO_2 with sensitivity analysis, only energy emissions considered per 1 kg of urea produced

Scenarios	**Avoided and emitted CO_2 emissions (kg)**			
	kg net CO_2 avoided	kg net CO_2 generated cdu	kg CO_2 emitted non-cdu	kg CO_2 emitted cdu
1	**0.0**	1.9	3.5	5.0
2	**1.4**	0.0	3.5	2.0
3	**0.0**	0.0	3.5	N/A
4	**0.0**	2.1	3.5	6.0
5	**1.2**	0.0	3.5	2.0

A normalised distribution curve was created for all CO_2 utilisation scenarios that use system expansion as the allocation method. 2,000 random iterations were run with a standard deviation from the mean of ± 100 %. The standard deviation of each process output was then used to calculate the standard error of the mean to obtain confidence levels of 95 %. The method has been described in **Section 5.3.1**.

Results (**Table 6.20**) show that outputs of Scenario 2 can all be varied for up to the 2nd standard deviation (95 % chance that it falls within that range) and the outcome is still the same. It is only in the 3rd standard deviation (99 % chance that it falls within that range) that the CO_2 emissions from H_2 production and urea synthesis contribute to higher total CO_2 emissions than the conventional process. For Scenario 4, the CO_2 emissions are lower than the conventional process until the 2nd deviation standard. This reflects a reasonable certainty that the CO_2 utilisation processes that use renewable energy have lower net CO_2 emissions than conventional processes.

Table 6.21 shows the results for the calculation of the standard error from the mean. The upper confidence interval from the CO_2 utilisation processes and the lower confidence interval from the conventional process are compared in **Table 6.22**. There is no "overlap" in the results, CO_2 utilisation processes connected to the electricity grid mix have higher emissions than the conventional process and CO_2 utilisation processes connected to wind power have lower emissions than the conventional process as expected.

Table 6.20 Showing standard deviations for urea scenarios applying system expansion

Scenario	**Input**	**kg CO_2 emitted**						
		Mean	**Standard deviation**	**68% min**	**68% max**	**95% min**	**95% max**	**99.7% max**
1	Power plant with CO_2 capture	0.1	0.1	0.1	0.2	0.0	0.3	0.4
	NH_3 synthesis	1.2	0.7	0.5	1.9	0.0	2.6	3.3
	H_2 generation	3.2	1.9	1.3	5.0	0.0	6.9	8.8
	Urea synthesis, CO_2 utilisation	0.9	0.5	0.4	1.4	0.0	1.9	2.4
	Power plant without CO_2 capture	0.7	0.4	0.3	1.1	0.0	1.5	1.9
	Urea synthesis, conventional	2.8	1.6	1.2	4.4	0.0	4.8	7.7
2	Power plant with CO_2 capture	0.1	0.1	0.1	0.2	0.0	0.3	0.4
	NH_3 synthesis	1.2	0.7	0.5	1.9	0.0	2.6	3.4
	H_2 generation	3.9×10^{-2}	2.3×10^{-2}	1.6×10^{-2}	6.2×10^{-2}	0.0	8.5×10^{-2}	0.1
	Urea synthesis, CO_2 utilisation	0.9	0.5	0.4	1.5	0.0	2.0	2.6
	Power plant without CO_2 capture	0.7	0.4	0.3	1.1	0.0	1.5	1.9
	Urea synthesis, conventional	2.8	1.6	1.2	4.5	0.0	4.7	7.7
4	Power plant with CO_2 capture	0.3	0.2	0.1	0.4	0.0	0.6	0.7
	NH_3 synthesis	1.2	0.7	0.5	1.9	0.0	2.6	3.3
	H_2 generation	3.2	1.9	1.3	5.0	0.0	6.9	8.8
	Urea synthesis, CO_2 utilisation	0.9	0.5	0.4	1.4	0.0	1.9	2.4
	Power plant without CO_2 capture	0.7	0.4	0.3	1.1	0.0	1.5	1.9
	Urea synthesis, conventional	2.8	1.6	1.2	4.5	0.0	4.8	7.7
5	Power plant with CO_2 capture	0.3	0.2	0.1	0.4	0.0	0.6	0.7
	NH_3 synthesis	1.2	0.7	0.5	1.9	0.0	2.6	3.3
	H_2 generation	3.9×10^{-2}	2.3×10^{-2}	1.6×10^{-2}	1.6×10^{-2}	0.000	8.5×10^{-2}	0.1
	Urea synthesis, CO_2 utilisation	0.9	0.5	0.4	1.5	0.0	2.0	2.6
	Power plant without CO_2 capture	0.7	0.4	0.3	1.1	0.0	1.5	1.9
	Urea synthesis, conventional	2.8	1.6	1.2	4.5	0.0	4.7	7.7

Table 6.21 Showing standard error from the mean for urea scenarios applying system expansion

Scenario	Input	kg CO_2 emitted			
		Standard error	95% confidence interval	Upper limit	Lower limit
1	Power plant with CO_2 capture	2.0×10^{-3}	3.0×10^{-3}	0.1	0.1
	NH_3 synthesis	1.6×10^{-2}	3.1×10^{-2}	1.2	1.2
	H_2 generation	4.2×10^{-2}	8.2×10^{-2}	3.3	3.1
	Urea synthesis, CO_2 utilisation	1.1×10^{-2}	2.2×10^{-2}	0.9	0.9
	Power plant without CO_2 capture	9.0×10^{-3}	1.8×10^{-2}	0.7	0.7
	Urea synthesis, conventional	6.3×10^{-2}	0.123	2.9	2.7
2	Power plant with CO_2 capture	2.0×10^{-3}	3.0×10^{-3}	0.1	0.1
	NH_3 synthesis	1.6×10^{-2}	3.0×10^{-2}	1.2	1.1
	H_2 generation	1.0×10^{-3}	1.0×10^{-3}	3.9×10^{-2}	3.8×10^{-2}
	Urea synthesis, CO_2 utilisation	1.2×10^{-2}	2.4×10^{-2}	0.9	0.9
	Power plant without CO_2 capture	9.0×10^{-3}	1.8×10^{-2}	0.7	0.7
	Urea synthesis, conventional	6.3×10^{-2}	0.1	2.9	2.7
4	Power plant with CO_2 capture	3.0×10^{-3}	7.0×10^{-3}	0.3	0.3
	NH_3 synthesis	1.6×10^{-2}	3.1×10^{-2}	1.2	1.2
	H_2 generation	4.2×10^{-2}	8.2×10^{-2}	3.3	3.1
	Urea synthesis, CO_2 utilisation	1.1×10^{-2}	2.2×10^{-2}	0.9	0.9
	Power plant without CO_2 capture	9.0×10^{-3}	1.8×10^{-2}	0.7	0.7
	Urea synthesis, conventional	6.3×10^{-2}	0.1	2.9	2.7
5	Power plant with CO_2 capture	3.0×10^{-3}	7.0×10^{-3}	0.3	0.2
	NH_3 synthesis	1.5×10^{-2}	3.0×10^{-2}	1.2	1.2
	H_2 generation	1.0×10^{-3}	1.0×10^{-3}	3.9×10^{-2}	3.8×10^{-2}
	Urea synthesis, CO_2 utilisation	1.2×10^{-2}	2.4×10^{-2}	0.9	0.9
	Power plant without CO_2 capture	9.0×10^{-3}	1.8×10^{-2}	0.7	0.7
	Urea synthesis, conventional	6.3×10^{-2}	0.1	2.9	2.7

Table 6.22 Scenario comparison for upper and lower kg CO_2 emissions for urea scenarios applying system expansion

Process description	Scenario			
	1	2	4	5
Upper value, CO_2 utilisation process (kg CO_2)	5.5	2.3	5.6	2.5
Lower value, Conventional process (kg CO_2)	3.3	3.4	3.4	3.4

The next step in the carbon accounting process was to calculate the overall greenhouse gas emissions that contribute to global warming. For this, the method chosen was CML-IA that uses the characterisation factor of global warming potential over 100 years (GWP_{100}). The same allocation rules also apply to global warming results as with direct

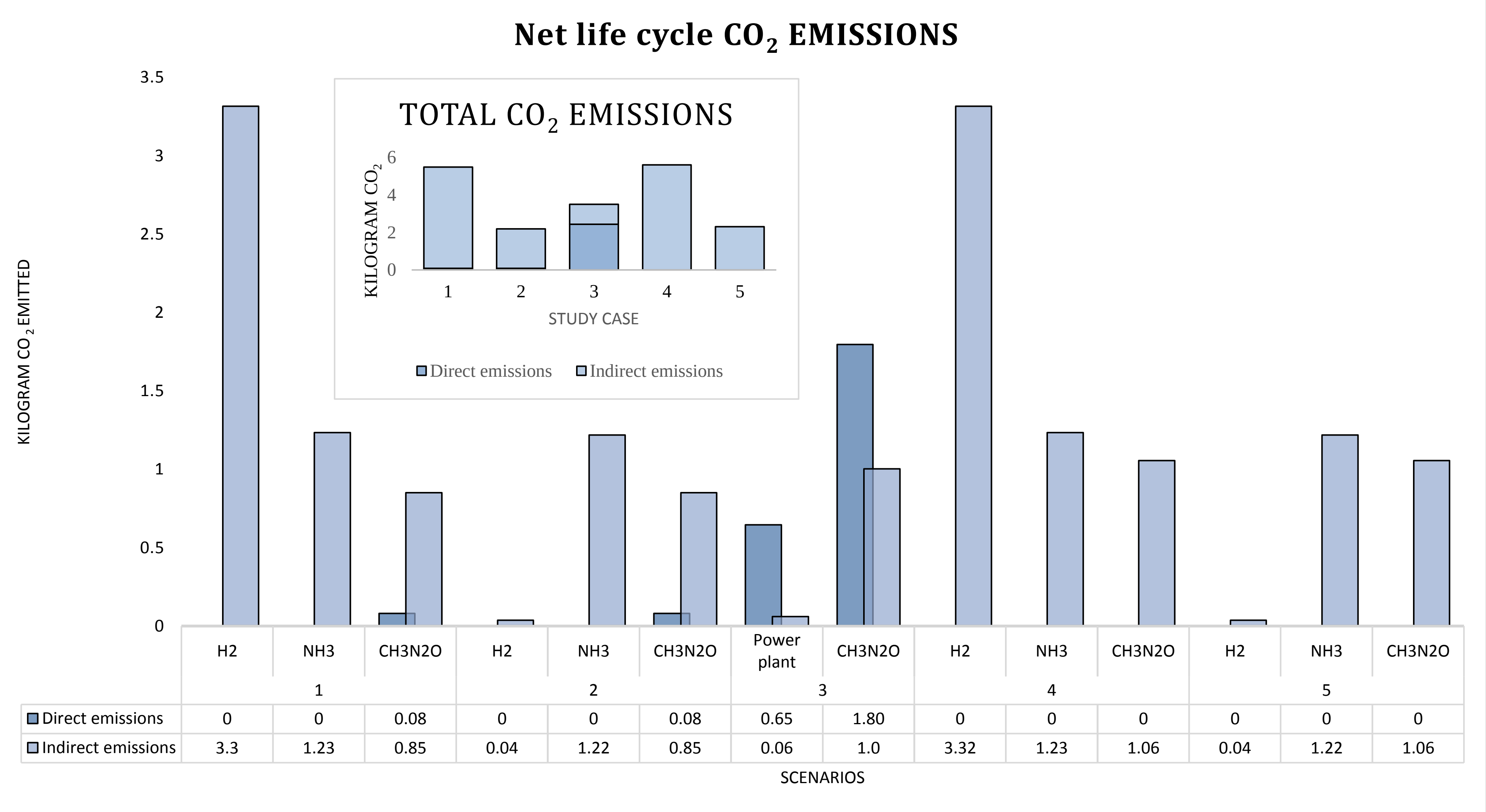
CO_2 emissions. The contribution of the main greenhouse gases to the CO_2 equivalent emitted in the CO_2 utilisation scenarios is summarised below in **Table 6.23**.

Table 6.23 Showing contribution of greenhouse gases to the global warming score for CO_2 based urea

Greenhouse gases	**Contribution to CO_2 eq in scenarios (%)**			
	1	**2**	**4**	**5**
Carbon dioxide (CO_2)	93	91	93	91
Methane (CH_4)	7	8	6	8
Nitrous oxide (N_2O)	1	1	1	1
Sulphur hexaflouride (SF_6)	4×10^{-5}	1×10^{-4}	9×10^{-9}	2×10^{-8}

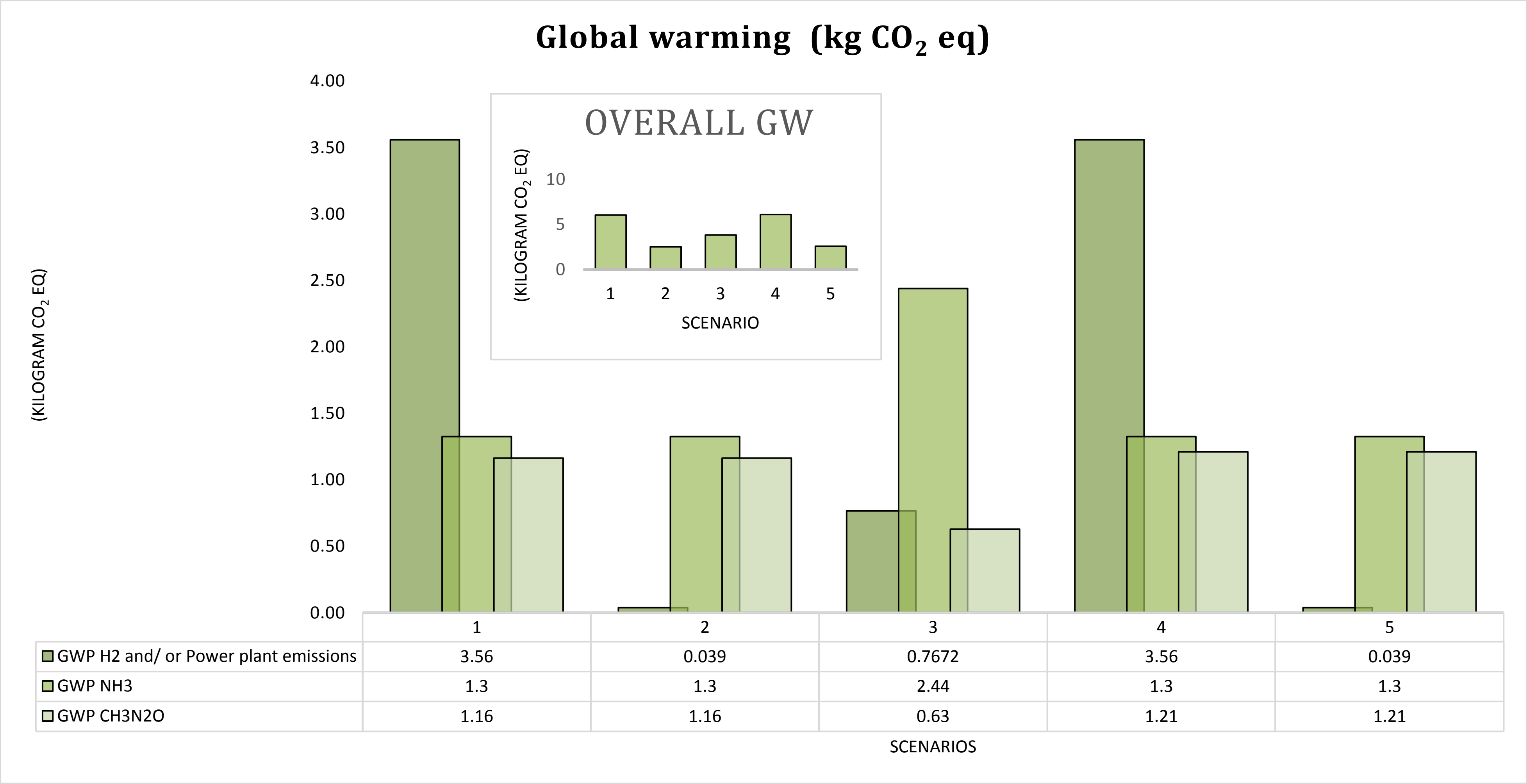
The table shows that methane is the second largest greenhouse gas contributor after carbon dioxide in all cases, with nitrous oxide as the third. Methane, nitrous oxide and sulphur hexafluoride are all emitted the most in the capture stage, with electricity from the grid as the second stressor for emissions (with 40% share from natural gas). The capture stage for Scenarios 1 and 2 also use chemicals such as triethylene glycol and monoethanolamine which are responsible for small amounts of sulphur hexafluoride emissions. Scenarios 2 and 5 have a higher methane percentage contribution than Scenario 1 and 4 (which are connected to the electricity grid mix); however, the total CO_2 equivalent emissions are less than half for scenarios powered by renewable energy.

Greenhouse gases besides CO_2 and water vapour account for 6 to 8 % of the total kg of CO_2 equivalent (eq). **Figure 6.13** shows the global warming scores comparison between all five scenarios with a final product of 1 kg of urea. For the full life cycle impact assessment (LCIA) results refer to **Appendix VI**. The results follow the same trend as the kg of CO_2 emitted for each scenario. The most promising scenarios are connected to decarbonised power sources (2 and 5) and the worst are connected to the electricity grid mix (1 and 4).



	H2	NH3	CH3N2O	H2	NH3	CH3N2O	Power plant	CH3N2O	H2	NH3	CH3N2O	H2	NH3	CH3N2O
		1			2		3			4			5	
▪ Direct emissions	0	0	0.08	0	0	0.08	0.65	1.80	0	0	0	0	0	0
▫ Indirect emissions	3.3	1.23	0.85	0.04	1.22	0.85	0.06	1.0	3.32	1.23	1.06	0.04	1.22	1.06

Figure 6.12 Net life cycle CO_2 emissions generated per functional unit (1 kg of urea ready for use phase). Scenarios 1 to 5 with up to 4 main stages in each: H_2 production, NH_3 production, CH_3N_20 and power plant electricity generation. 1) Case scenario 1 kg of urea-electricity grid mix, 2) Case scenario 1 kg of urea-wind power 3) Baseline scenario urea steam methane reforming (SMR) 4) Cases scenario 1 kg of urea-DAC (direct air capture) and H_2 using electricity grid mix 5) Case scenario 1 kg of urea-DAC (direct air capture) and H_2 from wind power.



	1	2	3	4	5
▨ GWP H2 and/ or Power plant emissions	3.56	0.039	0.7672	3.56	0.039
🟩 GWP NH3	1.3	1.3	2.44	1.3	1.3
☐ GWP CH3N2O	1.16	1.16	0.63	1.21	1.21

Figure 6.13 Global warming (GW) scores per functional unit (1 kg of urea ready for use phase). Scenarios 1 to 5 with up to 4 main stages in each: H_2 production, NH_3 production, CH_3N_20 and power plant electricity generation. 1) Case scenario 1 kg of urea-grid mix, 2) Case scenario 1 kg of urea-wind power 3) Baseline scenario urea steam methane reforming (SMR) 4) 1 kg of urea-DAC (direct air capture) and H_2 using electricity grid mix 5) Case scenario 1 kg of urea-DAC (direct air capture) and H_2 from wind power.

6.3.2 Other environmental impacts

For CO_2 utilisation processes, determining the net CO_2 uptakes and releases is fundamental for its success. However, it is not the only environmental flow to consider. Not analysing other environmental aspects aspect at least at initial screening level can lead to undetected higher impacts. To ensure a broad coverage as possible of the most common impact categories considered in life cycle assessments nine extra impact categories were assessed for this case study. Acidification, stratospheric ozone depletion, photochemical oxidation, freshwater and marine aquatic ecotoxicity potential, abiotic depletion, eutrophication and fossil fuel depletion. The ReCiPe (H) method was used for fossil depletion, while the other categories used CML-IA for characterisation factors.

Results were scaled to functional units of 1 kg of urea produced and 0.8 kWh electricity generated for the grid. Through **Figure 6.14** to **Figure 6.22**, the results for all impacts and scenarios are shown. There are impact categories where one scenario has a much larger impact than the rest, complicating the plotting of the collated results. In this case, a bubble graph (**Figure 6.20** to **Figure 6.22**) shows the overall difference between scenarios. While the range of impact units does not allow for direct comparison, a comparative analysis can simplify interpretation. **Figure 6.23** shows the impact percentage of each scenario for each impact category in this study. Overall, urea production from steam methane reforming to produce H_2 has higher environmental impacts in several categories. Abiotic depletion, stratospheric ozone depletion, marine aquatic, terrestrial and freshwater ecotoxicity have all higher scores for the conventional route than for CO_2 utilisation. However, the impact difference between global warming and fossil fuel depletion is not as clear between conventional process and utilisation.

Fossil fuel depletion

Fossil fuel depletion is another relevant impact category for assessing utilisation scenarios. This impact is highly linked to energy emissions from fossil-based sources. While global warming might not be as elevated for some scenarios, the fossil depletion rates could still be elevated under the same conditions. In this study, results show consistency with carbon emissions. Fossil depletion rates are in line with global warming scores. While utilisation processes come with higher energy penalties, conventional routes often use a wider range of hydrocarbons. The Haber-Bosch process relies on methane. A production of 1.23 kg NH_3 has a fossil depletion rate of 1.25 (kg oil eq). Where 0.8 (kg oil eq) of the fossil fuel depletion impact is from natural gas. Utilisation processes in this study rely on electricity, thus generally have lower fossil depletion values. As it is the case with almost every other impact in this study, only by lowering the impacts of the extra electricity required for CO_2 utilisation, can these processes be environmentally competitive. If no renewable energy source is available, then the conventional urea synthesis will deplete less hydrocarbons in the form of methane than CO_2 utilisation processes with electricity from the grid (**Figure 6.14**).

Acidification

The main known contributors of acidification impacts include SO_2, NOx and reduced nitrogen compounds ($NH_{x)}$ (Heij and Schneider, 1991). In all utilisation scenarios, SO_2 emissions were the highest of those species just listed. For Scenario 3 (conventional process), NH_3 converted to nitric acid was the largest emitter. As with the other impact categories, using a utilisation process with a decarbonised energy source (Scenario 2 and 5) generates the lowest impact. However, these processes still produce an ammonia-based fertilizer, hence there is still potential for related acidification emissions down the supply chain.

Eutrophication

As is the case for acidification, Scenario 3 showed the highest levels of PO_4^{-2} equivalent. This is a result from direct ammonia emissions to air by urea production (ecoinvent version 3.3 value). Nitrogen oxides come in second place in terms of contribution to the total, and its emission is highest in scenarios where electricity from the grid is used. (Scenario 1 and 4). Emissions from ammonia reduced by 99 % in all four utilisation scenarios. The initial assumption is that there are no direct ammonia emissions for Scenarios 1, 2, 4 and 5. However, this assumption should be revised once again when the design phase is completed.

Stratospheric ozone depletion

Although not all the compounds that contribute to stratospheric ozone depletion were traced in GaBi ts version 8.7.0.18, the highest value for this impact category is allocated to Scenario 3: Urea synthesis with hydrogen from steam methane reforming (SMR). Scenario 3 has the highest gas emissions due to its reliance on natural gas and heavy fuel oils. However, when ecoinvent version 3.3 is used, then the halogenated organic emissions lead to a much higher value. This can be explained by the lack of stratospheric ozone depletion potential factors found in GaBi ts version 8.7.0.18 and should only be considered as a rough estimate.

Resource depletion

According to the critical list of elements by the European Comission (2017), the three main scenarios (1, 2 and 3) use the following critical elements in larger quantities:

- Scenario 1: silicon (Si)
- Scenario 2: magnesium and manganese (Mg, Mn)
- Scenario 3 lead (Pb)

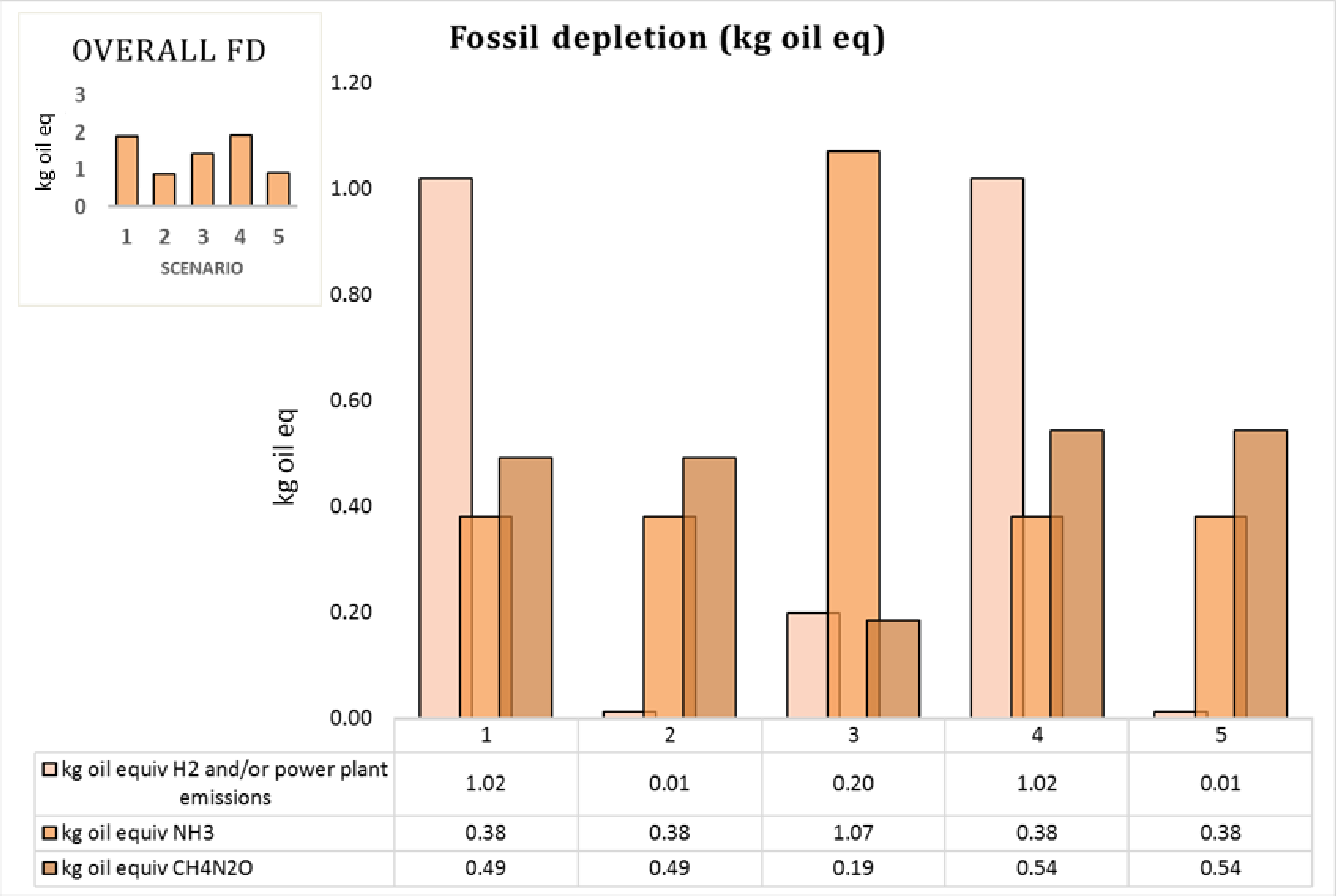
Overall (including non-critical elements), copper has the highest characterisation factor for abiotic depletion and it is the element with second highest concentration in scenarios with wind power (2 and 5). Although the use of several elements is associated with the production of turbines to utilise wind power, the impacts are minimum compared to hydrogen from steam methane reforming (SMR). In Scenario 3, ammonia synthesis is the largest contributor to resource depletion.

Photochemical oxidation

The main photochemical oxidant that has an impact on the environment is ozone (O_3) at ground level (Preiss, 2015). Tropospheric ozone has an effect on human health and plants, it is also highly linked with summer smog (World Health Organisation Europe, 2004; Royal Society, 2008). The main precursors to photochemical oxidants are NOx and non-methane volatile organic compounds (NMVOC) emissions. Results show higher non-methane volatile organic compounds (NMVOC) emissions for the CO_2 utilisation scenarios connected to the grid. This is associated to the higher energy penalties for water electrolysis if a renewable energy source is not used. As it is the case with several other impact categories, the use of wind power for water electrolysis has a lower photochemical oxidation score than the other alternatives. Urea synthesis with hydrogen from steam methane reforming (SMR) is the medium impact scenario compared to the other four CO_2 utilisation processes. If emissions from the CO_2 utilisation process are not managed, then the conventional routes have lower photochemical oxidation scores.

Marine aquatic, freshwater and terrestrial ecotoxicity

These impacts measure the effect of toxic emissions on aquatic and land ecosystems. Its effects are all on natural systems and resources. As mentioned in the CML-IA method, the characterisation of these impacts is still far from settled. The characterisation factor most used (since CML-IA is the most used method) is kg 1,4-DCB eq. The results in this study show that urea synthesis from steam methane reforming (SMR) generated hydrogen has the highest toxicity potential for all related impact categories. Direct ammonia emission and use of natural gas increase ecotoxicity impacts on this process.



	1	2	3	4	5
□ kg oil equiv H2 and/or power plant emissions	1.02	0.01	0.20	1.02	0.01
■ kg oil equiv NH3	0.38	0.38	1.07	0.38	0.38
■ kg oil equiv CH4N2O	0.49	0.49	0.19	0.54	0.54

Figure 6.14 Fossil depletion potential (FDP) scores per functional unit (1 kg of urea ready for use phase). Scenarios 1 to 5 with up to 4 main stages in each: H_2 production, NH_3 production, CH_4N_2O and power plant electricity generation (for system expansion in scenario 3). 1) Case scenario 1 kg of urea- electricity from grid mix, 2) Case scenario 1 kg of urea-wind power 3) Baseline scenario Urea steam methane reforming (SMR) 4) 1 kg of urea-DAC (direct air capture) and H_2 using electricity grid mix 5) Case scenario 1 kg of urea-DAC (direct air capture) and H_2 from wind power.

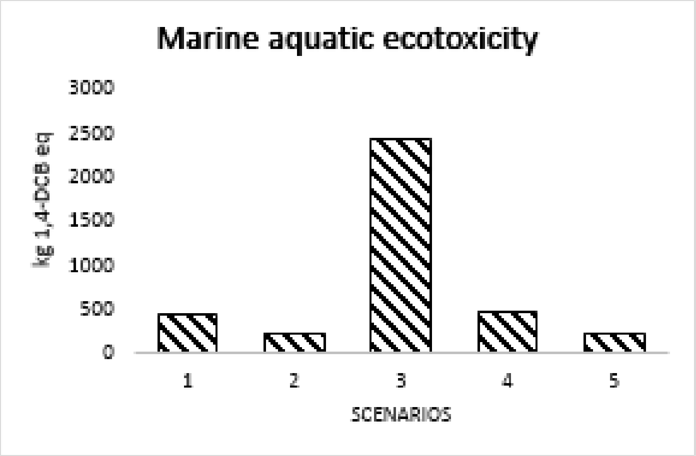


Figure 6.15 Marine aquatic ecotoxicity scores for all scenarios with system expansion, 1 kg of urea and 0.8 kWh as end products.

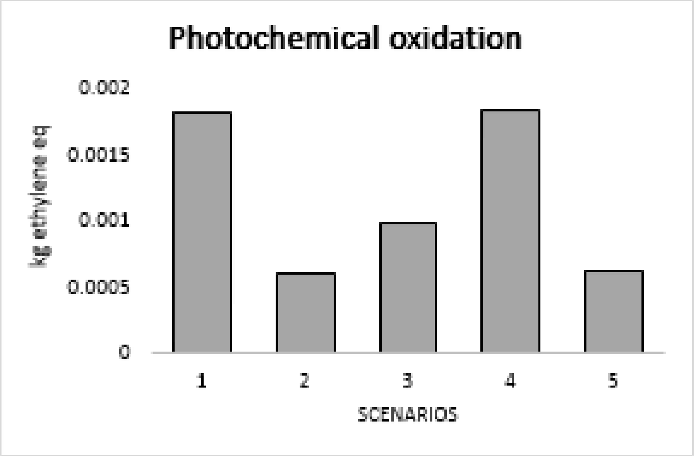


Figure 6.16 Photochemical oxidation scores for all scenarios with system expansion, 1 kg of urea and 0.8 kWh as end products.

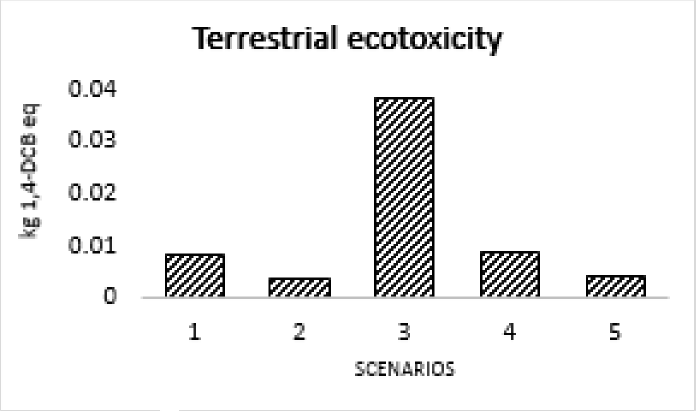


Figure 6.17 Terrestrial ecotoxicity scores for all scenarios with system expansion, 1 kg of urea and 0.8 kWh as end products.

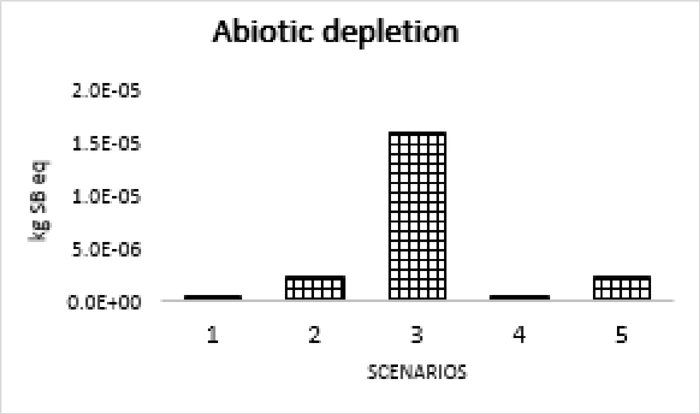


Figure 6.18 Abiotic depletion scores for all scenarios with system expansion, 1 kg of urea and 0.8 kWh as end products

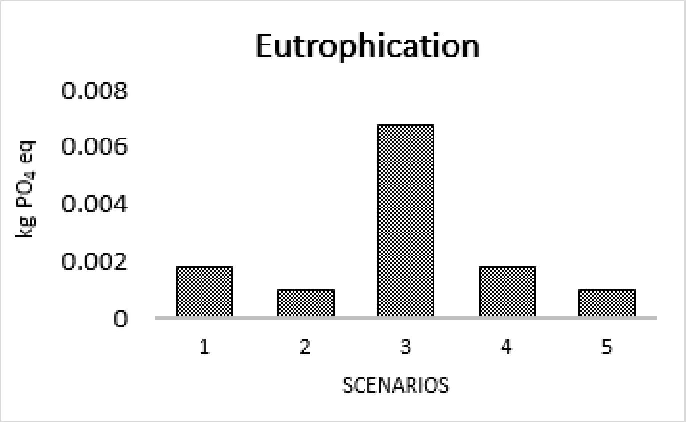


Figure 6.19 Eutrophication scores for all scenarios with system expansion, 1 kg of urea and 0.8 kWh as end products

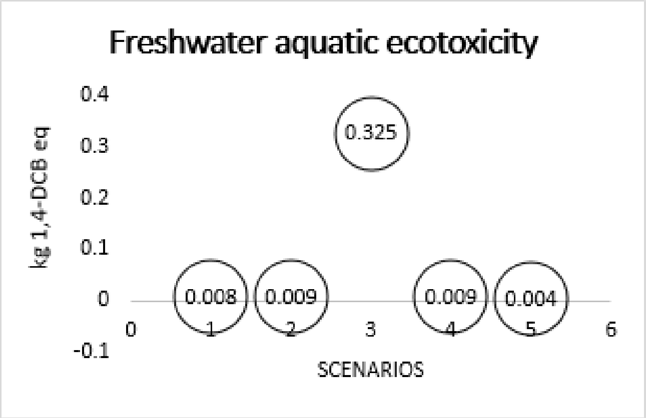


Figure 6.20 Freshwater aquatic ecotoxicity scores for all scenarios with system expansion, 1 kg of urea and 0.8 kWh as end products

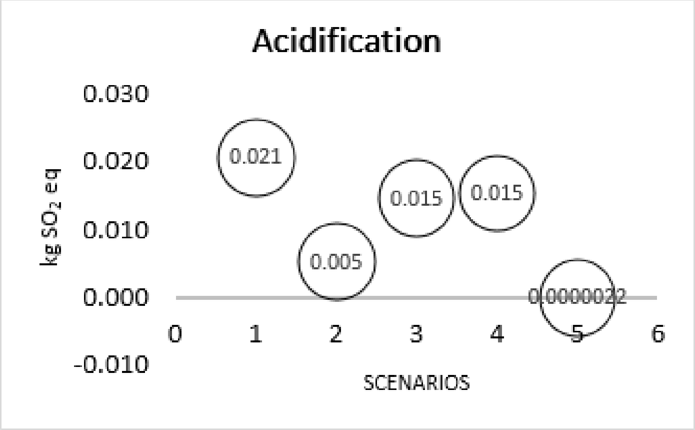


Figure 6.21 Acidification scores for all scenarios with system expansion, 1 kg of urea and 0.8 kWh as end products

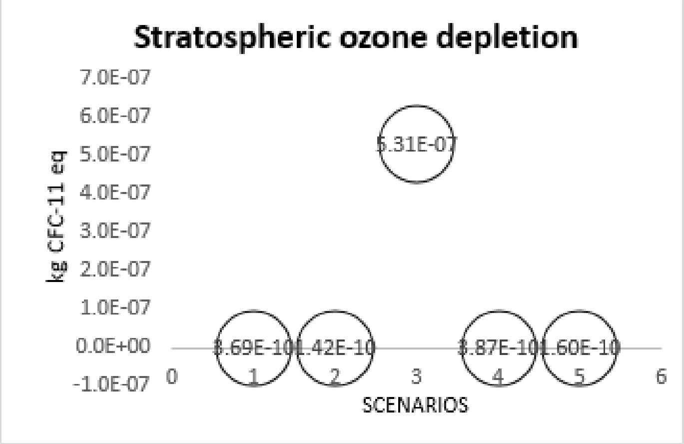


Figure 6.22 Stratospheric ozone depletion scores for all scenarios with system expansion, 1 kg of urea and 0.8 kWh as end products

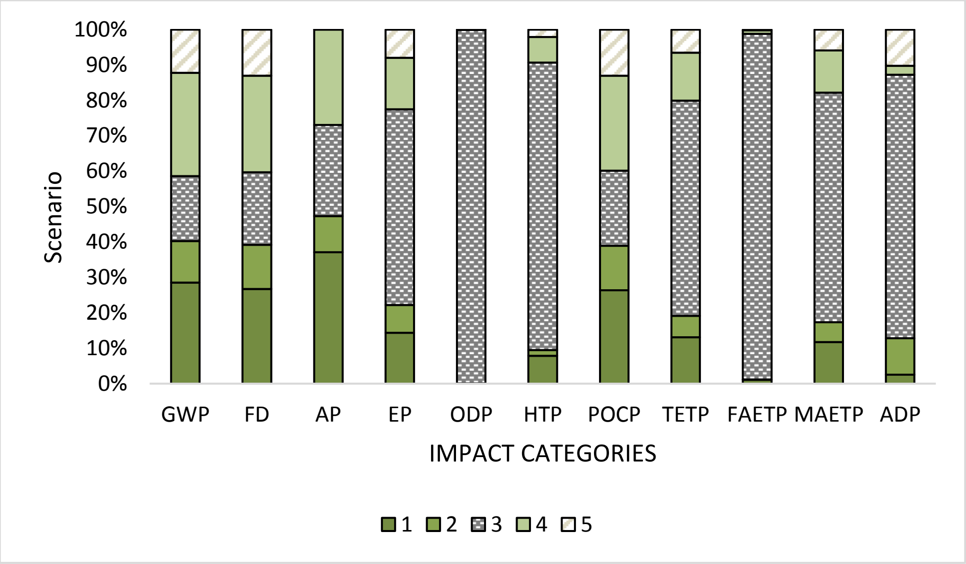


Figure 6.23 Comparative analysis of each scenario per impact category, based on results shown in Figures 6.13-6.22

6.4 Sensitivity and uncertainty analysis

The three most used allocation methods according to Von der Assen & Bardow (2014) are system expansion, avoided burden and economic allocation. Throughout the years, system expansion has been the method recommended for wider practice and for carbon dioxide utilisation technologies (von der Assen *et al.*, 2016). By comparing each method in **Table 6.24** and **Figure 6.24**, different interpretations are generated for the same set of results. This is a known problem with allocation where different methods result in different results with the same data. In this scenario, system expansion and economic allocation for urea are the most similar. Avoided burden has the greatest disparity; all emissions shift to either electricity generation or urea production. Both cases for avoided burden do not reflect the outcome; it is unlikely that one industry would be willing to take all of the burdens. For this sensitivity analysis, only net kg of CO_2 emitted for Scenario 1, 2, 4 and 5 were considered. Scenario 3 was used as an input to compare between conventional and CO_2 utilisation processes. The differences shown in this analysis are applicable to the other environmental categories, thus it was not necessary to replicate the analysis for other impacts. All impact assessments used system expansion throughout this work, unless stated.

Table 6.24 Net kg CO_2 emissions for each main scenario with allocation by different methods. Scaled to 1 kg of urea as final product, with 0.8 kWh generated from a coal fired power plant.

Allocation method		Net kg CO_2 emissions per scenario			
		1	2	4	5
System expansion	Utilisation	5.48	2.19	5.62	2.33
	Conventional	3.50	3.50	3.50	3.50
Avoided burden	Utilisation, primary product	4.78	1.48	4.92	1.62
	Electricity, secondary product	0.71	0.71	0.71	0.71
	Electricity, primary product	4.78	1.48	4.92	1.62
	Utilisation, secondary product	2.80	2.80	2.80	2.80
Economic allocation	Electricity	0.08	0.08	0.13	0.08
	CO_2 feedstock	0.36	0.36	0.36	0.36
	Urea	5.71	2.42	5.73	2.56

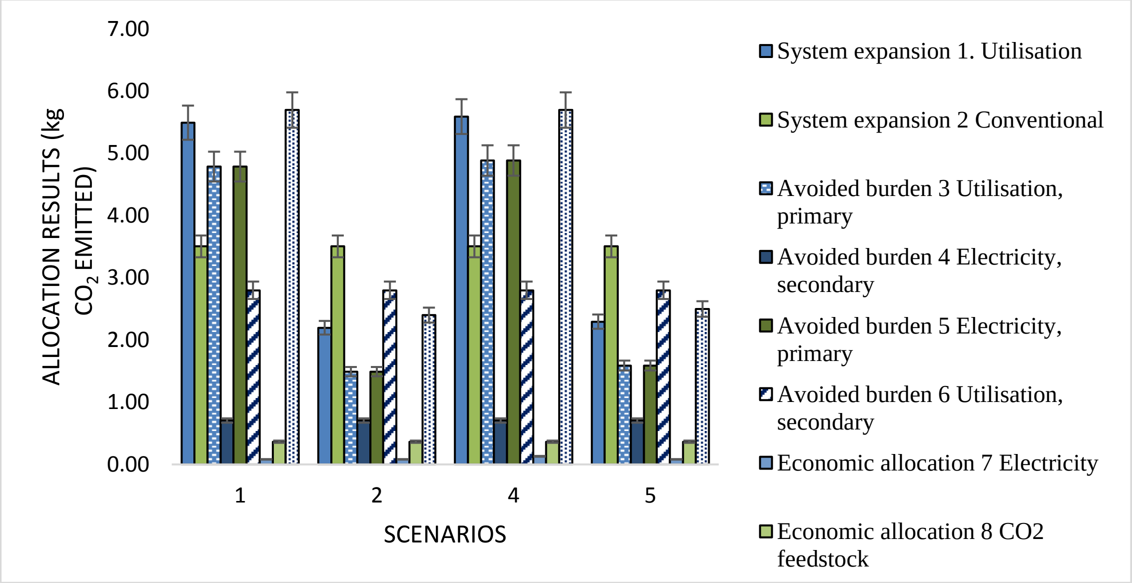


Figure 6.24 Net CO_2 emissions for each main scenario with allocation by different methods. Scaled to 1 kg of urea as final product, with 0.8 kWh generated from a coal fired power plant.

This study case used five alternative databases for global warming as sensitivity analysis. As can be seen in **Figure 6.25**, values change greatly when other databases are used. Hydrogen production has four different sources and ammonia production has two. In the ammonia case, steam methane reforming (SMR) to produce hydrogen was chosen as the baseline scenario since is the process most used worldwide (Methanol Institute, 2011). Partial oxidation does have a higher carbon footprint than steam methane reforming (SMR) but its lower production levels did not make it the most suitable case for comparison. The hydrogen databases considered include three ecoinvent version 3.3 processes and one by PlasticsEurope. However, all these processes use a chlor-alkali process that is not equivalent to the ITM Power Limited electrolyser as it not a process set for renewable energy. This same issue is also raised for H_2 from reforming by PlasticsEurope. Hence, Scenario 2 and 5 can still have similar carbon footprints to alternative databases by using renewable energy for hydrogen production.

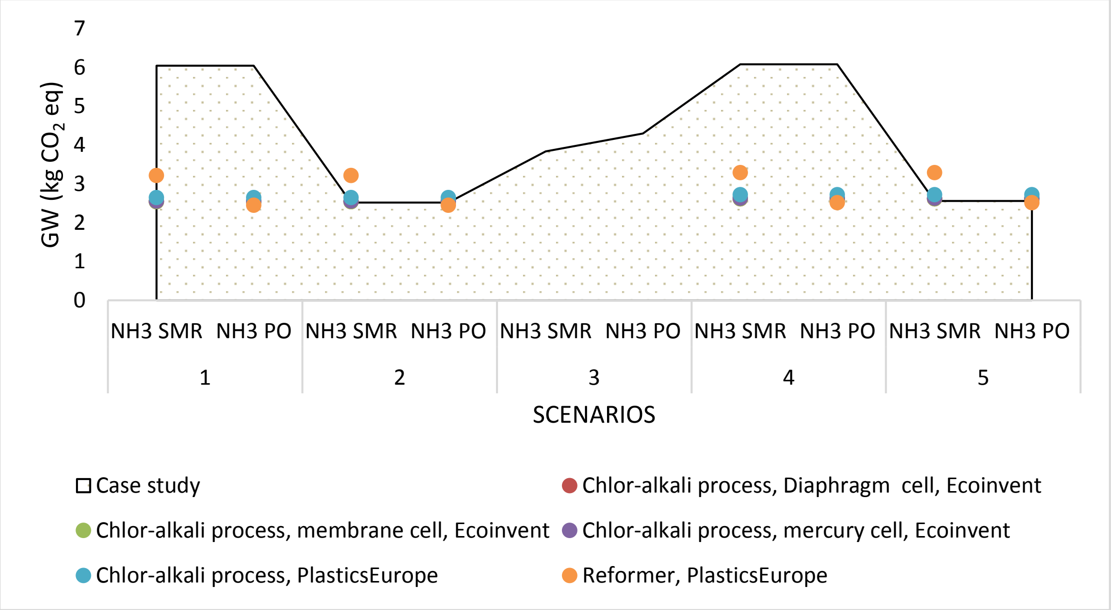


Figure 6.25 Global warming (GW) scores for all scenarios with different hydrogen database sources compared to a conventional urea production process with two ammonia production routes. The database used for ammonia from steam methane reforming (NH_3 SMR) and from partial oxidation (NH_3 PO) was obtained from ecoinvent version 3.3.

The uncertainty of net kg CO_2 emitted by the production of 1 kg of urea was calculated with a graphical distribution (**Figure 6.26**). The variance was set at ± 10% standard deviation scale, with 2,000 random data points plotted and considers all inputs in Scenario 1. The results show that the highest frequency can be found at 5.48 kg of CO_2 emissions per kg of NH_2CONH_2 with a probability of occurrence of 9.6% (**Figure 6.27**). Overall, 68% of the distributions stay within the range of 5.3 to 5.7 kg CO_2 emitted per kg of NH_2CONH_2.

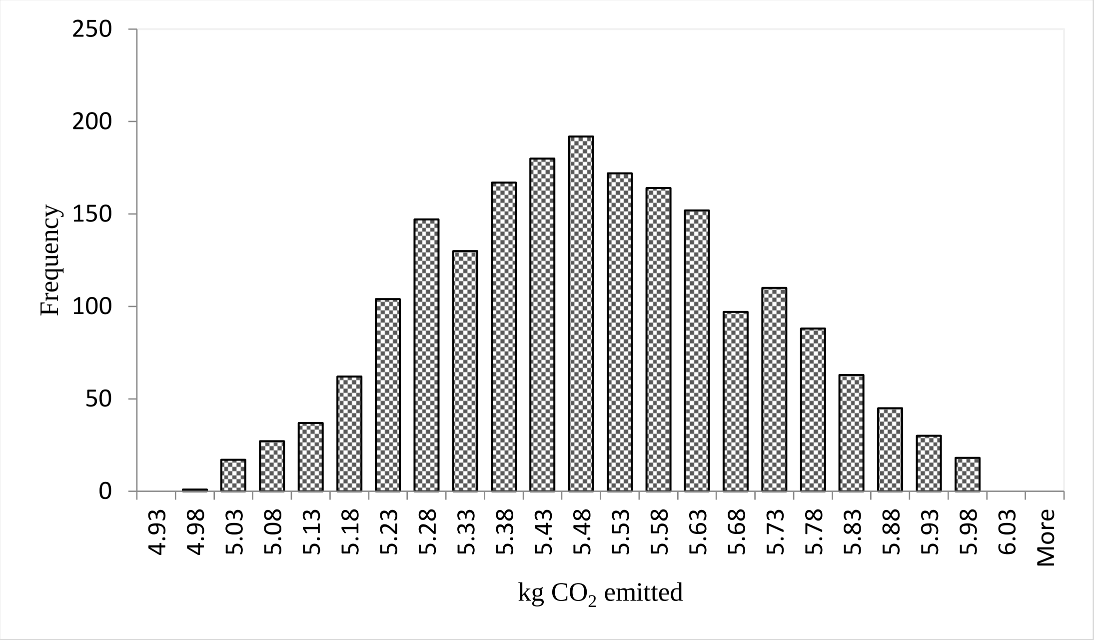


Figure 6.26 Uncertainty analysis of kg CO_2 emissions to produce 1 kg of urea and 0.8 kWh to the grid, using system expansion. Scenario 1 conditions. ± 10% standard deviation scale, 2,000 points calculated.

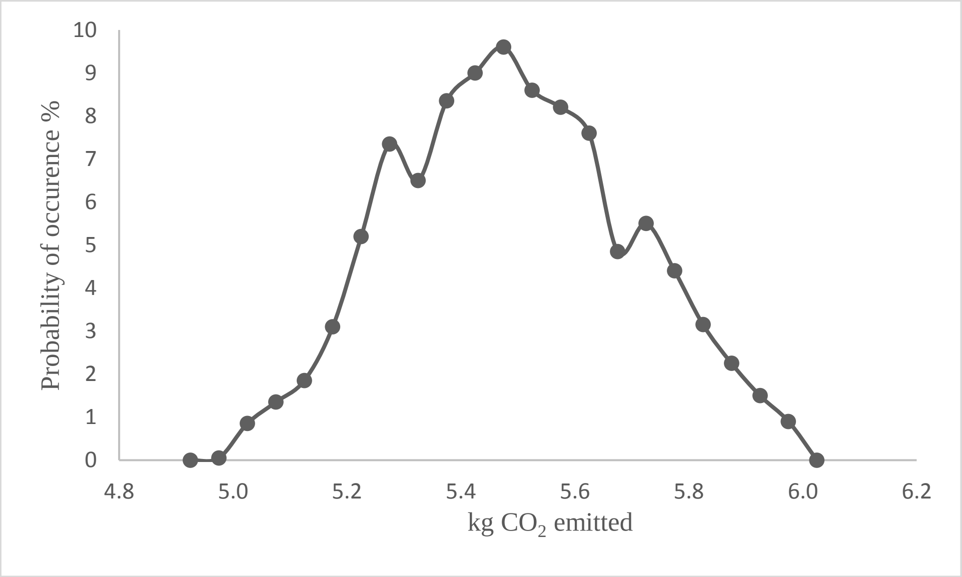


Figure 6.27 Probability distribution against the kg CO_2 emissions necessary to produce 1 kg of urea and deliver 0.8 kWh to the grid, using system expansion. Scenario 1 conditions. ± 10 standard deviation scale, 2000 points calculated.

Lastly, Indexed value graphs were created to determine the sensitivity of the impact categories for the CO_2 utilisation scenarios. The method is stated in **Section 5.4** and the same approach has been taken for consistency.

The results in **Figure 6.28** to **6.30** show that when the capture stage is varied, the global warming scores are one of the least sensitive categories while ozone depletion impacts are one of the highest. These trends were also seen in the methanol case study as they rely mostly on the outputs of the capture stage. When NH_3 and the electricity for H_2 is varied from 100 % (stoichiometric) to 200 % (stoichiometric + 100 % additional value) most of the impact categories have a similar sensitivity, abiotic depletion impacts are only relatively higher due to an increase in the use of renewable energy, while global warming impact results are more sensitive when electricity from the grid is used. This sensitivity analysis shows a reasonable level of confidence in the results and recommendations proposed in this cases study as there are no unexpected changes with any of the variations made.

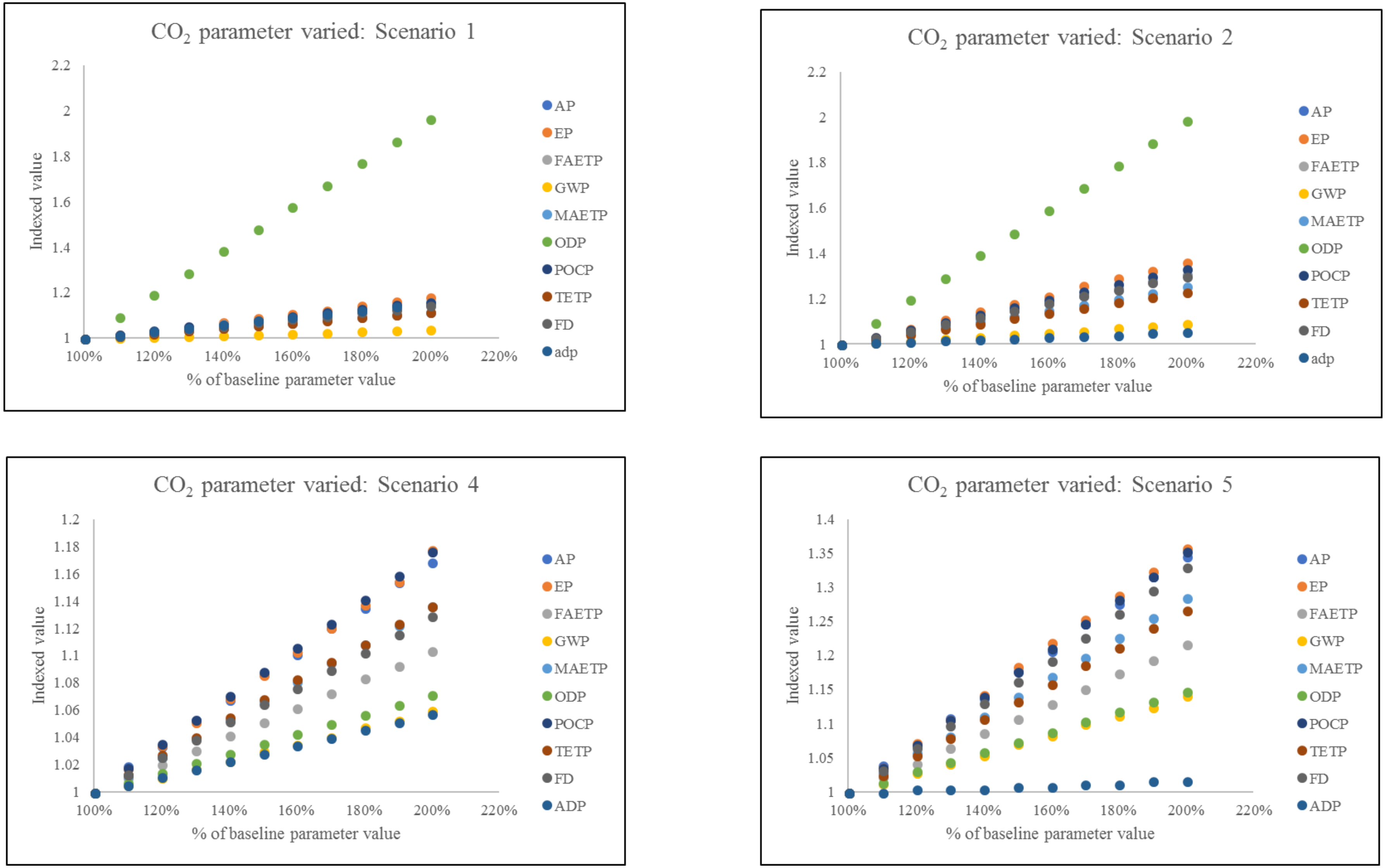


Figure 6.28 Sensitivity indexed graphs for the variation of the CO$_2$ parameter for CO$_2$ based urea scenarios using system expansion

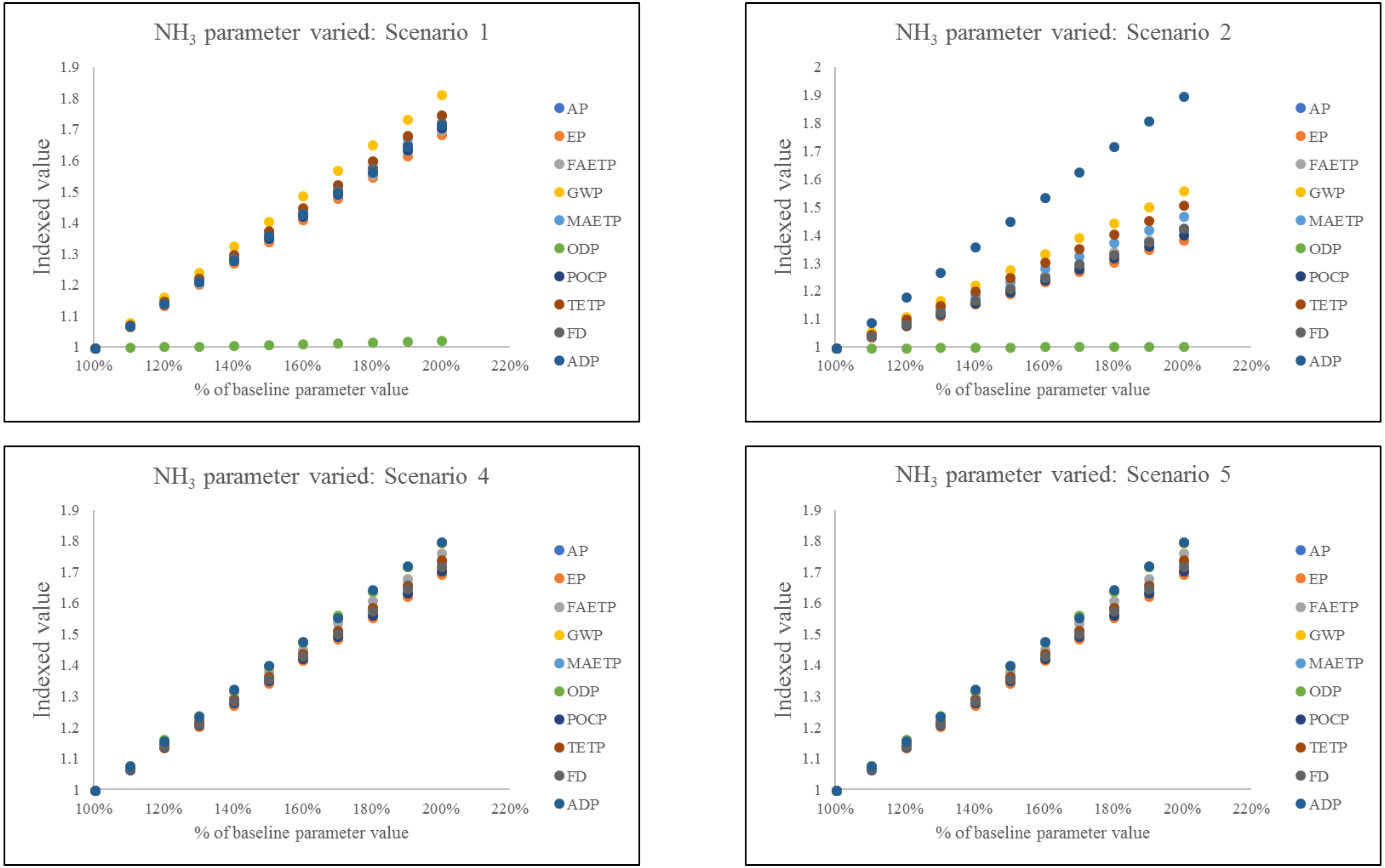


Figure 6.29 Sensitivity indexed graphs for the variation of the NH$_3$ parameter for CO$_2$ based urea scenarios using system expansion

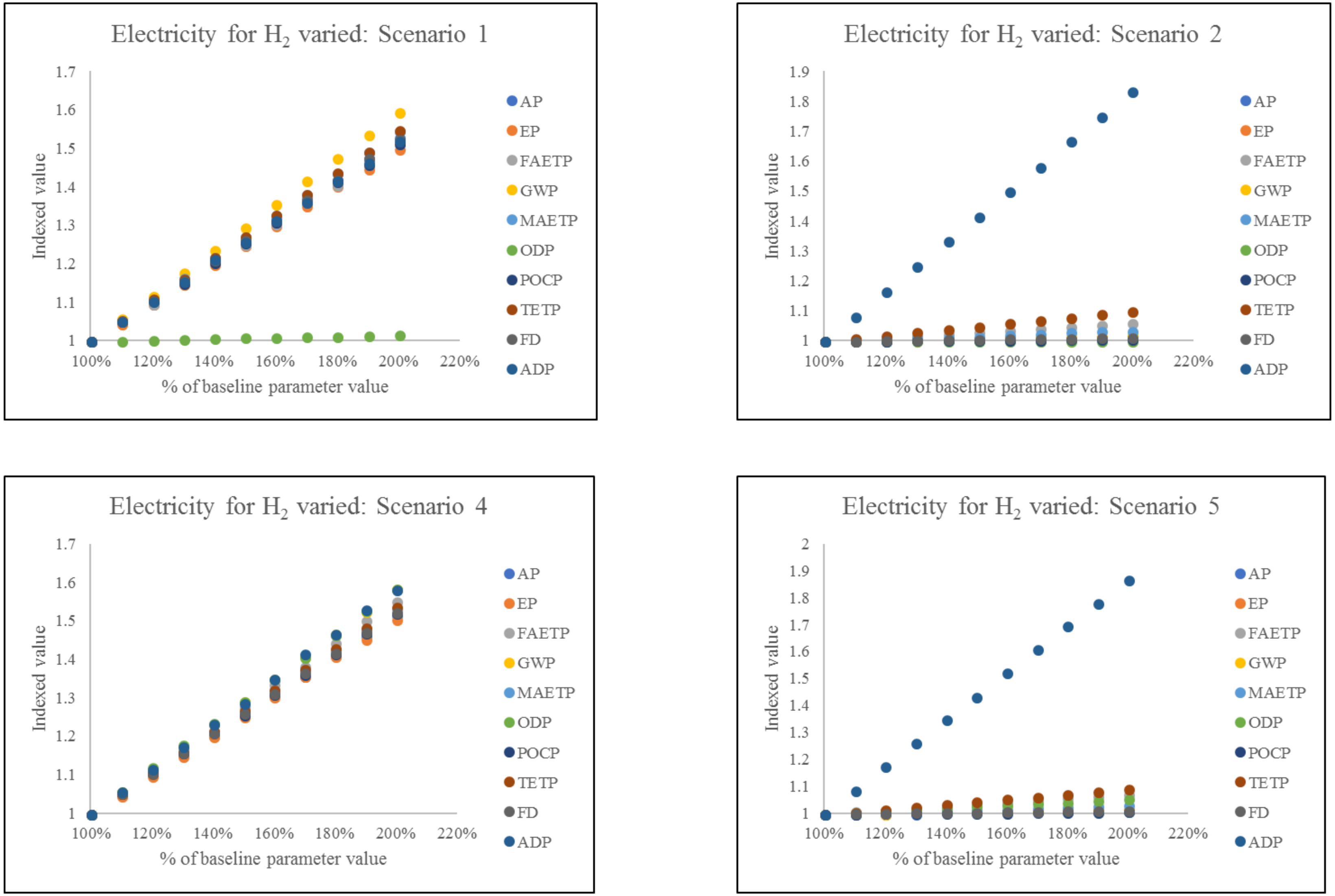


Figure 6.30 Sensitivity indexed graphs for the variation of the electricity required for H_2 production parameter for CO_2 based urea scenarios using system expansion

6.5 Chapter six summary

This chapter generated the life cycle inventory (LCI) and assessment for a carbon utilisation route with a production of 1 kg of urea (NH_2CONH_2). Urea synthesis included CO_2 from a capture process and NH_3 synthesised with H_2 from water electrolysis. The main inputs for a final production of 1 kg of urea were 0.102 kg H_2, 0.73 kg CO_2 and 0.57 kg NH_3. The main utilisation scenario considered CO_2 from a post-combustion capture process from a PC (pulverised coal) fired power plant with a 90% capture rate. H_2 supply was provided by an electrolyser (ITM Power Limited) powered by renewable energy; wind power in this scenario.

For the environmental assessment, results showed a net carbon avoidance of 1.3 kg of CO_2 per kg of urea for the utilisation scenario compared to urea produced in the conventional route (3.5 kg of CO_2 per kg of urea produced). This was the best-case scenario, where an electrolyser connected to wind power supplied H_2 for ammonia. Results also showed that the worst case is the same utilisation scenario connected directly to the grid. An extra 0.2 kg of CO_2 per 1 kg of urea was emitted, compared to the conventional baseline scenario (3.5 kg of CO_2 per kg of urea produced). A fourth and fifth scenario included direct air capture for supplying CO_2. However, results did not show an environmental benefit due to scope 2 emissions from purchasable electricity.

Results for other environmental impacts have higher difference between CO_2 utilisation and conventional processes. Ammonia by Haber-Bosch using hydrogen produced from steam methane reforming (SMR) contributes to larger toxicity impacts, eutrophication and stratospheric ozone depletion. In all categories, using renewable energy for water electrolysis, to produce hydrogen, for ammonia and then urea, has overall lowest environmental impacts. All scenarios used system expansion for 1 kg of urea and 0.8 kWh of electricity delivered to the grid. Sensitivity and uncertainty analysis repeated the results found in the assessment, where only by using renewable energy can the environmental impacts lower for this utilisation process.

6.6 Chapter six reference list

Althaus, H., Chudacoff, M., Hischier, R., Jungbluth, N., Osses, M., Primas, A. and Hellweg, S. (2007) ‘Life cycle inventories of chemicals. ecoinvent report No.8, v2.0.’, *Final report ecoinvent data …*, (8), pp. 1–957.

von der Assen, N. and Bardow, A. (2014) ‘Life cycle assessment of polyols for polyurethane production using CO2 as feedstock: insights from an industrial case study’, *Green Chemistry*, 16(6), p. 3272. doi: 10.1039/c4gc00513a.

von der Assen, N., Müller, L. J., Steingrube, A., Voll, P. and Bardow, A. (2016) ‘Selecting CO2 Sources for CO2 Utilization by Environmental-Merit-Order Curves’, *Environmental Science and Technology*, 50(3), pp. 1093–1101. doi: 10.1021/acs.est.5b03474.

European Comission (2017) *Critical Raw Materials*.

Galindo Cifre, P. and Badr, O. (2007) ‘Renewable hydrogen utilisation for the production of methanol’, *Energy Conversion and Management*, 48(2), pp. 519–527. doi: 10.1016/j.enconman.2006.06.011.

Heij, G. . and Schneider, T. (1991) *Acidification research in the Netherlands*.

Heijungs, R., Settanni, E. and Guin??e, J. (2013) ‘Toward a computational structure for life cycle sustainability analysis: Unifying LCA and LCC’, *International Journal of Life Cycle Assessment*, 18(9), pp. 1722–1733. doi: 10.1007/s11367-012-0461-4.

ITM Power Limited (2016) ‘Personal communication’.

Methanol Institute (2011) *Methanol Basics*.

Owen, R. (2016) ‘Personal communication’.

Preiss, P. (2015) ‘Photochemical Ozone Formation’, in Hauschild, M. Z. and Huijbregts, M. A. J. (eds) *Life Cycle Impact Assessment*. Dordrecht: Springer Netherlands, pp. 115–138. doi: 10.1007/978-94-017-9744-3_7.

Royal Society (2008) *Groun-level Ozone in the 21st Century: Future Trends, Impacts and Policy Implications*.

Soltanieh, M., Azar, K. M. and Saber, M. (2012) ‘Development of a zero emission integrated system for co-production of electricity and methanol through renewable hydrogen and CO2 capture’, *International Journal of Greenhouse Gas Control*. Elsevier Ltd, 7, pp. 145–152. doi: 10.1016/j.ijggc.2012.01.008.

Stamicarbon (2017) *Urea facts*.

Styring, P. (2016) ‘Personal communication’.

World Health Organisation Europe (2004) ‘Health Aspects of Air Pollution Results from the WHO Project “Systematic Review of Health Aspects of Air Pollution in Europe”’, *World Health*, p. 30.

Xiang, X., Guo, L., Wu, X., Ma, X. and Xia, Y. (2012) ‘Urea formation from carbon dioxide and ammonia at atmospheric pressure’, *Environmental Chemistry Letters*, 10(3), pp. 295–300. doi: 10.1007/s10311-012-0366-2.

7 Other Aspects of CO_2 Utilisation: Urea and Methanol Production Case Studies

The focus of this chapter is how other factors have an impact on a product from recovered CO_2. The methanol and urea study cases from **Chapters 5 and 6** are used as baseline. These factors include CO_2 availability in the UK and Europe, the UK electricity outlook until 2050, the prices of utilities and the role of hydrogen production in the UK, the global and UK market for CO_2 utilisation, associated human health impacts, and global warming and fossil depletion impacts. Together, they provide a qualitative assessment of the effects to both people and profit. This assessment provides the last set of indicators for calculating the utilisation potential of a process, shown in **Chapter 8**.

7.1 CO_2 availability by source in Europe

In **Chapters 5** and **6**, it is assumed that CO_2 is supplied from a subcritical PC (pulverised coal) power plant. While most utilisation studies currently use this CO_2 source, soon this might not be so suitable. Coal fired power plants are scheduled to be shut down by 2050, in an effort to meet carbon reduction targets (BIS, 2015). These power plants also have large-scale CO_2 emissions, while the utilisation products in this study use smaller quantities. For the total annual urea production, a minimum of only 30.4 t/year of CO_2 would be required (assuming four months in a season). In Europe, the processes with least CO_2 emissions still emit 100 t/year and large-scale processes can emit up to 36.6 Mt/year (Database, 2014). Thus, if a single utilisation process was to make a difference to the emissions of a company, only smaller emitters are applicable. To determine these emitters, all industrial and electricity generation sources with ≤ 0.2 Mt CO_2 emissions/year in Europe were mapped. Results are shown in **Figure 7.1**. The mapping included all industrial emitters that report to the European Union. The results showed better opportunities for small-scale CO_2 capture in Western Europe; Germany, France, Spain, the United Kingdom and Italy have the largest number of industries with lower CO_2 emissions. Specifically, in the UK, there are thirty-five registered small-scale industries that could supply CO_2 to a CO_2 utilisation process, based on the above criterion. Depending on the concentration of the CO_2 in the flue gas, the sources could be used for different CO_2 transformations. All sources were mapped by postcode to determine areas in the UK with the highest potential for carbon dioxide capture and possible future utilisation processes. These results are shown in **Figure 7.2** and showed a higher concentration of industrial activity in the Midlands, the East and in Yorkshire. Production of electricity dominates even at small-scale generation.

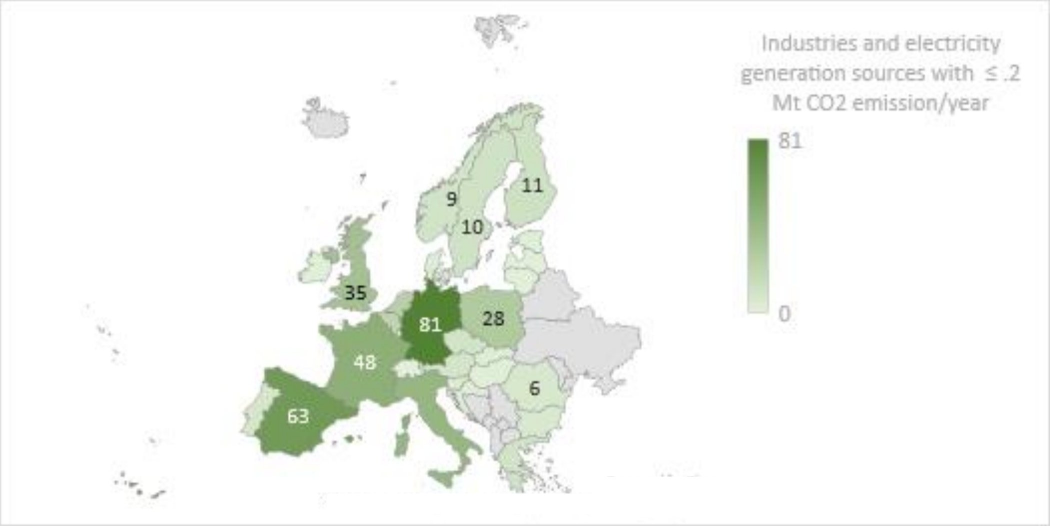


Figure 7.1 Mapping of number of industry and electricity generation sites that emit ≤ 0.2 Mt CO_2 emissions/year in Europe. Data adapted from European Commission report (database, 2014).

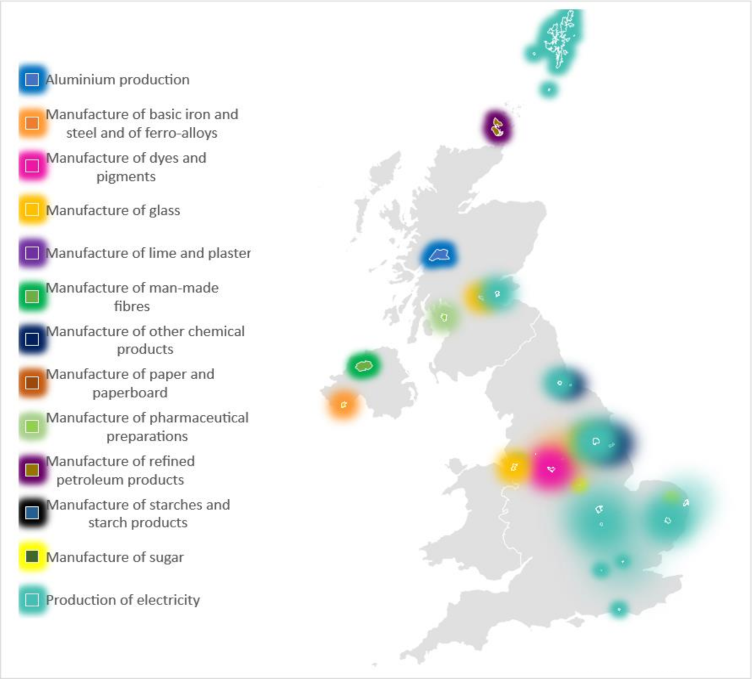


Figure 7.2 Mapping of industry and electricity generation sites that emit ≤ 0.2 Mt CO_2 emissions/year in the United Kingdom by commercial sector. Data adapted from European Commission report (database, 2014).

There is also the possibility that CO_2 utilisation could be used as a complimentary abatement technology for large-scale emitters. This would largely depend on a carbon capture and storage (CCS) application to take the excess CO_2. In the short-term, this could also include coal-fired power generation plants. **Figure 7.3** ranks European countries based on their net CO_2 emissions/year. This includes all industrial and energy sectors regardless of its size or its potential for carbon capture and storage. Results again show that western countries have the highest emissions. Overall, Germany leads by more than double of Poland's emissions (the next higher emitter). Unlike small-scale emissions, net emissions by country largely depend on the type of emitter. Therefore, countries such as France can have more small-scale processes than the UK, but less CO_2 emissions/year overall. France has a higher reliance on nuclear power for electricity generation than the UK, thus changing the net CO_2 emission map. All maps were created using map charts from Excel, powered by Bing ®.

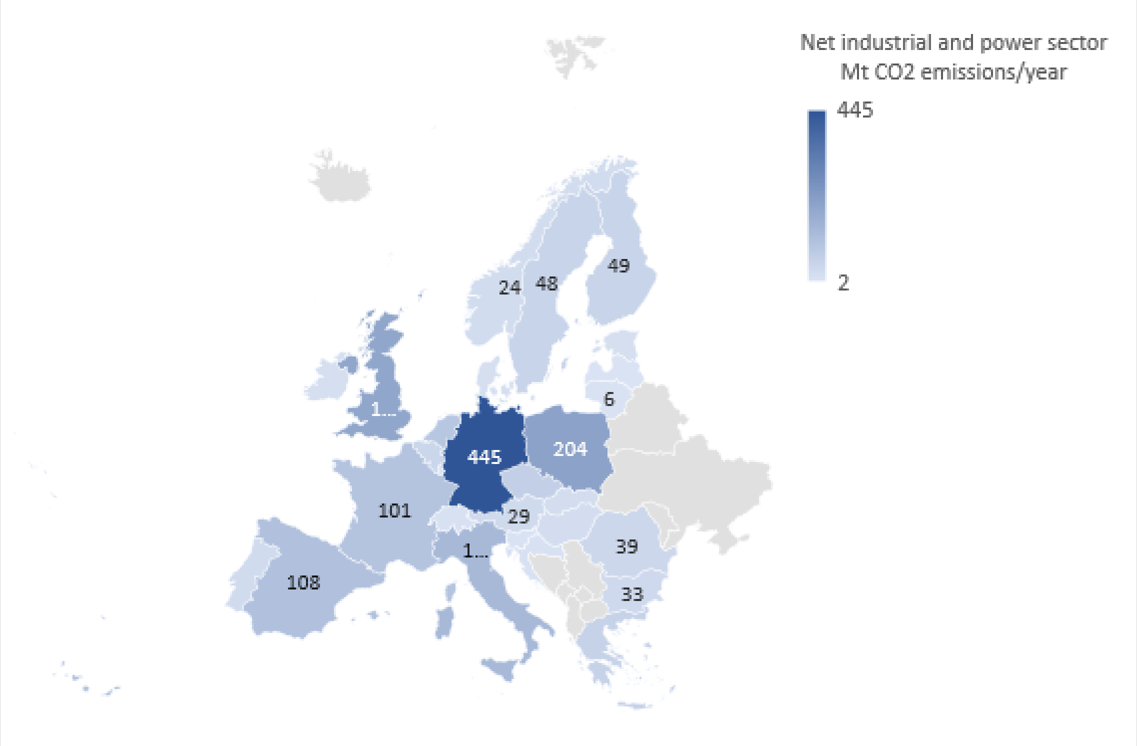


Figure 7.3 Mapping of the number of net industrial and power sector Mt CO_2 emissions/year in Europe

7.2 Electricity outlook for CO_2 utilisation

After securing a CO_2 stream for utilisation, the next step is to determine an adequate energy source to power this process. The CO_2 utilisation scenarios presented in **Chapters 5** and **6** depended on renewable energy, to avoid carbon emissions.

At the initial design stage of the urea plant and the worked example for methanol, heat integration is not considered. For urea production, the next iterations of the process will include energy recovery and heat integration, as discussed by Owen (2016). For methanol production, the results are used as benchmark in a worked example, which can be optimised in future assessments as required. With these results, the current electricity grid mix use was not decarbonised enough to reduce the impacts from energy consumed. However, this could change in the future, if the UK has a greener electricity grid mix. If this does not happen, then extra renewable energy specific for CO_2 conversion will be required.

In this section, scenarios are created to determine how renewable availability will affect the impact results of CO_2 utilisation processes in the near future. The results from **Chapters 5** and **6** for all five scenarios are used as baseline. The method CML-IA is used in all impacts except fossil fuel depletion, where ReCiPe (H) is used. Energy scenarios include the projected energy supply for years 2015, 2025 and 2035 according to BEIS (2017). A fourth scenario for 2050 is created by extrapolation.

Table 7.1 shows the percentage contribution of each electricity source for final consumption, for each year studied. According to the Renewable Energy Strategy, a 30% contribution of electricity from renewables by 2020 would help comply with the 15% overall renewable energy target set by the EU (National Grid, 2016).

Table 7.1 Scenarios 2015-2050 of the contribution of electricity sources for the grid mix in the UK (based on Annex J, BEIS (2017)).

Electricity source	**% of electricity contribution to the grid mix in the UK by year**			
	2015	**2025**	**2035**	**2050**
Coal	22.3	0.0	0.0	0.0
Coal and natural gas CCS[1]	0.0	0.0	1.9	0.0
Oil	0.6	1.1	0.7	0.5
Natural gas	30.4	42.2	13.4	4.9
Nuclear	19.8	14.0	35.6	31.0
Other Thermal	1.3	0.8	0.6	0.3
Renewables	24.7	40.4	46.4	61.3
Storage	1	1.5	1.3	1.5
% Total electricity supplied	100	100	100	100

[1] Carbon capture and storage

The renewable mix is not specified in Annex J (BEIS, 2017), thus an estimation was used based on Dukes 2016 Chapter 6: Renewable sources of energy (BEIS, 2016a) for 2015 and the National Grid scenarios road 2050 (National Grid, 2017a) for years 2025-2050. The percentage of total electricity generated from renewable sources (GWh) is used as reference for the year 2015. For these last years, the analysis uses the scenarios for renewable electricity supply based on the total output (TWh) created by the national grid. It specifically uses two scenarios, Two Degrees (TD) and Steady State (SS). Overall, there are four scenarios presented by the national grid:

- Consumer power (CP): Higher economic prosperity but less environmental focus. This scenario assumes that the target of limiting global temperature rise to two degrees Celsius above pre-industrial levels for 2050 will not be met. There is little inclination towards environmentally friendly options.
- Two degrees (TD): Higher focus on environmental sustainability and high economic prosperity. As the name suggests, the aim of this scenario is to portray the necessary conditions to restrict the global temperature rise to two degrees Celsius above pre-industrial levels for 2050.
- Steady state (SS): Less focus on the environment and low economic prosperity. This is a business as usual model where there is no inclination towards moving to a low carbon world. The targets of restricting the global temperature rise to two degrees Celsius above pre-industrial levels for 2050 are also not met.

- Slow progression (SP): High green ambitions for the long-term with lower economic prosperity. This scenario also does not meet all the UK carbon reductions targets since the slow economic growth reduces the pace of environmental progress.

For more information on these scenarios refer to National Grid (2017). The results from this report were used as estimates for renewable source contributions to complete **Table 7.1** and specify the renewable mix (see **Table 7.2**). Results for urea production are shown in **Figures 7.4** to **7.12** and show the impacts of connecting the carbon capture and utilisation system to the electricity grid in a specific year (Scenarios 1, 3 and 4). Scenarios 2 and 5 stay constant with time, assuming they are powered by the same wind power facilities. There are two graphs per impact; one considers a two-degree (TD) renewable scenario and the second a steady state case (SS). The first was chosen as the greenest case (a) and the second as the least environmental friendly (b) based on the projections by the national grid. This gave a range of results that facilitated analysis. Not all-renewable energy was mapped; if there was no specific database applicable then its contribution to the mix was not considered. This was standard for all scenarios and only included the following smaller processes: storage, other thermal processes, anaerobic digestion and co-firing with fossil fuels. For carbon capture and storage (CCS), the baseline model, created in **Chapter 5,** was also used for these calculations.

Results show that 39.9 MJ of electricity are required to produce 1 kg of urea (refer to **Chapter 6**). This electricity use has different impacts, depending on the electricity grid mix use. While initial results (**Chapter 6**) showed that using a baseline grid mix generated higher impacts than conventional routes, future projections show that a de-carbonised grid can be used to power CO_2 utilisation processes. The global warming impact of CO_2 utilisation scenarios drops below the conventional route by 2025 in both cases (a) and (b). By 2030, the global warming impact is below conventional values, when only wind power is used (scenarios 1,2,4 and 5)**.** The same trend can be seen for fossil fuel depletion and photochemical oxidation impacts.

Other impacts show a greater difference between the baseline scenario and the values for the year 2015. The variations in the standard grid mix used for the baseline (GaBi ts version 8.7.0.18 datasets) and the adaptations from the national grid account for these differences. However, the overall trendline is still downward for eutrophication, acidification, marine-aquatic and freshwater ecotoxicity impacts. Other impacts from using recovered CO_2 increase with the addition of renewables to the mix, although they are still significantly lower than for the conventional process (stratospheric ozone depletion, abiotic depletion, terrestrial ecotoxicity and human toxicity). There were also no major differences comparing between ‘greener’ and ‘least sustainable’ scenarios. The median is a swing of 3% in the electricity grid composition for all years. The highest changes are seen in biomass and carbon capture and storage (CCS), with up to 9% electricity increase projected in the mix. However, as biomass and carbon capture and storage (CCS) have a low influence in the general electricity mix, the increase is not perceptible in the impact results.

Table 7.2 Scenarios 2015-2050 of the contribution of electricity generation by renewable sources in the UK (based on projections from Chapter 6 BEIS (2016) for 2015 and National Grid (2017) scenarios for 2025-2050).

Renewable mix	**Contribution % of electricity generation by renewable sources in the UK by year**												
	2015	**2025**				**2035**				**2050**			
		TD[2]	SP[3]	SS[4]	CP[5]	TD[2]	SP[3]	SS[4]	CP[5]	TD[2]	SP[3]	SS[4]	CP[5]
Onshore wind	27.4	22.5	23.6	23.4	22.5	17.9	19.2	20.3	19.5	17.7	18.4	12.7	18.2
Offshore wind	20.9	34.2	33.8	31.0	30.3	40.7	40.6	46.0	39.4	41.4	38.4	50.6	35.4
Marine energy (wave and tidal stream)	2.0 x10^{-3}	2.5	1.1	0.2	1.1	6.0	3.5	0.2	2.1	10.7	8.9	0.2	9.5
Solar photovoltaics	9	8.4	8.6	8.7	11.6	10.0	9.6	8.8	14.5	10.7	10.4	8.1	14.9
Hydro total	7.5	3.7	4.2	5.5	4.5	2.7	3.1	5.2	3.5	2.5	2.9	5.7	3.1
Biomass	22	16.5	13.8	15.4	14.3	10.7	8.4	2.6	3.3	5.1	4.9	3.1	2.4
Other renewables[1]	12.9	12.2	14.9	15.8	15.7	12.1	15.6	16.9	17.8	12.0	16.0	19.6	16.5
Total generation %	100	100	100	100	100	100	100	100	100	100	100	100	100

[1] Taken from Energy Trends in Chapter 6 (BEIS, 2016a) as: landfill gas (16.6%), sewage sludge digestion (3%), biodegradable energy from waste (9.5%), co-firing with fossil fuels (0.6%), animal biomass (2.2%), anaerobic digestion (4.9%) and plant biomass (63.2%). Mix averages were used for all years as the general assumption. [2] Two degree [3] Consumer power [4] Slow progression [5] Consumer power ([2-5] From national grid scenarios)

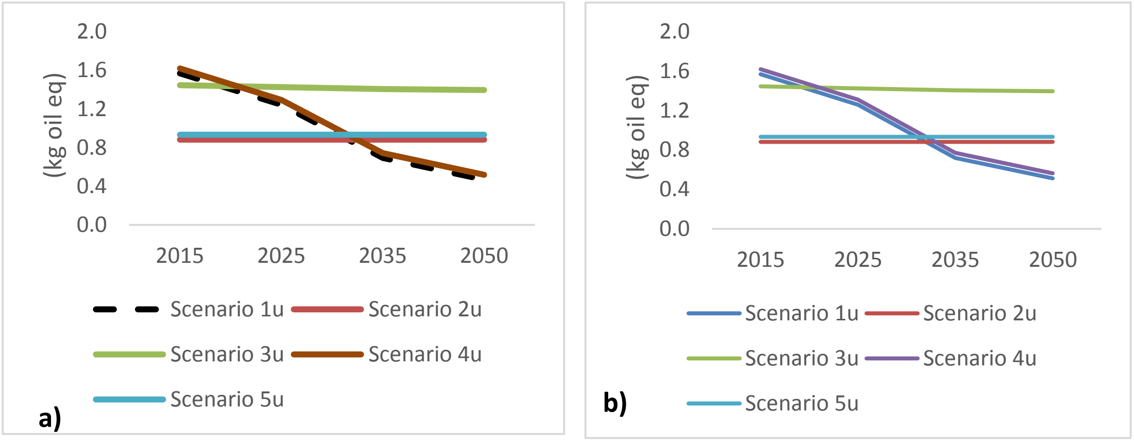


Figure 7.4 Fossil depletion scores for urea scenarios using (2015-2050) projected grid mixes by the national grid and BEIS. a) Renewables two degrees (TD) electricity scenario b) renewables steady state (SS) electricity scenario.

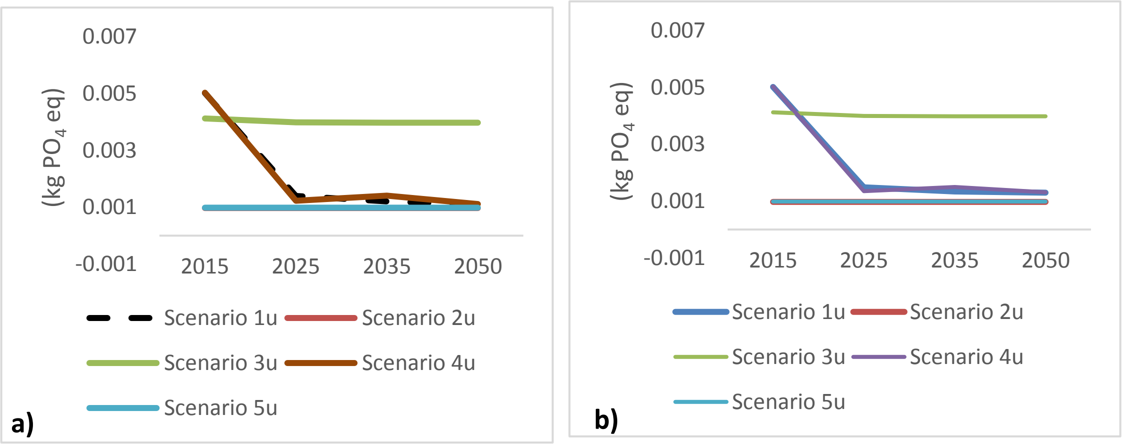


Figure 7.5 Eutrophication scores for urea scenarios using (2015-2050) projected grid mixes by the national grid and BEIS. a) Renewables two degrees (TD) electricity scenario b) renewables steady state (SS) electricity scenario.

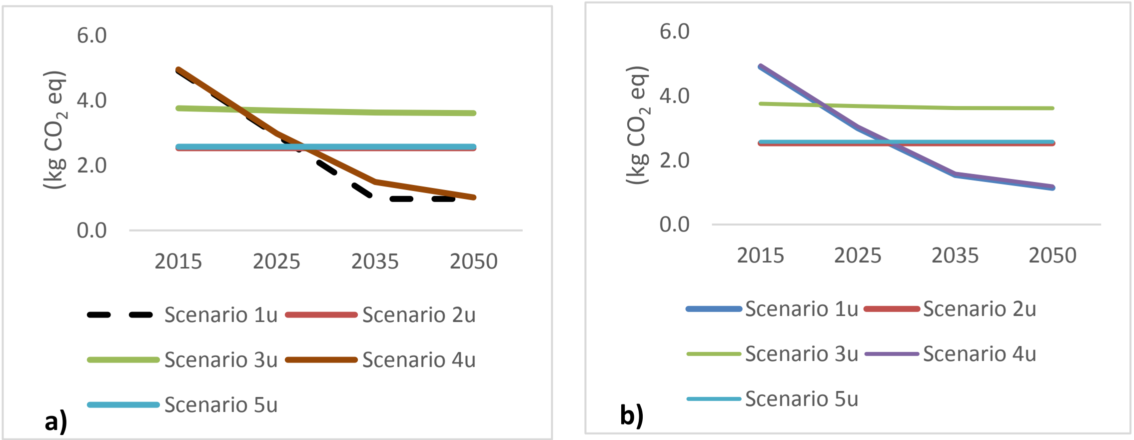


Figure 7.6 Global warming (GW) scores for urea scenarios using (2015-2050) projected grid mixes by the national grid and BEIS. a) Renewables two degrees (TD) electricity scenario b) renewables steady state (SS) electricity scenario.

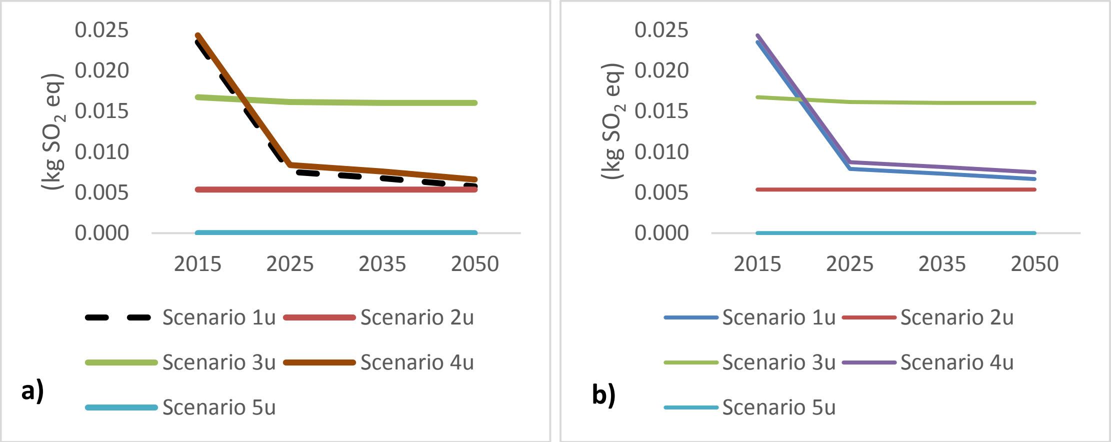


Figure 7.7 Acidification scores for urea scenarios using (2015-2050) projected grid mixes by the national grid and BEIS. a) Renewables two degrees (TD) electricity scenario b) renewables steady state (SS) electricity scenario.

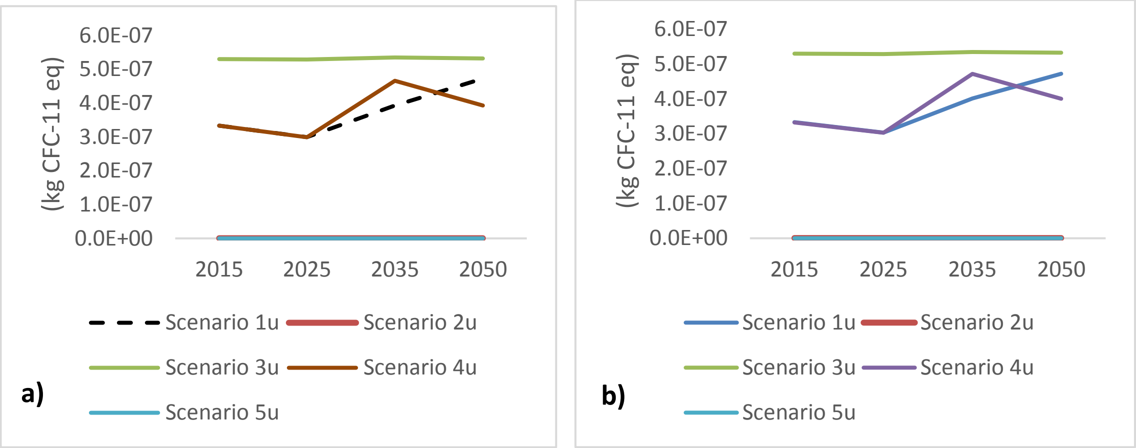


Figure 7.8 Stratospheric ozone depletion scores for urea scenarios using (2015-2050) projected grid mixes by the national grid and BEIS. a) Renewables two degrees (TD) electricity scenario b) renewables steady state (SS) electricity scenario.

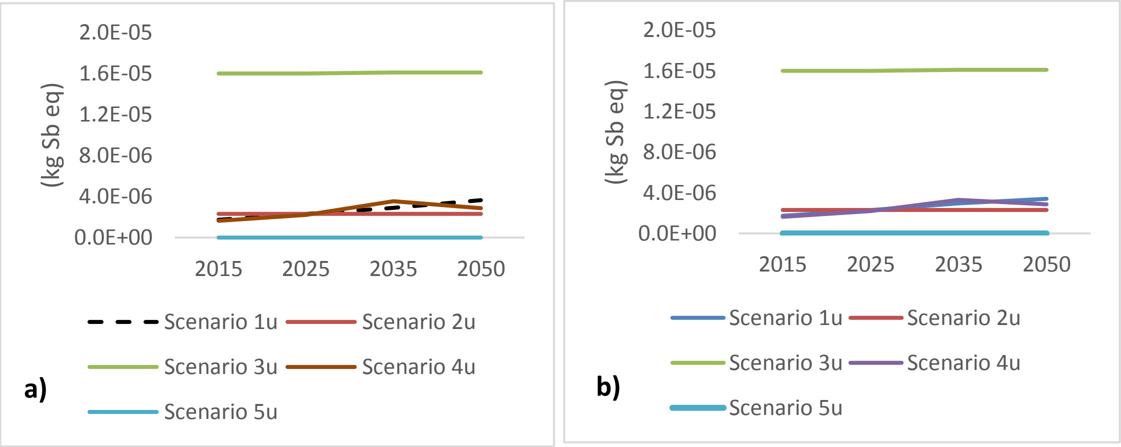


Figure 7.9 Abiotic depletion scores for urea scenarios using (2015-2050) projected grid mixes by the national grid and BEIS. a) Renewables two degrees (TD) electricity scenario b) renewables steady state (SS) electricity scenario.

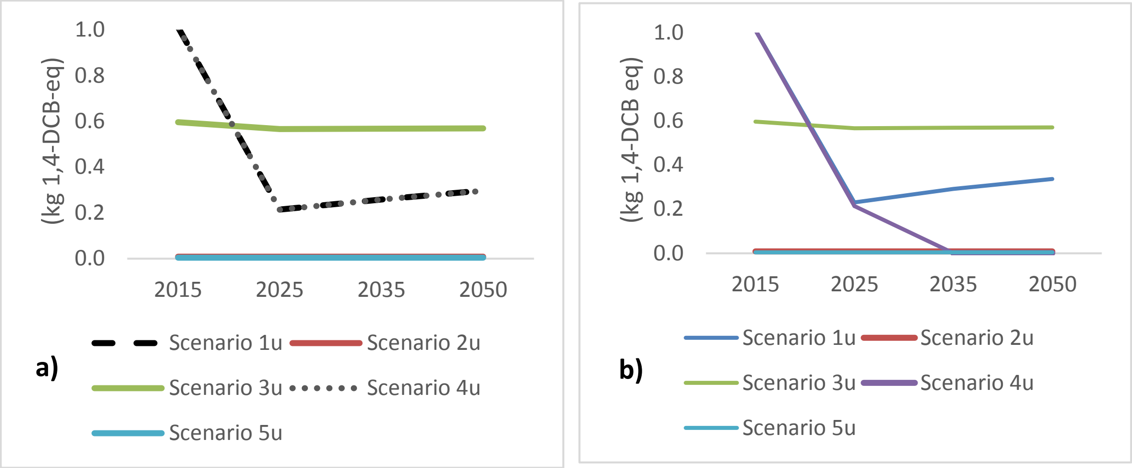


Figure 7.10 Freshwater ecotoxicity (FAET) scores for urea scenarios using (2015-2050) projected grid mixes by the national grid and BEIS. a) Renewables two degrees (TD) electricity scenario a) renewables steady state (SS) electricity scenario.

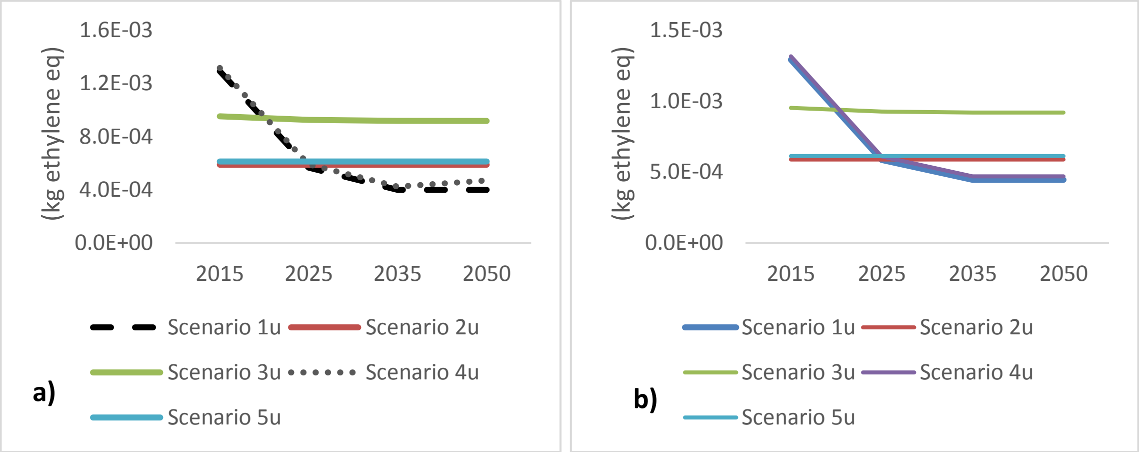


Figure 7.11 Photochemical oxidation scores for urea scenarios using (2015-2050) projected grid mixes by the national grid and BEIS. a) Renewables two degrees (TD) electricity scenario b) renewables steady state (SS) electricity scenario.

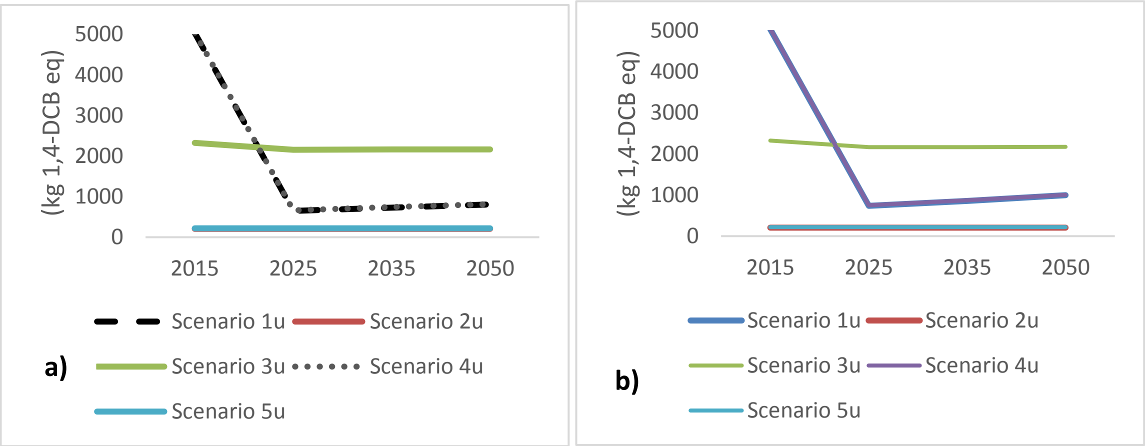


Figure 7.12 Marine aquatic ecotoxicity (MAET) scores for urea scenarios using (2015-2050) projected grid mixes by the national grid and BEIS. a) Renewables two degrees (TD) electricity scenario b) renewables steady state (SS) electricity scenario.

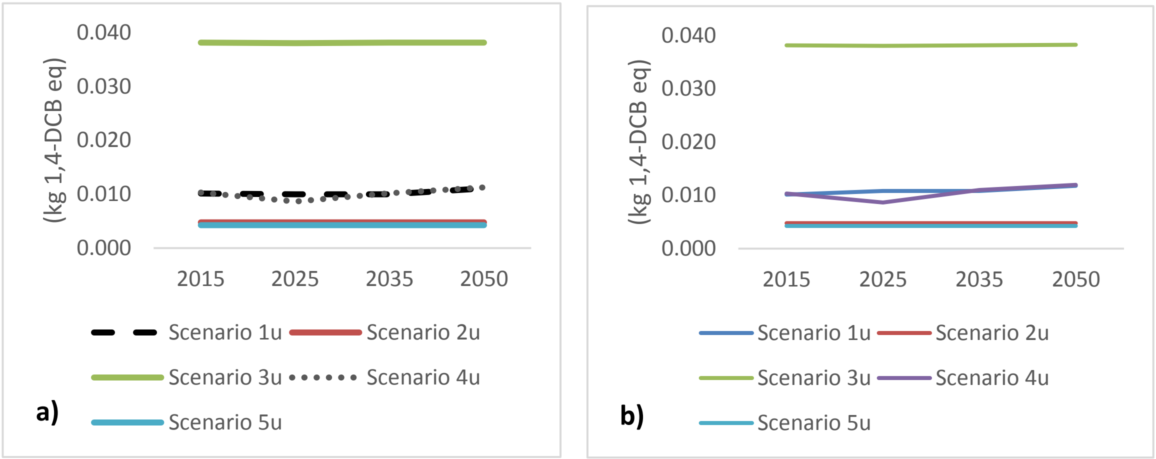


Figure 7.13 Terrestrial ecotoxicity (TAET) scores for urea scenarios using (2015-2050) projected grid mixes by the national grid and BEIS. a) Renewables two degrees (TD) electricity scenario b) renewables steady state (SS) electricity scenario.

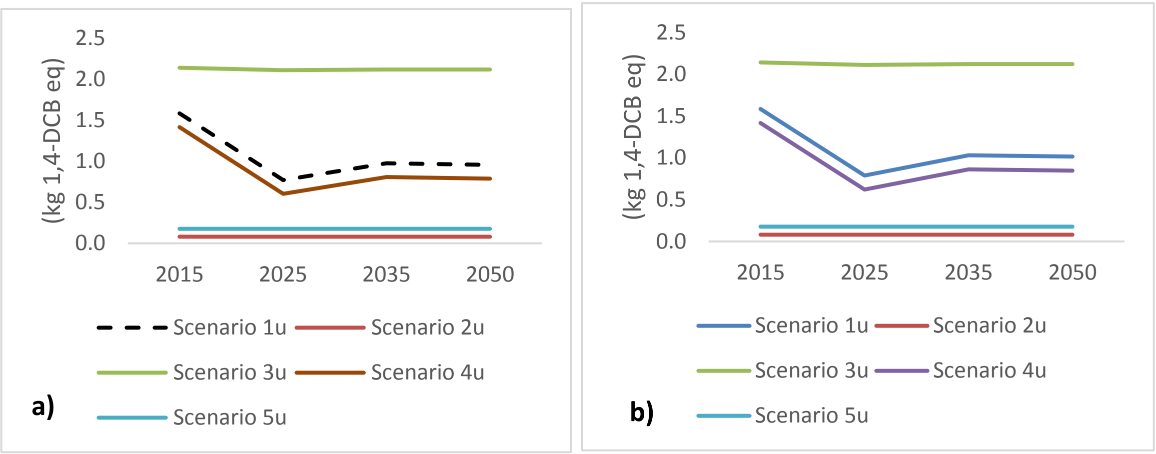


Figure 7.14 Human toxicity scores for urea scenarios using (2015-2050) projected grid mixes by the national grid and BEIS. a) Renewables two degrees (TD) electricity scenario b) renewables steady state (SS) electricity scenario.

The same analysis was applied to the methanol production scenarios from **Chapter 5**. This includes the same grid mixes and the same renewable contribution as in the urea case study. The electricity input is higher than for urea: 56.2 MJ is required per kg of CH_3OH produced with recovered CO_2.

The analysis showed less favourable results than for urea production. With the suggested grid mix, the utilisation process is not competitive in terms of carbon avoidance until the year 2050. Overall, nine out of eleven categories have lower impacts for methanol production from natural gas (Scenario 3). These results are dependent on the electricity grid mix. As seen in **Figure 7.15** to **Figure 7.25**, only scenarios with renewables come close to being competitive to the conventional route.

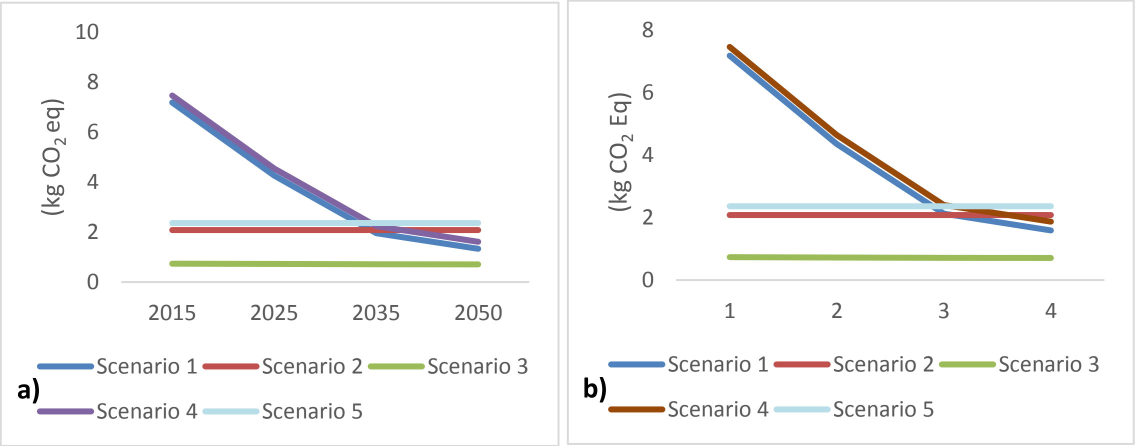


Figure 7.15 Global warming (GW) scores for methanol scenarios using (2015-2050) projected grid mixes by the national grid and BEIS. a) Renewables two degrees (TD) electricity scenario b) renewables steady state (SS) electricity scenario.

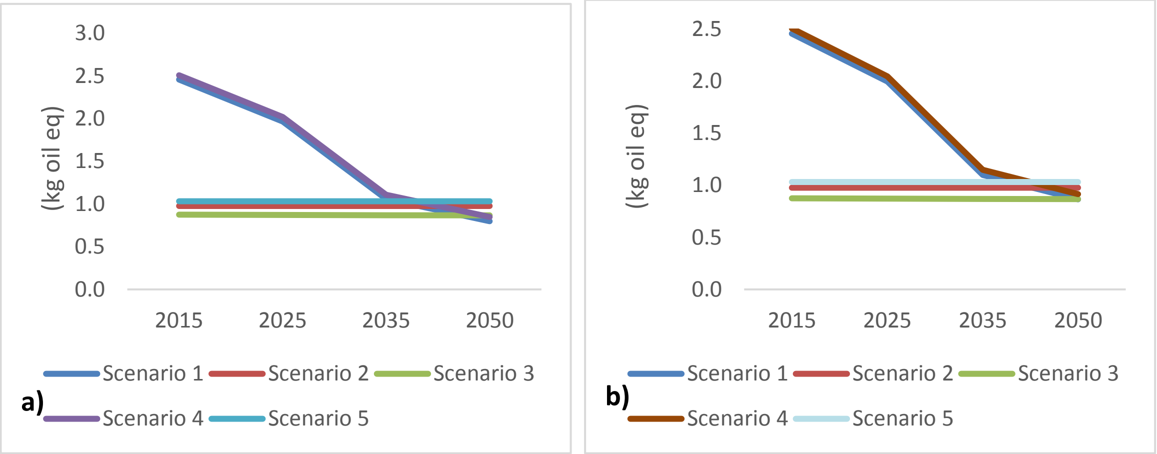


Figure 7.16 Fossil depletion scores for methanol scenarios using (2015-2050) projected grid mixes by the national grid and BEIS. a) Renewables two degrees (TD) electricity scenario b) renewables steady state (SS) electricity scenario.

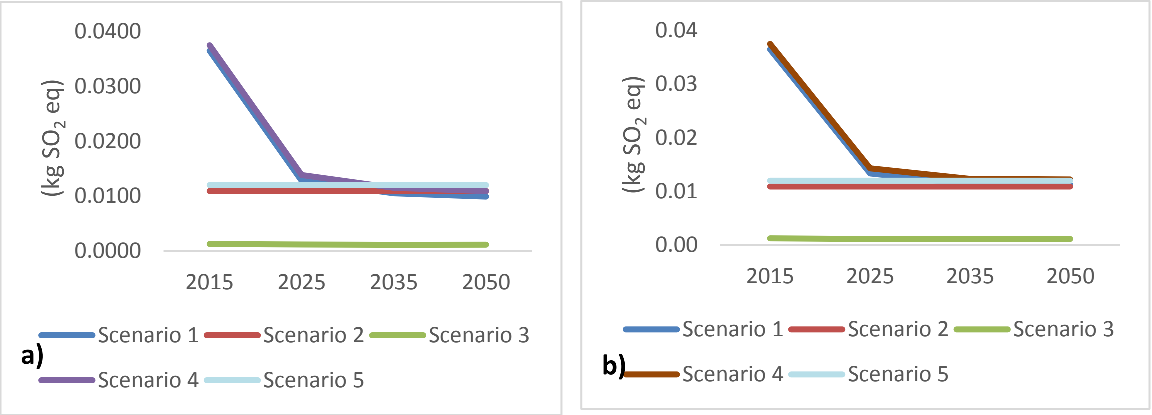


Figure 7.17 Acidification scores for methanol scenarios using (2015-2050) projected grid mixes by the national grid and BEIS. a) Renewables two degrees (TD) electricity scenario b) renewables steady state (SS) electricity scenario.

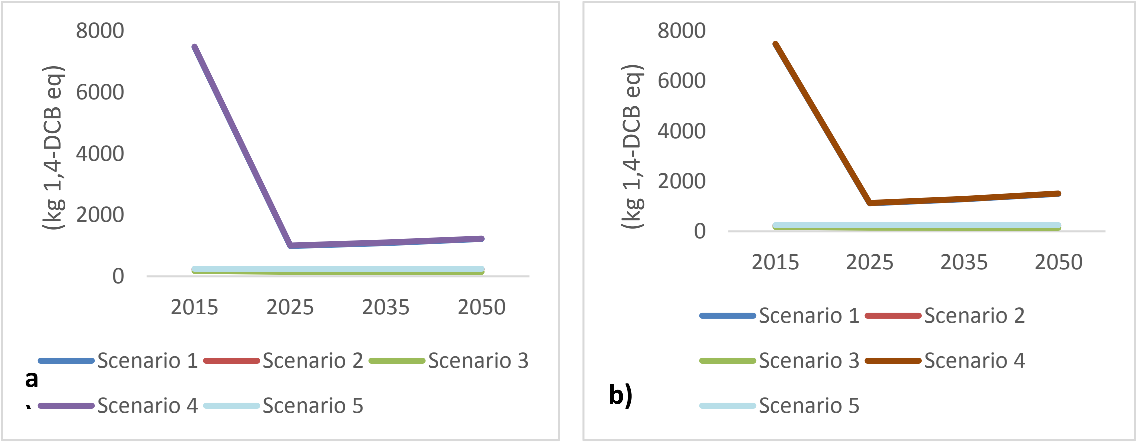


Figure 7.18 Marine aquatic eco-toxicity (MAET) scores for methanol scenarios using (2015-2050) projected grid mixes by the national grid and BEIS. a) Renewables two degrees (TD) electricity scenario b) renewables steady state (SS) electricity scenario.

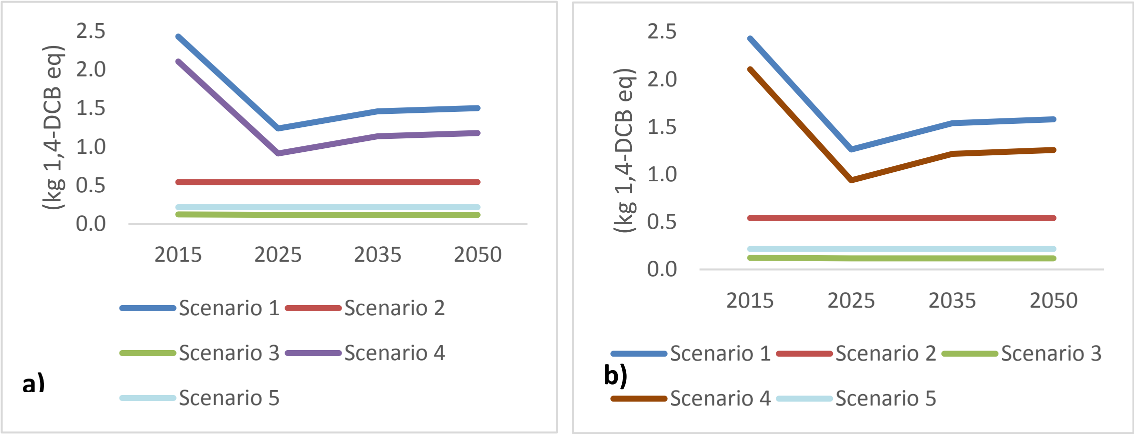


Figure 7.19 Human toxicity scores for methanol scenarios using (2015-2050) projected grid mixes by the national grid and BEIS. a) Renewables two degrees (TD) electricity scenario b) renewables steady state (SS) electricity scenario.

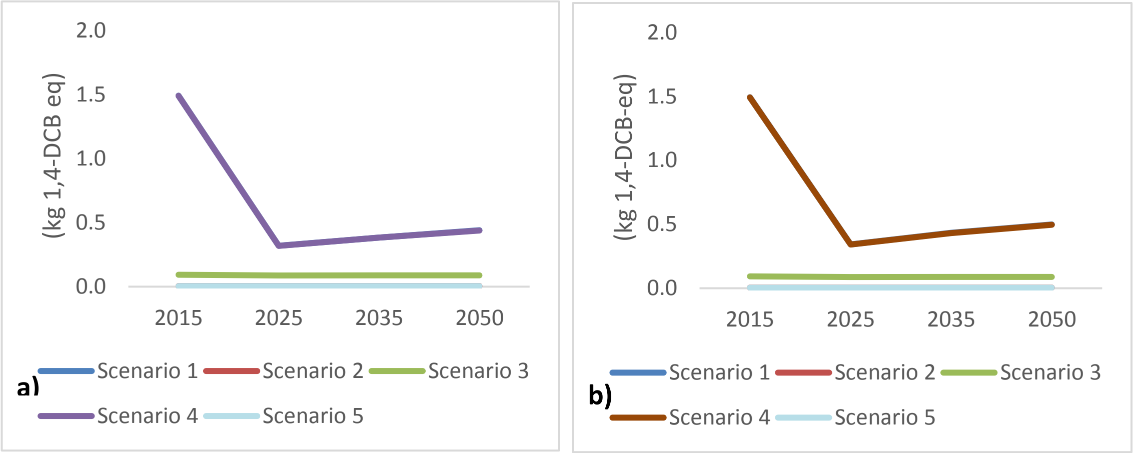


Figure 7.20 Freshwater ecotoxicity scores for methanol scenarios using (2015-2050) projected grid mixes by the national grid and BEIS. a) Renewables two degrees (TD) electricity scenario b) renewables steady state (SS) electricity scenario.

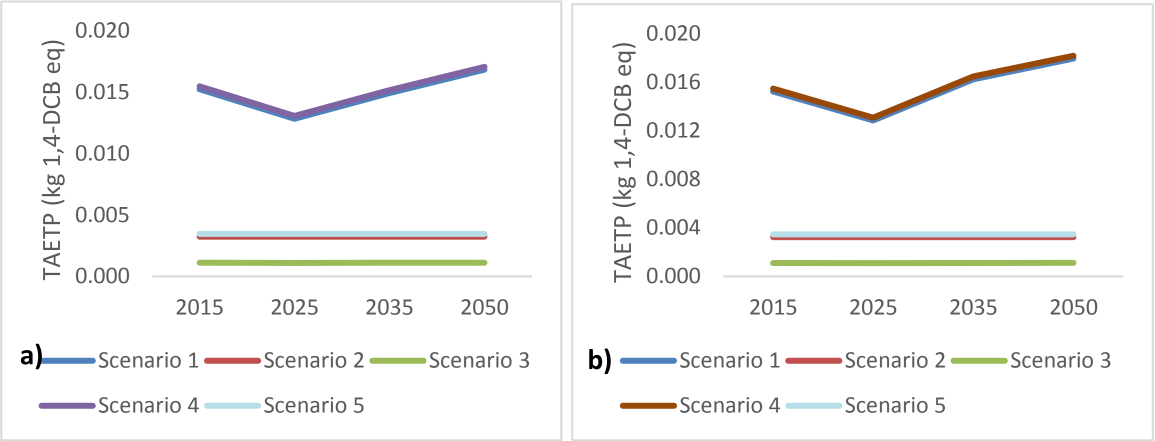


Figure 7.21 Terrestrial ecotoxicity (TAET) scores for methanol scenarios using (2015-2050) projected grid mixes by the national grid and BEIS. a) Renewables two degrees (TD) electricity scenario b) renewables steady state (SS) electricity scenario.

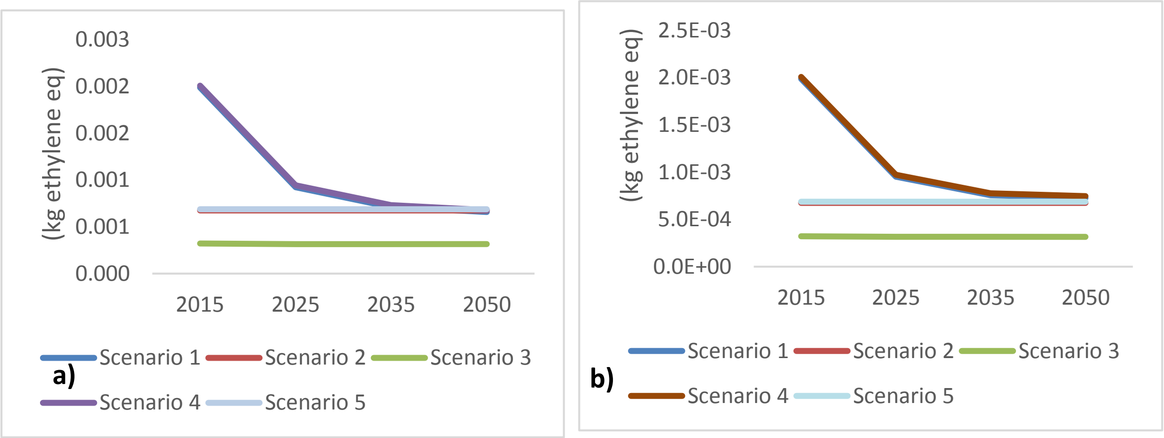


Figure 7.22 Photochemical oxidation scores for methanol scenarios using (2015-2050) projected grid mixes by the national grid and BEIS. a) Renewables two degrees (TD) electricity scenario b) renewables steady state (SS) electricity scenario.

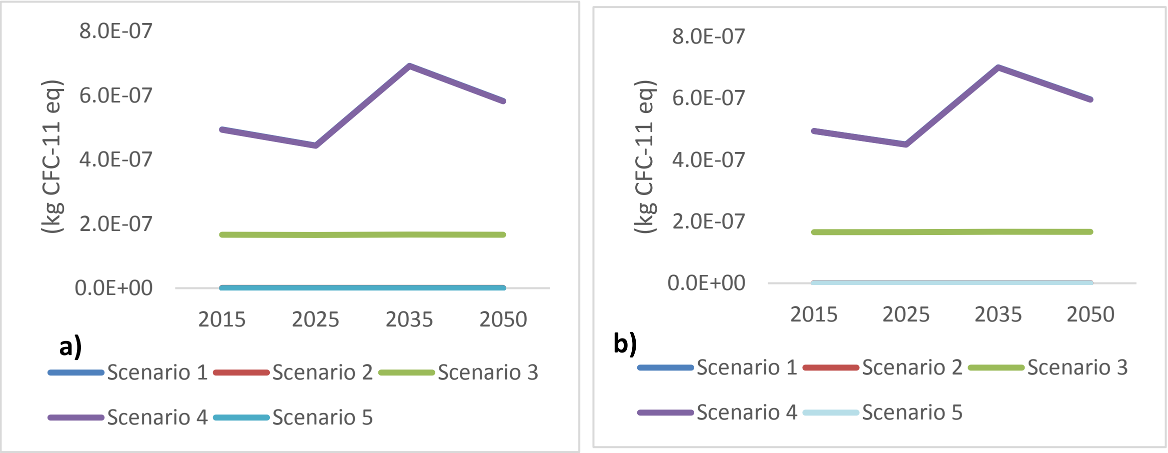


Figure 7.23 Stratospheric ozone depletion scores for urea scenarios using (2015-2050) projected grid mixes by the national grid and BEIS. a) Renewables two degrees (TD) electricity scenario b) renewables steady state (SS) electricity scenario.

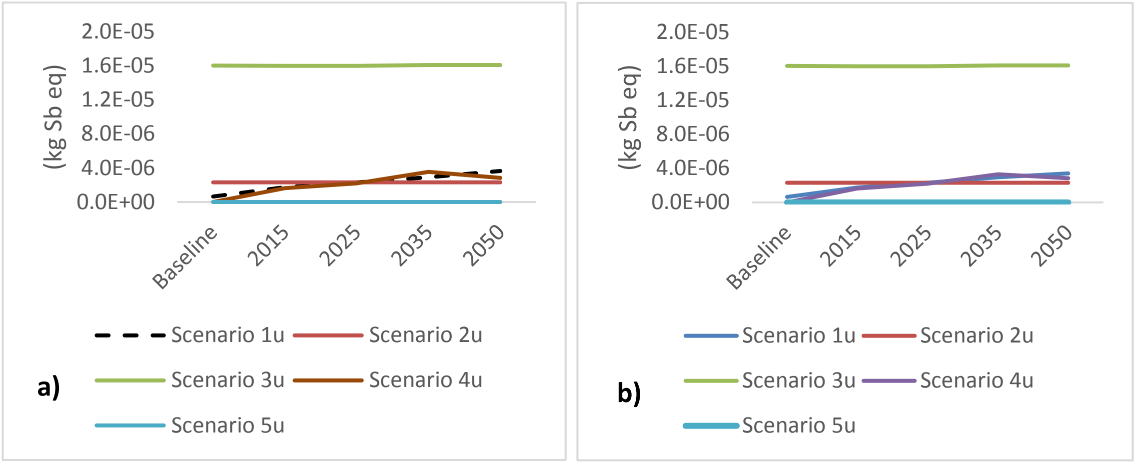


Figure 7.24 Abiotic depletion scores for urea scenarios using (2015-2050) projected grid mixes by the national grid and BEIS. a) Renewables two degrees (TD) electricity scenario b) renewables steady state (SS) electricity scenario.

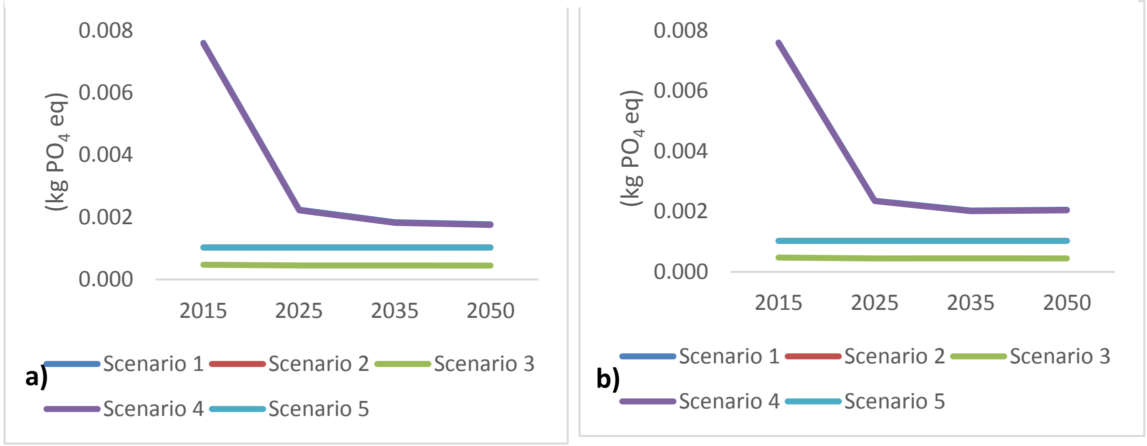


Figure 7.25 Eutrophication scores for urea scenarios using (2015-2050) projected grid mixes by the national grid and BEIS. a) Renewables two degrees (TD) electricity scenario b) renewables steady state (SS) electricity scenario.

7.3 Main utilities and costs for urea and methanol synthesis

Results in **Chapters 5** and **6** showed that utilisation systems are dependent on the environmental impacts of the utilities. This also has a direct impact on the overall operational costs. **Table 7.3** shows the costs considered in this work for each utility for all baseline scenarios. Gas and electricity costs are taken from UK statistics for the 4th quarter of 2016 (Department of Energy & Climate Change, 2016). Process and cooling water rates are the EU average for the year 2013 (European Commission, 2016). Water costs are set every three years in the UK (Ofwat, 2016), thus it is assumed that 2013 costs will cover up to 2016. Obtaining the price of electricity from wind power is more complicated than when the electricity is supplied from the grid; it depends on how it is traded in a region and there is no single price for wind-generated electricity (Krohn *et al.*, 2009). Therefore, for this analysis, the levelised cost of electricity (LCOE) was used to estimate CO_2 utilisation scenarios, as discussed in **Section 4.5.3**. The value in £/kWh was obtained from BEIS (2016b) for the year 2016, with medium capital costs for onshore wind <5 MW in the UK, and an average load factor of 32%.

Table 7.3 Process utilities costs for non-domestic consumers

Utilities	Size of consumer (MWh)	Cost
Gas (£/kWh)^1	2,778-27,777	0.10
Electricity grid mix (£/kWh)^1	2,000-19,999	0.02
Electricity wind power (£/kWh)^2	N/A	0.07
Process water (£/ton)^3	N/A	0.02
Cooling water (£/ton)^3	N/A	0.03

[1] Values from 4th quarter 2016 from (Department of Energy & Climate Change, 2016), including climate change levy [2] Values from BEIS (2016b), year 2016 with medium capital costs [3] Values from year 2013, EU average (European Commission, 2016)

Results for urea scenarios (**Table 7.4**) show a positive outlook for utilisation. Although electricity costs are much higher in all carbon dioxide utilisation (CDU) scenarios, fuel costs are lower or non-existent. In comparison, traditional ammonia and urea synthesis require large quantities of natural gas, thus off-setting the benefit of low electricity and water consumption. For utilisation, there is a cost-benefit from using the current electricity grid mix, but not an environmental one. The environmental- and cost-benefit could come from a scenario where the regulatory-price driven mechanisms are strong. (Refer to **Section 3.4** for more information). In all CO_2 utilisation scenarios, water electrolysis has the highest energy penalty; 63% to 66% of the electricity costs are linked to the electrolyser.

Table 7.4 Cost of main utilities for urea production in £/kg of product for all five baseline case scenarios (refer to Chapter 6 for a description).

Utilities	**Urea production case scenarios (£/kg of product)**				
	1	**2**	**3**	**4**	**5**
Electricity					
Compression	3.2 x 10^{-2}	3.2 x 10^{-2}	0.0	3.2 x 10^{-2}	3.2 x 10^{-2}
Electrolysis	0.1	0.4	0.0	0.1	0.4
CO_2 capture[1]	1.0 x 10^{-3}	1.0 x 10^{-3}	0.0	1.2 x 10^{-2}	1.2 x 10^{-2}
Ammonia synthesis	1.8 x 10^{-2}	1.8 x 10^{-2}	1.0 x 10^{-3}	1.8 x 10^{-2}	1.8 x 10^{-2}
Urea synthesis	1.7 x 10^{-2}	1.7 x 10^{-2}	6.0 x 10^{-3}	1.7 x 10^{-2}	1.7 x 10^{-2}
Sub-total	0.2	0.5	7.0 x 10^{-3}	0.2	0.5
Process and cooling water					
CO_2 capture	5.0 x 10^{-5}	8.0 x 10^{-5}	0.0	8.0 x 10^{-5}	8.0 x 10^{-5}
Electrolysis	5.0 x 10^{-5}	5.0 x 10^{-5}	0.0	5.0 x 10^{-5}	5.0 x 10^{-5}
Ammonia synthesis	0.0	0.0	3.0 x 10^{-5}	0.0	0.0
Sub-total	1.3 x 10^{-4}	1.3 x 10^{-4}	3.0 x 10^{-5}	1.3 x 10^{-4}	1.3 x 10^{-4}
Gas					
Urea synthesis	0.0	0.0	0.3	0.0	0.0
Ammonia synthesis	0.0	0.0	0.8	0.0	0.0
Sub-total	0.0	0.0	1.1	0.0	0.0
Total (£/kg NH_2CONH_2)	0.2	0.5	1.1	0.2	0.5

The results for methanol production (**Table 7.5**) show a less positive outlook than for urea, which is mainly due to:

- Increased hydrogen consumption required per kg of methanol produced using recovered CO_2
- Lower natural gas rates per kg of methanol produced through conventional production

Elevated hydrogen requirements have a strain on scenarios that depend on renewables (see **Section 7.3.2**). As this is the case with urea, only by using renewables can the process have less environmental impact than a conventional process. This becomes challenging when renewables (wind power in this case study) have higher costs than other fuels. While results are not directly comparable between levelised cost of electricity (LCOE) of wind and direct prices of electricity grid mix, it is useful for identifying these cost hotspots. For the direct air capture (DAC) process, there was no major overall cost increase associated with higher electricity consumption rates than with post-combustion capture. The use of renewable in utilisation processes is discussed further in **Sections 2.4.3** and **3.4**.

Table 7.5 Cost of main utilities for methanol production in £/kg of product for all five baseline case scenarios (refer to Chapter 6 for a description).

Utilities	**Methanol production case scenarios (£/kg of product)**				
	1	**2**	**3**	**4**	**5**
Electricity					
Compression	0.0	0.0	0.0	0.0	0.0
Electrolysis	0.3	0.8	0.0	0.3	0.8
CO_2 capture[1]	4.0×10^{-3}	4.0×10^{-3}	0.0	2.2×10^{-2}	2.2×10^{-2}
Other	3.0×10^{-5}	3.0×10^{-5}	0.0	3.0×10^{-5}	3.0×10^{-5}
Methanol synthesis	6.0×10^{-2}	6.0×10^{-2}	2.2×10^{-2}	5.9×10^{-2}	5.9×10^{-2}
Sub-total	0.3	0.9	2.0×10^{-3}	0.3	0.9
Process and cooling water					
CO_2 capture	1.7×10^{-4}	1.7×10^{-4}	0.0	1.7×10^{-4}	1.7×10^{-4}
Electrolysis	3.0×10^{-5}	3.0×10^{-5}	0.0	3.0×10^{-5}	3.0×10^{-5}
Methanol synthesis	0.0	0.0	2.0×10^{-5}	0.0	0.0
Sub-total	1.0×10^{-2}	1.0×10^{-2}	2.0×10^{-5}	1.0×10^{-2}	2.0×10^{-4}
Gas					
Methanol synthesis	0.0	0.0	0.5	0.0	0.0
Sub-total	0.0	0.0	0.5	0.0	0.0
Total (£/kg NH_2CONH_2)	0.3	0.9	0.5	0.3	0.9

7.3.2 Hydrogen production, renewables and associated costs

Hydrogen production through water electrolysis is energy intensive and can therefore lead to elevated costs (Sayah and Sayah, 2011; Boretti, 2013; Dincer and Acar, 2017). However, there are also several advantages to using an electrolyser: it has a flexible operation that can be controlled, it can eliminate direct emissions from grid-connected electrolysis and it eliminates extra requirements for stand-alone hydrogen facilities (Owen, 2016; Bazzanella, Ausfelder and DECHEMA, 2017). **Table 7.6** shows general system costs for average low-hydrogen production routes. These are the current costs according to Bazzanella & Ausfelder (2017); future predictions expect costs to lower for all technologies.

Table 7.6 Average system costs for low-hydrogen production routes

Hydrogen production routes	**Costs**	
	Current system costs	2030 costs projections
PEM-Electrolysis (€/kW)[1]	1,800-2,300	700
Alkaline Electrolysis (€/kW)[1]	1,000-1,200	600
High-temperature solid-oxide electrolysis (€/kW)[2]	2,000	1,000

[1](Bertuccioli *et al.*, 2014) [2] (Bazzanella, Ausfelder and DECHEMA, 2017)

A positive environmental impact of electrolytic production of hydrogen will depend on the energy source. While this is a challenge, there are steps towards connecting it to low carbon electricity sources. One of the main benefits of certain electrolysers is the availability to switch between the electricity grid and renewables on-site (Owen, 2016). This is a potential solution to managing production costs according to renewable energy availability.

Taking wind power as the baseline renewable energy source, hydrogen production can also serve as energy storage. One of the main limitations with wind power is that it is intermittent. There are days where there is no wind power available during peak hours but extra generation at night. There could also be a surplus of electricity during summer and a lack of it during winter (National Grid, 2017b). This leads to an imbalance in the grid that incurs extra costs. According to the National Grid, the cost of balancing the UK network in the years 2012 to 2013 amounted to £803 million pounds. Three main scenarios are discussed in which utilisation technologies and wind power could play different roles:

1.- The capacity of the National Grid did not support the intermittent renewable energy projection thus constraints costs continued. CO_2 utilisation processes will need to be balanced between the grid and renewable energy.

2.- All electricity is fed into the grid and there are no further constraints. Utilisation processes could be linked directly to the grid if the renewable energy mix is high.

3.- There is a range of intermittent electricity allowing CO_2 utilisation to operate with extra electricity.

The first scenario considers a case where wind power continues to be a strain to the National Grid, elevating the costs of electricity delivery. In this case, there is an opportunity for utilisation processes to take the renewable energy loads off the grid when there is a surplus. A mix of renewable and grid mix would suit this scenario.

The second possibility allows utilisation processes to connect only to the electricity grid, assuming a balance in supply and demand. This scenario would fit with the projections shown at the beginning of this section.

The third option considers a case where the utilisation process is supplied only by wind energy and assumes that there will be enough wind energy to supply the production rate regardless of intermittency. This seems the least likely scenario unless the main product was wind and utilisation is a by-product. If a product is not required all year long, as in the urea case study, there could be a case of matching renewable energy peaks to production seasons. This would require wind power (as an example) to peak during seeding season.

Finally, wind power costs in the UK are expected to decrease by 0.5 % over the next 20 years (BEIS, 2016b). Projections for the levelised cost of wind power in the UK from 2015-2030 are shown in **Table 7.7**. If this outlook is accurate, then it would continue to benefit urea production but not methanol, as seen in utilities costs results (**Table 7.4** and **Table 7.5)**.

Table 7.7 Projections for the levelised cost of electricity (LCOE) of electricity year 2015-2030 for onshore wind > 5 MW UK (BEIS, 2016b)

Capital cost £/MWh	**Levelised cost of electricity for onshore wind > 5 MW per year**			
	2015	2020	2025	2030
High	81	79	74	72
Medium	67	65	61	60
Low	50	49	46	45

7.4 Market for CO_2 utilisation product

Beyond the environmental and technical performance of a utilisation product, there must be a market to introduce this product. This section qualitatively assesses current and future trends for the supply and demand of methanol and urea. While there is no specific information available for a utilisation product, comparing it to the conventional product is a way to envision future scenarios.

Methanol

The global market for methanol was estimated at USD 31.02 billion in 2016, and is expected to grow within the next five years (BusinessWire, 2017). However, the market for methanol in the UK is small; according to BusinessWire (2017) it only takes up 4% of the overall demand in Europe. Petrochemical-based industries have been struggling in the UK; however, there is an increase in other applications that could revive the market. Alternative fuels, fuel cells and dimethyl ether (DME) are all options for the methanol market.

Methanol prices are currently lower than road fuels (see **Table 7.8**); this presents an opportunity for cheaper and cleaner fuels. According to Methanex (2017), the retail price for summer 2017 in Europe is set at € 0.2 per litre of methanol. Although costs have increased from last year, methanol prices tend to be stable.

Table 7.8 Comparison between the cost of methanol and road fuel in the UK for summer 2017

Cost	**Fuels in the UK**		
	Methanol[1]	**Petrol**[2]	**Diesel**[2]
		Ultra-low sulphur unleaded petrol	Ultra-low sulphur diesel
£/L	0.18	0.94	0.95

[1] Cost valid for Europe from July 1, 2017 to September 30,2017 (Methanex, 2017) [2] July 2017 average from Department for Environment Food and Rural Affairs (DEFRA) (2017b), excluding VAT

Even though retail costs for methanol are lower, there is still blending to consider. After purchase, methanol can either be transported to a refinery, to blend with gasoline, or transported directly to gasoline distribution terminals and blended when tanks are loading. For this second process, gasoline must be previously treated to ensure optimum performance (Methanol Institute, 2011). This would increase the final fuel price, but it is still expected to be lower than an only fossil-based fuel.

There is a push to move away from petrol and diesel vehicles to improve air quality. Alone in the UK, there is an intention to end conventional car sales by 2040 and reach zero emission vehicle levels by 2050 (Department for Environment Food and Rural Affairs (DEFRA), 2017a). Therefore, there are some constraints to using blended methanol and petrol.

While the utilisation market in the fuel transportation sector for pure methanol could reduce, there are other uses for methanol and overall worldwide demand is still growing. Worldwide demand reached 70 million tonnes by 2015, with 40% for use in emerging energy applications. According to the Methanol Institute (2017), approximately 200,000 tons of methanol per year are used as chemical feedstock or as transportation fuel. According to Statista (2017), imports reached a value of 201,506 million GBP in 2015 and exports reached 4,605 million GBP. Products like dimethyl ether (DME), alternative marine fuel, fuel cells and power generation are all new contributors to the worldwide energy sector (Methanol Institute, 2017).

Urea

Urea is one of the most produced chemicals in the world and is the most important nitrogen-based fertiliser. According to Stamicarbon (2017), more than 190 million tons of urea are produced each year and the demand is growing at over 3%. Out of the total amount produced, 80% of urea is used as fertiliser. Overall, urea prices have been on the rise since 2016. In the UK, urea supply relies mainly on imports from the European Union (EU). Import rates reached 21,037 million GBP in 2015; 99.9% of these were from the EU. Exports for the same year added up to 2,531 million GBP, mostly to the EU (Statista, 2017). With trade uncertainty due to Brexit, there is an opportunity to increase national fertiliser production; this includes alternative options such as CO_2 utilisation. Nitrogen-based fertiliser will continue to play an important role in agriculture, thus the market for urea will remain high.

For the specific process under study, the project is set to work at a small scale. According to the British Survey of Fertiliser practice (DEFRA, 2015), the general application rate of N-fertiliser in 2016 was 141 kg/ha (all tillage). For crops and grass, the application rate was 94 kg/ha. Over the last 30 years of the survey, the use rates have been within 140 to 150 kg/ha of total nitrogen use. The production rate for the utilisation scenarios in this work is set at 250 kg/day of urea. This provides enough fertiliser to supply the seeding season of a small farm. This would close a cradle to gate cycle for urea production, thus reducing intermediates, transportation, delivery and so on, which come with additional costs.

7.5 Human health impacts

The scope of a life cycle assessment (LCA) does not include a risk assessment, hence a hazards metric is used to calculate human toxicity potential (McKone and Hertwich, 2001). This work analyses initial indicators for detecting hotspots in CO_2 utilisation processes, thus the life cycle assessment (LCA) approach is applicable. The human toxicity impact category expresses the potential for health impacts by exposure of harmful agents by using an *exposure ratio* (Guinée *et al.*, 2001). General results for both urea and methanol scenarios are shown in **Figure 7.26** and **Figure 7.27.** The method stated in **Section 4.5.5** was used to generate these results.

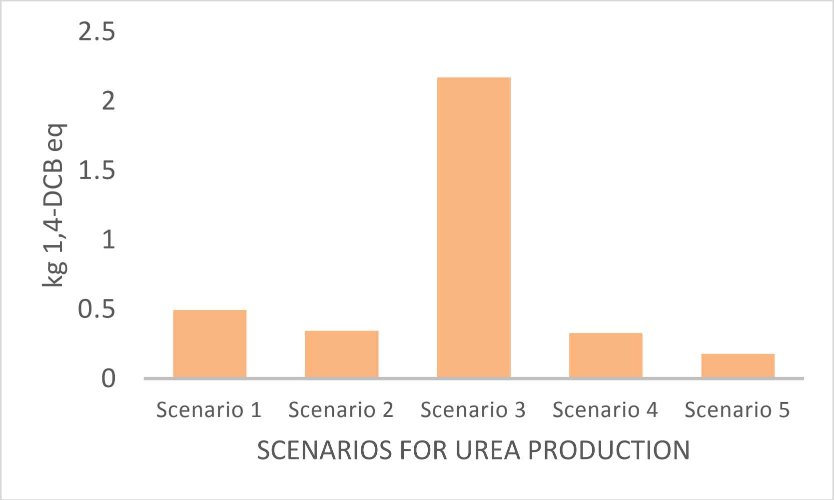


Figure 7.26 CML-IA general results for human toxicity scores using urea scenarios from Chapter 6.

For urea synthesis, there is a direct benefit from using any of the utilisation scenarios, which is linked to ammonia synthesis. In the UK, ammonia from the Haber-Bosh process has an impact of 1.25 (kg 1,4-DCB eq)/kg urea, compared to an average impact of 0.62 (kg 1,4-DCB eq)/kg urea for ammonia for utilisation. The use of natural gas in ammonia from the Haber-Bosch process is responsible for higher human toxicity scores.

Activities such as drilling, extracting and transporting natural gas lead to methane emissions through leakage. Methane emissions can cause health and air quality problems by being an O_3 precursor (Anenberg *et al.*, 2012). Tropospheric O_3 is a harmful pollutant that is linked to respiratory-related hospitalisations, asthma-related emergency room visits and premature human mortality (Melvin, Sarofim and Crimmins, 2016; Saari, Thompson and Selin, 2017). According to the Department for Environment Food and Rural Affairs (2017), in the UK, there has been a long-term increase in urban background ozone pollution between 2003 and 2016, but remains fairly stable.

Overall, by decreasing natural gas in urea production, there is an opportunity to reduce potential health impacts associated with methane emissions in the UK.

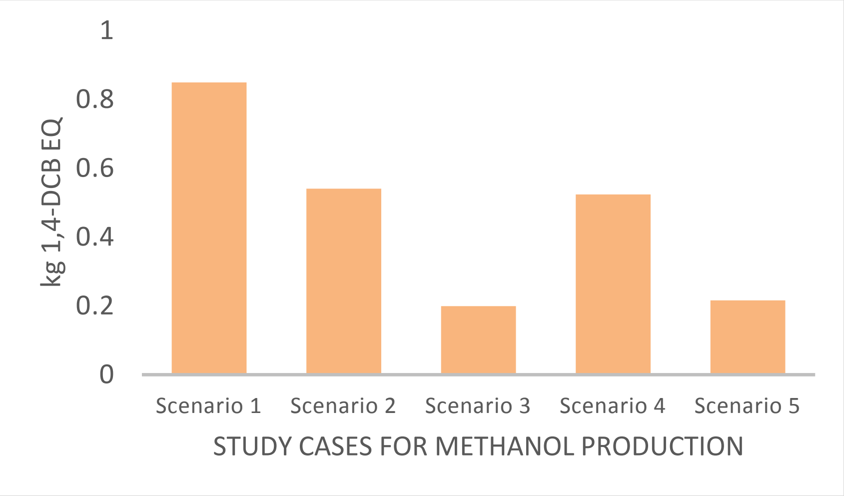


Figure 7.27 CML-IA general results for human toxicity scores using methanol scenarios from Chapter 5.

The result for methanol production is the opposite of those for urea scenarios; utilisation cases contribute to higher health impacts than for methanol from natural gas. This is the result of higher health impacts in post-combustion capture than in natural gas extraction and processing. For Scenarios 1 and 4, where the electricity grid mix is used, 50% of the human toxicity results are from the capture stage and 50% from electricity grid mix use. For the capture stage, 80% of the impacts are generated from CO_2 dehydration.

Ethylene glycol is a solvent used for CO_2 dehydration, and is produced by reacting ethylene oxide (EO) with water (Database from GaBi ts version 8.7.0.18). The effects on human health, according to the World Health Organization, include: intoxication for ingestion (which can lead to mortality), nasal and throat irritation following inhalation, and ocular and dermal irritation (WHO, 2004). However, some of these health effects have only been documented in small-scale trials. Ethylene glycol is not classified as a carcinogen.

To reduce the health impacts of methanol from CO_2 capture, a different dehydration process in combination with a decarbonised grid mix should be considered, as it is only the combination of the two that could lower the human toxicity scores for utilisation processes towards the result for the conventional process. Other dehydration alternatives that could be explored include: compression and cooling, adsorption using solid desiccants and cooling below the initial dew point (Abbas, Mezher and Abu-Zahra, 2013).

7.6 Main impacts for carbon utilisation

The assessment of CO_2 utilisation processes mainly focuses on their potential to transform CO_2, lower CO_2 emissions and displace raw materials. The aim is to design a process with less environmental impact than a fossil fuel-based process, which can also compete in the market. Ultimately, this aim is linked to the well-being of our society.

Providing a ‘more sustainable product’ is a way to ensure that not only future generations can have access to this product, but that they also suffer less from the impacts of its production. Therefore, selecting climate change and fossil fuel depletion as the main impacts also fit within a social perspective. Comparisons between gases and their global warming impact can be made, through the global warming score, and the security of hydrocarbons through conventional production routes can be measured using the fossil depletion score.

The effects of climate change in the UK according to the Met Office Hadley Center (2011) include the following projections:

- A strong food security for the next 40 years; however, this depends mainly on imports.
- A vulnerability to water stress in the south and south east of the UK, while the remaining of the UK is not predicted to be affected.
- Rainfall is expected to increase, especially in the winter months.
- A greater tendency towards increased flood risk, although international and national studies report different projections.
- A potential for major impacts on coastal flooding from sea level rise (LSR) by 2080, if no climate change mitigation is set in place.

This reiterates the benefits of a successful utilisation process that can contribute to mitigating the effects of climate change on either a small or larger scale. This will depend mostly on finding suitable decarbonised energy sources. Global warming and fossil depletion scores for each scenario under study were calculated in **Chapters 5** and **6**. A summary of the final score is shown again in **Table 7.9** and **Table 7.10**.

Table 7.9 Global warming scores for urea and methanol production, based on five case scenarios

Scenarios	**Urea production**	**Methanol production**
	(kg CO_2 eq)	(kg CO_2 eq)
1	6.0	9.2
2	2.5	2.1
3	3.8	2.2
4	6.10	9.6
5	2.6	2.4

Table 7.10 Fossil depletion scores for urea and methanol production, based on five case scenarios

Scenarios	**Urea production**	**Methanol production**
	(kg Oil eq)	(kg Oil eq)
1	1.9	3.0
2	0.8	0.9
3	1.4	1.4
4	1.9	3.0
5	0.9	1.0

7.7 Results for indicators for CO_2 utilisation with no aggregation/weighting

Through **Chapters 5** to **7**, quantitative and qualitative aspects of CO_2 utilisation processes have been assessed. To this point, the results are not weighted, normalised or aggregated in any form.

In this study the major environmental impacts assessed were fossil fuel depletion and global warming following the work done by Von der Assen & Bardow (2014), Assen *et al*. (2016) and Sternberg & Bardow (2015). The aforementioned studies agree that these two categories should form the basis of any primary screening for CO_2 based products. This work considers this as a reasonable basis for screening as unless the net outcome of the two categories is positive (i.e. fossil fuel depletion is reduced, and global warming impact is reduced) then the likelihood of the CO_2 based product having a more sustainable production is low.

The CML-IA and ReCiPe methods were chosen to assess these impacts. As discussed previously in **Chapter 4**, these methods were selected as they have been used in other published work such as Troy *et al*. (2016), von der Assen & Bardow (2014), Morales Mora *et al*. 2016, Sternberg & Bardow (2015) and Corsten *et al*. (2013) and are thus useful for comparing results. Other main environmental impacts from the CML-IA method were also assessed considering at “an initial screening level”, with this being open to further research if the focus shifts to determining specific characterisation factors for CO_2 utilisation. As of now, as part of the recommendations we suggest to utilise an established method such as CML-IA or ReCiPe, to screen potential environmental impacts at midpoint level as a starting point in the impact assessment.

In a second stage we suggest that once the environmental impact categories from established tools have been assessed at an initial screening level, the research should be dedicated to selecting environmental impacts using statistical analysis such as Monte Carlo simulations and fuzzy set theory, to determine the most sensitive impacts to change.

Table 7.11 and **Table 7.12** show a summary of the results for each scenario and each indicator under study. The first table only considers the results for baseline scenarios. The second table shows the changes between grid mix possibilities and year of consumption.

Only global warming and fossil fuel depletion impact categories are considered for the summary; however, all results are shown in **Section 7.2**.

The matrix created to assess the environmental impacts of the case studies follows the methodology stated in **Section 4.4** and **4.6**. The matrix considers the different process configurations in form of scenarios and the indicators for the environmental impact assessment.

With these results, scenarios can be compared in this graph, without further aggregation. Carbon hotspots can be detected as well as environmental benefits/drawbacks. The next chapter explores weighting methods and the benefits of analysing weighting results against un-aggregated values.

Table 7.11 Results of each indicator for methanol and urea synthesis baseline scenarios from Chapter 5 and 6.

Indicators	Methanol synthesis scenarios					Urea synthesis scenarios				
	1	**2**	**3**	**4**	**5**	**1**	**2**	**3**	**4**	**5**
Extra energy for capture (kWh/kg CO_2 captured)	0.1	0.1	N/A	0.8	0.8	0.1	0.1	N/A	0.8	0.8
Energy penalty for utilisation (kWh/kg utilisation product)	15.6	15.6	N/A	15.6	15.6	10.5	10.5	N/A	10.5	10.5
Renewable energy consumption ($kWh_{renewables}$/kg utilisation product)	N/A	12.7	N/A	N/A	12.7	N/A	6.6	N/A	N/A	6.6
Total energy consumption (kWh/kg final product)	15.7	15.7	4.6	16.4	16.4	10.6	10.6	11.1	11.3	11.3
Net CO_2 avoided (Kg CO_2/kg product)	-7.1	0.1	0	-7.3	0.5	-2.0	1.3	0	-2.1	1.2
Net CO_2 utilised (Kg CO_2/kg product)	1.4	1.4	0	1.4	1.4	0.7	0.7	0.7	0.7	0.7
CO_2 capture efficiency (%)	90	90	N/A	90	90	90	90	N/A	90	90
Global warming (kg CO_2 eq/kg product)	9.2	2	2.1	9.5	2.3	6	2.5	3.8	6.1	2.6
Eutrophication (kg PO_4 eq/kg product)	2.0 x 10^{-3}	1.0 x 10^{-3}	3.0 x 10^{-3}	3.0 x 10^{-3}	1.0 x 10^{-3}	1.7 x 10^{-3}	9.0 x 10^{-4}	6.8 x 10^{-3}	1.8 x 10^{-3}	9.0 x 10^{-4}
Acidification (kg SO_2 eq/kg product)	3.3 x 10^{-2}	1.1 x 10^{-2}	6.0 x 10^{-3}	3.5 x 10^{-2}	1.1 x 10^{-2}	2.1 x 10^{-2}	5.0 x 10^{-3}	1.5 x 10^{-2}	1.5 x 10^{-2}	2.2 x 10^{-6}
Stratospheric ozone depletion (kg CFC-11 eq/kg product)	1.3 x 10^{-9}	9.1 x 10^{-10}	1.6 x 10^{-7}	6.0 x 10^{-10}	1.4 x 10^{-10}	7.9 x 10^{-10}	5.6 x 10^{-10}	5.3 x 10^{-7}	3.8 x 10^{-10}	1.6 x 10^{-10}
Photochemical oxidation (kg ethylene eq/kg product)	2.0 x 10^{-3}	1.0 x 10^{-3}	1.0 x 10^{-3}	2.0 x 10^{-3}	1.0 x 10^{-3}	2.0 x 10^{-3}	6.0 x 10^{-4}	1.0 x 10^{-3}	2.0 x 10^{-3}	6.0 x 10^{-4}
Marine aquatic ecotoxicity (kg 1,4-DCB eq/kg product)	706.0	233.0	270.0	722.0	248.0	435.0	206.0	2,420.0	448.0	219.0

Indicators	**Methanol synthesis scenarios**					**Urea synthesis scenarios**				
	1	**2**	**3**	**4**	**5**	**1**	**2**	**3**	**4**	**5**
Freshwater aquatic ecotoxicity (kg 1,4-DCB eq/kg product)	1.5 x 10^{-2}	5.0 x 10^{-3}	8.3 x 10^{-2}	1.4 x 10^{-2}	4.0 x 10^{-3}	9.0 x 10^{-3}	9.0 x 10^{-3}	0.3	9.0 x 10^{-3}	4.0 x 10^{-3}
Terrestrial ecotoxicity (kg 1,4-DCB eq/kg product)	8.0 x 10^{-3}	3.0 x 10^{-3}	2.0 x 10^{-3}	9.0 x 10^{-3}	3.0 x 10^{-3}	9.0 x 10^{-3}	4.0 x 10^{-3}	3.2 x 10^{-2}	8.0 x 10^{-3}	4.0 x 10^{-3}
Human toxicity (kg 1,4-DCB eq/kg product)	0.8	0.5	0.2	0.5	0.2	0.5	0.3	2.2	0.3	0.2
Particulate matter (kg PM_{10} eq/kg product)	8.0 x 10^{-3}	3.0 x 10^{-3}	4.0 x 10^{-3}	8.0 x 10^{-4}	3.0 x 10^{-3}	5.0 x 10^{-3}	2.0 x 10^{-3}	5.0 x 10^{-3}	6.0 x 10^{-3}	3.0 x 10^{-3}
Fossil depletion (kg oil eq/kg product)	3.0	0.9	1.4	3.1	1.03	1.9	0.9	1.4	1.2	0.9
Abiotic depletion (kg Sb eq)/kg product)	1.1 x 10^{-6}	4.2 x 10^{-06}	6.5 x 10^{-7}	9 x 10^{-7}	4 x 10^{-6}	6.4 x 10^{-7}	2.3 x 10^{-06}	1.6 x 10^{-5}	5.4 x 10^{-7}	2.2 x 10^{-6}
Cost of utilities (£/kg of product)	0.3	0.9	0.5	0.3	0.9	0.2	0.5	1.1	0.2	0.5
Product demand worldwide (million tonnes/year)	NA	NA	70	NA	NA	NA	190	NA	NA	NA
CO_2 source availability < 0.2 Mt CO_2 (% in UK/total EU)	7.8	7.8	7.8	NA	7.8	7.8	7.8	7.8	7.8	7.8

*Check glossary list for full details

Table 2 Global warming (GW) and fossil depletion (FD) results for future CO_2 utilisation scenarios for methanol and urea synthesis, for baseline scenarios from Chapter 5 and 6, projections 2025 and 2050.

Indicators	Methanol synthesis scenarios										Urea synthesis scenarios									
	1		2		3		4		5		1		2		3		4		5	
	TD[1]	SS[2]	TD[1]	SS[2]	TD[1]	SS[2]	TD[1]	SS[2]	TD[1]	SS[2]	TD[1]	SS[2]	TD[1]	SS[2]	TD[1]	SS[2]	TD[1]	SS[2]	TD[1]	SS[2]
GW[3]$_{100}$ year 2025 ((kg CO_2 eq)/kg product)	4.2	4.3	2.1	2.1	0.7	0.7	4.5	4.6	2.3	2.3	2.9	3	2.5	2.5	3.7	3.7	2.3	3	2.5	2.5
GW[3]$_{100}$ year 2050 ((kg CO_2 eq)/kg product)	1.3	1.6	2.1	2.1	0.7	0.7	1.6	1.8	2.4	2.4	1.0	1.1	2.5	2.5	3.6	3.6	1.0	1.2	2.6	2.6
FD[3] year 2025 ((kg oil eq)/kg product)	1.9	2.0	1.0	1.0	0.9	0.9	1.1	1.1	1.0	1.0	1.2	1.3	0.9	0.9	1.4	1.4	1.3	1.3	0.9	0.9
FD[3] year 2050 ((kg oil eq) /kg product)	0.8	0.9	1.0	1.0	0.9	0.9	0.8	0.9	1.0	1.0	0.5	0.5	0.9	0.9	1.4	1.4	0.5	0.6	0.9	0.9

[1]Two degrees [2]Steady state [3]Global warming [4]Fossil depletion

7.8 Chapter seven summary

In this chapter other aspects that affect the production of CO_2 based products are assessed, focusing on renewable energy availability as well as other impacts. The aim of CO_2 utilisation is to design a process with a smaller environmental impact than a fossil fuel-based process that can also compete in the market. This is linked to the well-being of our society, by providing a 'more sustainable product'. This aim includes understanding how CO_2 availability will affect CO_2 utilisation. For this, industrial and electricity generation sources with ≤ 0.2 Mt CO_2 emissions/year in Europe were mapped. The results showed better opportunities for small-scale CO_2 capture in Western Europe. Specifically, in the UK, thirty-five registered small-scale industries were found that could supply CO_2 for a transformation process. After securing a CO_2 stream for utilisation, the next step was to assess the security of the energy source to power these processes. Scenarios were created to determine how renewable availability would affect impact results in the near future. While initial results in **Chapter 6** showed that using a baseline electricity grid mix generated higher impacts than conventional routes, future projections show that a de-carbonised grid can be used to power utilisation processes. The global warming score of urea scenarios drops below that of the conventional route by 2025, and by 2030 there is a further drop, with only wind power as an energy source. For methanol production, the analysis showed less favourable results. With the suggested electricity grid mix, the utilisation process is not competitive in terms of carbon avoidance at least until the year 2050.

Utilisation systems are dependent on the environmental impacts of utilities. This has a direct impact on the overall operational costs. For urea production, there is a cost-benefit from using the current electricity grid mix, but not an environmental benefit. In all CO_2 utilisation scenarios, water electrolysis has the highest energy penalty; between 63% and 66% of operational electricity costs are associated with the electrolyser. For methanol, there is currently no cost-benefit from using a CO_2 utilisation process. High levels of hydrogen required per kg of methanol and lower natural gas rates per kg of methanol from the conventional route makes current costs non-competitive. Other aspects that were assessed included the current market for methanol and urea. With a yearly demand of 70 and 190 million tonnes respectively, the market for the product is secure regardless of the feedstock. Human health impacts showed a benefit in switching to urea from recovered

CO_2 and a drawback when methanol is obtained from recovered CO_2. Higher health impacts are associated with post-combustion capture and related processes. Lastly, a summary of all indicator results is shown in **Table 7.11.**

7.9 Chapter seven reference list

Abbas, Z., Mezher, T. and Abu-Zahra, M. R. M. (2013) ‘CO2 purification. Part I: Purification requirement review and the selection of impurities deep removal technologies’, *International Journal of Greenhouse Gas Control*. Elsevier Ltd, 16, pp. 324–334. doi: 10.1016/j.ijggc.2013.01.053.

Anenberg, S. C., Schwartz, J., Shindell, D., Amann, M., Faluvegi, G., Klimont, Z., Janssens-maenhout, G., Pozzoli, L., Dingenen, R. Van, Vignati, E., Emberson, L., Muller, N. Z., West, J. J., Williams, M., Demkine, V., Hicks, W. K., Kuylenstierna, J., Raes, F. and Ramanathan, V. (2012) ‘Global Air Quality and Health Co-benefits of Mitigation Near-Term Climate Change through Methane and Black Carbon Emissions Controls’, *Environmental and Health Perspectives*, 120(6), pp. 831–839. doi: 10.1289/ehp.1104301.

von der Assen, N. and Bardow, A. (2014) ‘Life cycle assessment of polyols for polyurethane production using CO2 as feedstock: insights from an industrial case study’, *Green Chemistry*, 16(6), p. 3272. doi: 10.1039/c4gc00513a.

von der Assen, N., Müller, L. J., Steingrube, A., Voll, P. and Bardow, A. (2016) ‘Selecting CO2 Sources for CO2 Utilization by Environmental-Merit-Order Curves’, *Environmental Science and Technology*, 50(3), pp. 1093–1101. doi: 10.1021/acs.est.5b03474.

Bazzanella, A. M., Ausfelder, F. and DECHEMA (2017) *Technology study: Low carbon energy and feedstock for the European Chemical Industry*. Frankfurt.

BEIS (2016a) *Digest of United Kingdom Energy Statistics (DUKES) 2016*.

BEIS (2016b) *Electricity generation costs*.

BEIS (2017) *UPDATED ENERGY AND EMISSIONS PROJECTIONS 2016*.

Bertuccioli, L., Chan, A., Hart, D., Lehner, F., Madden, B. and Standen, E. (2014) ‘Study on development of water electrolysis in the EU’, *Fuel Cells and hydrogen Joint Undertaking*, (February), pp. 1–160. Available at: http://www.fch-ju.eu/sites/default/files/study electrolyser_0-Logos_0_0.pdf.

BIS (2015) ‘Industrial Decarbonisation & Energy Efficiency Roadmaps to 2050: Cross Sector Summary’, (March), p. 31.

Boretti, A. (2013) ‘Renewable hydrogen to recycle CO2 to methanol’, *International Journal of Hydrogen Energy*. Elsevier Ltd, 38(4), pp. 1806–1812. doi: 10.1016/j.ijhydene.2012.11.097.

BusinessWire (2017) *Global Methanol Market 2016-2021: Growing Petrochemicals Demand & Development of New Industrial Sectors is Driving Growth - Research and Markets*.

Corsten, M., Ramírez, A., Shen, L., Koornneef, J. and Faaij, A. (2013) ‘Environmental impact assessment of CCS chains – Lessons learned and limitations from LCA literature’, *International Journal of Greenhouse Gas Control*. Elsevier Ltd, 13, pp. 59–71. doi: 10.1016/j.ijggc.2012.12.003.

Database, E.-P. (2014) *CO2 emission data*.

DEFRA (2015) ‘The British Survey of Fertiliser Practice - Fertiliser use on farm for the 2014 crop year’, (April), p. 6.

Department for Environment Food and Rural Affairs (DEFRA) (2017) ‘Department for Environment, Food and Rural Affairs : Air Quality Statistics in the UK’, *Defra National Statistics Release: Air Quality Statistics in the UK 1987 to 2016*, (April), pp. 1–17.

Department for Environment Food and Rural Affairs (DEFRA) (2017) ‘UK plan for tackling roadside nitrogen dioxide concentrations’, (July).

Department for Environment Food and Rural Affairs (DEFRA) (2017) *Weekly Road Fuel Prices*.

Department of Energy & Climate Change (2016) ‘Quarterly energy prices tables. Annex, June 2016’, (MARCH).

Dincer, I. and Acar, C. (2017) ‘Innovation in hydrogen production’, *International Journal of Hydrogen Energy*. Elsevier Ltd, 42(22), pp. 14843–14864. doi: 10.1016/j.ijhydene.2017.04.107.

European Commission (2016) *Production costs from energy-intensive industries in the EU and third countries*. doi: 10.2790/79502.

Guinée, J. B., Gorrée, M., Heijungs, R., Huppes, G., Kleijn, R., De Koning, A., Van Oers, L., Sleeswijk, A. W., Suh, S. and Udo de Haes, H. A. (2001) *Life Cycle Assessment-An operational guide to the ISO standards Part 2A*.

Krohn, S., Morthorst, P.-E., Awerbuch, S. and The European Wind Energy Association (2009) ‘The Economics of Wind Energy’, *International Journal of Energy Technology and Policy*, 3(1/2), p. 158. doi: 10.1504/IJETP.2005.006769.

McKone, T. E. and Hertwich, E. G. (2001) ‘The Human Toxicity Potential and a strategy for evaluating model performance in Life Cycle Impact Assessment’, *International Journal of Life Cycle Assessment*, 6(2), pp. 106–109. doi: 10.1007/BF02977846.

Melvin, A. M., Sarofim, M. C. and Crimmins, A. R. (2016) ‘Climate Benefits of U.S. EPA Programs and Policies That Reduced Methane Emissions 1993-2013’, *Environmental Science and Technology*, 50(13), pp. 6873–6881. doi: 10.1021/acs.est.6b00367.

Met Office Hadley Center (2011) *Climate: Observations, projections and impacts*.

Methanex (2017) *Methanex posts regional contract methanol prices for North America, Europe and Asia*.

Methanol Institute (2011) *Methanol gasoline blends: Alternative Fuel for Today’s Automobiles and Cleaner Burning Octane for Today’s Oil Refinery*.

Methanol Institute (2017) *The Methanol Industry*.

Morales Mora, M. a., Vergara, C. P., Leiva, M. a., Martínez Delgadillo, S. a. and Rosa-Domínguez, E. R. (2016) ‘Life cycle assessment of carbon capture and utilization from ammonia process in Mexico’, *Journal of Environmental Management*. Elsevier Ltd, 183, pp. 998–1008. doi: 10.1016/j.jenvman.2016.09.048.

National Grid (2016) ‘Future Energy Scenarios 2016’, (July), pp. 1–194.

National Grid (2017a) ‘Future Energy Scenarios (FES)’, (July).

National Grid (2017b) *National Grid*.

Ofwat (2016) *Business retail price review 2016 : final determinations*.

Owen, R. (2016) ‘Personal communication’.

Saari, R. K., Thompson, T. M. and Selin, N. E. (2017) ‘Human Health and Economic Impacts of Ozone Reductions by Income Group’, *Environmental Science & Technology*, p. acs.est.6b04708. doi: 10.1021/acs.est.6b04708.

Sayah, A. K. and Sayah, A. K. (2011) ‘Wind-hydrogen utilization for methanol production: An economy assessment in Iran’, *Renewable and Sustainable Energy Reviews*. Elsevier Ltd, 15(8), pp. 3570–3574. doi: 10.1016/j.rser.2011.05.013.

Stamicarbon (2017) *Urea facts*.

Statista (2017) *Statista The portal for statistics*.

Sternberg, A. and Bardow, A. (2015) ‘Power-to-What? – Environmental assessment of energy storage systems’, *Energy Environ. Sci.*, pp. 389–400. doi: 10.1039/C4EE03051F.

Troy, S., Schreiber, A. and Zapp, P. (2016) ‘Life cycle assessment of membrane-based carbon capture and storage’, *Clean Technologies and Environmental Policy*. Springer Berlin Heidelberg, 18(6), pp. 1641–1654. doi: 10.1007/s10098-016-1208-x.

WHO (2004) ‘Concise International Chemical Assessment Document Ethylene glycol: Human Health Aspects’, 61.

8 Multi Criteria Decision Analysis (MCDA) and General Discussion

This chapter interprets the environmental impacts by analysing and presenting them in a format that will guide the decision maker. With this, the decision maker can compare between scenarios and alternatives for better understanding of a process. The conceptual framework includes a multi criteria decision analysis (MCDA) method to rank all scenarios, based on the methodology from **Section 4.6**. An equal weights approach and a specific rank using simple attribute tanking technique (SMART) was used to compare results and show the applicability of the framework. This chapter also provides a final and general discussion of the work done by the author.

8.1 Equal weighting of results using Multi Value Attribute Theory (MVAT)

A matrix for scenario analysis with un-aggregated results was created. This matrix can be found in **Appendix VII**. It includes all baseline and future electricity grid mix scenarios. The results were ranked using equal weights for all quantitatively measurable indicators. The values showed repeated ranks, this was due to the similarities of the future electricity grid mixes.

For this section and for clarity of results, only the baseline scenarios were considered. By using the baseline cases, an indication on how a decision-making step can be applied to a CO_2 utilisation process is shown. Fifteen out of twenty indicators were ranked. The other five indicators are descriptive of the process and are considered within other impacts. The weight of each indicator was set at 6.6%.

The scenarios for each production route are:

Methanol and Urea

*1a** Post-combustion capture unit from subcritical PC (pulverised coal) power plant + utilisation product synthesis + hydrogen from water electrolyses powered by the electricity grid

*2a** Post-combustion capture unit from subcritical PC (pulverised coal) power plant + utilisation product synthesis + hydrogen from water electrolyses powered by wind power

*3a** Non-utilisation route for product synthesis

*4a** Direct air capture unit for CO_2 supply + utilisation product synthesis + hydrogen from water electrolyses powered by the electricity grid

*5a** Direct air capture unit for CO_2 supply + utilisation product synthesis + hydrogen from water electrolyses powered by wind power

Table 8.1 shows the weighted results for methanol scenarios. A rank repetition occurs in scenarios where the energy mixes are the same (Scenario 1a and 4a, 2a and 5a).

Table 8.1 Multi criteria decision analysis (MCDA) results with equal weighting for methanol scenarios

Indicators	**Scenarios**					
	1a	**2a**	**3a**	**4a**	**5a**	**Weight (%)**
Net CO_2 avoided	5	1	4	2	2	6.6
Net CO_2 utilised	1	1	5	1	1	6.6
Global warming	5	1	2	3	3	6.6
Eutrophication	4	1	5	1	1	6.6
Acidification	5	2	1	2	2	6.6
Stratospheric ozone depletion	4	3	5	1	1	6.6
Photochemical oxidation	5	1	3	3	1	6.6
Marine aquatic eco-toxicity	5	1	4	2	2	6.6
Freshwater aquatic eco-toxicity	4	3	5	1	1	6.6
Terrestrial eco-toxicity	5	2	1	2	2	6.6
Human toxicity	5	4	1	1	1	6.6
Particulate matter	5	2	1	2	2	6.6
Fossil depletion	5	1	4	2	2	6.6
Abiotic depletion	2	4	1	5	3	6.6

Indicators	**Scenarios**					
	1a	**2a**	**3a**	**4a**	**5a**	**Weight (%)**
Utilities costs	2	4	1	3	5	6.6
Total	4	2	3	3	2	N/A
Rank	**5**	**2**	**3**	**4**	**1**	N/A

Figure 8.1 shows the graph with the final rankings, where the lower the value, the better the scenario (with lower impacts). The graph shows Scenario 5 and 2 as the best options. These results show a better overall score for this CO_2 based product than when the results are un-aggregated (as seen at the end of **Chapter 7**).

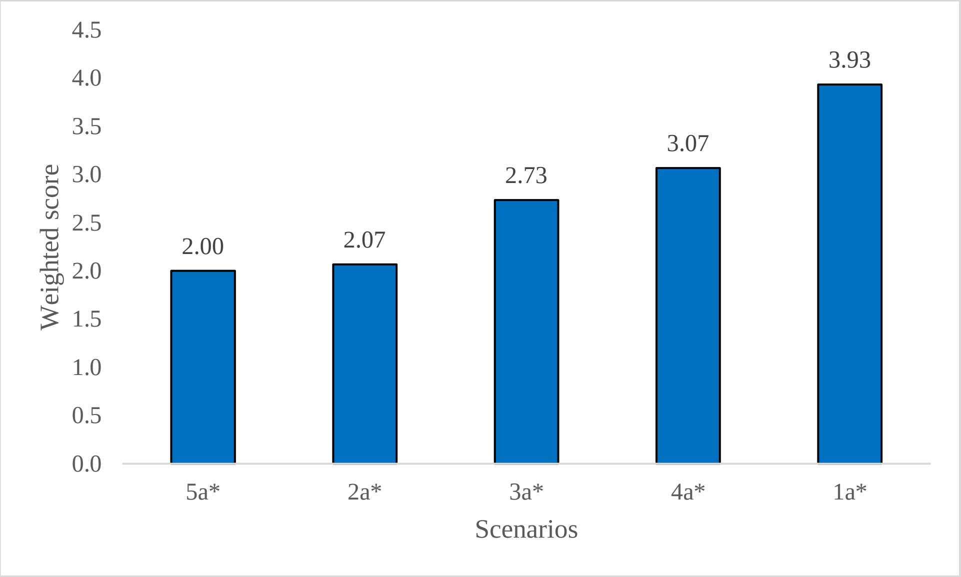


Figure 8.1 Ranking of methanol scenarios with equal weighted score

Table 8.2 shows the weighted results for urea scenarios. As is the case with methanol, there is also rank repetition on some indicators due to the use of the same electricity mixes. The rank repetition is seen in Scenarios 1a and 4a, 2a and 5a.

Figure 8.2 shows the graph with the final ranks; the overall results are consistent with the individual indicators. The scenarios with the most CO_2 utilisation potential are the ones connected to renewable sources. There was no major difference between changing the CO_2 capture route. The conventional route overall has the least favourable score despite having lower global warming and fossil depletion scores than scenarios 1 and 4. The same was found with methanol, these results show a better general score for this CO_2 based product than when calculated un-aggregated (Shown in **Chapter 7**).

Table 8.2 Multi criteria decision analysis (MCDA) results with equal weighting for urea scenarios

Indicators	**Scenarios**					
	1a	**2a**	**3a**	**4a**	**5a**	**Weight (%)**
Net CO_2 avoided	4	1	3	5	2	6.6
Net CO_2 utilised	1	1	5	1	1	6.6
Global warming	4	1	3	5	2	6.6
Eutrophication	3	1	5	4	1	6.6
Acidification	5	2	3	3	1	6.6
Stratospheric ozone depletion	4	3	5	2	1	6.6
Photochemical oxidation	4	1	3	4	1	6.6
Marine aquatic eco-toxicity	3	1	5	4	2	6.6
Freshwater aquatic eco-toxicity	2	2	5	2	1	6.6
Terrestrial eco-toxicity	4	1	5	3	1	6.6
Human toxicity	4	3	5	2	1	6.6
Particulate matter	3	1	3	5	2	6.6
Fossil depletion	5	1	4	3	2	6.6
Abiotic depletion	2	4	5	1	3	6.6
Utilities costs	1	3	5	1	4	6.6
Total	3.2	1.7	4.3	3	1.7	N/A
Rank	**4**	**2**	**5**	**3**	**1**	N/A

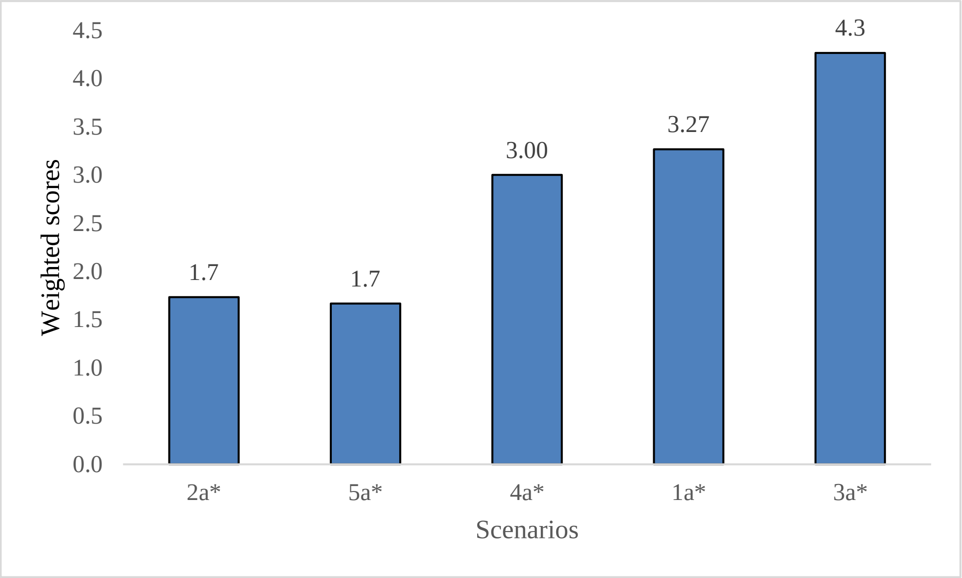


Figure 8.2 Ranking of urea scenarios with equal weighted score

8.2 Specific weighting of the environmental impact results

As stated in the ILCD handbook (European Commission 2010), specific weighting can support the interpretation of a study. However, it can only serve as a sensitivity analysis and not as a comparative study intended for public viewing.

In the case of CO_2 utilisation, global warming and fossil fuel depletion are the main impacts assessed (as discussed previously in **Chapter 3** and seen in studies such as Sternberg & Bardow (2015)). It is therefore suggested in this work, that all environmental assessments of CO_2 utilisation should include a weighting factor for a minimum of global warming and fossil fuel depletion impacts. These results can be used for sensitivity analysis and are of interest for the CO_2 utilisation area as life cycle assessment studies are increasingly used as decision support tools. A similar approach was found for ranking electricity scenarios in Santoyo-Castelazo & Azapagic (2014) and the fundamentals are taken as basis for the approach taken in this work. A simple multi attribute rating technique (SMART) was used to assign and apply the weight of the impacts. The assessment with the assigned weights is shown in **Appendix VII**. The decision makers in this worked example are the author and the research group involved. This streamlined group was used for the completion of a “proof a concept” study. This shows the applicability and validity of the decision step in the conceptual framework for impact assessment. For future work, it is envisioned that the involvement of a larger group of stakeholders in the decision-making process would be beneficial in ensuring a more robust outcome. A smaller group was used to meet the time constraints of this study as a more extensive stakeholder engagement stage fell outside of the scope of this project (with proof of concept being the major aim). This does show a limitation in the stakeholder approach as it requires increased engagement from a larger, targeted working group.

Weighted rank

This ranking included the general weighted score of each case study after applying the simple multi attribute rating technique and is shown in **Figure 8.3**. For both methanol and urea the scenarios were ranked in similar order where the best cases were the alternatives connected to renewable energy. The worst scenarios for methanol were the CO_2 based processes coupled to the electricity grid. The worst case for urea production was the conventional route option.

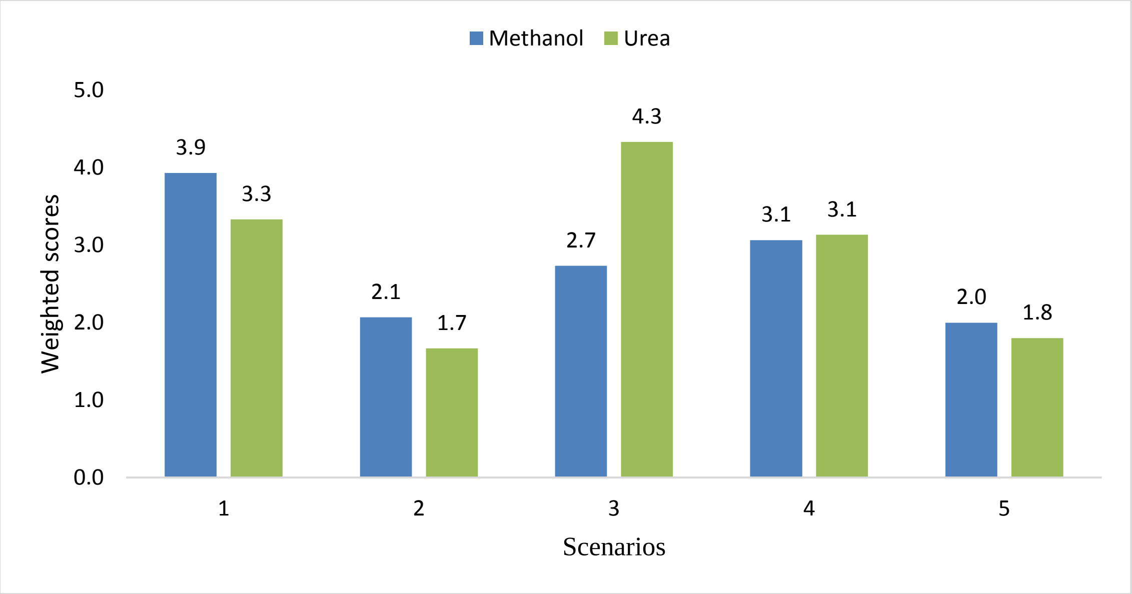


Figure 8.3 Overall weighted results for methanol and urea case studies

Weights assigned to global warming

Two weights were assigned to global warming scores. In the first, global warming is given 100% relevance and the rest of the impacts are given 25% (little relevance). Results for methanol and urea alternatives (**Figure 8.4**) do not change from the weighted rank case shown previously (**Figure 8.3**).

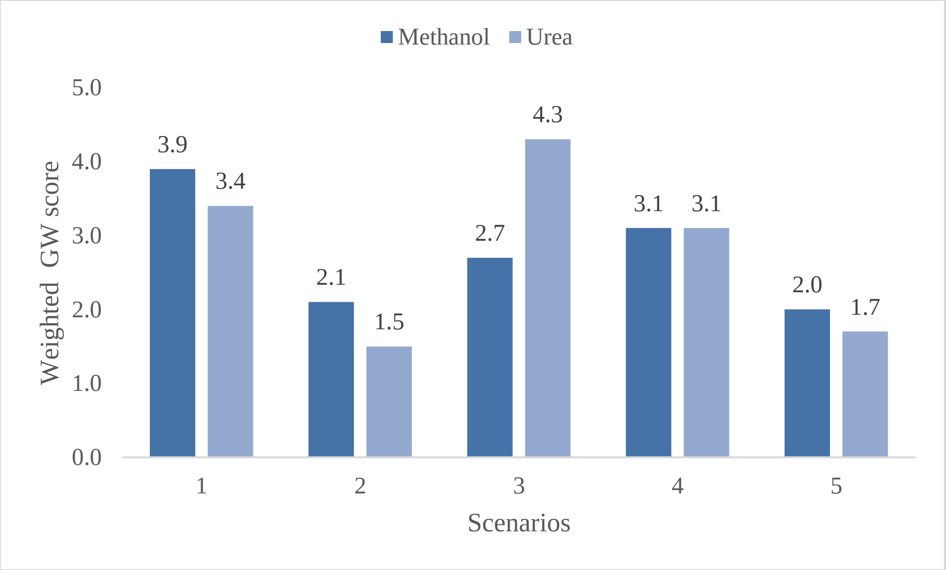


Figure 8.4 Global warming (GW) weighted scores for methanol and urea case studies, 100:25 weight

The second weight considers a case where global warming has 100% relevance and the rest of the impacts have 0% (no relevance). Results in **Figure 8.5** show closer results between CO_2 utilisation processes and conventional production routes. However, the number one ranked scenario is still a CO_2 utilisation process coupled with renewables for both products. Any other weight combination will give the same result as with a 100:25 ratio.

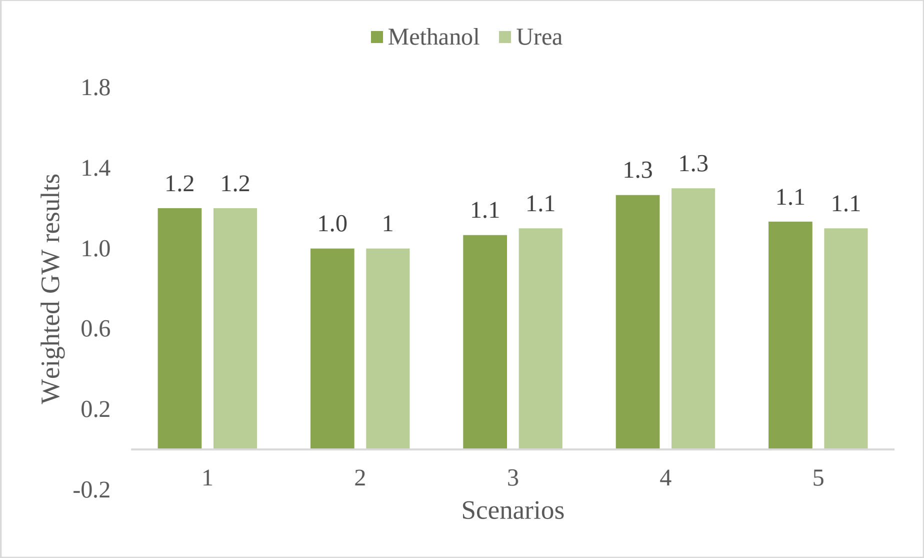


Figure 8.5 Global warming (GW) weighted scores for methanol and urea case studies, 100:0 weight

Fossil fuel depletion weights

The same weights were assigned to both global warming and fossil depletion scores. **Figure 8.6** shows the results for the 100:25 ratio weight Methanol and urea ranks do not change with this weight ratio and remain the same as the initial weighted ranks case (**Figure 8.3**).

Figure 8.6 Fossil depletion (FD) weighted scores for methanol and urea case studies, 100:25 weight

Results in **Figure 8.7** show for the second weight ratio considered; fossil depletion with 100% relevance and the rest with 0% (no relevance). For methanol and urea production, CO_2 utilisation coupled with renewables are the best cases. The worst case for methanol is CO_2 utilisation coupled with the electricity grid mix. For urea, the worst case is a conventional production process.

Figure 8.7 Fossil depletion potential (FD) weights for methanol and urea case studies, 100:0 weight

8.2.1 Comparison of all weights

Methanol

Six different weights were used to analyse the sensitivity of the results. These results are summarised in **Table 8.3**. Overall, the scenario with direct air capture (DAC) and renewables for hydrogen production has the lowest impacts in 66% of the cases. The case with the highest impacts is a combination of post-combustion capture and hydrogen production connected to the electricity grid mix. The conventional process is mostly stable with comparably average impacts. Changes in the ranking order can also be seen in scenarios with 100% relevance compared to 0% no relevance.

Table 8.3 Summary of methanol production weighting results for each case study and each weight variable

Weight	**Scenario**				
	1a*	***2a****	***3a****	***4a****	***5a****
Equal weights	5	2	3	4	1
Weighted ranks	5	2	3	4	1
GW^1 weight 100:25	5	2	3	4	1
GW^1 weight 100:0	4	1	2	5	3
FD^2 weight 100:25	5	2	3	4	1
FD^2 weight 100:0	4	1	3	5	2

^{1}Global warming ^{2}Fossil depletion

Urea

The summary of weighted results for the urea case studies is shown in **Table 8.4**. The sensitivity levels are lower than for methanol production. 83% of the weight variables have post-combustion capture and hydrogen production from renewables as the case study with the lowest impacts. 66% of the weighting options have the conventional route as the case study with the highest impacts.

Table 8.4 Summary of urea production weighting results for each case study and each weight variable

Weight	**Scenario**				
	1a*	**2a***	**3a***	**4a***	**5a***
Equal weights	4	2	5	3	1
Weighted ranks	4	1	5	3	2
GW^1 weight 100:25	4	1	5	3	2
GW^1 weight 100:0	4	1	3	5	2
FD^2 weight 100:25	4	1	5	3	2
FD^2 weight 100:0	5	1	4	3	2

^{1}Global warming ^{2}Fossil depletion

8.3 General uncertainties and discussion points

Multi criteria decision analysis (MCDA)

The major uncertainty in the ranking system is the weight of the ranks. These are decided by a set of questions proposed by the author and discussed with the research group involved. Although the research group has experience in CO_2 utilisation, the study would benefit from a larger group of stakeholders and stakeholder engagement such as industrial experts, policy makers and other academics/consultants. The results are as expected; the best CO_2 utilisation scenarios are the ones connected to renewable energy. While this ranking system is practical and easy to implement, currently it can only be applied to measurable results. This left five indicators out that although discussed, were not in the final ranking system and did not contribute to calculating the CO_2 utilisation potential. In future work, fuzzy set theory will be applied to translate the linguistic values to numerical.

Although final scenario rankings were similar for both products, the net impacts were not. Urea production has lower environmental impacts than methanol through CO_2 utilisation. Since the ranking systems compare similar traits (renewable, vs non-renewable, post-combustion capture vs direct air capture), the rank results are still similar. This method is not applicable to comparing utilisation products versus CO_2 utilisation products if the final product is not the same. Hence, this framework can be applied to CO_2 utilisation versus non-CO_2 utilisation or CO_2 utilisation versus CO_2 utilisation if the end-product is the same.

Study boundaries

Although this point has been discussed in **Chapter 3** and **4**, it is important to state it once more: the boundaries of a study will depend on the final product and what is it being compared to. This is no different for CO_2 utilisation technologies. There are efforts to unify the outcome of the studies to make them more comparable. However, this will only work within the same boundary: cradle to gate, gate to gate, etc. This will depend on the final use of the CO_2 based product, whether it is a chemical, fuel or material. As of now, in this work it is suggested to use cradle to gate since the end-product is the same for methanol and urea when produced by both CO_2 utilisation and conventional routes. This does not negate the temporary storage CO_2 issue as it is acknowledged that from gate to grave the impacts will be the same for both CO_2 based and conventional products. The focus of this boundary is to detect any environmental benefit/drawback of producing a CO_2 based chemical compared to ca conventional chemical.

Data limitations

The uncertainty of results (**Section 5.4** and **6.4**) increases when data availability is limited. This difference in uncertainty can be seen between methanol and urea case studies. Methanol is based on literature available, while urea is a mix of simulations, data provided by the stakeholder and literature. Although there are final results for both cases, the methanol results are much more conservative. It is useful to see how both case studies can be analysed within their own limitations and how the assessment method is flexible enough to tailor for each case. They are both worked examples that show the applicability of the framework developed.

For a final interpretation, only the baseline scenarios were fully assessed. These scenarios included two main capture routes. While these are not the only ones, they do represent two of the biggest capture concepts: CO_2 from fixed point sources and from direct air capture, hence the decision to assess these. Within these areas, many processes can be assessed, and some are use to investigate sensitivity in this work too analysed in this work. By using the two capture routes, a general picture of CO_2 utilisation was created, allowing for general comparisons and the development of an environmental impact assessment framework. The main limitation encountered was that the capture routes are not at the same research stage/ TRL and data was not evenly available for both processes. Sensitivity analyses were used to determine how this would change final impacts, but the results were negligible at a broader scope.

Other data differences include transportation. The methanol case studies include CO_2 transportation for 500 km through a pipeline. Urea cases do not include any form of transport. This showed the CO_2 transport contributions to the CO_2 utilisation potential. The impacts were too small to have a significant impact on the overall environmental impact values. In practice, if the information is available, it should be included. Other data limitations can include the optimisation of the processes such as heat integration. If they are not considered in this environmental impact assessment, then it is assumed that the results are operating from a non-optimised scenario. This leaves optimisation to the process engineer/optimiser to make the changes necessary and the LCA practitioner to assess the process as many times as required. For future work, the framework will include guidelines for assessing the CO_2 utilisation process according to the development stage of the process.

Electricity outlook

There are two main uncertainties with the electricity scenarios created. The first is extrapolating grid mix to the year 2050. A more accurate approach collects data for this year, but this data would have been an approximation in itself. Nevertheless, this uncertainty was accepted as one of the many future possibilities. This also led to an inclusion of several databases and projections to create the scenarios. As the number of projections used increased, the outcome had higher variance. This is seen in the disparity of the results between the baseline scenario and the projections from literature. This is attributed to using different electricity mixes. Baseline cases use commercial life cycle assessment datasets and the projections use information from the National Grid and BEIS. The timeframes of both datasets are not equal. To overcome this, the scenario planning approach was used, where there is no one solution, but a series of potential options. Therefore, it is the general trends that are useful for interpretation.

Utilities

This work considers utility costs for all case studies. These results are comparable except for renewable energy cost (wind power). Because of the way renewable energy is charged, there is no average cost that can be used for a general assessment. Therefore, the levelised cost of electricity (LCOE) was used instead. While this gives an initial insight of the costs of CO_2 utilisation, the uncertainty level is high and still needs to be addressed at macro-economic scale. This is an initial attempt to develop a life cycle costing method and is an important part of the proposed future work.

CO_2 captured as waste, non-waste or by product

Is captured carbon dioxide a waste, a non-waste or by-product? After revising the waste regulations set in place by the Waste Framework Directive (see **Section 3.4**), the objective is to ensure that carbon dioxide can be a non-waste flow after capturing. This means that the CO_2 stream should have a marketable value, be of certain use and comply with health and environmental regulations. Before capturing, the source of carbon dioxide (i.e. flue gases) will be considered a waste as it is a substance or object that is discarded. It is what happens after capturing that will determine its legal state. Whilst considering CO_2 as a by-product would be ideal, this is not possible unless it can be used directly without further processing prior to its use. If there is a capture stage, CO_2 will not be a product. This leaves the possibility to explore processes that use direct flue gas utilisation, in which the flue gas could potentially act as a by-product.

There is also the question whether utilising carbon dioxide is a recovery, recycling or reuse process. Again, the Waste Framework Directive (WFD) has clear definitions on each of these terms and when to apply them. A recovery definition seems to be aligned with carbon capture; waste that can serve a useful purpose by replacing other materials to fulfil a function. In this instance, the CO_2 capture method would be considered a recovering process. While it is tempting to also use the term CO_2 recycling, the original substance (i.e. flue gas) or object did not have an original purpose; hence, recycling is not a correct term. The last term is re-use, which is any product or component that is used again. Since the CO_2 was not used before in any form, this is also would be an incorrect term. To clarify the situation, the following statement was made:

> *"CO_2 captured for carbon dioxide utilisation processes is considered a non-waste substance obtained through a recovery process that aims to replace conventional materials to conserve natural resources and help create a marketable end-product."*

CO_2 utilisation and EU Emissions Trading Scheme (EU ETS)

To qualify in the trading scheme, carbon dioxide utilisation would need to be a legitimate low carbon technology. This reiterates the importance of having environmental assessments that can help prove its contribution towards meeting emission reduction targets. This also means that utilisation technologies would need to be operational at large scale if they are to play a role in carbon trades. There is also an interest in whether only the recovered carbon dioxide could contribute in the emissions trading scheme. At this moment and at a basic level, CO_2 would only contribute to the EU emission trading scheme (EU ETS) if it can reduce its carbon allowance needs. This means that the capturing and/or utilisation process would have a contribution to the program only if it is at least carbon neutral.

Comparability with other studies

The most important research gap found in this area is the lack of comparability of life cycle assessment results for CO_2 utilisation processes. It is difficult to express the benefits and drawbacks of utilisation system when there are no basic guidelines to follow. Through this work, a set of indicators and a ranking system are presented that will facilitate the interpretation of results. While un-aggregated results should be presented to avoid misinterpretation by the LCA practitioner, a final interpretation with the same boundaries for all studies can help to convey the message of the results. This is particularly useful for policy makers and non-governmental organizations (NGOs) that need to form a decision based on scientific data. As the demand for sustainability assessments increases, the ways to present these assessments should also improve without compromising scientific knowledge.

8.4 Chapter eight summary

This chapter discusses weighting of indicators, uncertainties and general discussion points. First, results from **Chapter 5** and **6** are calculated by applying weighting factors to the CO_2 utilisation indicators. The calculated results are similar for all weighting scenarios in both urea and methanol cases. The major differences are seen when either global warming or fossil depletion scores are assigned a weight of 100% (relevance). When this happens, the ranking results favour conventional routes over utilisation processes using electricity grid mixes. In general, case studies that use 100% renewable energy for hydrogen production are better ranked than those that do not, since the total kg of CO_2 emitted is lower than when using a carbonised electricity grid. This is consistent with all the weighting factors used. The weight of the ranks was calculated by using a simple multi-attribute rating technique (SMART). The results found give an overview of how the environmental impact assessment framework can be applied and what is the outcome. As with any study, there are uncertainties and limitations to consider. Some of these uncertainties include:

- Data gaps that limit the parts of the process that can be analysed (i.e. catalyst use that has been omitted for all processes). This leads to cutting back on other processes that might have more information to ensure comparability.
- It is difficult to obtain electricity costs at consumption point for renewable energy therefore in this work levelised cost of electricity (LCOE) values are used instead.
- Extrapolating future electricity scenarios leads to inaccuracies. However, since future calculations will always be estimations, the results can be used for loose interpretations provided the future extrapolations reflect an expected reality.
- The study boundaries make the CO_2 based products only comparable with other products that have identical chemical composition (in this case cradle to gate).

8.5 Chapter eight reference list

European Commission, 2010. *International Reference Life Cycle Data System (ILCD) Handbook -- General guide for Life Cycle Assessment -- Detailed guidance*, Available at: http://lct.jrc.ec.europa.eu/pdf-directory/ILCD-Handbook-General-guide-for-LCA-DETAIL-online-12March2010.pdf.

Santoyo-Castelazo, E. & Azapagic, A., 2014. Sustainability assessment of energy systems: Integrating environmental, economic and social aspects. *Journal of Cleaner Production*, 80, pp.119–138. Available at: http://dx.doi.org/10.1016/j.jclepro.2014.05.061.

Sternberg, A. & Bardow, A., 2015. Power-to-What? – Environmental assessment of energy storage systems. *Energy Environ. Sci.*, pp.389–400. Available at: http://xlink.rsc.org/?DOI=C4EE03051F [Accessed January 26, 2015].

9 Conclusions, Recommendations and Future Work

Through this work, the possibilities of assessing a CO_2 utilisation process from an environmental point of view are reviewed, analysed and discussed. For this, a framework was created tailored to the needs of a process that uses a waste flow of carbon dioxide and chemically transforms it into a new commodity. To prove the validity of the framework, two main products were used as case studies: methanol and urea. Methanol was selected for its ability to be produced from various feedstocks, including CO_2. It is also one of the most studied CO_2 utilisation processes, making it a suitable case for "proof of concept". Urea was chosen as the specific case to test the robustness of the framework. Urea can be produced with captured CO_2 and H_2 from renewable energy to produce NH_3 through Haber-Bosch.

9.1 Framework recommendations

Finding the data for the life cycle inventory can be challenging. There is much information available that is aggregated and un-aggregated. However, most of this information is not tailored for CO_2 utilisation processes or chemical processes in general. This can complicate performing the life cycle assessment. After trying several modelling approaches, the following recommendations are suggested:

- Find a life cycle assessment platform that is user friendly and supports at least the commonly used characterisation methods, i.e. CML-IA and ReCiPe (H) methods.
- The platform should be able to integrate databases such as ecoinvent or other commercially available. It should be able to load supply chains for chemical processes and not only products.
- If simulation data is available, the inputs/outputs and utilities can be useful. From the experience obtained in this work, it is better to start from a black box model approach than replicating the simulation systematically. By doing this broken flows are avoided without changing the outcome as anything in between with no environmental connection will appear as an empty flow. Examples of successful

and failed life cycle assessment models for CO_2 utilisation are shown in **Appendix VIII**.

- Add allocation steps within the life cycle assessment (LCA) model, this facilitates the interpretation phase. This can be done by adding negative CO_2 values where required.
- At least two types of allocations should be applied and compared between each other. In this work, we suggest system expansion as the first option and a economic allocation as the second.
- Use commonly applied environmental impact categories in LCA when the assessment is at screening level, but as a minimum global warming, fossil depletion, CO_2 avoided and used must be analysed first. If the results for these categories are negative, it is difficult to see a scenario where CO_2 utilisation would be feasible. As the depth of the assessment increases, analytical tools such as Monte Carlo can be used to screen sensitive impact categories.
- It is suggested to at least use a midpoint approach such as CML-IA for the characterisation factors when the assessment is at screening level. This makes it easier to compare to other LCA studies on CO_2 utilisation studies. Extra methods and approaches can be included to check sensitivity.
- Future scenarios should be planned according to the information available and the hotspots detected. i.e in this work, the scenarios were based around electricity as this was the most sensitive input.

9.2 Future work

- Mapping CO_2 availability in a country is useful at present time and was relevant in this work. However, this is not a fixed value, as industrial priorities change with time so will CO_2 sources. Future work will consider CO_2 source projections and how this will by mapping high to low probability of a CO_2 source availability in the next 20 to 30 years.
- There is an opportunity to improve the ranking method by increasing stakeholder engagement and including a panel of experts to determine the weight of each

indicator. There is also the option of using a ranking system that can also include qualitative indicators such as the inclusion of fuzzy numbers.

- Future work considers expanding the environmental impact assessment framework to include social and economic categories to create a sustainability life cycle assessment.

- Finally, the framework can be presented in a template format (technical summary) with easy guidelines for life cycle assessment/carbon dioxide utilisation practitioners. There is still much discussion in this area, since it is unclear until which point it is useful to aggregate results. However, a preliminary format can be created towards unifying the indicators of relevance and the acceptable ways to assess them. This format would have variations to accommodate different type of products from CO_2 utilisation processes.

9.3 Framework conclusions

A guideline was specified on how to use process simulations as database sources for life cycle inventories as well as the minimum data required to build the inventory. To assess the environmental aspects, analyse and quantify their impacts, a life cycle assessment approach was used. The ISO standard 14040:2006 was used as baseline and adapted to CO_2 utilisation processes; this included using a subtraction method to allocate. A cradle to gate approach was used for all scenarios. This assessment also considered all processes to be linear using a matrix method for process based modelling following the work of Heijungs *et al.* (2013). CML-IA method was used to assess the 11 impact categories.

Since electricity plays a large role in CO_2 utilisation, it is suggested to include electricity outlooks. These scenarios reflect the probable electricity grid mixes of a region under certain conditions and timeframes. All impacts are assessed for the year 2015, 2025, 2050 and a baseline case with the current available datasets. Other aspects included in the framework include utilities cost and the market for CO_2 based products.

As a last step in the framework, it is suggested to include scenario analysis to interpret results. The recommendations of this study include using a multi criteria decision analysis

(MCDA) approach to evaluate possible routes, alternatives or decisions. While un-aggregated results should always be available, there is also a requirement to unify results in CO_2 utilisation assessments, make them more comparable and reduce uncertainty of interpretations.

The framework was tested by assessing two CO_2 based products. The main conclusions for each case are drawn out in the following sections.

9.4 Case study conclusions

9.4.1 Methanol case study

A comparative assessment is made between methanol production from CO_2 and renewable hydrogen and methanol from natural gas and from syngas. The functional unit is defined as the production of 1 kg of CH_3OH per 1.43 kWh of electricity generated for the grid.

- Two capture routes were considered: CO_2 is captured from a subcritical 550 MW Pulverised Coal power plant with post-combustion capture. The capture method used is absorption with amines at a 90% capture. In the second option, CO_2 is captured from a direct air capture (DAC) plant using a sodium hydroxide solution in an absorption process.
- Hydrogen is supplied through water electrolysis. The system is powered using both renewables and the current electricity grid (depending on the scenario). As an alternative process, data from chlor-alkali databases were also used to compare processes. Sixteen different databases and variations of methanol synthesis were tested.
- Five main scenarios were assessed. Scenario 1 and 4 do not use renewables for CO_2 utilisation, Scenario 1 uses post-combustion capture process, Scenario 4 uses direct air capture theoretic principles. Scenarios 2 and 5 use renewable energy to power water electrolysis to produce hydrogen. Scenario 2 uses post-combustion capture and Scenario 5 uses direct air capture. Scenario 3 is the conventional production route of methanol from natural gas.

- Results show that only the CO_2 utilisation scenarios coupled with renewable energy can at least be carbon neutral. No major improvement was found between using post-combustion capture and direct air capture (DAC). This was due to the high indirect emissions associated currently with capturing CO_2 from air. Overall, CO_2 emissions contribute from 88 to 91% of the global warming score to CO_2 utilisation scenarios.
- Other impacts such as fossil fuel depletion show similar trends as with carbon avoidance. Methanol synthesis needs to lower its energy penalties or be sourced from decarbonised energy to reduce its fossil fuel depletion impact to at least 2.4 times its current value. Eutrophication scores have the lowest levels when using renewables in CO_2 utilisation cases. Acidification scores are negative in all utilisation cases due to high SO_2 emissions linked to the electricity grid and dehydration of CO_2. For stratospheric ozone depletion, methanol from natural gas has the worst results due to its reliance on fossil fuels. Resource depletion is worse in scenarios that use renewable energy from wind power; the impacts are attributed to the manufacturing stage, specifically the use of molybdenum. Photochemical oxidation score is its lowest in Scenario 3 (methanol from natural gas). Finally, ecotoxicity scores showed varied results. Marine aquatic and terrestrial ecotoxicity results do not favour CO_2 utilisation routes due to the high-energy penalties. Freshwater ecotoxicity has lower impact in utilisation cases due to the lack of methane requirements for methanol production.
- Sensitivity tests showed that by allocating with the avoided burden method, environmental burdens shift to only one part of the process instead of distributing them according to the impact of each product and co-product. System expansion was chosen as the preferable allocation method.
- Seven different hydrogen sources were compared against three methanol synthesis routes and two carbon sources. This showed close results between theoretical case studies and a case with stakeholder information. This reinforces the usefulness of carrying a pre-assessment study of this sort for life cycle assessment processes.
- The electricity outlook with the suggested grid mixes did not favour methanol production through CO_2 utilisation processes until the year 2050 when the grid is decarbonised unless renewable energy is used. This also has an impact on

operational costs, where utilities costs are high due to increased hydrogen requirements per kg of CH_3OH produced.

- If environmental and cost hurdles can be overcome, there is a strong market for CH_3OH. While the demand for it in the UK is small (4% total in Europe), there is an increase in other applications such as: alternative fuels, fuel cells, DME, etc.
- The highest utilisation potential is seen with CO_2 captured from air and hydrogen produced from renewable energy. 66% of the ranking methods selected this combination as the process with lowest environmental impacts.

9.4.2 Urea case study

A comparative assessment is made between urea production from CO_2 with NH_3 (from renewable hydrogen) and urea from fossil fuel based NH_3. The functional unit is defined as the production of 1 kg of NH_2CONH_2 per 0.8 kWh of electricity generated for the grid.

- NH_3 is produced by using H_2 from a PEM electrolyser that delivers 33 kg H_2/day and uses 55 kWh. Urea is synthesised by the reaction of ammonia and carbon dioxide at high temperatures and pressures.
- The principles used in the methanol case study for selecting five scenarios were also applied in this case. Scenarios 1, 2, 4 and 5 are CO_2 utilisation cases, while Scenario 3 is the conventional route. Scenarios 1 and 4 use electricity from the grid to produce green hydrogen and are coupled to CO_2 from post-combustion capture. Scenario 2 and 5 use renewable energy to produce hydrogen and is coupled with CO_2 from direct air capture (DAC).
- Results show that up to 37% of carbon emissions can be avoided compared to the conventional route if H_2 is produced from renewable energy (wind power) in CO_2 utilisation scenarios. If 100% renewables are not used, then CO_2 emissions can rise up to 57% compared to the conventional route. 61% of the carbon emissions are associated with H_2 production. The greenhouse contribution to global warming without CO_2 ranges from 8 % to 11%.
- All CO_2 utilisation scenarios have less potential for environmental impacts than the conventional urea route in the following categories: marine aquatic eco-toxicity, terrestrial eco-toxicity, freshwater eco-toxicity, abiotic depletion, acidification, eutrophication, and stratospheric ozone depletion. For photochemical oxidation and fossil depletion, only CO_2 utilisation scenarios that

use renewable energy for hydrogen production can have favourable results compared to the conventional route. System expansion was applied to all impact calculations.

- The electricity outlook with the grid mix projections, suggests that by 2025 the global warming and fossil depletion scores of urea from CO_2 utilisation processes can be lower than urea from a conventional route. Other environmental impacts also trend towards lower values in CO_2 utilisation scenarios compared to the conventional route.
- There is also a positive outlook for urea production utilities costs from recovered CO_2 at small scale. This is due to the high fuel costs of traditional urea synthesis compared to CO_2 utilisation processes where fuel is low or non-existent. In the utilisation scenarios, water electrolysis accounts for most of the operational costs. 63% to 66% of total operational electricity costs come from the electrolyser.
- The highest utilisation potential is seen with CO_2 capture from post-combustion capture and hydrogen production from renewable energy. 83% of the ranking methods calculated this process as the one with lowest environmental impacts.

9.5 General conclusion

The relevance of this research is the contribution to lessen the impacts of man-made processes through an environmental impact assessment. Finding efficient methods to analyse carbon mitigation technologies can help guide these processes towards reaching sustainability targets. For carbon dioxide utilisation, specifically, it can help to determine if there is a contribution to climate change mitigation and/or lessening of other impacts and whether this technology can be scalable.

An environmental impact assessment framework that is applicable to carbon dioxide utilisation processes that chemically transform CO_2 has been developed. This is a novel multidisciplinary assessment approach to determine and interpret the carbon utilisation potential of a process. The results showed the benefits of using specific indicators and scenarios to overcome the challenges of measuring processes that use a captured CO_2 source. It also provides the initial guidelines to create a template for carbon dioxide utilisation assessments in the future. This work has been tested on two main products with a supply chain based in the UK and can be adapted to other regions.

Appendices

Appendix I

Initial scenario analysis for the environmental impact assessment framework design, divided into four stages:

Locational availability of renewable energy

Region/country

- Energy mix and associated impacts
  .-Are there **unlimited/limited/no renewable** energy sources?
  .-Do the associated impacts compare **low/equal/high** to other potential countries?

- Energy production
  Is there a **surplus/sufficient/insufficient** rate of energy production?

Environmental

CO_2 emissions and fossil depletion

- Allocation of emissions and fossil depletion rates for CO_2 source, capture stage, utilisation transport and extra processes
  .- Are levels **low/moderate/high** compared to other production routes?

  .- **Yes/most likely/no** there are process alternatives to reducing emissions and fossil depletion scores?

Environmental impacts

- Allocation of main impacts according to study boundaries
  .- Are impacts **low/moderate/high** compared to other production routes?

.- **Yes/most likely/no** there are process alternatives to reducing environmental impacts?

carbon dioxide utilisation (CDU)/conventional

- Analysis on net emissions/impacts between carbon dioxide utilisation and conventional production methods

Other aspects of CO_2 utilisation

Capture cost

- Cost of CO_2 avoided

  .- Is the net CO_2 avoided cost **lower/equal/higher** than other carbon dioxide utilisation (CDU) and conventional processes

Utilisation cost

- Cost of CO_2 avoided

  .- Is the net CO_2 avoided cost **lower/equal/higher** than other carbon dioxide utilisation (CDU) and conventional processes

Market for product

- Demand for carbon dioxide utilisation (CDU) product

  .- Is there a **low/medium/high** demand for utilisation product?

- 20 year outlook for product

  .- Is the demand for the product trending towards **down/stable/up**?

Energy outlook

- Renewable energy costs

  .- Will renewable energy costs be **low/feasible/non feasible**?

- 20 year outlook for renewable energy
  .- Are the projections for renewable energy cost **positive/neutral/negative** in the next 20 years?

Design of the CO_2 utilisation process

CO_2 source

.- Will the CO_2 be supplied via **air capture/biogenic point source/non biogenic point source**?

.-Will the CO_2 concentration in the stream be **low/medium/high**?

.-**No/most likely/yes** dehydration method will be required?

Capture

.-Will the CO_2 capture method be via **direct air capture (DAC)/direct flue gas utilisation/flue gas**?

.-It will **not/most likely/will require** extra processes such as compression and impurities removal?

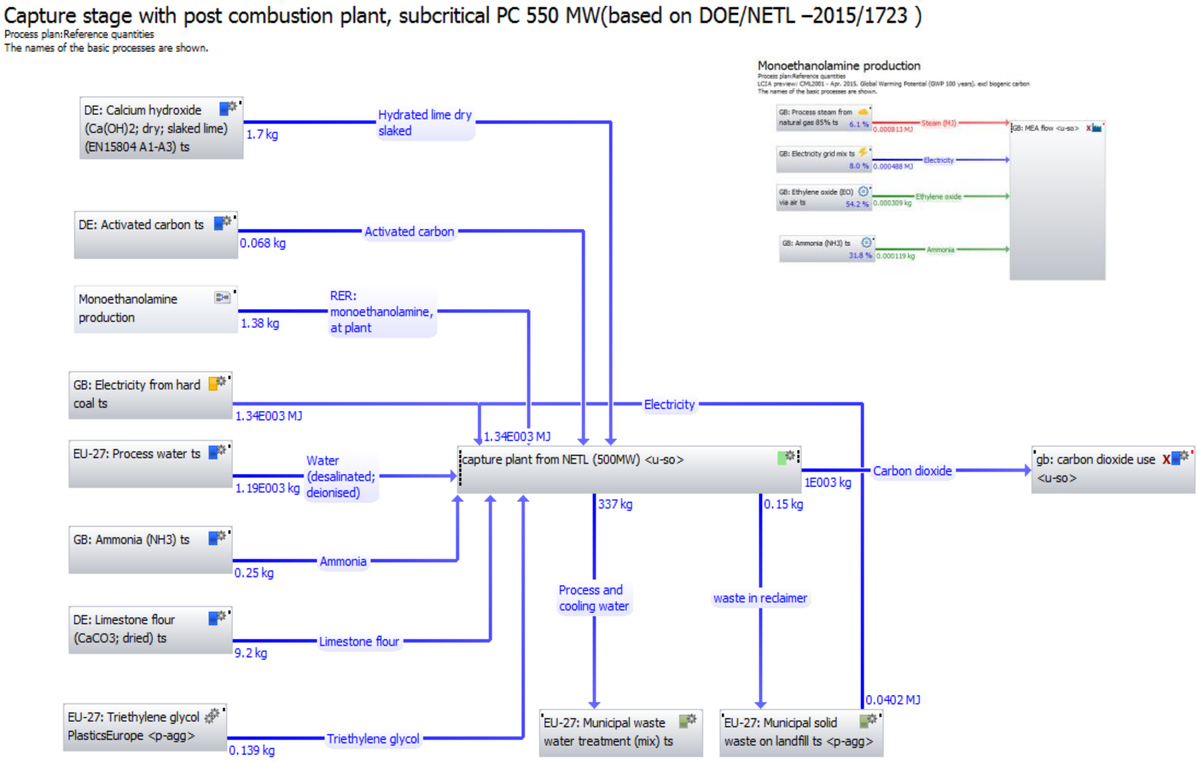
Utilisation

.- Will the utilisation route require **no extra energy/renewable energy/fossil based energy**?

.-Will the energy/requirements be **low/medium/high** compared to conventional routes?

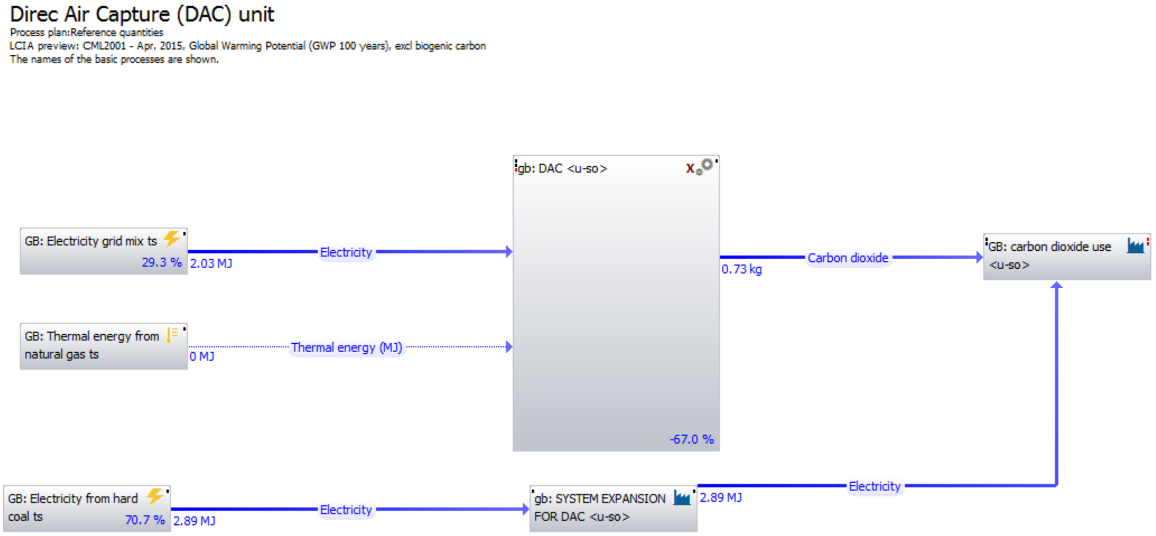
Appendix II

Mapping of carbon capture processes for fixed point sources:



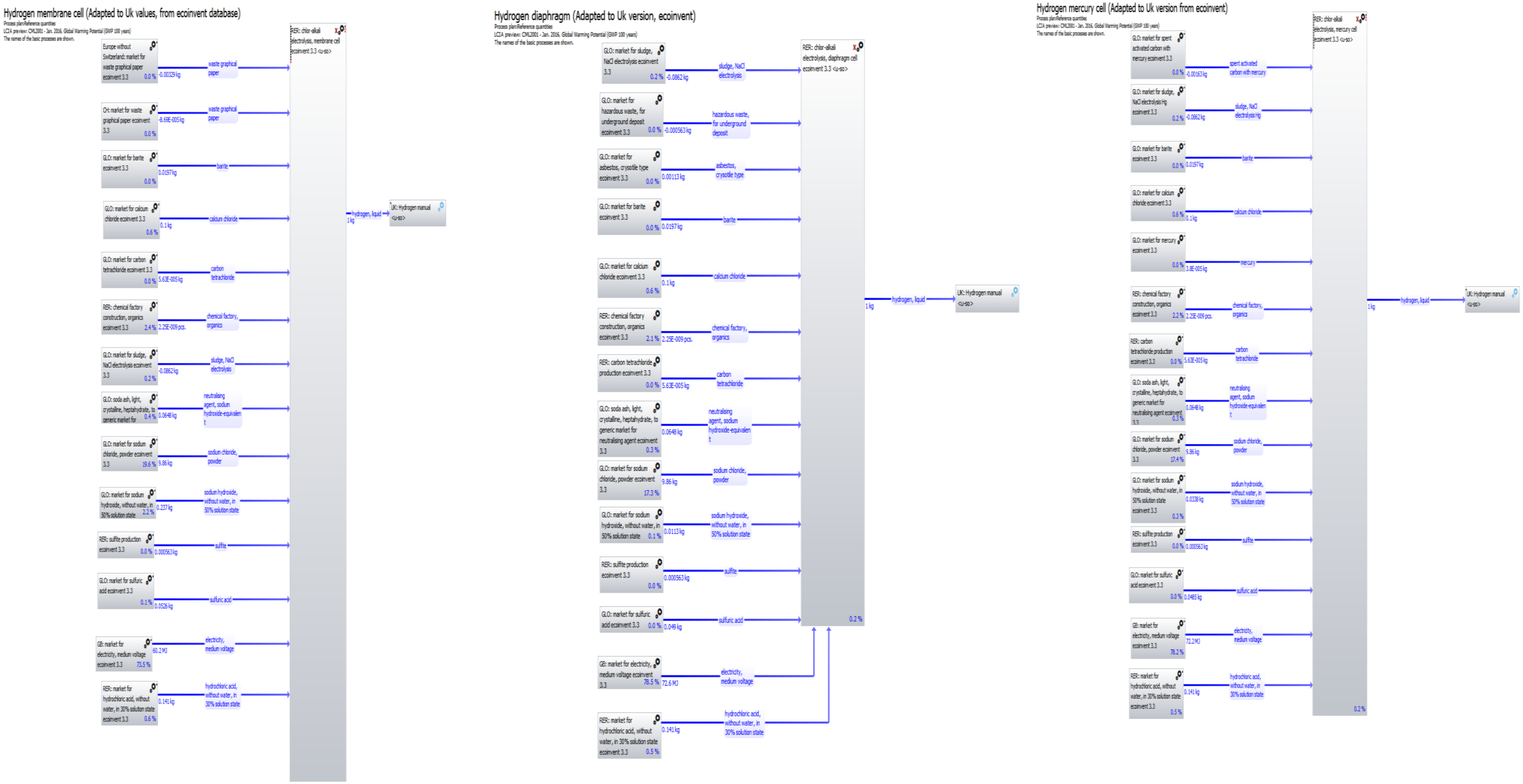
Inputs/outputs for capture stage with post-combustion capture, subcritical pulverised coal (PC), based on NETL (2015). GaBi ts version 8.7.0.18 software used for mapping.

Mapping of Direct Air Capture processes:



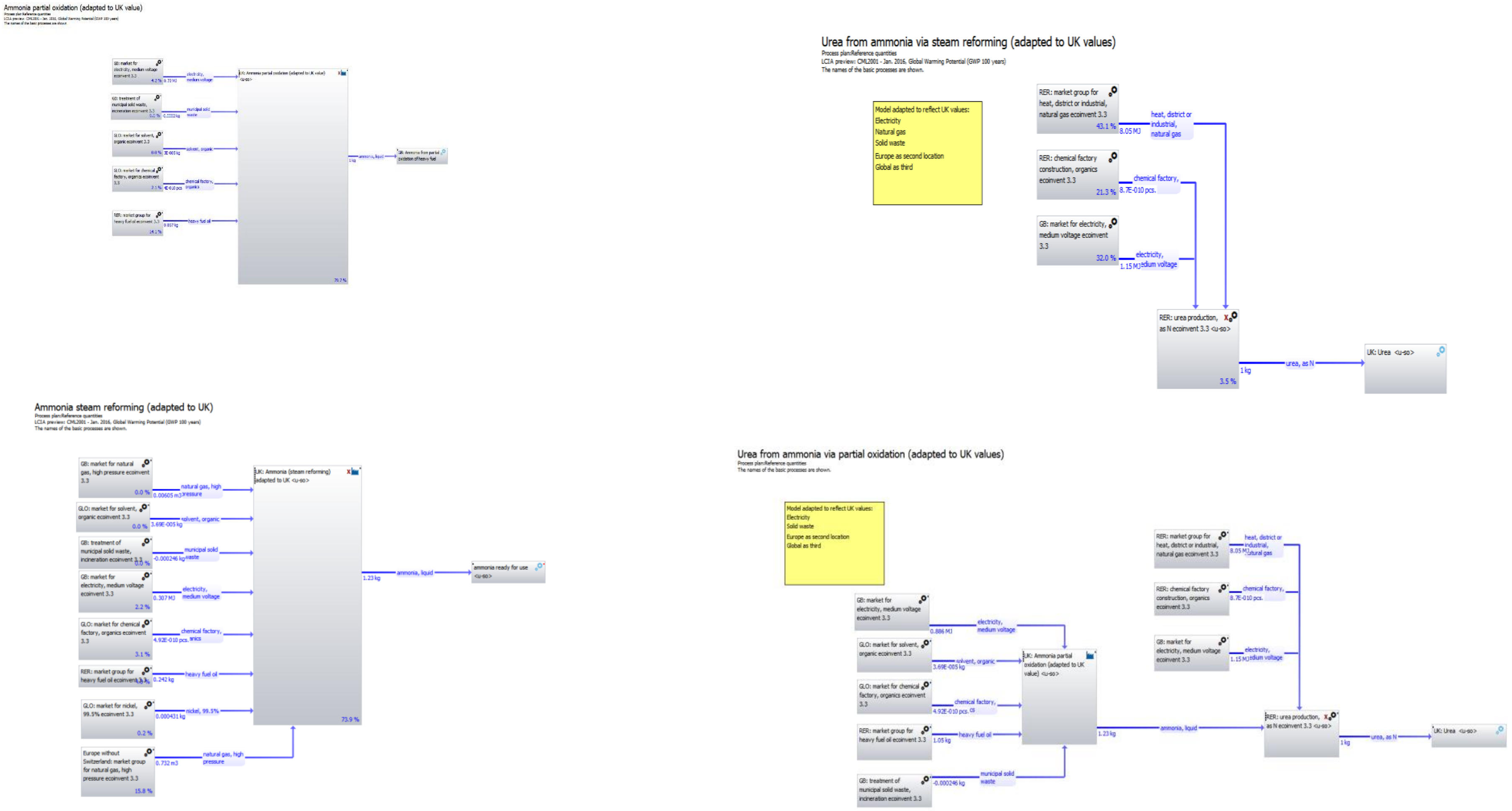
Inputs/outputs for a direct air capture unit (DAC) based on Zeman (2014). GaBi ts version 8.7.0.18 software used for mapping.

Mapping of hydrogen production through chlor-alkali electrolysis (adapted to UK values):



Inputs/outputs for chlor-alkali electrolysis for hydrogen production, based on Althaus *et al.* (2007). GaBi ts version 8.7.0.18 software used for mapping.

Mapping of ammonia and urea process for Scenario 3 (adapted to UK values)



Inputs/outputs for ammonia and urea production using GaBi TS version 8.7.0.18 software for modelling and ecoinvent version 3.3

Appendix III

Quality indicators selected and adapted to carbon dioxide processes. Based on inventories by NETL (2013).

- Source reliability: Describes where the life cycle inventory (LCI) data is obtained from. There is a higher tolerance for secondary sources do to the general lack of primary information for carbon dioxide utilisation (CDU). However, data cross checks are still required with secondary data.
- Database within date: This quality indicator determines whether the data for the life cycle inventory (LCI) is still relevant in the assessment. Since CO_2 utilisation processes are relatively new, there are not many timeframe problems associated with it.
- Geographical correlation: Determines whether the impacts of a database are aligned with the region of study. For carbon dioxide utilisation (CDU), the index is flexible. As information advances in this area, the quality index can tighten.
- Technical similarities: This last indicator determines whether the database to use is representative of the process under study. Again, the general limitations in carbon dioxide utilisation (CDU) data limit how close this indicator can be. It is assumed that if the process is the same or very similar, it can be used for general assessments.

Quality indicators for carbon dioxide utilisation processes

Score	Source reliability	Database within date	Geographical correlation	Technical similarities
1	Data based on measurements, calculations and some assumptions, data cross checks	Within 3 years of study	Database from area of study	Data from process under study
2	Data based on secondary sources, data cross checks	Within 6 years of study	Database from the larger area of study	Data from similar process
3	Data based on many assumptions no secondary databases used, data cross checks	Within 10 years of study	Database from similar area/region	Data from similar process using different materials
4	Informed estimate	Within 15 years of study	Known location of database from other area with similar process	Data on related process
5	Non-informed estimate	> 15 years of study	Unknown location of database with similar process	Data for different technology

Appendix IV

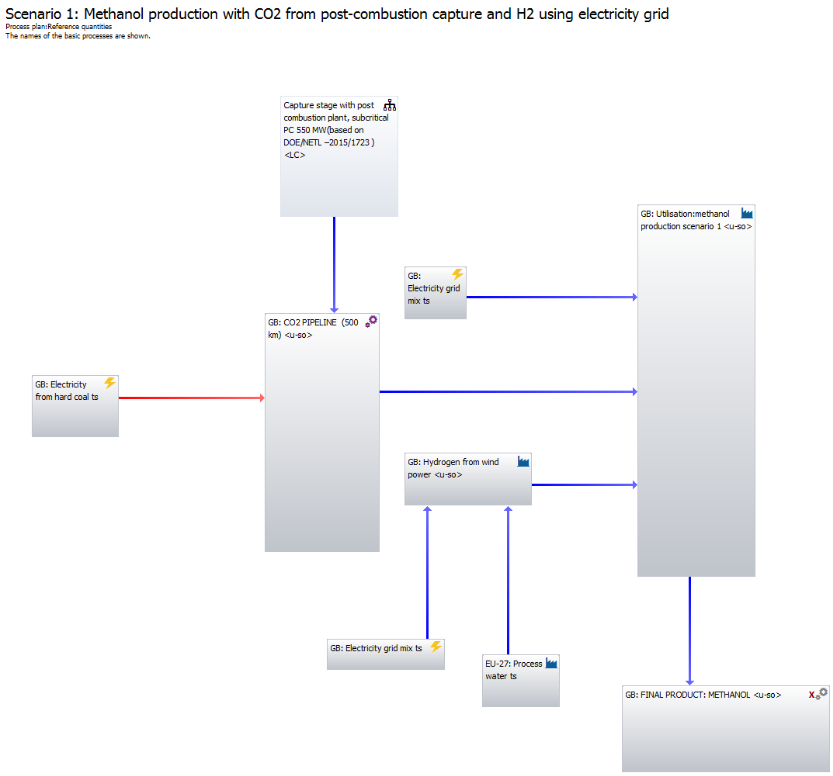
Process parameters for carbon capture processes from a fixed-point sources, based on the report by NETL (2015) and adapted to the conditions of the study cases

	Subcritical PC			Supercritical PC			NGCC		
Total kg CO_2 captured	*0.73*	*1.37*	*1000*	*0.73*	*1.37*	*1000*	*0.73*	*1.37*	*1000*
Power Output									
Net power output (MWe)	550	550	550	550	550	550	559	559	559
Capacity factor (%)	85	85	85	85	85	85	85	85	85
Net electricity output (kWh)	11220000	11220000	11220000	11220000	11220000	11220000	11403600	11403600	11403600
kWh needed for case study	0.803	1.513	1100	0.84	1.575	1146	2	3.8	1000
TOTAL CO_2 Emissions (kg)	1133220	1133220	1133220	1088340	1088340	1088340	456144	456144	456144
CO_2/Day									
kg CO_2 emitted/MWh	101	101	101	97	97	97	40	40	40
total kg CO_2 emitted	0.081	0.153	111	0.08	0.15	111	0.082	0.15	40
kg CO_2 needed for capture/total MWh	0.811	1.528	1111	0.81	1.5	1111	0.82	1.5	400
CO_2 capture rate (%)	90	90	90	90	90	90	90	90	90
CO_2 captured (kg)	0.73	1.375	1000	0.73	1.4	1000	0.73	1.38	360
Emission factor (kg CO_2/kWh)	1.01	1.01	1.01	0.97	0.97	0.97	0.4	0.4	0.4
Auxiliary electricity for capture									
Auxiliary power for capture (MWe)	63	63	63	61	61	61	31	31	31
Auxiliary electricity for capture (kWh)	1285200	1285200	1285200	1244400	1244400	1244400	632400	632400	632400
Auxiliary electricity for capture (additional kWh/kWh generated)	0.1145	0.1145	0.1145	0.11	0.11	0.11	0.06	0.06	0.06
Net auxiliary electricity for capture (kWh)	0.09	0.17	126	0.09	0.17	127	0.11	0.21	55
Consumables									
Limestone (kg/ total kg CO_2 captured)	0.0397	0.0749	54.4	0.04	0.075	54.5	0	0	0
Hydrated lime (kg/ total kg CO_2 captured)	0.0081	0.0153	11.1	0.008	0.015	11.1	0	0	0

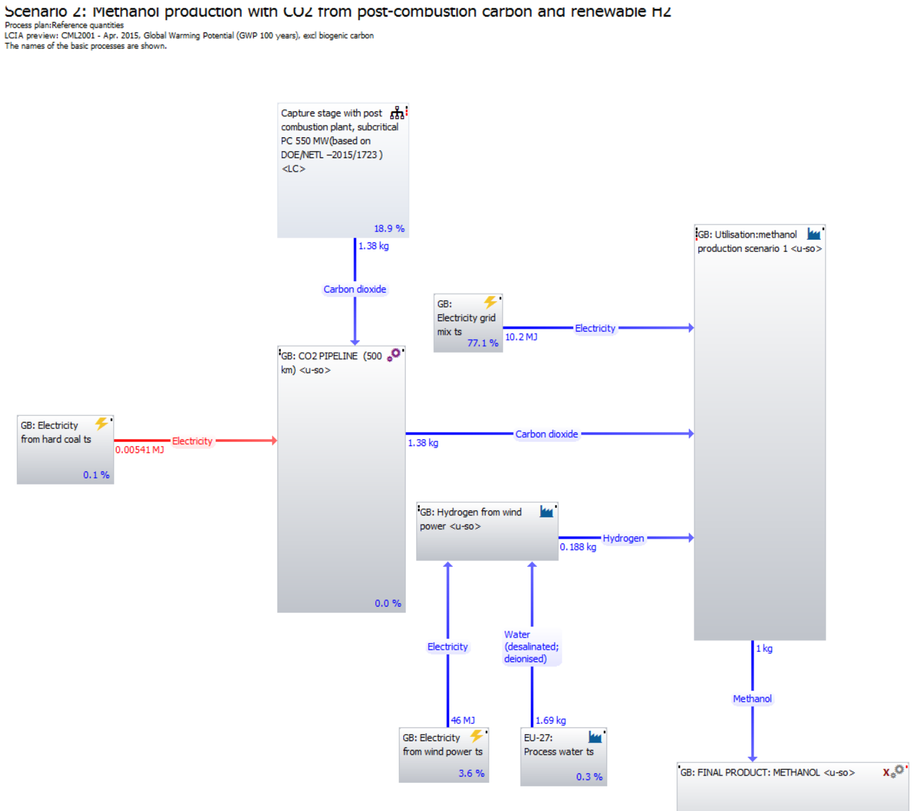
	Subcritical PC			**Supercritical PC**			**NGCC**		
Total kg CO_2 captured	*0.73*	*1.37*	*1000*	*0.73*	*1.37*	*1000*	*0.73*	*1.37*	*1000*
Activated carbon (kg/ total kg CO_2 captured)	0.0003	0.0005	0.4	2.04E-04	3.82E-04	0.28	0	0	0
Triethylene glycol (kg/ total kg CO_2 captured)	0.0264	0.0498	36.2	0.03	0.05	36.5	1.44E-07	2.69E-07	7.04E-05
SCR Catalyst (kg/ total kg CO_2 captured)	2.93E-08	5.53E-08	4.02E-05	2.65E-05	4.97E-05	0.04	1.43E-08	2.68E-08	7.02E-06
Ammonia (kg/ total kg CO_2 captured)	0.0011	0.0021	1.55	0.0011	0.002	1.53	9.4E-05	0.0002	0.05
Thermal reclaimer unit waste (kg/ total kg CO_2 captured)	0.0001	0.0002	0.18	0.0001	0.0003	0.19	6E-05	0.0001	0.03
Makeup and wastewater treatment chemicals (kg/ total kg CO_2 captured)	0.0010	0.0018	1.3	0.0009	0.0017	1.3	1	1	1
Water (kg/ total kg CO_2 captured)	1.98	3.7	2708.5	1.9	3.6	2635	2.4	4.41172	1155
Gypsum (kg/ total kg CO_2 captured)	NA	NA	NA	0.007	0.013	9.36	NA	NA	NA
Water balance									
Process water discharge (lpm)	7268	7268	7268	6863	6863	6863	3782	3782	3782
Process water discharge (m^3/day)	10466	10466	10466	9883	9883	9883	5446	5446	5446
Process water discharge (m3/kWh required for case study)	0.00075	0.0014	1.03	0.0007	0.0014	1.01	0.0010	0.0018	0.5
Process water withdrawal (lpm)	31960	31960	31960	29840	29840	29840	15230	15230	15230
Process water withdrawal (m^3/day)	46022	46022	46022	42970	42970	42970	21931	21931	21931
Process water withdrawal (m^3/kWh required for case study)	0.003	0.006	4.5	0.003	0.006	4.4	0.004	0.007	1.9

Appendix V

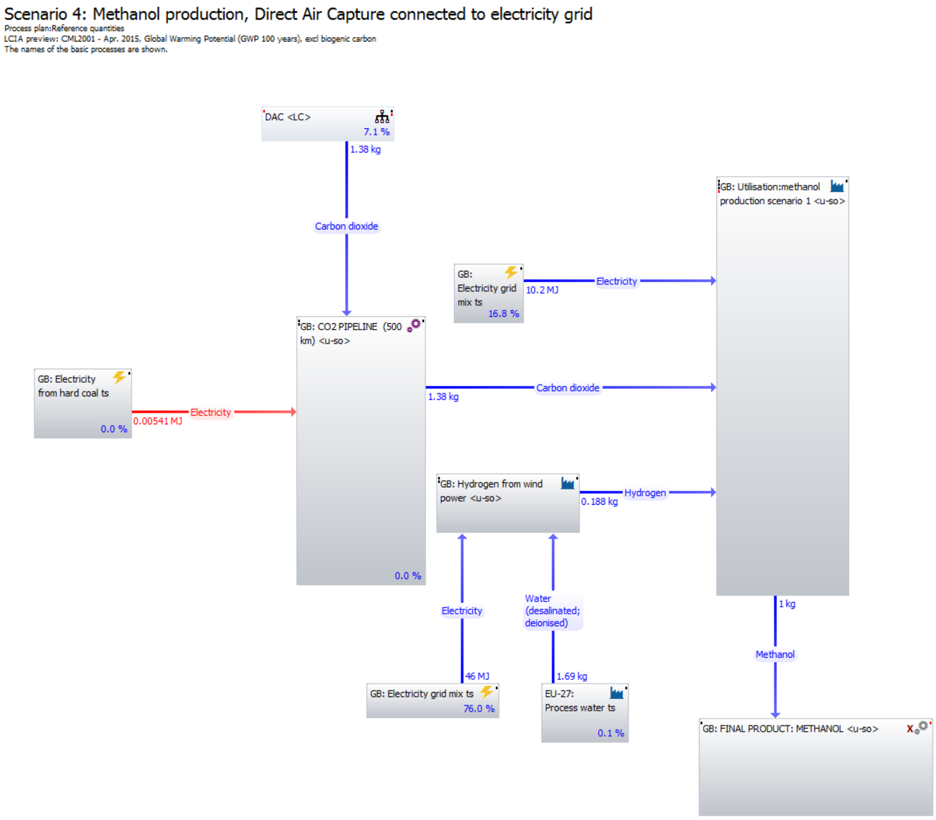
Mapping of methanol case studies, Scenarios 1, 2,4 and 5:



Inputs/outputs for Scenario 1, methanol production using GaBi ts version 8.7.0.18 software

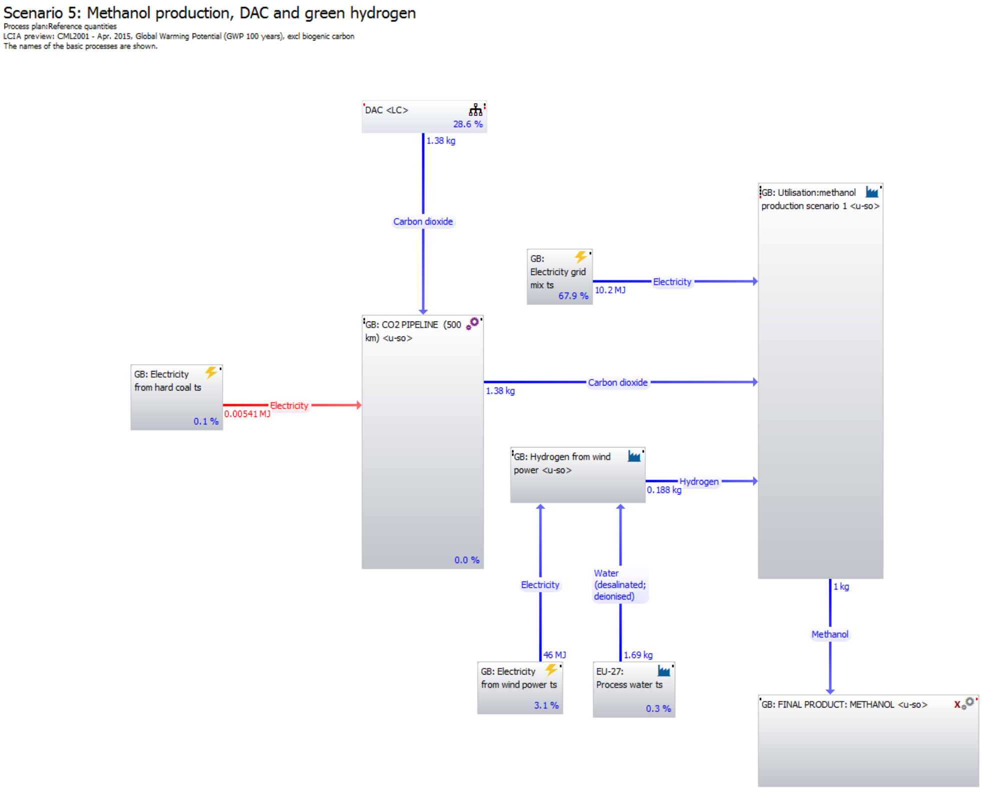


Inputs/outputs for Scenario 2, methanol production using GaBi ts version 8.7.0.18 software



Scenario 4: Methanol production, Direct Air Capture connected to electricity grid
Process plan:Reference quantities
LCIA preview: CML2001 - Apr. 2015, Global Warming Potential (GWP 100 years), excl biogenic carbon
The names of the basic processes are shown.

Inputs/outputs for Scenario 4, methanol production using GaBi ts version 8.7.0.18 software



Scenario 5: Methanol production, DAC and green hydrogen
Process plan:Reference quantities
LCIA preview: CML2001 - Apr. 2015, Global Warming Potential (GWP 100 years), excl biogenic carbon
The names of the basic processes are shown.

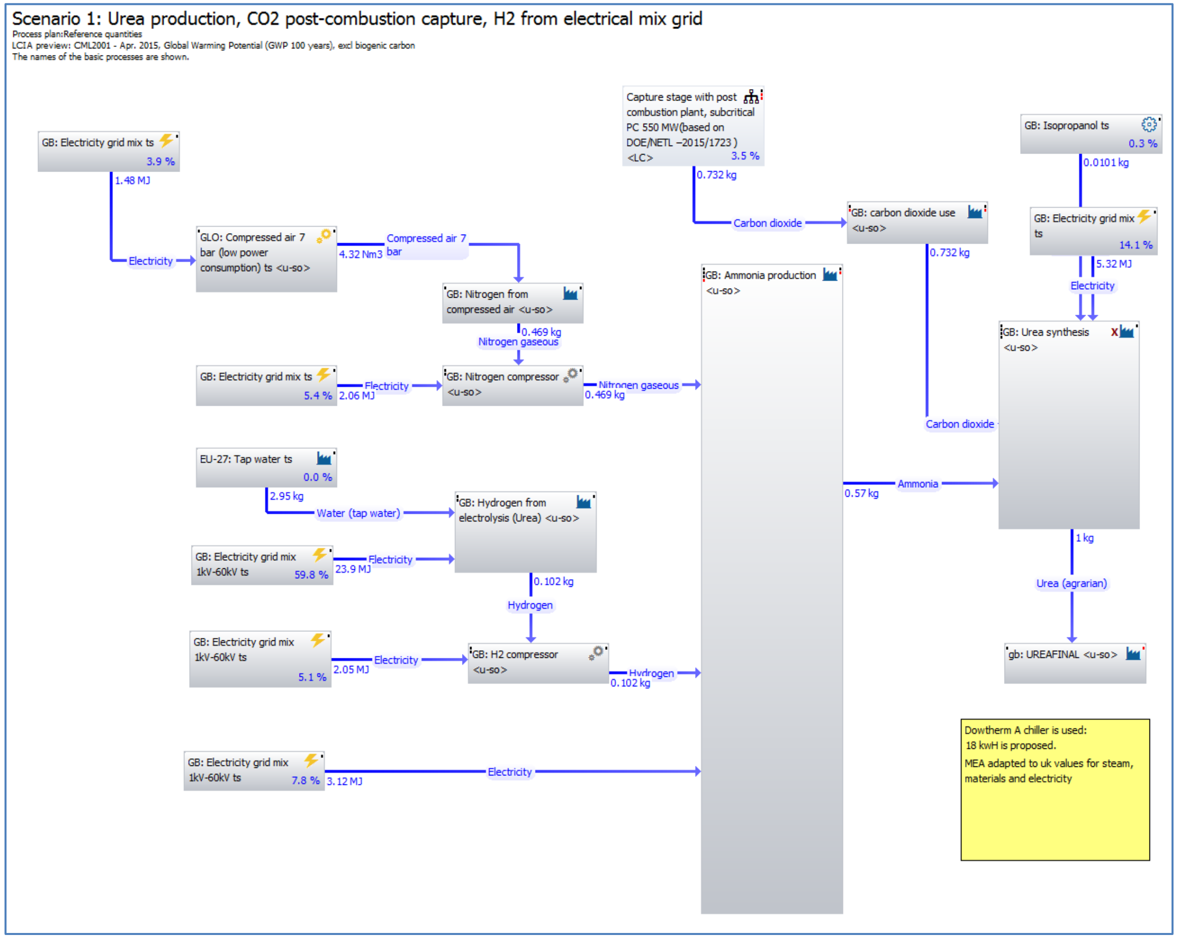
Inputs/outputs for Scenario 5, methanol production using GaBi ts version 8.7.0.18 software

Life cycle impact assessment (LCIA) results for methanol case studies: Scenarios 1 to 5 using GaBi ts version 8.7.0.18 software

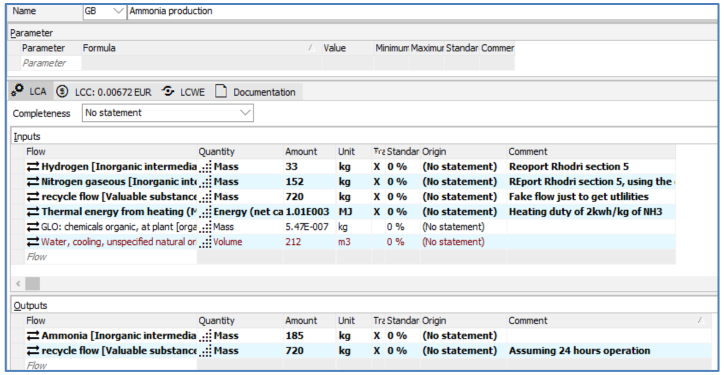
	1			2			3		4			5		
Impact categories	CO_2 *capture*	H_2	CH_3OH	CO_2	H_2	CH_3OH	*Power plant*	CH_3OH	CO_2 *capture*	H_2	CH_3OH	CO_2 *capture*	H_2	CH_3OH
kg CO_2 Direct emissions	0.15	0	0	0.15	0	0	1.2105	0	0	0	0	0	0	0
kg CO_2 Indirect emissions	0.1	6.7	1.5	0.1	0.1	1.5	0.1	0.6	0.5	6.7	1.5	0.5	0.1	1.5
kg CO_2 Total emissions	0.3	6.7	1.5	0.3	0.1	1.5	1.3	0.6	0.5	6.7	1.5	0.5	0.1	1.5
ADP elements [kg Sb-eq]	0.0000003	0.0000007	0.0000001	0.0000003	0.0000039	0.0000001	0.0000000	0.0000007	0.0000001	0.0000007	0.0000001	0.0000001	0.0000039	0.0000001
AP [kg SO_2-eq.]	0.0056	0.0228	0.0051	0.0056	0.0002	0.0051	0.0048	0.0012	0.0067	0.0228	0.0051	0.0067	0.0002	0.0051
EP [kg PO_4 eq]	0.0006	0.0019	0.0004	0.0006	0.0000	0.0004	0.0004	0.0005	0.0006	0.0019	0.0004	0.0006	0.00003	0.0004
FAETP inf. [kg 1,4-DCB eq]	0.0028	0.0098	0.0022	0.0028	0.0006	0.0022	0.0009	0.0823	0.0017	0.0098	0.0022	0.0017	0.0006	0.0022
GWP 100 years [kg CO_2 eq]	0.4	7.2	1.6	0.4	0.1	1.6	1.4	0.7	0.7	7.2	1.6	0.7	0.1	1.6
HTP inf. [kg 1,4-DCB eq]	0.4	0.3	0.1	0.4	0.03	0.1	0.1	0.1	0.1	0.3	0.1	0.1	0.03	0.1
MAETP inf. [kg 1,4-DCB eq]	109.1	489.7	108.0	109.1	15.6	108.0	82.8	145.7	124.1	489.7	108.0	124.1	15.6	108.0
ODP, steady state [kg CFC-11 eq]	8.04E-10	4.65E-10	1.03E-10	8.04E-10	2.86E-12	1.03E-10	7.61E-13	1.64E-07	3.93E-11	4.65E-10	1.03E-10	3.93E-11	2.86E-12	1.03E-10
POCP [kg ethylene eq]	0.0004	0.0013	0.0003	0.0004	0.0000	0.0003	0.0003	0.0003	0.0004	0.0013	0.0003	0.0004	0.00001	0.0003
TETP inf. [kg DCB-Equiv.]	0.0013	0.0061	0.0013	0.0013	0.0006	0.0013	0.0010	0.0013	0.0016	0.0061	0.0013	0.0016	0.0006	0.0013
FD [kg oil eq]	0.5	2.1	0.5	0.5	0.02	0.5	0.4	0.9	0.5	2.1	0.5	0.5	0.02	0.5

Appendix VI

Mapping of urea case studies, Scenarios 1, 2,4 and 5



Dowtherm A chiller is used:
18 kwH is proposed.
MEA adapted to uk values for steam, materials and electricity



Name GB Ammonia production

Parameter

Parameter	Formula	Value	Minimum	Maximur	Standar	Commer
Parameter						

LCC: 0.00672 EUR

LCWE

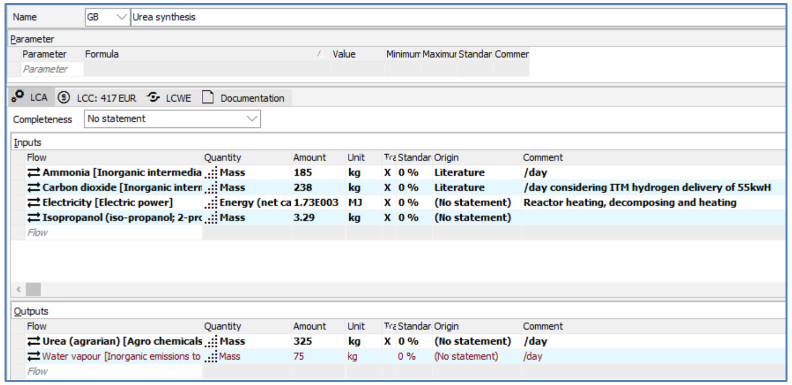
Completeness: No statement

Inputs

Flow	Quantity	Amount	Unit	Tra	Standar	Origin	Comment
Hydrogen [Inorganic intermedia	**Mass**	**33**	**kg**	**X**	**0 %**	**(No statement)**	**Reoport Rhodri section 5**
Nitrogen gaseous [Inorganic inte	**Mass**	**152**	**kg**	**X**	**0 %**	**(No statement)**	**REport Rhodri section 5, using the**
recycle flow [Valuable substance	**Mass**	**720**	**kg**	**X**	**0 %**	**(No statement)**	**Fake flow just to get utlilities**
Thermal energy from heating (N	**Energy (net ca**	**1.01E003**	**MJ**	**X**	**0 %**	**(No statement)**	**Heating duty of 2kwh/kg of NH3**
GLO: chemicals organic, at plant [orga	Mass	5.47E-007	kg		0 %	(No statement)	
Water, cooling, unspecified natural or	Volume	212	m3		0 %	(No statement)	
Flow							

Outputs

Flow	Quantity	Amount	Unit	Tra	Standar	Origin	Comment
Ammonia [Inorganic intermedia	**Mass**	**185**	**kg**	**X**	**0 %**	**(No statement)**	
recycle flow [Valuable substance	**Mass**	**720**	**kg**	**X**	**0 %**	**(No statement)**	**Assuming 24 hours operation**
Flow							



Name GB Urea synthesis

Parameter

Parameter	Formula	Value	Minimum	Maximur	Standar	Commer
Parameter						

LCC: 417 EUR

LCWE

Completeness: No statement

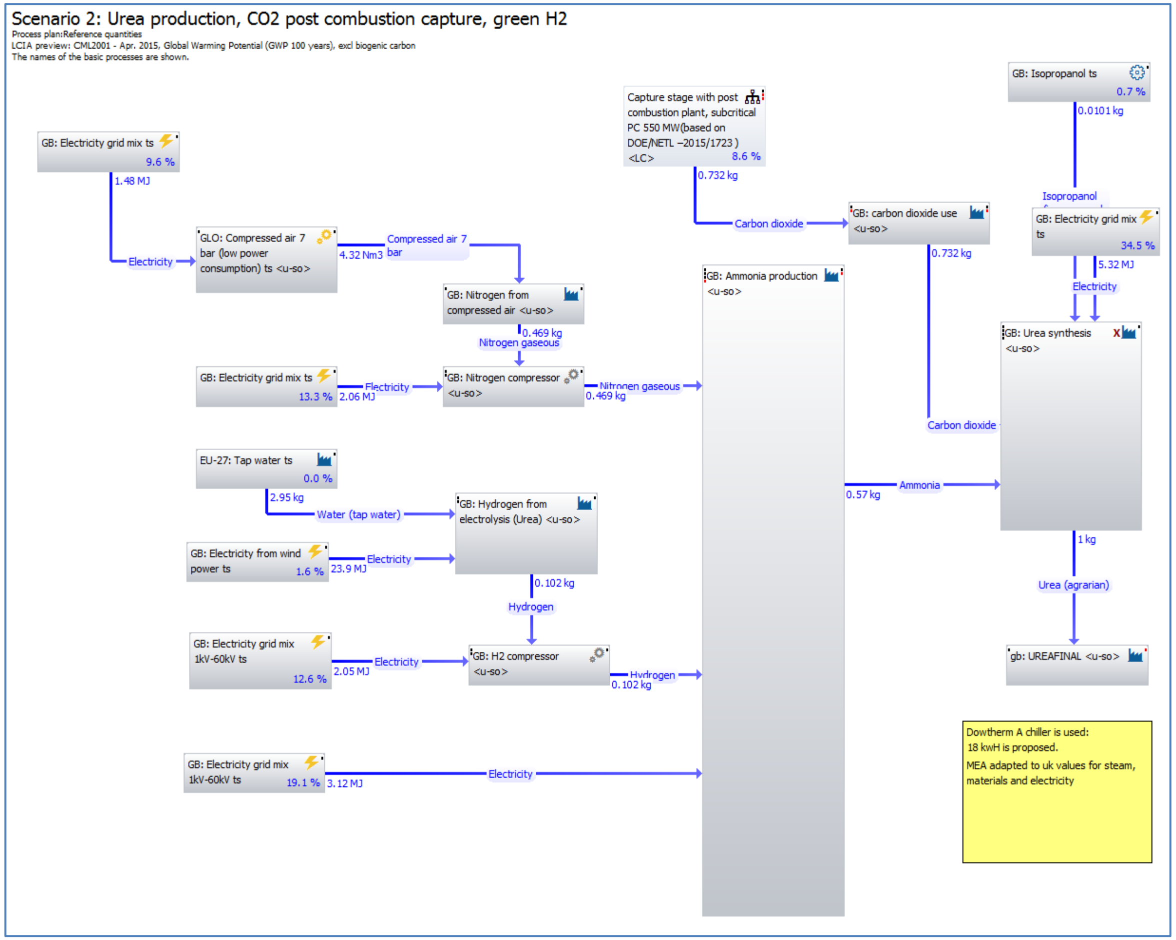
Inputs

Flow	Quantity	Amount	Unit	Tra	Standar	Origin	Comment
Ammonia [Inorganic intermedia	**Mass**	**185**	**kg**	**X**	**0 %**	**Literature**	**/day**
Carbon dioxide [Inorganic intern	**Mass**	**238**	**kg**	**X**	**0 %**	**Literature**	**/day considering ITM hydrogen delivery of 55kwH**
Electricity [Electric power]	**Energy (net ca**	**1.73E003**	**MJ**	**X**	**0 %**	**(No statement)**	**Reactor heating, decomposing and heating**
Isopropanol (iso-propanol; 2-prc	**Mass**	**3.29**	**kg**	**X**	**0 %**	**(No statement)**	
Flow							

Outputs

Flow	Quantity	Amount	Unit	Tra	Standar	Origin	Comment
Urea (agrarian) [Agro chemicals	**Mass**	**325**	**kg**	**X**	**0 %**	**(No statement)**	**/day**
Water vapour [Inorganic emissions to	Mass	75	kg		0 %	(No statement)	/day
Flow							

Inputs/outputs for Scenario 1, urea production using GaBi ts version 8.7.0.18 software



Scenario 2: Urea production, CO2 post combustion capture, green H2

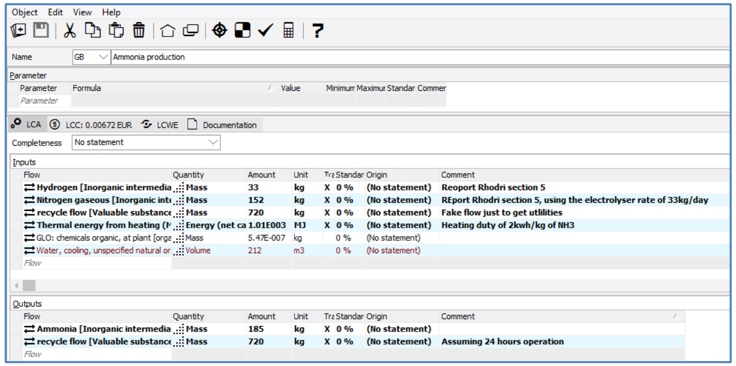
Process plan:Reference quantities

LCIA preview: CML2001 - Apr. 2015, Global Warming Potential (GWP 100 years), excl biogenic carbon

The names of the basic processes are shown.

Dowtherm A chiller is used:
18 kwH is proposed.

MEA adapted to uk values for steam, materials and electricity



Name: GB Ammonia production

Parameter

Parameter	Formula	Value	Minimum	Maximum	Standard	Comment
Parameter						

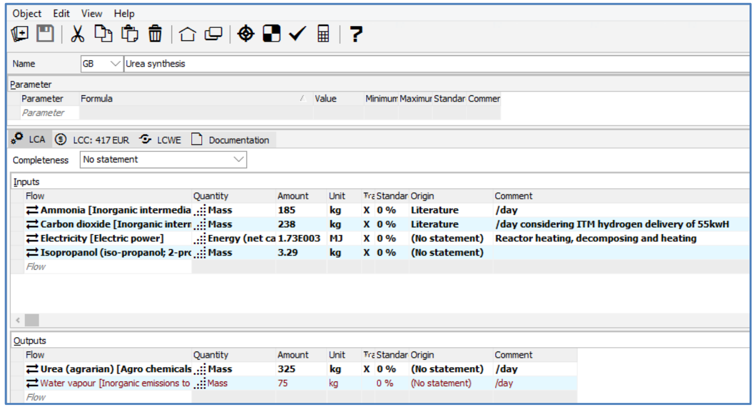
Completeness: No statement

Inputs

Flow	Quantity	Amount	Unit	Tra	Standar	Origin	Comment
Hydrogen [Inorganic intermedia	Mass	33	kg	X	0 %	(No statement)	Reoport Rhodri section 5
Nitrogen gaseous [Inorganic int	Mass	152	kg	X	0 %	(No statement)	REport Rhodri section 5, using the electrolyser rate of 33kg/day
recycle flow [Valuable substance	Mass	720	kg	X	0 %	(No statement)	Fake flow just to get utlilities
Thermal energy from heating (M	Energy (net ca	1.01E003	MJ	X	0 %	(No statement)	Heating duty of 2kwh/kg of NH3
GLO: chemicals organic, at plant [orga	Mass	5.47E-007	kg		0 %	(No statement)	
Water, cooling, unspecified natural or	Volume	212	m3		0 %	(No statement)	
Flow							

Outputs

Flow	Quantity	Amount	Unit	Tra	Standar	Origin	Comment
Ammonia [Inorganic intermedia	Mass	185	kg	X	0 %	(No statement)	
recycle flow [Valuable substance	Mass	720	kg	X	0 %	(No statement)	Assuming 24 hours operation
Flow							



Name: GB Urea synthesis

Parameter

Parameter	Formula	Value	Minimum	Maximum	Standard	Comment
Parameter						

Completeness: No statement

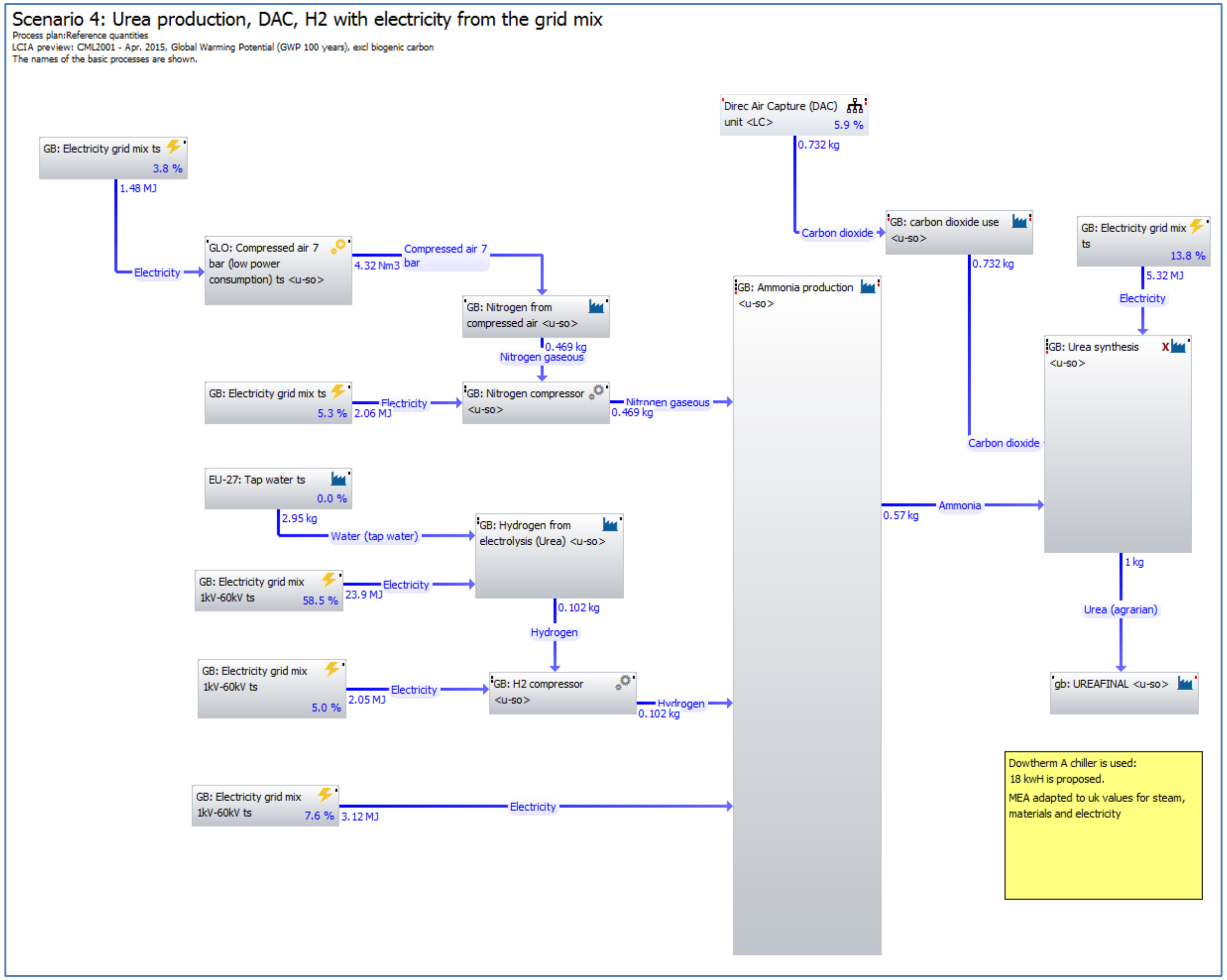
Inputs

Flow	Quantity	Amount	Unit	Tra	Standar	Origin	Comment
Ammonia [Inorganic intermedia	Mass	185	kg	X	0 %	Literature	/day
Carbon dioxide [Inorganic intern	Mass	238	kg	X	0 %	Literature	/day considering ITM hydrogen delivery of 55kwH
Electricity [Electric power]	Energy (net ca	1.73E003	MJ	X	0 %	(No statement)	Reactor heating, decomposing and heating
Isopropanol (iso-propanol; 2-pro	Mass	3.29	kg	X	0 %	(No statement)	
Flow							

Outputs

Flow	Quantity	Amount	Unit	Tra	Standar	Origin	Comment
Urea (agrarian) [Agro chemicals	Mass	325	kg	X	0 %	(No statement)	/day
Water vapour [Inorganic emissions to	Mass	75	kg		0 %	(No statement)	/day
Flow							

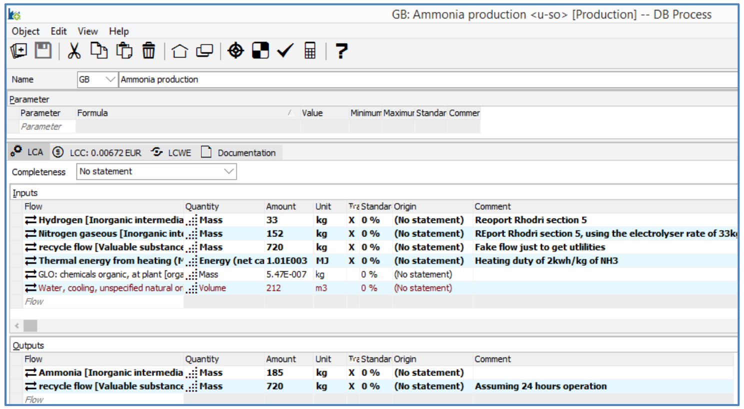
Inputs/outputs for Scenario 2, urea production using GaBi ts version 8.7.0.18 software



Scenario 4: Urea production, DAC, H2 with electricity from the grid mix

Process plan:Reference quantities
LCIA preview: CML2001 - Apr. 2015, Global Warming Potential (GWP 100 years), excl biogenic carbon
The names of the basic processes are shown.

Dowtherm A chiller is used:
18 kwH is proposed.
MEA adapted to uk values for steam, materials and electricity



GB: Ammonia production <u-so> [Production] -- DB Process

Name: GB Ammonia production

Parameter

Parameter	Formula	Value	Minimum	Maximur	Standar	Commer
Parameter						

LCA | LCC: 0.00672 EUR | LCWE | Documentation

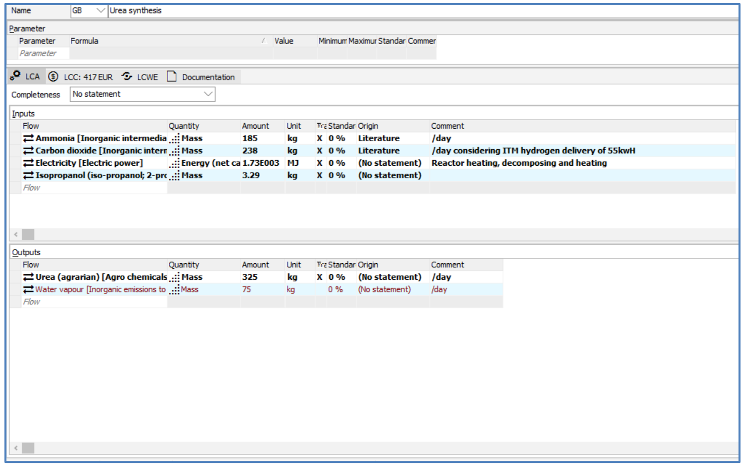
Completeness: No statement

Inputs

Flow	Quantity	Amount	Unit	Tra	Standar	Origin	Comment
Hydrogen [Inorganic intermedia	**Mass**	**33**	**kg**	**X**	**0 %**	**(No statement)**	**Reoport Rhodri section 5**
Nitrogen gaseous [Inorganic inte	**Mass**	**152**	**kg**	**X**	**0 %**	**(No statement)**	**REport Rhodri section 5, using the electrolyser rate of 33k**
recycle flow [Valuable substance	**Mass**	**720**	**kg**	**X**	**0 %**	**(No statement)**	**Fake flow just to get utlilities**
Thermal energy from heating (M	**Energy (net ca**	**1.01E003**	**MJ**	**X**	**0 %**	**(No statement)**	**Heating duty of 2kwh/kg of NH3**
GLO: chemicals organic, at plant [orga	Mass	5.47E-007	kg		0 %	(No statement)	
Water, cooling, unspecified natural or	Volume	212	m3		0 %	(No statement)	
Flow							

Outputs

Flow	Quantity	Amount	Unit	Tra	Standar	Origin	Comment
Ammonia [Inorganic intermedia	**Mass**	**185**	**kg**	**X**	**0 %**	**(No statement)**	
recycle flow [Valuable substance	**Mass**	**720**	**kg**	**X**	**0 %**	**(No statement)**	**Assuming 24 hours operation**
Flow							



Name: GB Urea synthesis

Parameter

Parameter	Formula	Value	Minimum	Maximur	Standar	Commer
Parameter						

LCA | LCC: 417 EUR | LCWE | Documentation

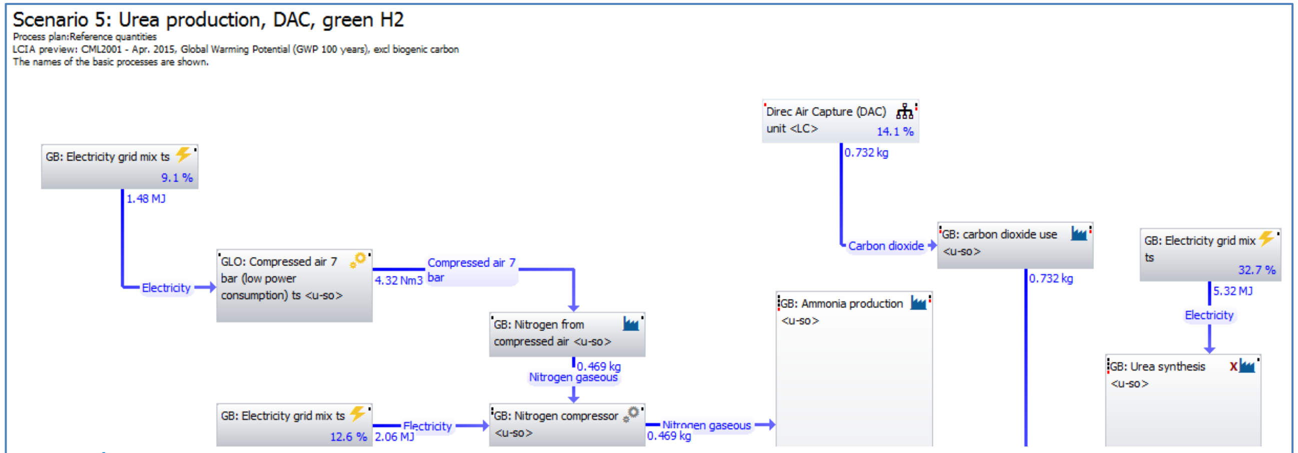
Completeness: No statement

Inputs

Flow	Quantity	Amount	Unit	Tra	Standar	Origin	Comment
Ammonia [Inorganic intermedia	**Mass**	**185**	**kg**	**X**	**0 %**	**Literature**	**/day**
Carbon dioxide [Inorganic interr	**Mass**	**238**	**kg**	**X**	**0 %**	**Literature**	**/day considering ITM hydrogen delivery of 55kwH**
Electricity [Electric power]	**Energy (net ca**	**1.73E003**	**MJ**	**X**	**0 %**	**(No statement)**	**Reactor heating, decomposing and heating**
Isopropanol (iso-propanol; 2-prc	**Mass**	**3.29**	**kg**	**X**	**0 %**	**(No statement)**	
Flow							

Outputs

Flow	Quantity	Amount	Unit	Tra	Standar	Origin	Comment
Urea (agrarian) [Agro chemicals	**Mass**	**325**	**kg**	**X**	**0 %**	**(No statement)**	**/day**
Water vapour [Inorganic emissions to	Mass	75	kg		0 %	(No statement)	/day
Flow							



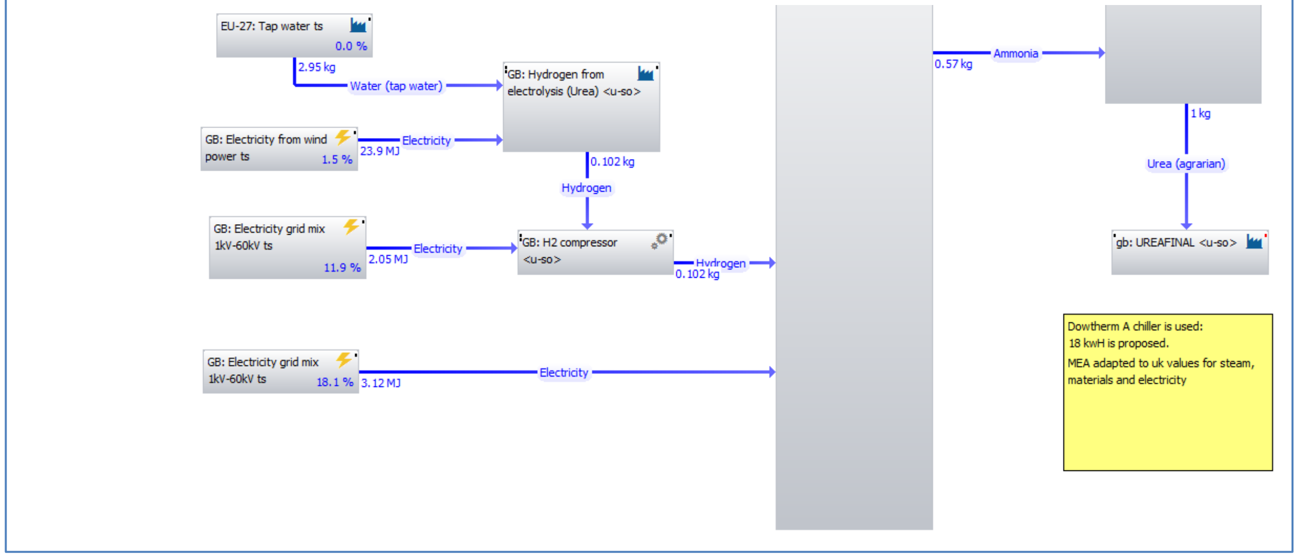
Scenario 5: Urea production, DAC, green H2

Process plan:Reference quantities

LCIA preview: CML2001 - Apr. 2015, Global Warming Potential (GWP 100 years), excl biogenic carbon

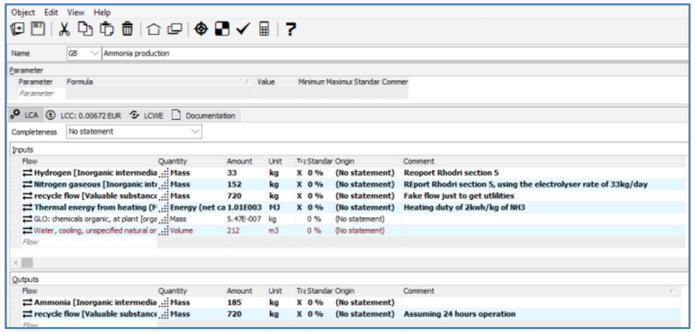
The names of the basic processes are shown.

Inputs/outputs for Scenario 4, urea production using GaBi ts version 8.7.0.18 software



Dowtherm A chiller is used:
18 kwH is proposed.
MEA adapted to uk values for steam, materials and electricity

Inputs/outputs for Scenario 5, urea production using GaBi ts version 8.7.0.18 software



Name: GB Ammonia production

Parameter

Parameter	Formula	Value	Minimum	Maximum	Standard	Comment
Parameter						

LCC: 0.00672 EUR

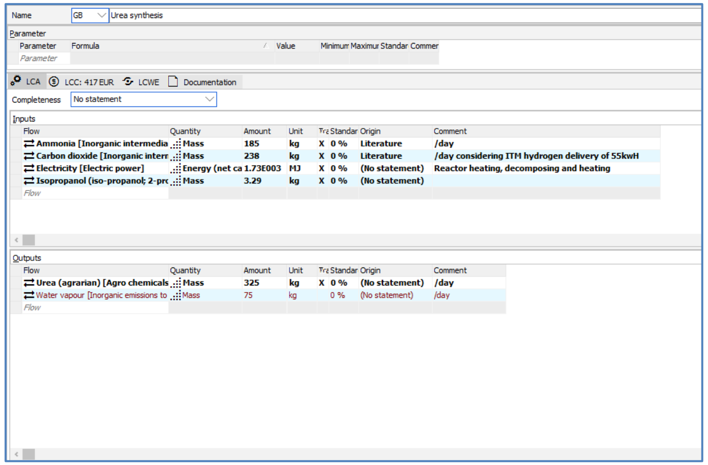
Completeness: No statement

Inputs

Flow	Quantity	Amount	Unit	Tra	Standar	Origin	Comment
Hydrogen [Inorganic intermedia	Mass	33	kg	X	0 %	(No statement)	Reoport Rhodri section 5
Nitrogen gaseous [Inorganic inte	Mass	152	kg	X	0 %	(No statement)	REport Rhodri section 5, using the electrolyser rate of 33kg/day
recycle flow [Valuable substance	Mass	720	kg	X	0 %	(No statement)	Fake flow just to get utlilities
Thermal energy from heating (M	Energy (net ca	1.01E003	MJ	X	0 %	(No statement)	Heating duty of 2kwh/kg of NH3
GLO: chemicals organic, at plant [orga	Mass	5.47E-007	kg		0 %	(No statement)	
Water, cooling, unspecified natural or	Volume	212	m3		0 %	(No statement)	
Flow							

Outputs

Flow	Quantity	Amount	Unit	Tra	Standar	Origin	Comment
Ammonia [Inorganic intermedia	Mass	185	kg	X	0 %	(No statement)	
recycle flow [Valuable substance	Mass	720	kg	X	0 %	(No statement)	Assuming 24 hours operation



Name: GB Urea synthesis

Parameter

Parameter	Formula	Value	Minimum	Maximum	Standard	Comment
Parameter						

LCC: 417 EUR

Completeness: No statement

Inputs

Flow	Quantity	Amount	Unit	Tra	Standar	Origin	Comment
Ammonia [Inorganic intermedia	Mass	185	kg	X	0 %	Literature	/day
Carbon dioxide [Inorganic intern	Mass	238	kg	X	0 %	Literature	/day considering ITM hydrogen delivery of 55kwH
Electricity [Electric power]	Energy (net ca	1.73E003	MJ	X	0 %	(No statement)	Reactor heating, decomposing and heating
Isopropanol (iso-propanol; 2-pro	Mass	3.29	kg	X	0 %	(No statement)	
Flow							

Outputs

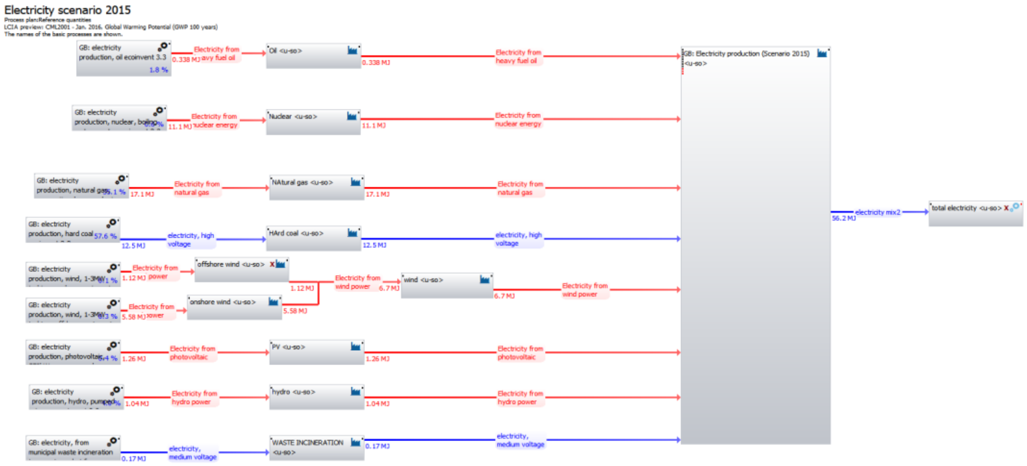
Flow	Quantity	Amount	Unit	Tra	Standar	Origin	Comment
Urea (agrarian) [Agro chemicals	Mass	325	kg	X	0 %	(No statement)	/day
Water vapour [Inorganic emissions to	Mass	75	kg		0 %	(No statement)	/day
Flow							

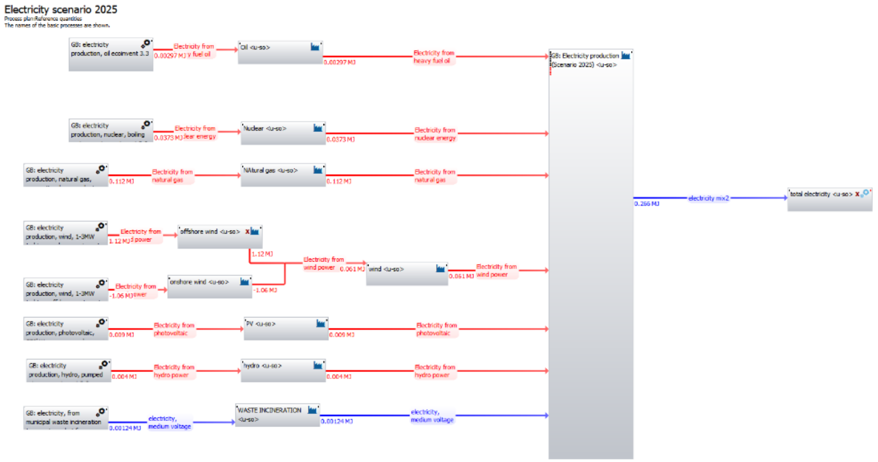
Life cycle impact assessment (LCIA) results for urea case studies: Scenarios 1 to 5 using GaBi ts version 8.7.0.18 software

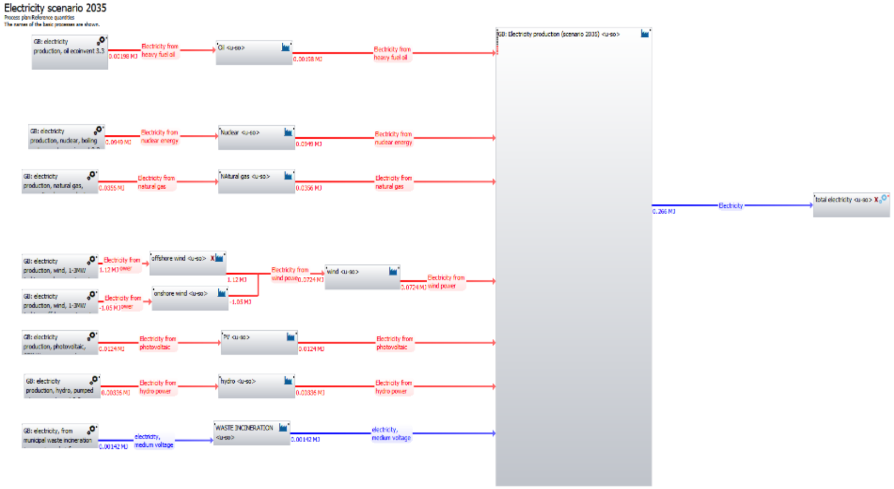
Impact categories	H_2	NH_3	NH_2CONH_2	H_2	NH_3	NH_2CONH_2	Power plant	NH_2CONH_2	H_2	NH_3	NH_2CONH_2	H_2	NH_3	NH_2CONH_2
kg CO_2 Direct emissions	0	0	0.08	0	0	0.08	0.65	1.80	0	0	0	0	0	0
kg CO_2 Indirect emissions	3.3	1.23	0.85	0.04	1.2	0.9	0.06	1.0	3.3	1.2	1.1	0.04	1.2	1.1
kg CO_2 Total emissions	3.3	1.2	0.93	0.04	1.2	0.9	0.71	2.8	3.3	1.2	1.1	0.04	1.2	1.1
ADP elements [kg Sb-eq]	3.13E-07	1.17E-07	2.14122E-07	1.98E-06	1.17E-07	2.14122E-07	3.66E-09	0.000016	3.13E-07	1.17E-07	1.10378E-07	1.98E-06	1.17E-07	1.10378E-07
AP [kg SO_2-eq.]	0.011	0.004	0.005	0.00011	0.004	0.005	0.003	0.015	0.011201	0.004158	0.0062	0.00011	0.004	0.006
EP [kg PO_4 eq]	0.001	0.0003	0.001	0.00001	0.0003	0.001	0.0002	0.004	0.000922	0.000344	0.0005	1.25E-05	0.000	0.001
FAETP inf. [kg 1,4-DCB eq]	0.005	0.0018	0.0027	0.0003	0.0018	0.0027	0.0005	0.631	0.005	0.002	0.002	0.0003	0.002	0.002
GWP 100 years [kg CO_2 eq]	3.6	1.3	1.2	0.04	1.3	1.2	0.770077	3.0	3.6	1.3	1.2	0.04	1.3	1.2
HTP inf. [kg 1,4-DCB eq]	0.17	0.063	0.264	0.018	0.063	0.264	0.041	2.13	0.1681	0.0627	0.0962	0.0179	0.0627	0.0962
MAETP inf. [kg 1,4-DCB eq]	237.1	88.7	109.6	7.9	88.7	109.6	44.3	2420.0	237.1	88.7	122.7	7.9	88.7	122.7
ODP, steady state [kg CFC-11 eq]	2.28E-10	8.49E-11	4.80718E-10	8.44E-13	8.49E-11	4.80718E-10	4.07E-13	0.000000531	2.28E-10	8.49E-11	7.46696E-11	8.44E-13	8.49E-11	7.46696E-11
POCP [kg ethylene eq]	0.0006	0.0008	0.0003	0.0000	0.0002	0.0003	0.0001	0.001	0.0006	0.0008	0.0004	0.0000	0.0002	0.0004
TETP inf. [kg DCB-Equiv.]	0.0030	0.0011	0.0013	0.0003	0.0011	0.0013	0.0006	0.038	0.0030	0.0011	0.0015	0.0003	0.0011	0.0015
FD [kg oil eq]	1.02	0.4	0.5	0.01	0.4	0.5	0.2	1.3	1.02	0.38	0.54	0.01	0.38	0.54
PM [kg PM10 eq]	0.00274	0.00102	0.00105	0.00005	0.00102	0.00105	0.00035	0.005	0.003	0.001	0.002	0.000	0.001	0.002

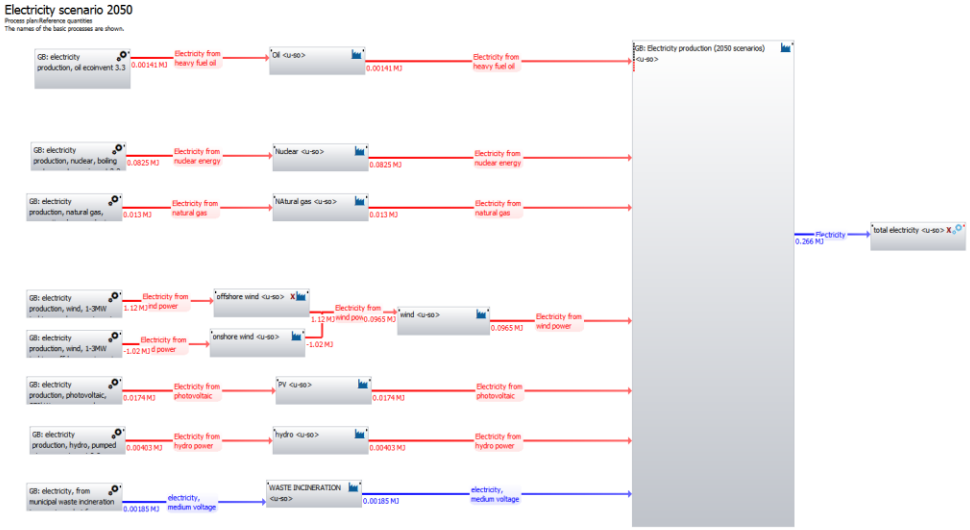
Appendix VII

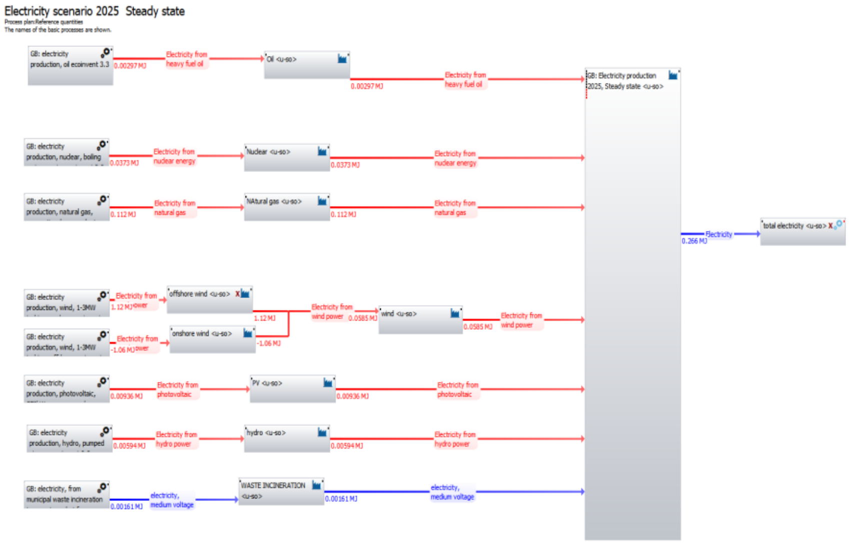
Mapping of electricity projections and matrices with scenario results

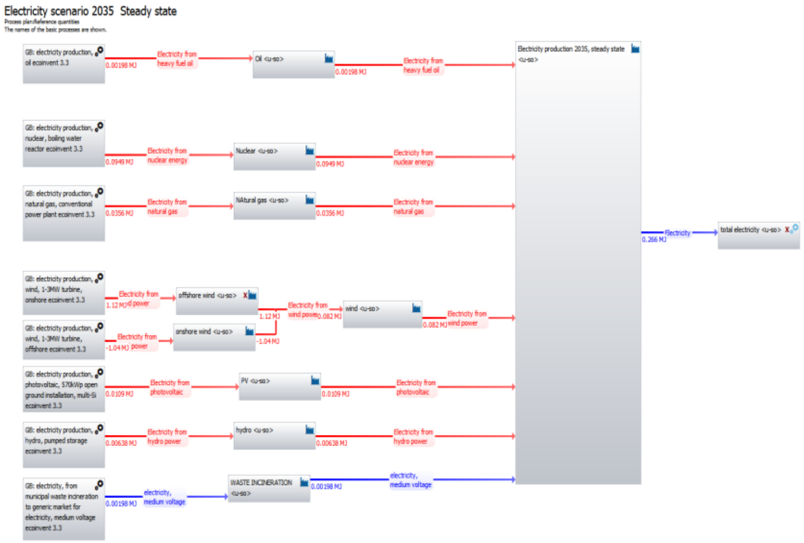


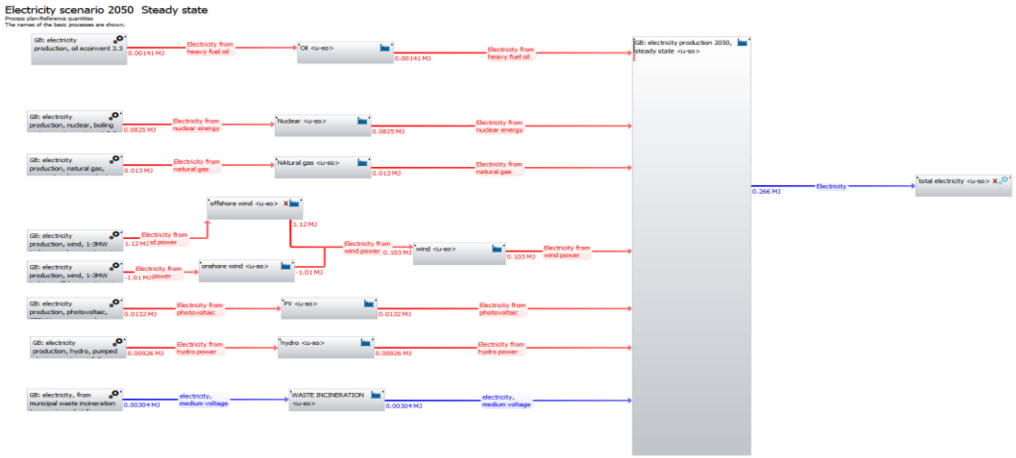












Inputs/outputs for electricity scenarios based on projections by BEIS (2017) and the National Grid (2017a) using GaBi ts version 8.7.0.18 software

Matrix for scenario analysis, methanol production results. Where criteria = indicators, variables = grid mix/year, scenarios = capture and utilisation routes. No weighting. 1 to 5 = number of case study a*) baseline scenario year b*) 2025 based on BEIS (2017) and National Grid (2017a) reports for two degrees (TD) scenario c*) 2050 based on BEIS (2017) and National Grid (2017a) reports for two degrees (TD) scenario

		Indicators													
		Net kg CO_2 avoided	*Net kg CO_2 utilised*	*GWP*	*EP*	*AP*	*ODP*	*POCP*	*MAETP*	*FAETP*	*TETP*	*HTP*	*PM*	*FD*	*ADP*
Case study for each electricity production	1a*	-6.1	1.38	9.2	0.002	0.03	1.3 x 10^{-9}	0.002	706.0	0.02	0.01	0.8	0.008	3.0	1.1 x 10^{-6}
	1b*	-5.8	1.38	4.2	0.002	0.01	4.4 x 10^{-7}	0.001	991.0	0.3	0.01	1.2	0.003	1.9	3.5 x 10^{-6}
	1c*	-5.8	1.38	1.3	0.002	0.01	5.8 x 10^{-7}	0.001	1220.0	0.4	0.02	1.5	0.003	0.8	5.5 x 10^{-6}
	2a*	0.1	1.38	2.0	0.001	0.01	9.1 x 10^{-10}	0.001	233.0	0.01	0.003	0.5	0.003	1.0	4.2 x 10^{-06}
	2b*	0.1	1.38	2.1	0.001	0.01	9.1 x 10^{-10}	0.001	233.0	0.01	0.003	0.5	0.003	1.0	4.2 x 10^{-06}
	2c*	0.1	1.38	2.1	0.001	0.01	9.1 x 10^{-10}	0.001	233.0	0.01	0.003	0.5	0.003	1.0	4.2 x 10^{-06}
	3a*	0.0	0.0	2.1	0.003	0.01	1.6 x 10^{-7}	0.001	270.0	0.1	0.002	0.2	0.0002	1.4	6.5 x 10^{-7}
	3b*	0.0	0.0	0.7	0.004	0.001	1.6 x 10^{-7}	3.2 x 10^{-4}	147.0	0.1	0.001	0.1	0.003	0.9	33.2
	3c*	0.0	0.0	0.7	0.004	0.001	1.6 x 10^{-7}	3.1 x 10^{-4}	148.0	0.1	0.001	0.1	0.003	0.9	33.2
	4a*	-6.3	1.38	9.5	0.003	0.04	1.4 x 10^{-10}	0.001	248.0	0.004	0.003	0.2	0.004	1.0	94 x 10^{-7}
	4b*	-6.3	1.38	4.5	0.002	0.01	4.4 x 10^{-7}	0.001	1006.0	0.3	0.01	0.9	0.003	1.1	0.01
	4c*	-6.3	1.38	1.6	0.002	0.01	5.8 x 10^{-7}	0.0007	1235.0	0.4	0.02	1.2	0.003	0.8	0.01
	5a*	0.1	1.38	2.3	0.001	0.01	1.4 x 10^{-10}	0.0007	248.0	0.004	0.003	0.2	0.003	1.0	4 x 10^{-6}
	5b*	0.1	1.38	2.3	0.001	0.01	1.4 x 10^{-10}	0.0007	248.0	0.004	0.003	0.2	0.003	1.0	4 x 10^{-6}
	5c*	0.1	1.38	2.4	0.001	0.01	1.4 x 10^{-10}	0.0007	248.0	0.004	0.003	0.2	0.003	1.0	4 x 10^{-6}

Matrix for scenario analysis, urea production results. Where criteria = indicators, variables = grid mix/year, scenarios = capture and utilisation routes. No weighting. 1 to 5 = number of study a*) baseline scenario b*) 2025 based on BEIS (2017) and National Grid (2017a) reports for two degrees (TD) scenario c*) 2050 based on BEIS (2017) and National Grid (2017a) reports for two degrees (TD) scenario

		Indicators														
		Net CO_2 avoided	*Net CO_2 utilised*	*GWP*	*EP*	*AP*	*ODP*	*POCP*	*MAETP*	*FAETP*	*TETP*	*HTP*	*PM*	*FD*	*ADP*
Case study for each electricity projection	1a*	-2	0.73	6	0.0017	0.011	7.8 x 10^{-10}	0.002	435	0.009	0.006	0.5	0.005	1.9	6.4 x 10^{-7}
	1b*	-2	0.73	2.9	0.0014	0.008	3 x 10^{-7}	0.0006	648	0.21	0.01	0.8	0.002	1.2	2.3 x 10^{-6}
	1c*	-2	0.73	1	0.0011	0.006	4.7 x 10^{-7}	0.0004	805	0.3	0.01	0.9	0.002	0.5	3.6 x 10^{-6}
	2a*	1.3	0.73	2.5	0.0009	0.005	5.6 x 10^{-10}	0.0006	206	0.009	0.004	0.08	0.002	0.88	2.3 x 10^{-06}
	2b*	1.3	0.73	2.5	0.001	0.005	5.6 x 10^{-10}	0.0006	206	0.009	0.004	0.08	0.002	0.9	2.3 x 10^{-06}
	2c*	1.3	0.73	2.5	0.001	0.005	5.6 x 10^{-10}	0.0006	206	0.009	0.004	0.08	0.002	0.9	2.3 x 10^{-06}
	3a*	0	0	3.8	0.0068	0.015	5.3 x 10^{-7}	0.001	2420	0.325	0.038	2.17	0.005	1.45	1.6 x 10^{-5}
	3b*	0	0	3.7	0.004	0.016	5.3 x 10^{-7}	0.001	2154	0.57	0.038	2.11	0.005	1.4	1.6 x 10^{-5}
	3c*	0	0	3.6	0.004	0.016	5.3 x 10^{-7}	0.001	2164	0.57	0.038	2.12	0.005	1.4	1.6 x 10^{-5}
	4a*	-2.1	0.73	6.1	0.0018	0.015	3.8 x 10^{-10}	0.002	448	0.009	0.008	0.3	0.006	1.2	5.4 x 10^{-7}
	4b*	-2.1	0.73	2.3	0.0122	0.008	3 x 10^{-7}	0.0006	661	0.21	0.009	0.6	0.003	1.3	2.2 x 10^{-6}
	4c*	-2.1	0.73	1	0.0011	0.007	4 x 10^{-7}	0.0005	818	0.3	0.011	0.8	0.003	0.5	2.8 x 10^{-6}
	5a*	1.2	0.73	2.6	0.0009	2.2 x 10^{-6}	1.6 x 10^{-10}	0.0006	219	0.004	0.004	0.18	0.003	0.93	1.6 x 10^{-10}
	5b*	1.2	0.73	2.5	0.001	2.2 x 10^{-6}	1.6 x 10^{-10}	0.0006	220	0.004	0.004	0.18	0.003	0.9	1.6 x 10^{-10}
	5c*	1.2	0.73	2.6	0.001	2.2 x 10^{-6}	1.6 x 10^{-10}	0.0006	220	0.004	0.004	0.18	0.003	0.9	1.6 x 10^{-10}

General weighting scores for carbon utilisation processes and simple multi attribute ranking technique (SMART) ranking

Questions for ranking (SMART)	Net CO$_2$ avoided	Net CO$_2$ utilised	GWP	EP	AP	ODP	POCP	MAETP	FAETP	TETP	HTP	PM	FD	ADP	Utilities costs
1. Does the indicator have an Importance in the overall carbon balance of the process?	100	100	100	0	0	0	0	0	0	0	0	0	50	0	0
2. Does the impact determines/describes the utilisation of CO$_2$?	75	100	50	0	0	0	0	0	0	0	0	0	50	0	50
3. Does the impact affects/describes de displacement of fossil-based fuel due to CO$_2$ utilisation?	50	25	50	0	0	0	0	0	0	0	0	0	100	0	0
4. Does the impact indicate additional costs for CO$_2$ utilisation?	0	0	0	0	0	0	0	0	0	0	0	0	0	0	100
5. Are there any categories that show the impact of energy penalties for utilisation?	0	0	100	75	75	75	75	75	75	75	75	75	100	50	100
6. Do the indicators show how much CO$_2$ can be utilised in a CDU process?	50	100	50	0	0	0	0	0	0	0	0	0	0	0	0
7. Do the indicators show additional impacts due to renewable energy use?	0	0	75	50	50	50	50	50	50	50	50	50	50	75	100
8. Do the indicators affect utilisation scenarios more than conventional?	100	100	100	25	25	25	25	25	25	25	25	25	100	25	25
9. Are there indicators that assess the health risks of CO$_2$ utilisation processes?	0	0	0	0	0	0	0	0	0	0	100	100	0	0	0
10. Overall, according to their importance in CO2 utilisation, what order of relevance should the indicators have?	75	50	100	25	25	25	25	25	25	25	25	25	100	50	50
Total	450	475	625	175	175	175	175	175	175	175	275	275	550	200	425
Weighted average	0.100	0.106	0.139	0.039	0.039	0.039	0.039	0.039	0.039	0.039	0.061	0.061	0.122	0.044	0.094
Rank	4	3	1	9	9	9	9	9	9	9	6	6	2	8	5

Value	Rank
0	No relevance
25	Little relevance
50	Relevant
100	Very relevant

Rank results for general weighted scores for both methanol and urea products

Indicators	Scenarios for Methanol					*Weight (%)*
	1a	*2a*	*3a*	*4a*	*5a*	
Net CO_2 avoided	0.58	-0.08	0	-0.05	-0.05	10.0
Net CO_2 utilised	-0.145666667	-0.145666667	0	-0.145666667	-0.145666667	10.6
GWP	1.277777778	0.277777778	0.291666667	1.319444444	0.319444444	13.9
EP	7.77778E-05	3.88889E-05	0.000132222	3.88889E-05	3.88889E-05	3.9
AP	0.001283333	0.000427778	0.000233333	0.001166667	0.000427778	3.9
ODP	5.05556E-11	3.53889E-11	6.22222E-09	2.33333E-11	5.44444E-12	3.9
POCP	7.77778E-05	2.72222E-05	3.88889E-05	3.88889E-05	2.72222E-05	3.9
MAETP	27.45555556	9.061111111	10.5	28.06844444	9.644444444	3.9
FAETP	0.000583333	0.000194444	0.003227778	0.000528889	0.000155556	3.9
TETP	0.000311111	0.000116667	7.77778E-05	0.00035	0.000116667	3.9
HTP	0.051333333	0.033	0.012222222	0.031777778	0.012222222	6.1
PM	0.000488889	0.000183333	2.44444E-05	0.000183333	0.000183333	6.1
FD	0.366666667	0.118555556	0.174777778	0.377666667	0.125888889	12.2
ADP	4.88889E-08	1.86667E-07	2.88889E-08	4.00E-08	1.77778E-07	4.4
Utilities costs	0.062333333	0.17	0.044388889	0.066111111	0.179444444	9.4
Sum	29.7	9.4	11.0	29.7	10.1	100

Methanol ranks						
	1a*	2a*	3a*	4a*	5a*	Weight (%)
Net CO2 avoided	5	1	4	2	2	10.0
Net CO2 utilised	1	1	5	1	1	10.6
GWP	4	1	2	5	3	13.9
EP	4	1	5	1	1	3.9
AP	5	2	1	4	2	3.9
ODP	4	3	5	2	1	3.9
POCP	5	1	3	3	1	3.9
MAETP	4	1	3	5	2	3.9
FAETP	4	2	5	3	1	3.9
TETP	4	2	1	5	2	3.9
HTP	5	4	1	3	1	6.1
PM	5	2	1	2	2	6.1
FD	4	1	3	5	2	12.2
ADP	3	5	1	2	4	4.4
Utilities costs	2	4	1	3	5	9.4
Total	3.9	2.1	2.7	3.1	2.0	
Rank	5	2	3	4	1	

Indicators	Scenarios for Urea					*Weight (%)*
	1a	*2a*	*3a*	*4a*	*5a*	
Net CO_2 avoided	0.200000	-0.130000	0.000000	0.210000	-0.120000	10.0
Net CO_2 utilised	-0.077056	-0.077056	0.000000	-0.077056	-0.077056	10.6
GWP	0.833333	0.347222	0.527778	0.847222	0.361111	13.9
EP	0.000066	0.000035	0.000264	0.000070	0.000035	3.9
AP	0.000817	0.000194	0.000583	0.000583	0.000000	3.9
ODP	3.03E-11	2.18E-11	2.06E-08	1.48E-11	6.22E-12	3.9
POCP	0.000078	0.000023	0.000039	0.000078	0.000023	3.9
MAETP	16.916667	8.011111	94.111111	17.422222	8.516667	3.9
FAETP	0.000350	0.000350	0.012639	0.000350	0.000156	3.9
TETP	0.000350	0.000156	0.001478	0.000311	0.000156	3.9
HTP	0.030556	0.004889	0.132611	0.018333	0.011000	6.1
PM	0.000306	0.000122	0.000306	0.000367	0.000183	6.1
FD	0.232222	0.107556	0.177222	0.146667	0.113667	12.2
ADP	2.84E-08	1.02E-07	7.11E-07	2.40E-08	9.78E-08	4.4
Utilities costs	0.043444	0.100111	0.107667	0.043444	0.101056	9.4
Sum	18.181133	8.364714	95.071699	18.612592	8.906997	100

Urea ranks						
	1a*	2a*	3a*	4a*	5a*	Weight (%)
Net CO2 avoided	4	1	3	5	2	10.0
Net CO2 utilised	1	1	5	1	1	10.6
GWP	4	1	3	5	2	13.9
EP	3	1	5	4	1	3.9
AP	5	2	3	3	1	3.9
ODP	4	3	5	2	1	3.9
POCP	4	1	3	4	1	3.9
MAETP	4	2	6	5	3	3.9
FAETP	2	2	5	2	1	3.9
TETP	4	1	5	3	1	3.9
HTP	4	1	5	3	2	6.1
PM	3	1	3	5	2	6.1
FD	5	1	4	3	2	12.2
ADP	2	4	5	1	3	4.4
Utilities costs	1	3	5	1	4	9.4
Total	3.3	1.7	4.3	3.1	1.8	
Rank	4	1	5	3	2	

Indicators	**Methanol Scenarios (FD weight 100)**					*Weight (%)*
	1a	*2a*	*3a*	*4a*	*5a*	
Net CO_2 avoided	0	0	0	0	0	0.0
Net CO_2 utilised	0	0	0	0	0	0.0
GWP	0	0	0	0	0	0.0
EP	0	0	0	0	0	0.0
AP	0	0	0	0	0	0.0
ODP	0	0	0	0	0	0.0
POCP	0	0	0	0	0	0.0
MAETP	0	0	0	0	0	0.0
FAETP	0	0	0	0	0	0.0
TETP	0	0	0	0	0	0.0
HTP	0	0	0	0	0	0.0
PM	0	0	0	0	0	0.0
FD	3	0.97	1.43	3.09	1.03	100.0
ADP	0	0	0	0.00E+00	0	0.0
Utilities costs	0	0	0	0	0	0.0
Sum	3.0	1.0	1.4	3.1	1.0	100

Indicators	**Urea Scenarios (FD weight 100)**					*Weight (%)*
	1a	*2a*	*3a*	*4a*	*5a*	
Net CO_2 avoided	0.00	0.00	0.00	0.00	0.00	0.0
Net CO_2 utilised	0.00	0.00	0.00	0.00	0.00	0.0
GWP	0.00	0.00	0.00	0.00	0.00	0.0
EP	0.00	0.00	0.00	0.00	0.00	0.0
AP	0.00	0.00	0.00	0.00	0.00	0.0
ODP	0.00	0.00	0.00	0.00	0.00	0.0
POCP	0.00	0.00	0.00	0.00	0.00	0.0
MAETP	0.00	0.00	0.00	0.00	0.00	0.0
FAETP	0.00	0.00	0.00	0.00	0.00	0.0
TETP	0.00	0.00	0.00	0.00	0.00	0.0
HTP	0.00	0.00	0.00	0.00	0.00	0.0
PM	0.00	0.00	0.00	0.00	0.00	0.0
FD	1.90	0.88	1.45	1.20	0.93	100.0
ADP	0.00	0.00	0.00	0.00	0.00	0.0
Utilities costs	0.00	0.00	0.00	0.00	0.00	0.0
Sum	1.90	0.88	1.45	1.20	0.93	100

Methanol ranks (FD weight 100)						
	1a*	2a*	3a*	4a*	5a*	Weight (%)
Net CO_2 avoided	1	1	1	1	1	0.0
Net CO_2 utilised	1	1	1	1	1	0.0
GWP	1	1	1	1	1	0.0
EP	1	1	1	1	1	0.0
AP	1	1	1	1	1	0.0
ODP	1	1	1	1	1	0.0
POCP	1	1	1	1	1	0.0
MAETP	1	1	1	1	1	0.0
FAETP	1	1	1	1	1	0.0
TETP	1	1	1	1	1	0.0
HTP	1	1	1	1	1	0.0
PM	1	1	1	1	1	0.0
FD	4	1	3	5	2	100.0
ADP	1	1	1	1	1	0.0
Utilities costs	1	1	1	1	1	0.0
Total	1.2	1.0	1.1	1.3	1.1	
Rank	4	1	3	5	2	

Urea ranks (FD weight 100)						
	1a*	2a*	3a*	4a*	5a*	Weight (%)
Net CO_2 avoided	1	1	1	1	1	0.0
Net CO_2 utilised	1	1	1	1	1	0.0
GWP	1	1	1	1	1	0.0
EP	1	1	1	1	1	0.0
AP	1	1	1	1	1	0.0
ODP	1	1	1	1	1	0.0
POCP	1	1	1	1	1	0.0
MAETP	1	1	1	1	1	0.0
FAETP	1	1	1	1	1	0.0
TETP	1	1	1	1	1	0.0
HTP	1	1	1	1	1	0.0
PM	1	1	1	1	1	0.0
FD	5	1	4	3	2	100.0
ADP	1	1	1	1	1	0.0
Utilities costs	1	1	1	1	1	0.0
Total	1.3	1.0	1.2	1.1	1.1	
Rank	5	1	4	3	2	

Indicators	**Methanol Scenarios (FD weight 100:25)**					*Weight (%)*
	1a	*2a*	*3a*	*4a*	*5a*	
Net CO_2 avoided	0.322222	-0.04444	0	-0.02778	-0.0278	5.6
Net CO_2 utilised	-0.07667	-0.07667	0	-0.07667	-0.0767	5.6
GWP	0.511111	0.111111	0.116667	0.527778	0.12778	5.6
EP	0.000111	5.56E-05	0.000189	5.56E-05	5.6E-05	5.6
AP	0.001833	0.000611	0.000333	0.001667	0.00061	5.6
ODP	7.22E-11	5.06E-11	8.89E-09	3.33E-11	7.8E-12	5.6
POCP	0.000111	3.89E-05	5.56E-05	5.56E-05	3.9E-05	5.6
MAETP	39.22222	12.94444	15	40.09778	13.7778	5.6
FAETP	0.000833	0.000278	0.004611	0.000756	0.00022	5.6
TETP	0.000444	0.000167	0.000111	0.0005	0.00017	5.6
HTP	0.046667	0.03	0.011111	0.028889	0.01111	5.6
PM	0.000444	0.000167	2.22E-05	0.000167	0.00017	5.6
FD	0.666667	0.215556	0.317778	0.686667	0.22889	22.2
ADP	6.11E-08	2.33E-07	3.61E-08	5.00E-08	2.2E-07	5.6
Utilities costs	0.036667	0.1	0.026111	0.038889	0.10556	5.6
Sum	40.7	13.3	15.5	41.3	14.1	100

Indicators	**Urea Scenarios (FD weight 100:25)**					*Weight (%)*
	1a	*2a*	*3a*	*4a*	*5a*	
Net CO_2 avoided	0.11111	-0.0722	0	0.11667	-0.0667	5.6
Net CO_2 utilised	-0.04	-0.04	0.00	-0.04	-0.04	5.6
GWP	0.33	0.14	0.21	0.34	0.14	5.6
EP	0.0001	0.0001	0.0004	0.0001	0.0001	5.6
AP	0.0012	0.0003	0.0008	0.0008	0.0000	5.6
ODP	4.33E-11	3.11E-11	2.94E-08	2.11E-11	8.89E-12	5.6
POCP	0.0001	0.0000	0.0001	0.0001	0.0000	5.6
MAETP	24.17	11.44	134.44	24.89	12.17	5.6
FAETP	0.0005	0.0005	0.0181	0.0005	0.0002	5.6
TETP	0.0005	0.0002	0.0021	0.0004	0.0002	5.6
HTP	0.03	0.00	0.12	0.02	0.01	5.6
PM	0.0003	0.0001	0.0003	0.0003	0.0002	5.6
FD	0.42	0.20	0.32	0.27	0.21	22.2
ADP	1.28E-07	3.56E-08	8.89E-07	3.00E-08	1.22E-07	5.6
Utilities costs	0.03	0.06	0.06	0.03	0.06	5.6
Sum	25.0	11.7	135.2	25.6	12.5	100

Methanol ranks (FD weight 100:25)						
	1a*	2a*	3a*	4a*	5a*	Weight (%)
Net CO_2 avoided	5	1	4	2	2	5.6
Net CO_2 utilised	1	1	5	1	1	5.6
GWP	4	1	2	5	3	5.6
EP	4	1	5	1	1	5.6
AP	5	2	1	4	2	5.6
ODP	4	3	5	2	1	5.6
POCP	5	1	3	3	1	5.6
MAETP	4	1	3	5	2	5.6
FAETP	4	2	5	3	1	5.6
TETP	4	2	1	5	2	5.6
HTP	5	4	1	3	1	5.6
PM	5	2	1	2	2	5.6
FD	4	1	3	5	2	22.2
ADP	3	5	1	2	4	5.6
Utilities costs	2	4	1	3	5	5.6
Total	3.9	2.1	2.7	3.1	2.0	
Rank	5	2	3	4	1	

Urea ranks (FD weight 100:25)						
	1a*	2a*	3a*	4a*	5a*	Weight (%)
Net CO_2 avoided	4	1	3	5	2	5.6
Net CO_2 utilised	1	1	5	1	1	5.6
GWP	4	1	3	5	2	5.6
EP	3	1	5	4	1	5.6
AP	5	2	3	3	1	5.6
ODP	4	3	5	2	1	5.6
POCP	4	1	3	4	1	5.6
MAETP	3	1	5	4	2	5.6
FAETP	2	2	5	2	1	5.6
TETP	4	1	5	3	1	5.6
HTP	4	1	5	3	2	5.6
PM	3	1	3	5	2	5.6
FD	5	1	4	3	2	22.2
ADP	4	2	5	1	3	5.6
Utilities costs	1	3	5	1	4	5.6
Total	3.4	1.5	4.3	3.1	1.7	
Rank	4	1	5	3	2	

Indicators	Methanol Scenarios (GWP weight 100:25)					*Weight (%)*
	1a	*2a*	*3a*	*4a*	*5a*	
Net CO$_2$ avoided	0.322222	-0.04444	0	-0.02778	-0.0278	5.6
Net CO$_2$ utilised	-0.07667	-0.07667	0	-0.07667	-0.0767	5.6
GWP	2.044444	0.444444	0.466667	2.111111	0.51111	22.2
EP	0.000111	5.56E-05	0.000189	5.56E-05	5.6E-05	5.6
AP	0.001833	0.000611	0.000333	0.001667	0.00061	5.6
ODP	7.22E-11	5.06E-11	8.89E-09	3.33E-11	7.8E-12	5.6
POCP	0.000111	3.89E-05	5.56E-05	5.56E-05	3.9E-05	5.6
MAETP	39.22222	12.94444	15	40.09778	13.7778	5.6
FAETP	0.000833	0.000278	0.004611	0.000756	0.00022	5.6
TETP	0.000444	0.000167	0.000111	0.0005	0.00017	5.6
HTP	0.046667	0.03	0.011111	0.028889	0.01111	5.6
PM	0.000444	0.000167	2.22E-05	0.000167	0.00017	5.6
FD	0.166667	0.053889	0.079444	0.171667	0.05722	5.6
ADP	6.11E-08	2.33E-07	3.61E-08	5.00E-08	2.2E-07	5.6
Utilities costs	0.036667	0.1	0.026111	0.038889	0.10556	5.6
Sum	41.8	13.5	15.6	42.3	14.4	100

Indicators	Urea Scenarios (GWP weight 100:25)					*Weight (%)*
	1a	*2a*	*3a*	*4a*	*5a*	
Net CO$_2$ avoided	0.11	-0.07	0.00	0.12	-0.07	5.6
Net CO$_2$ utilised	-0.04	-0.04	0.00	-0.04	-0.04	5.6
GWP	1.33	0.56	0.84	1.36	0.58	22.2
EP	0.0001	0.0001	0.0004	0.0001	0.0001	5.6
AP	0.0012	0.0003	0.0008	0.0008	0.0000	5.6
ODP	4.33E-11	3.11E-11	2.94E-08	2.11E-11	8.89E-12	5.6
POCP	0.0001	0.0000	0.0001	0.0001	0.0000	5.6
MAETP	24.17	11.44	134.44	24.89	12.17	5.6
FAETP	0.001	0.001	0.018	0.001	0.000	5.6
TETP	0.001	0.000	0.002	0.0004	0.0002	5.6
HTP	0.028	0.004	0.121	0.017	0.010	5.6
PM	0.0003	0.0001	0.0003	0.0003	0.0002	5.6
FD	0.11	0.05	0.08	0.07	0.05	5.6
ADP	1.28E-07	3.56E-08	8.89E-07	3.00E-08	1.22E-07	5.6
Utilities costs	0.03	0.06	0.06	0.03	0.06	5.6
Sum	25.73	12.00	135.58	26.43	12.76	100

Methanol ranks (GWP weight 100:25)						
	1a*	2a*	3a*	4a*	5a*	Weight (%)
Net CO$_2$ avoided	5	1	4	2	2	5.6
Net CO$_2$ utilised	1	1	5	1	1	5.6
GWP	4	1	2	5	3	22.2
EP	4	1	5	1	1	5.6
AP	5	2	1	4	2	5.6
ODP	4	3	5	2	1	5.6
POCP	5	1	3	3	1	5.6
MAETP	4	1	3	5	2	5.6
FAETP	4	2	5	3	1	5.6
TETP	4	2	1	5	2	5.6
HTP	5	4	1	3	1	5.6
PM	5	2	1	2	2	5.6
FD	4	1	3	5	2	5.6
ADP	3	5	1	2	4	5.6
Utilities costs	2	4	1	3	5	5.6
Total	3.9	2.1	2.7	3.1	2.0	
Rank	5	2	3	4	1	

Urea ranks (GWP weight 100:25)						
	1a*	2a*	3a*	4a*	5a*	Weight (%)
Net CO$_2$ avoided	4	1	3	5	2	5.6
Net CO$_2$ utilised	1	1	5	1	1	5.6
GWP	4	1	3	5	2	22.2
EP	3	1	5	4	1	5.6
AP	5	2	3	3	1	5.6
ODP	4	3	5	2	1	5.6
POCP	4	1	3	4	1	5.6
MAETP	3	1	5	4	2	5.6
FAETP	2	2	5	2	1	5.6
TETP	4	1	5	3	1	5.6
HTP	4	1	5	3	2	5.6
PM	3	1	3	5	2	5.6
FD	5	1	4	3	2	5.6
ADP	4	2	5	1	3	5.6
Utilities costs	1	3	5	1	4	5.6
Total	3.4	1.5	4.3	3.1	1.7	
Rank	4	1	5	3	2	

Indicators	Methanol Scenarios (GWP weight 100)					*Weight (%)*
	1a	*2a*	*3a*	*4a*	*5a*	
Net CO_2 avoided	0	0	0	0	0	0.0
Net CO_2 utilised	0	0	0	0	0	0.0
GWP	9.2	2	2.1	9.5	2.3	100.0
EP	0	0	0	0	0	0.0
AP	0	0	0	0	0	0.0
ODP	0	0	0	0	0	0.0
POCP	0	0	0	0	0	0.0
MAETP	0	0	0	0	0	0.0
FAETP	0	0	0	0	0	0.0
TETP	0	0	0	0	0	0.0
HTP	0	0	0	0	0	0.0
PM	0	0	0	0	0	0.0
FD	0	0	0	0	0	0.0
ADP	0	0	0	0.00E+00	0	0.0
Utilities costs	0	0	0	0	0	0.0
Sum	9.2	2.0	2.1	9.5	2.3	100

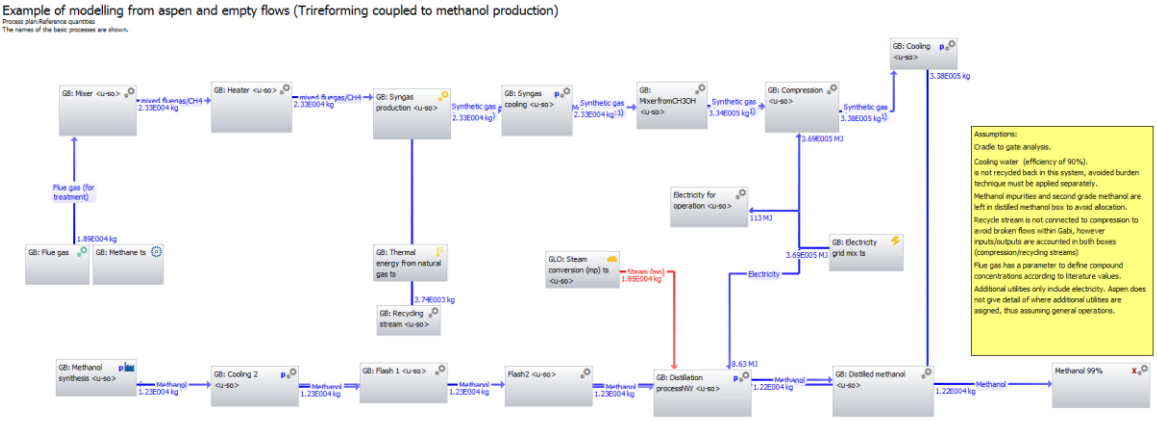
Methanol ranks (GWP weight 100)						
	1a*	2a*	3a*	4a*	5a*	Weight (%)
Net CO_2 avoided	1	1	1	1	1	0.0
Net CO_2 utilised	1	1	1	1	1	0.0
GWP	4	1	2	5	3	100.0
EP	1	1	1	1	1	0.0
AP	1	1	1	1	1	0.0
ODP	1	1	1	1	1	0.0
POCP	1	1	1	1	1	0.0
MAETP	1	1	1	1	1	0.0
FAETP	1	1	1	1	1	0.0
TETP	1	1	1	1	1	0.0
HTP	1	1	1	1	1	0.0
PM	1	1	1	1	1	0.0
FD	1	1	1	1	1	0.0
ADP	1	1	1	1	1	0.0
Utilities costs	1	1	1	1	1	0.0
Total	1.2	1.0	1.1	1.3	1.1	
Rank	4	1	2	5	3	

Indicators	Urea Scenarios (GWP weight 100)					*Weight (%)*
	1a	*2a*	*3a*	*4a*	*5a*	
Net CO_2 avoided	0.00	0.00	0.00	0.00	0.00	0.0
Net CO_2 utilised	0.00	0.00	0.00	0.00	0.00	0.0
GWP	6.00	2.50	3.80	6.10	2.60	100.0
EP	0.00	0.00	0.00	0.00	0.00	0.0
AP	0.00	0.00	0.00	0.00	0.00	0.0
ODP	0.00	0.00	0.00	0.00	0.00	0.0
POCP	0.00	0.00	0.00	0.00	0.00	0.0
MAETP	0.00	0.00	0.00	0.00	0.00	0.0
FAETP	0.00	0.00	0.00	0.00	0.00	0.0
TETP	0.00	0.00	0.00	0.00	0.00	0.0
HTP	0.00	0.00	0.00	0.00	0.00	0.0
PM	0.00	0.00	0.00	0.00	0.00	0.0
FD	0.00	0.00	0.00	0.00	0.00	0.0
ADP	0.00	0.00	0.00	0.00	0.00	0.0
Utilities costs	0.00	0.00	0.00	0.00	0.00	0.0
Sum	6.00	2.50	3.80	6.10	2.60	100

Urea ranks (GWP weight 100)						
	1a*	2a*	3a*	4a*	5a*	Weight (%)
Net CO_2 avoided	1	1	1	1	1	0.0
Net CO_2 utilised	1	1	1	1	1	0.0
GWP	4	1	3	5	2	100.0
EP	1	1	1	1	1	0.0
AP	1	1	1	1	1	0.0
ODP	1	1	1	1	1	0.0
POCP	1	1	1	1	1	0.0
MAETP	1	1	1	1	1	0.0
FAETP	1	1	1	1	1	0.0
TETP	1	1	1	1	1	0.0
HTP	1	1	1	1	1	0.0
PM	1	1	1	1	1	0.0
FD	1	1	1	1	1	0.0
ADP	1	1	1	1	1	0.0
Utilities costs	1	1	1	1	1	0.0
Total	1.2	1.0	1.1	1.3	1.1	
Rank	4	1	3	5	2	

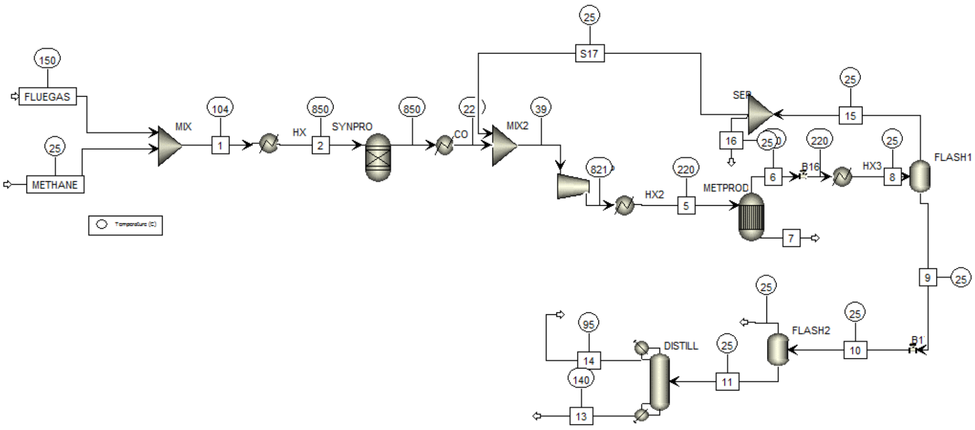
Appendix VIII

Examples of models adapted directly from Aspen Plus© version 8.4 simulations to test how information can be used for the inventory (these cases were not used for results).

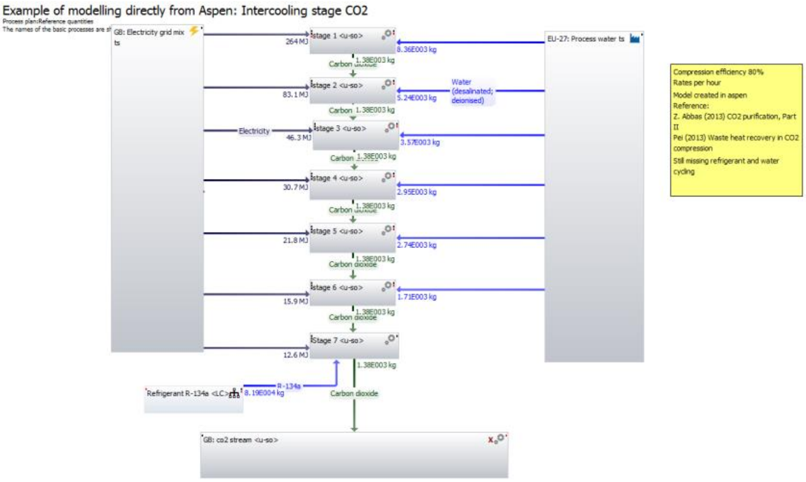

Example of modelling from aspen and empty flows (Trireforming coupled to methanol production)

Process plan:Reference quantities
The names of the basic processes are shown.

Assumptions:
Cradle to gate analysis.
Cooling water (efficiency of 90%).
is not recycled back in this system, avoided burden technique must be applied separately.
Methanol impurities and second grade methanol are left in distilled methanol box to avoid allocation.
Recycle stream is not connected to compression to avoid broken flows within Gabi, however inputs/outputs are accounted in both boxes (compression/recycling streams)
Flue gas has a parameter to define compound concentrations according to literature values.
Additional utilities only include electricity. Aspen does not give detail of where additional utilities are asigned, thus assuming general operations.



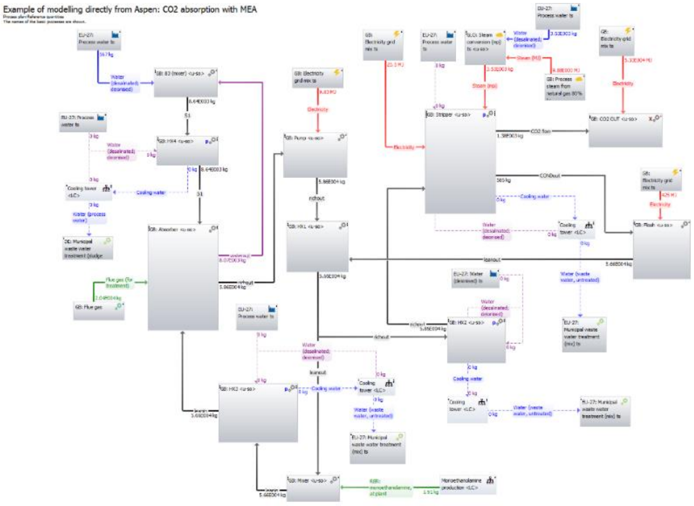
Direct flue gas utilisation process example based on the work by Zhang (2013) and using Aspen Plus© version 8.4 and GaBi ts version 8.7.0.18 software for modelling

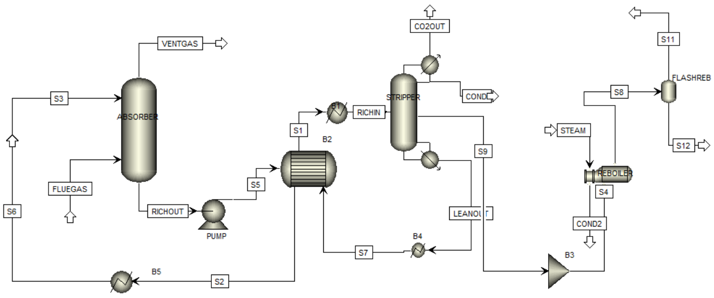

Example of modelling directly from Aspen: Intercooling stage CO2

Process plan:Reference quantities
The names of the basic processes are s

Compression efficiency 80%
Rates per hour
Model created in aspen
Reference:
Z. Abbas (2013) CO2 purification, Part II
Pei (2013) Waste heat recovery in CO2 compression
Still missing refrigerant and water cycling

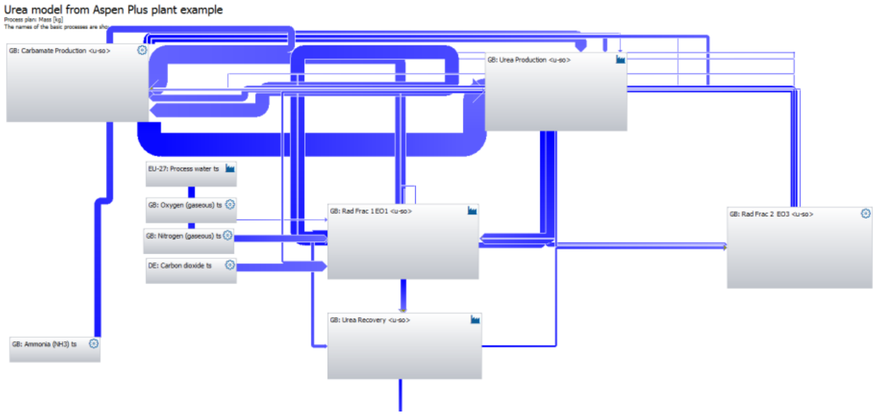
Inputs/outputs for a seven-stage compressor for CO_2 intercooling based on Abbas *et al.* (2013) and Pei (2013) using GaBi ts version 8.7.0.18 software





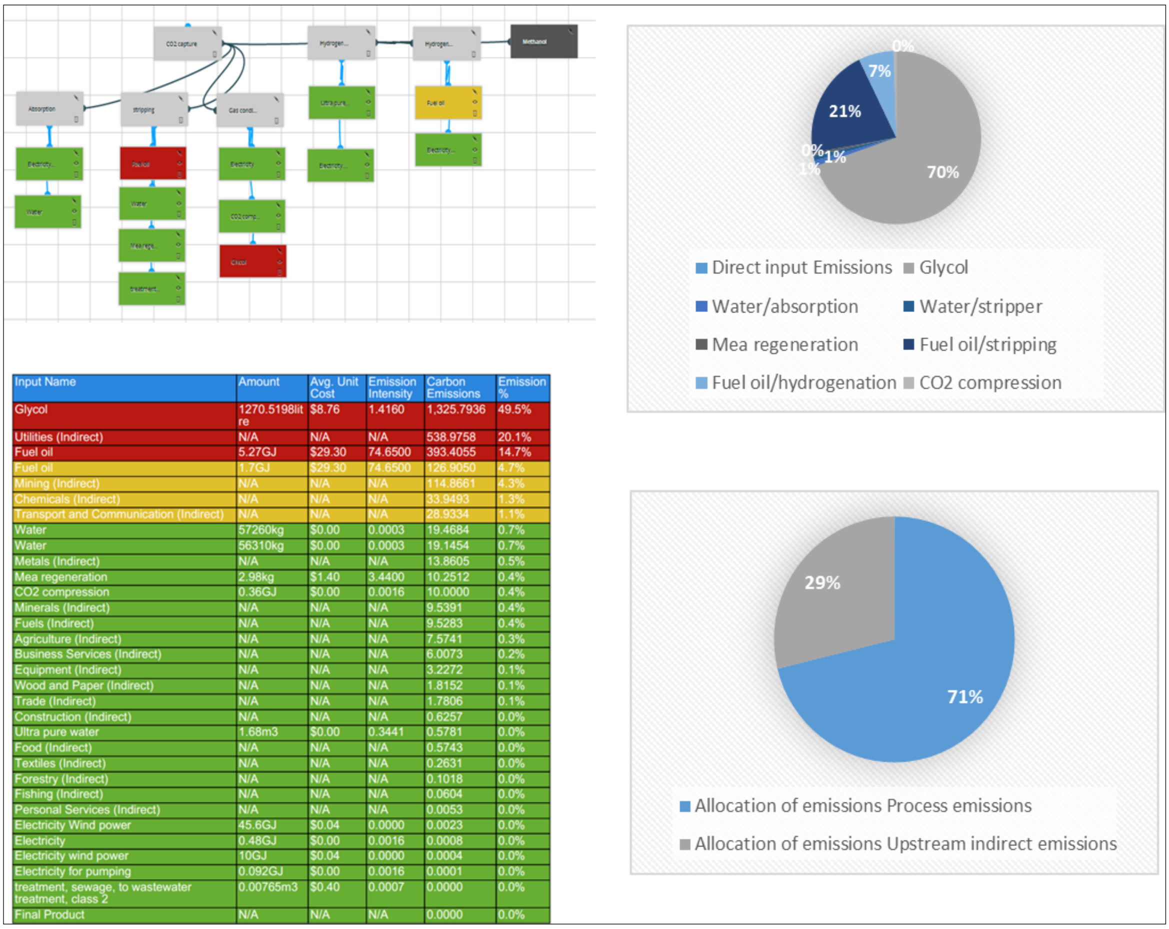
Absorption column for CO_2 capture model ENRTL-RK-Rate based monoethanolamine (MEA) by Aspen Plus® version 8.4. Inputs/outputs using GaBi version 8.7.0.18 ts for modelling.

An example on how by connecting every stream from a simulation model to a life cycle assessment (LCA) software by following every input and out will lead to unnecessary loops and broken flows is shown below.



Inputs/outputs using GaBi ts version 8.7.0.18 for modelling. Based on a urea pilot plant from by Aspen Plus® version 8.4.

An example of using other carbon footprint tools to model CO_2 utilisation processes is shown below. In this case, the Supply Chain Environmental Analysis tool (scenat) was used to calculate methanol production with a similar process used in **Chapter 5**. The results gave basic information: direct vs indirect emissions, emission intensity and input/output hotspot. However, using a tool such as this one proved of limited use for carbon dioxide utilisation (CDU). These commercial tools are suited for complete supply chains that have a place in the economic sector, unlike utilisation processes. Mapping full processes is difficult since there is no flexibility with the database (fixed hybrid input/output method), complicates allocation and does not have access to other environmental impact categories. It can be used for a quick reference for some established processes, but it is not a tool to create new CO_2 utilisation processes and assess them.



Input Name	Amount	Avg. Unit Cost	Emission Intensity	Carbon Emissions	Emission %
Glycol	1270.5198litre	$8.76	1.4160	1,325.7936	49.5%
Utilities (Indirect)	N/A	N/A	N/A	538.9758	20.1%
Fuel oil	5.27GJ	$29.30	74.6500	393.4055	14.7%
Fuel oil	1.7GJ	$29.30	74.6500	126.9050	4.7%
Mining (Indirect)	N/A	N/A	N/A	114.8661	4.3%
Chemicals (Indirect)	N/A	N/A	N/A	33.9493	1.3%
Transport and Communication (Indirect)	N/A	N/A	N/A	28.9334	1.1%
Water	57260kg	$0.00	0.0003	19.4684	0.7%
Water	56310kg	$0.00	0.0003	19.1454	0.7%
Metals (Indirect)	N/A	N/A	N/A	13.8605	0.5%
Mea regeneration	2.98kg	$1.40	3.4400	10.2512	0.4%
CO2 compression	0.36GJ	$0.00	0.0016	10.0000	0.4%
Minerals (Indirect)	N/A	N/A	N/A	9.5391	0.4%
Fuels (Indirect)	N/A	N/A	N/A	9.5283	0.4%
Agriculture (Indirect)	N/A	N/A	N/A	7.5741	0.3%
Business Services (Indirect)	N/A	N/A	N/A	6.0073	0.2%
Equipment (Indirect)	N/A	N/A	N/A	3.2272	0.1%
Wood and Paper (Indirect)	N/A	N/A	N/A	1.8152	0.1%
Trade (Indirect)	N/A	N/A	N/A	1.7806	0.1%
Construction (Indirect)	N/A	N/A	N/A	0.6257	0.0%
Ultra pure water	1.68m3	$0.00	0.3441	0.5781	0.0%
Food (Indirect)	N/A	N/A	N/A	0.5743	0.0%
Textiles (Indirect)	N/A	N/A	N/A	0.2631	0.0%
Forestry (Indirect)	N/A	N/A	N/A	0.1018	0.0%
Fishing (Indirect)	N/A	N/A	N/A	0.0604	0.0%
Personal Services (Indirect)	N/A	N/A	N/A	0.0053	0.0%
Electricity Wind power	45.6GJ	$0.04	0.0000	0.0023	0.0%
Electricity	0.48GJ	$0.00	0.0016	0.0008	0.0%
Electricity wind power	10GJ	$0.04	0.0000	0.0004	0.0%
Electricity for pumping	0.092GJ	$0.00	0.0016	0.0001	0.0%
treatment, sewage, to wastewater treatment, class 2	0.00765m3	$0.40	0.0007	0.0000	0.0%
Final Product	N/A	N/A	N/A	0.0000	0.0%

Inputs/outputs example for methanol production using the modelling tool scenat (Supply Chain Environmental Analysis tool)