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Frauzem, Rebecca; Vooradi, Ramsagar ; Bertran, Maria-Ona; Frauzem, Rebecca; Anne, Sarath Babu; Gani, Rafiqul

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Sustainable chemical processing and energy-carbon dioxide management: review of challenges and opportunities

Ramsagar Vooradi², Maria-Ona Bertran¹, Rebecca Frauzem¹, Sarath Babu Anne², Rafiqul Gani¹

¹Department of Chemical & Biochemical Engineering, Technical University of Denmark, DK-2800 Lyngby, Denmark

²Chemical Engineering Department, National Institute of Technology Warangal, Telangana-506004, India

Abstract

This paper presents a brief review of the available energy sources for consumption, their effects in terms of CO₂-emission and its management, and sustainable chemical processing where energy-consumption, CO₂-emission, as well as economics and environmental impacts are considered. Not all available energy sources are being utilized efficiently, while, the energy source causing the largest emission of CO₂ is being used in the largest amount. The CO₂ management is therefore looking at “curing” the problem rather than “preventing” it. Examples highlighting the synthesis, design and analysis of sustainable chemical processing in the utilization of biomass-based energy-chemicals production, carbon-capture and utilization with zero or negative CO₂-emission to produce value added chemicals as well as retrofit design of energy intensive chemical processes with significant reduction of energy-consumption are presented. These examples highlight issues of energy-sustainable design, energy-CO₂ neutral design, energy-retrofit design, and energy-process intensification. Finally, some perspectives on the status and future directions of carbon dioxide management are given.

Keywords

Carbon dioxide management; Energy efficiency; Process synthesis; Sustainable process design
Process intensification; Process Systems Engineering

1. Introduction

Energy consumption per capita is one of the most important parameters to assess the quality of life of the population of a country. Thus, sustainable harnessing of the available energy resources with a view to meet the necessities of increasing world population, to ensure a safe and healthy living of the present as well as the future generations on earth, is an essential ingredient of all governmental planning (Brundtland Commission, 1987). As Figure 1 shows, the total world energy consumption is reported to rise to 815 quadrillion Btu in 2040 from 549 quadrillion Btu in 2012, that is, an increase of 48% in a span of 28 years (The International Energy Outlook, 2016). As can be seen from Figure 1, fossil fuels are going to be the mainstay for global energy requirements, for several decades to come. However, if adequate measures are not employed, the use of fossil fuels for power generation is bound to result in increased CO₂ releases.

Additionally, use of fossil fuels for transportation, industrial operations and agricultural activities are associated with massive global CO₂ emissions and the resultant increase in the atmospheric CO₂ levels. It is established that carbon dioxide alone accounts for nearly (77%) of the global Green House Gas (GHG) emissions (IPCC, 2007). Recently, in view of generation of energy from renewable sources (solar energy, wind energy, tidal energy, etc.) as well as the need for more efficient usage of energy, supplementing, and/or replacing non-renewable sources (coal, crude-oil, natural gas, etc.) as well as reducing their usage has become an alternative worth investigating. The availability of these resources is however, dependent on geographic location as well as the seasonal and nocturnal variations. Furthermore, the requirement of land for exploitation of solar and wind is considerably high.

[Insert Figure 1 here]

A target level of 450 ppm CO₂-equivalent concentration has been predicted by many models as the concentration needed to stabilize the global average temperature increase to 2 °C at the end of 21st century (Hare, et al. 2011; OECD, 2012). Global CO₂ monitoring at Mauna Loa in Hawaii shows that the concentration of CO₂ is already above 400 ppm (CO₂-Earth, 2017), that is, almost nearing the established target limit. To limit the CO₂-equivalent concentration to 450 ppm, between 40% to 70 % of the total anthropogenic emissions need to be reduced by 2050, compared to 2010 emissions, and no anthropogenic emissions by 2100 (IPCC, 2014). Hence the present practice of using fossil fuels as the energy source must not continue and there is an urgent need to reduce the CO₂ emission and thereby, global warming through better management of energy-consumption, CO₂-emission and their management. To reduce the global carbon dioxide emissions, different approaches have been proposed:

- improvement of process efficiencies to reduce energy consumption (Duflo, et al. 2012; Tula, et al. 2017);
- utilization of alternative energy sources (e.g., solar energy, wind power and geothermal) and renewable (e.g., biomass and biofuel) as opposed to currently dominant fossil fuel based sources (Karakosta, et al. 2013; Hussain, et al. 2017);
- application of carbon dioxide capture, sequestration & utilization (CCS & U) technologies (Cuellar-Franca and Azapagic, 2015; Dowell, et al. 2017).

For a sustainable energy management scenario, not just one of the above approaches, but a judicious mix of all three needs to be employed. However, such an integrated approach would need to address issues of economic feasibility, energy consumption and related direct-indirect CO₂ emissions together with other performance factors. Therefore, the availability of energy sources, the CO₂-emission and management and sustainability of manufacturing process alternatives need to be carefully studied to determine the best options.

Due to the increasing emissions from industrial sources, natural removal of GHG via photosynthesis and absorption on the sea surface are not able to balance the emission sources and therefore cannot keep the CO₂ concentration within the desired threshold limit of 450 ppm (Peters, et al. 2012). The scope of some recent techno-economic studies (Rubin, et al. 2012;

Yuan, et al. 2016; and Rahman, et al. 2017) on combined CO₂ capture and sequestration (CCS), and CO₂ capture and utilization (CCU) are highlighted in Figure 2. Frauzem et al (2017) have reported results from sustainable design of CCU for the production of higher value chemicals like dimethyl carbonate.

[Insert Figure 2 here]

Although CCS and CCU have the potential to significantly impact the stabilization of CO₂ concentration in the atmosphere, in their execution, challenges such as additional cost, storage related problems, technical competences, organizational policies and environmental complexities have not yet been adequately addressed (Rahman, et al. 2017). The enormity of the energy management-CO₂ mitigation problem raises the question - would the current CCS and CCU efforts actually reduce the global warming (or CO₂ concentration in the atmosphere) to the desired level? The current global emission rate of CO₂ is about 35.5 Gt per year due to various anthropogenic activities, requiring a volume of 1,033 million barrels per day of emitted CO₂ at a possible storage condition of pressure=10 MPa, temperature=40 °C and density=600 kg/m³. This volume is approximately 10 times greater than the current global oil production. Presently more than 60 million tons per year of CO₂ is used for enhanced oil recovery (EOR) application and a similar amount is captured and sequestered (Wallace and Kuuskraa, 2014; Dowell, et al., 2017). In 2013, 200 Mt of CO₂ was utilized to yield different products and in 2016 the forecasted CO₂ utilization is about 299 Mt. In order to stabilize the global CO₂ concentration at 450 ppm, it is expected that about 120-160 Gt of CO₂ will need to be sequestered by 2050 (IEA, 2013). The analysis by Dowell, et al., 2017 shows that about 800 Gt of CO₂ need to be captured during the 2010-2150 period in order to ensure that global temperature rise will not exceed by 2 °C. In order to meet the mitigation challenge of 800 Gt of CO₂ in a sustainable manner, recent technologies, such as the use of CO₂ in enhanced oil recovery (CO₂-EOR) and carbon capture and utilization (CCU), will need to be well established to take equal share along with carbon capture and sequestration (CCS), which could be considered as a mature technology compared with the other two.

As can be observed from the above discussion, much of the effort put on reducing the CO₂ concentration levels in the atmosphere appears to be trying to “cure” the problem rather than “preventing” the problem. That is, curing the problem is to capture the CO₂ after it has been generated and released mostly because of the use of fossil fuel based energy. Preventing the problem, on the other hand, is generating and releasing significantly lower amounts of CO₂, by for example, reducing the consumption of fossil fuel through improved process design-synthesis-intensification.

Sustainability is defined as “the ability to meet current needs without compromising the ability of future generations to meet their needs” (Brundtland Commission, 1987). The past environmental issues, including global warming, prompted the Brundtland Commission to recommend the search for sustainable solutions. In this respect, sustainable chemical and biochemical processes must perform better than existing process alternatives measured in terms of a set of sustainability

(performance) metrics (ICHEME, 2002). Among the sustainability metrics, the need for energy per kg product, the carbon foot-print, the global warming potential, among others are included, as well as economic-social factors such as profit and jobs created. Therefore, finding more sustainable process alternatives means, for example, more profit, less energy consumption and lower carbon foot-print.

The objective of this paper is to briefly review the current state of the art in availability-utilization of different energy sources, the consequent CO₂-emission management as well as developments in sustainable chemical process synthesis-design. In section 2, a brief review on the utilization of fossil fuels and other energy sources, including renewable sources are presented along with the associated challenges with respect to production costs and associated CO₂-emissions. Also, perspectives on replacing the fossil fuels with renewable and green sources are discussed. In section 3, issues related to CO₂ emission and management, including capture, sequestration and conversion are highlighted together with perspectives on their efficient management. Section 4 highlights developments in sustainable chemical process synthesis-design in terms of economics, energy conservation, safety, environmental, and social impacts. Section 5 presents examples of application of a 3-stage method for sustainable chemical process design for biorefinery, net CO₂ negative sustainable designs of CO₂ capture and utilization processes for production of value-added chemicals as well as applications of hybrid and process intensification methods to retrofit design with significant reduction of energy consumption.

2. Available Energy Sources

Energy is defined as capacity to do work and it manifests itself in many forms. Planet earth contains different forms of energy sources such as fossil fuels, renewables (biomass), nuclear and green energy sources (such as solar, wind, geothermal and hydro) from which high grade thermal energy can be obtained. This section briefly reviews the different energy sources, their usage statistics and associated environmental and technical challenges.

2.1. Energy from fossil fuels

Since the industrial revolution, fossil fuels such as coal, gas and oil have been considered to be the main energy sources to meet the ever increasing energy demand (Huber, 2009). Because of their ease of use, availability and price, compared to other energy sources, fossil fuels are currently the dominant energy source. In general, the use of fossil-based energy had a positive impact on economic growth and at the same time it had a negative impact on environment due to GHG emissions. One way to control these emissions is to implement energy-electricity conservation policies. However, the impact of such conservation policies on economic growth can be negative or positive depending on specific locations (Sharma, 2010). Also, this introduces a “social” dimension to the problem, which though very important, is outside the scope of this article.

Figure 3 shows CO₂ emission from the use of fossil fuels. Because of their abundance and relatively lower costs, fossil fuels are used widely in domestic as well as transport sectors in

addition to major applications in various industrial sectors. Figure 3(a) shows the emissions from use of fossil fuels in all sectors while Figure 3(b) shows only those from industrial sectors. As can be seen from the Fig 3(b), electric power plants are mainly responsible for the atmospheric CO₂ emissions, with a share of about 50%. In view of the unavoidable dependence on fossil fuels, at least for several decades, for meeting the global energy demand along with effective CCS or CCU techniques are essential to contain the CO₂ emissions. This, however, is “curing” the problem after it has occurred. According to IPCC report on Climate Change 2014, in order to maintain CO₂ concentration at 450 ppm by 2100, CO₂ emissions from the energy supply sector are expected to decline significantly over the next decade and in between 2040 and 2070 the emissions are supposed to reduce by 90% or more below 2010 levels. The “curing” strategies alone cannot handle this task efficiently due to the large volume of CO₂ that need to be captured and sequestered or utilized. Green energy technologies (solar, hydro, wind) along with energy efficient industrial processes can substantially reduce the burden on curing strategies by minimizing emissions. That is, to “prevent” the problem, it is necessary to implement energy efficient process designs and green energy technologies that significantly reduce the process energy demand and GHG emissions.

[Insert Figures 3a-3b here]

2.2. Renewable & green energy sources

Renewable energy is the energy obtained from renewable resources, which naturally restore on earth and/or in atmosphere on a human timescale. The main stream of renewable resources is biomass. Energy from renewables is a potential alternative to fossil fuel energy. In 2015, 1823 million tons of oil equivalents (Mtoe) of world Total Primary Energy Supply (TPEC) was from renewable and green energy sources (see Figure 4a). Renewable and green energy sources produce 22.8% of the total world electricity, which is the third largest contributor to global electricity production in 2015 (see Figure 4b). In this sub-section, the current state of art related to some of the important emerging renewable and green energy sources is discussed. Finally this sub-section is concluded with, some research facts on “do alternative energy sources displace fossil fuels?”

[Insert Figures 4a and 4b here]

Bioenergy: Energy in the form of heat/electricity/transportation fuel, which is derived from the any biomass is referred to as Bioenergy (Creutzig, et al. 2014). Currently bioenergy accounts for about 10% of global primary energy supply (Anselm and Adam, 2014). Currently 90 % of the total domestic heating requirement and 7 % of the industrial heat requirement are by biomass (REN21, 2017). In the year 2012, about 1900 barrels per day bio fuel and approximately 400 trillion kilowatt hours of electricity is produced from biomass (Faik, et al. 2017). In 2016, 4% of the world’s transport fuel demand is supplemented using biofuels. Recently, bioenergy attracted much attention due to the following advantages: substantial sources (Teske, et al. 2011), techno economic feasibility (Bhattacharya, et al. 2003), ensuring national energy security (Van Loo and Koppejan, 2008), enhancing rural employment and agricultural economy (Demirbas, et al. 2009), low CO₂ emissions (Faik, et al. 2017). However, the use of biomass on a large scale may not be a

sustainable option due to the following challenges: Natural vegetation has to be sacrificed for crop-based biofuels to accommodate their increase in demand (Elshout, et al. 2015), deforestation due to massive production of bioenergy (Rajcaniova, et al. 2014).

Solar energy: Solar energy is a primary source of energy that is abundantly available in most parts of the world. Sun emits solar energy at the rate of 3.8×10^{23} KW, of which only 1.8×10^{14} KW is intercepted by earth (Panwar, et al. 2011). There is sufficient scope to utilize available solar energy via solar thermal and solar photovoltaic (PV) based systems. In spite of several advantages, such as abundance, low contribution to carbon footprints, major barriers for solar energy are its fluctuating nature and high cost technology (Devabhaktuni, et al. 2013, Mohanty, et al. 2017). Many researchers investigated global solar energy scenarios, developments in solar power generation, photovoltaic collectors, solar heaters, design improvements and sizing, materials for efficient light absorption to overcome barriers and upgrade solar industry as a potential application (Kannan and Vakeesan, 2016; Modi, et al. 2017; Devbhaktuni, 2013; Mekhilef, et al. 2011). Figure 5 highlights the global capacity of solar photovoltaic (PV), Concentrating Solar Power (CSP) energy production and solar water heating applications, for the year 2015-2016 (REN21, 2017). Significant increase of total capacity generation in solar thermal energy applications represent the incorporation of new technologies and design improvements.

[Insert Figure 5 here]

Wind energy: Much like solar energy, wind energy also comprises only a small amount of the total energy that reaches the earth surface. It can be used either directly as mechanical power or indirectly by converting the kinetic energy of wind into electrical energy by means of wind turbine. In this technology, wind turbine is sub-divided into two categories, onshore wind turbines and offshore wind turbines. Both these turbine technologies bear striking similarities, the only significant difference being the design of the offshore wind turbines that require floating or other special foundations to account for underwater tower submergence (Kumar, 2016). Some of the main advantages of wind energy are its easy accessibility, pollution free energy source and feasibility for installation in rural areas. Wind energy also preserves the land and environment in rural areas and agriculture and animal husbandry in the vicinity can be easily dealt with. Although there are many advantages of wind energy, some of its main disadvantages are its unreliability, due to varying wind speed and noise pollution in the vicinity (Kaplan, 2015).

Figure 6 shows the installed wind power capacity in the world from 2001 to 2016. It is seen from Fig 6 that the world's total installed capacity was 486.749 GW with more than 12% growth rate in the annual market at the end of 2016. The steady increase of global wind energy generation capacity clearly indicates that there is a very large and growing global demand for emissions-free wind power almost throughout the world (GWEC, 2017). The wind industry sector also creates many new jobs, nearly half a million people are employed in this industry, and this number is expected to increase further (GWEC, 2012).

[Insert Figure 6 here]

Geothermal energy: The thermal energy available on earth's crust is called geothermal energy and energy is released due to radioactive decay of minerals including potassium, uranium and

thorium (Bahadori, et al. 2013). In the year 2016, 157 TWh of geothermal energy is produced in the form of electricity and thermal output (REN21, 2017). The main competing advantages of geothermal energy are low carbon emissions in energy production compared to fossil fuels and power production not being intermittent in nature, unlike solar and wind power (Abbas et al. 2014). Indonesia and Turkey installed the highest capacity (205 MW and 197 MW respectively) geothermal power plants in the year 2016 (REN21, 2017). To produce geothermal energy in a sustainable manner, research should be focused on addressing the issues highlighted in Figure 7 (Jiang, et al. 2017; Shortall, et al. 2015; Fridleifsson, et al. 2001; Chen and Jiang 2015; Kagel, et al. 2007).

[Insert Figure 7 here]

Hydro energy: Hydropower is a clean, efficient and hassle-free technology of power generation, as compared to other renewable energy sources. The flexibility and storage capacity of hydropower not only makes it possible to improve grid stability but also support the deployment of other intermittent renewable energy sources such as wind and solar power. Among all renewable energy sources, plant life of hydro power is the highest, about 35 years and generation tariff is the lowest, between 63.33-87.50 USD/MWh (Mishra et al., 2015). These advantages make it one of the best options as a renewable and sustainable energy source. Hydropower plants are categorized as reservoir based and run of river type. The run of river scheme harnesses energy from flow of water to produce power. Consequently, it has a low environmental impact and does not necessitate rehabilitation of people. Hydropower currently contributes to more than 50% of electricity derived from green energy sources (see Figure 4). Despite these advantages, large hydro projects face continued opposition due to their environmental and social repercussions (landscape, biodiversity, wildlife, population settlement, health, and water quality). The percentage of undeveloped hydropower capacity is very high in certain regions: Africa (92%), followed by Asia (80%), Oceania (80%) and Latin America (74%) (Ardizzon, 2014). With small size projects and improved designs for minimizing the environmental effects, hydropower production can be a viable option.

Tidal energy: Around 70% of the earth's mass is covered by oceans, which are a great green energy source. Energy is stored in oceans in the form of thermal energy (heat), kinetic energy (tides and waves), chemical energy (chemicals) and biological energy (biomass). Uninterrupted supply of tidal energy due to dynamic behavior of the oceans makes it a reliable energy source (Khan, 2017). As it depends only on the gravitational attraction between the moon and the sun and the centrifugal forces due to the rotation of the earth and moon, it is predictable in nature (Rourke, 2010). Among the ocean energy technologies, wave and ocean thermal technologies are at an early stage of development (Uihlein, 2016). Small to medium capacity tidal power generation plants (3.2-250 MW) are under operation globally and big capacity projects (2000-1200 MW) are being planned (Khan, 2017). Segura, (2017) carried out life-cycle cost assessment of different energy systems and presented in terms of levelized cost of energy (LCOE), showing that LCOE is very high for wave and tidal, due to premature technologies.

2.3. Nuclear energy

Nuclear energy is the only base load power source that can replace/supplement fossil fuels. During 2014 about 10% of total world energy consumption has been met from nuclear energy and in 2016, total nuclear capacity supplying electricity to the grid is 350 GWe (WNN, 2017). The International Energy Outlook 2016 reports that nuclear power generation is expected to increase from 2.3 trillion kWh in 2012 to 3.1 trillion kWh in 2020 and to 4.5 trillion kWh in 2040. The main advantages of nuclear energy are high capacity factor, low CO₂ emissions and relatively small amount of fuel required (the energy of 1 kg of Uranium is equivalent to 2.7 million kg coal). Presently, all nuclear reactors producing energy are based on nuclear fission reaction and various types of reactors and fuel cycles are developed. The amount of vitrified High Level Waste generated from the nuclear fission plants is very small and can be safely managed. In spite of the above advantages, the nuclear power production by fission is still associated with the following challenges: Management of very hazardous radioactive wastes, including final disposal, non-ecofriendly production of nuclear fuel, radiation released during accidents and low thermal efficiency in case of electric power production. However, improvements in the thermal efficiency, safety and waste management practices, will favor nuclear energy usage towards the sustainable development (Pioro and Duffey, 2015). Research on nuclear fusion is in advanced stages in different countries. In November 2006, seven countries, China, India, Japan, Russia, South Korea, the USA and the European Union, signed an agreement for construction and operation of a 500 MW an International Thermonuclear Experimental Reactor (ITER) and work is under progress (NPE, 2017). As fusion reactors do not generate long-lived High Level Waste and are safer to operate, when this technology matures, it could be a very effective replacement for fossil fuels.

2.4. Perspectives on replacement of fossil fuels with alternative energy sources

Extensive studies establishing a link between energy and growth have been reported (Ozturk, 2010; Omri, 2014). In order to make the growth sustainable and inclusive, recent studies have mainly focused on establishing the link between energy, emission and growth (Adeolu & Olabanji, 2017). Life cycle analysis performed (Amponsah, 2014) to assess the total burden of CO₂ emission on environment by including all the stages of energy production processes such as upstream stage: resource extraction, plant construction, material and component manufacturing; operation stage (combustion, plant maintenance and operation); downstream stage (dismantling, decommissioning, disposal and recycling) not surprisingly point to energy production from fossil fuels has high life cycle emissions compared to renewable, green and nuclear sources.

The extraction of energy from renewable, green and nuclear sources is a promising option to minimize the use of energy from fossil fuels, which could be used mainly for transportation and value added chemical productions. During the period 2012 to 2040, renewable and green sources are projected to be fastest-growing energy source with an increase in consumption by 2.6 percent per year and nuclear increasing by 2.3 percent per year. Currently research is focused on enhancing the energy extraction efficiency from renewable and green sources. However, with the

present growth rate and capacity (see Table 1), the renewable and green energy sources cannot completely replace the fossil fuels, to meet the global base load energy demand, in foreseeable future. Efforts also need to be made to use green energy sources for power generation and integrate them with CO₂ capture and utilization processes (Roh et al. 2016a).

[Insert Table 1 here]

3. CO₂ Emissions and Management

Due to the various anthropogenic activities, it is very difficult to maintain the CO₂ concentration in atmosphere at acceptable levels. Most of the research has been aimed at addressing this problem through CCS and CCU techniques. A number of authors have reviewed the technologies and current challenges with respect to CCS (Li, et al. 2013; Rahman, et al. 2017) and CCU (Almomoori, et al 2017; Karimi and Kawi, 2016; Lin and Biddinger, 2017; Yuan, et al. 2015; Kongpanna et al. 2015; Roh, et al. 2016a). The approach primarily being employed is to manage the CO₂ concentrations after it has been released, that is “cure” the problem. With this approach, there are two main concerns: how to capture the released CO₂ and then what to do with it?

3.1. Capture technologies

The industrial sector alone accounts for about 50% of the total CO₂ emissions. The concentration of CO₂ in flue gas emissions from stationary sources is relatively high compared with other mobile sources. Therefore, preventing the emission of CO₂ from stationary sources is a feasible option to control the global CO₂ concentration. To capture CO₂ from stationary sources and the atmosphere, different mass transfer techniques may be used including absorption, adsorption and membrane separations. Techniques are well established to capture CO₂ at the different stages (post combustion or pre combustion) for emissions from stationary sources, i.e., mainly from chemical processes and power plants. CO₂ capture from air (dynamic source), however, is very challenging because of thermodynamic limitations resulting from the extremely dilute CO₂ concentrations, and the energy cost for driving large volumes of air through a capturing process. Classical CO₂ separation processes such as cryogenic distillation and membrane-based separation are not economically competitive. During the past several years, numerous contributions have been devoted to evaluating different approaches for CO₂ capture from the ambient air (Lackner, et al. 1999; Kulkarni & Sholl, 2012; Sehaqui, et al. 2015). Another option worth investigating is enhancing the engineered cultivation of biomass, which can then be used as a raw material for biofuel production (Rodionova, 2017).

Pre-combustion: In pre-combustion capture process H₂ and CO₂ are produced from fuel gasification followed by water gas shift reaction. Well established processes are available to separate CO₂ from the flue gas by physical absorption using selexol or rectisol solvents (IEA, 2016). Research is in progress to synthesize efficient sorbents and membranes to overcome the challenges associated with these technologies at commercial scale implementation (Bolisetty, et al. 2015; NETL/DOE. 2015).

Oxy-fuel combustion: The combustion processes utilize pure oxygen rather than air. Therefore, the exhaust gas contains mainly CO₂ and water vapor that can be easily separated to CO₂ and water by condensation. Oxygen-fuel combustion avoids complex post-combustion separation and have higher power generation efficiencies. The main disadvantages associated with oxy-fuel combustion are oxygen separation and repowering (Kocs, 2017). Most of the studies on oxy-fuel combustion are at laboratory or small scale and these technologies need be demonstrated at a large scale such as power plants (Ferrari, et al. 2017).

Post-combustion: In post-combustion capture process, CO₂ is separated from flue gas consisting of high amounts of N₂. At present the amine based post combustion capture process is considered to be the most mature technique among all solvent based CO₂ capture processes. However, active research is striving towards process improvement to address the issues such as: effect of oxidized impurities, handling bulk volumes and energy requirement (Liang, et al. 2016). Membrane technology is also a potential option for post-combustion CO₂ capture due to the inherent advantages: simple in operation, less energy requirement, compact size, stable at high acid concentrations and less water requirement (Khalilpour, et al. 2015). However, it is still not an economical option compared with solvent based capture in handling bulk volumes of captured gas. The challenges associated with membrane at high throughput are: permeability not as desirable, significant energy required to create vacuum/high pressure and interference of harmful contaminants (NETL/DOE. 2015). In the CO₂ capture by adsorption processes, CO₂ is adsorbed on a solid surface by physical/chemical adsorption followed by adsorbent exposed to high temperature or pressure swing to release the adsorbate. Extensive studies are being carried out using different adsorbents— including metal organic frameworks, zeolites, sodium oxides, amine-enriched sorbents and carbonates to synthesize the efficient process prototype with following characteristics: high adsorption capacity, low cost, high selectivity, thermal stability, chemical stability, low attrition rates (Samanta, et al. 2012; Yaumi, et al. 2017). In addition to the above techniques, the use of ionic liquids and hybrid approaches are being explored rigorously to intensify the CO₂ capture process (Liu et al. 2016).

Perspectives: Research during the last two decades on carbon capture from stationary sources has reached a high level of sophistication. It is possible to capture the maximum amount of CO₂ using techniques that are continuously being improved. In order to mitigate the CO₂ concentration in atmosphere, the captured CO₂ from industries (about 50% of the total emission) has to be sequestered and utilized. However, the enormity of this problem with present limitations on sequestration and utilization techniques raises the questions – would it be viable to sequester large volumes of CO₂ or convert it to useful products?

3.2. Sequestration technologies

There is without doubt a need for reduction of CO₂ concentration in the atmosphere and an alternative already being tried is to capture the CO₂ from emission sources and then sequester it (see Figure 2). Storage or sequestration involves the transportation of the captured and pressurized CO₂ to storage tanks or the injection into underwater formations and other

underground options (IPCC, 2005). The storage in geological formations and mineralization are the most frequently discussed; especially the option for use in oil fields as geological storage and the use in mineralization using cement emissions (IPCC, 2005). There have been projects involving the use of CO₂ as storage in Enhanced Oil Recovery (EOR) as is the case in Canada at the Boundary Dam Facility (Consoli and Wildgust, 2017). In addition, there are industrialized sequestration projects in the North Sea and other offshore basins (Consoli and Wildgust, 2017). However, this, ultimately, does not solve the problem of CO₂ concentrations in the atmosphere as they are merely relocated to long-term storage options, from which the CO₂ will come out again. In addition, large scale deployment of CCS is associated with following challenges: energy requirement, capture cost, transport infrastructure availability, geological storage availability, technical and integration risks and public perception (REN21, 2017). As a consequence, there is a clear shift towards CCU because of its advantages over CCS. However, the challenges associated with CCU have to be further addressed in more detail.

3.3. Conversion technologies

Conversion of CO₂ to useful products is limited by, for example, lack of knowledge about the products that can be made by converting CO₂, about the catalysts that may be needed, and the associated reaction kinetics. Therefore, most carbon dioxide conversion technologies are currently in their early stages of development. As a result of this, carbon dioxide conversion processes have been limited to the production of bulk chemicals like methanol, syngas or dimethyl carbonate, although in principle, hundreds of chemicals can be produced through carbon dioxide conversion reactions (Otto et al., 2015). There are almost no process-level studies dealing with production of CO₂-based fine chemicals. Also, there exist only limited industrial application cases, like the CO₂-based methanol plants in Iran (Aasberg-Petersen et al., 2008), Qatar (Al-Hitmi, 2012) and Iceland (Carbon Recycling International, 2016). Some of the useful products that can be obtained by converting CO₂ have been studied recently by Roh, et al. 2016a-b and Bertran, et al. 2017.

Industrially, conversion processes have been used for the production of urea and certain carbonates (Mikkelsen, 2010). However, the development of this technology to other products is relatively limited; methanol production is the most mature technology. In addition, the amount of CO₂ that can be converted is severely hampered by the supply-demand scenario of these useful products. Even if the conversion processes to different products are mature enough and sustainable enough, the amount of emissions that can be reduced is still limited by the demands of all these products. If the production of all these products were replaced by conversion processes, only about 1% of emissions would be reduced (Frauzem et al., 2017). This amount could be greatly increased if more sustainable routes to fuels could be found. In this respect conversion of CO₂ into biofuel can offer an attractive solution. However, any such conversion process should be sustainable and result in a net negative CO₂ emission.

3.4. CO₂ emission reduction technologies

This option looks at the core of the CO₂ management problem – that is, how to reduce the current levels of CO₂ emission by more efficient use of energy? The list of energy using equipment and processes are many and therefore, in this paper only a few major ones are considered briefly and one (chemical processes) considered in greater detail.

Transportation: Gasoline and other liquid fuels are primary sources of fuel for transportation vehicles. In 2012, total 104 quadrillion Btu of energy is consumed by transportation sector and the energy consumption is expected to reach 155 quadrillion Btu by the year 2040 in this sector (The International Energy Outlook, 2016). At present fossil fuels are being used as a primary energy source for vehicles. In order to limit the global temperature rise to 2⁰C, the emission from transportation sector should be reduced by 21% of the total emissions relative to the 4 degree scenario by the year 2050 (IEA, Global EV Outlook. 2013). Research is more focused towards the development of biofuels (Bio-ethanol and diesel) and blends to replace the use of fossil fuels. The biofuels are more favorable to sustainable environment as they emit less CO₂ compared to fossil fuels. However, the entire world's attention is towards the use of electric vehicles, which will eventually reduce dependence on petroleum and biofuels. In the long-term, the use of electric vehicles decarbonizes the entire transportation sector. At present the market transformation is constrained by the challenges in the following fields: technical, financial, policy challenges and market fluctuations.

Equipment: The equipment, which alters the pressure and temperature of systems, may require significant energy input. Turbines, pumps, compressors and heat exchangers, etc., handle energy intensive tasks at the industrial level. Improvements in technology: steps towards equipment efficiency increase, compact design, equipment integration, cogeneration and heat integration, etc. will increase the overall performance. These steps along with energy auditing will conserve the energy and leads to less CO₂ emissions. Process design that may reduce the energy demand for any equipment may also be considered as a means for CO₂ emission reduction.

Residential: The total energy consumption by the residential sector is significantly high and consistently increasing with time. As per “The International Energy Outlook 2016 projections”, the energy use in residential sector will account for about 13% of the world total delivered energy consumption by 2040. The energy consumption is due to the following activities: cooling, heating, lighting, and consumer products. The energy consumption in the residential sector can vary significantly from region to region because of geographical variations, energy access, equipment efficiency, and income levels. The energy consumption in this sector can be significantly reduced by using advanced and cost effective technologies such as: use of LED's for lighting, centralized heating systems, use of high efficient consumer products including heat pumps, water heaters, air conditioners, dish washers and electric stoves. Engineered construction and retrofitting of structures with the objective of energy conservation and encouraging the use of energy from renewables will be able to reduce the carbon foot print. In addition to this people should be self-motivated and socially responsible towards the energy saving which can create sustainable environment by minimizing CO₂ emissions.

Chemical processes: Industrial sector including manufacturing and non-manufacturing units account for 54% of total world delivered energy which is the maximum compared with any other end-use sector (The International Energy Outlook, 2016). Most of the chemical industries are known as energy intensive manufacturing units which include: petrochemicals, pulp and paper, basic chemicals, refining, nonferrous metals, iron and steel, nonmetallic minerals and food. Basic chemical industries are the largest consumer of delivered energy compared with all other energy intensive industries. Many of the chemical processes (distillation, evaporation, drying, etc.) require energy at high temperature, which can be facilitated by using renewable or fossil fuel energy. Chemical industries have extensive use of auxiliary equipment such as: pumps, compressors and conveyers, which also require significant amounts of high grade energy.

Until last two decades the chemical process industries were designed using traditional methods and the main focus was on primary tasks (reaction & separation) and economics (Hernandez, 2017). At present, the energy consumption and waste release in manufacturing industries are serious concerns that need to be addressed to avoid the disruption of environmental cycles which in turn make the process sustainable. Therefore, currently the vision of sustainable process design is to conceptualize new processes considering reactions, separations and economics along with energy conservation, safety, environmental and social impacts. Recent publications highlighting integrated solution approaches (Celebi et al, 2017; Roh et al, 2016a, Yue & You, 2014) are options worth investigating.

3.5. Perspectives on CO₂ emission and management

Mature technologies are available for CO₂ capture and sequestration. CCS is one of the potential options to mitigate the climate change. However, different technical and economic issues must first be resolved in order to use this option on a large scale. CCS is perceived to be an unprofitable activity that requires large capital investment and energy (Cuellar-Franca and Azapagic, 2015), while delaying the problem and not resolving it. As an alternative to CCS, CCU is considered to be a more attractive option as it adds value to the captured CO₂ by producing useful chemicals. In CCU process, the captured CO₂ could also be used as a C1 building block for producing high carbon number compounds. However, the CCU technologies are not implemented on a large scale (Yuan, et al. 2016), although, Hasan et al. (2014) and Gencer et al. (2015) have reported substantial and interesting new developments. Also, exactly how much of the captured CO₂ may be converted to useful chemicals with negative or zero net CO₂ emission needs to be established.

Additionally, research is also focused on improvisation of energy technologies through innovative and sustainable designs to substantially reduce the CO₂ emissions (EIA, 2015; Tula, et al. 2017). For example, a global increase of 7% in the efficiency of coal-fired power plants will reduce the global carbon dioxide emissions by 1.7 billion tons per year (World Energy Resource, 2016).

A summary on CO₂ emission and management towards the creation of a sustainable environment by 2050 is given in Table 2 in terms of selected variable values. The energy related CO₂ emissions need to be reduced significantly by 2050. To meet this target the following alternatives need to be encouraged judiciously: use of renewable, green and nuclear energy, CCS and CCU for CO₂ capture, fuel switching and energy efficient technologies. The impact on cumulative CO₂ reduction by CCS and CCU technologies need to be significant. But, the CO₂ emission reductions by energy efficient technologies have higher impact compared with capture technologies. To meet the target energy reduction technologies need to double the global rate of improvement in energy efficiency by 2030 (UN, 2015). Energy generation technology in thermal power plants is fully matured and there is little scope to improve the energy efficiency. Also, energy efficiency of industrial, transportation and building sectors need to be improved significantly to reduce the cumulative CO₂ emissions. The industrial sector alone has the target of 120 Gt of cumulative CO₂ reduction by improving the energy efficiency (EIA, 2015). Therefore, the research should be more focused on sustainable chemical process synthesis, design and innovation to reduce the energy consumption.

[Insert Table 2 here]

4. Sustainable Chemical Process Design

Process systems engineering (PSE) has evolved into becoming a field of chemical engineering, that can provide systematic methods and tools for sustainable and innovative synthesis-design of chemical and biochemical processes. Different solution approaches may be applied to determine sustainable process designs: hierarchical methods based on heuristics (Klemes, et al. 2013); mathematical optimization methods (Chen and Grossmann, 2017); hybrid-integrated methods based on process intensification (Babi, et al. 2015), based on superstructure optimization of biorefinery (Bertran, et al. 2017), and, CO₂ capture-utilization (Frauzem, et al 2017). Figure 8 shows different levels of boundaries that have to be considered in process design to analyze the sustainability at every stage. Sustainability is measured in terms of, among others, usage of energy, water, material; environmental impacts as well as economic and social factors. With respect to energy consumption and CO₂ emission, the sustainability of a new innovative/alternative process need to be established in terms of energy consumption, environmental impacts as well as overall profit while converting the same raw material to the same products. The resulting process design should also be sustainable with respective to safety, operability and other sustainability-LCA factors. In this paper sustainable process design is highlighted through the application of an extended version (Bertran, et al. 2017) of a 3-stages sustainable process synthesis-design methodology (Babi, et al. 2015).

[Insert Figure 8 here]

The objective of sustainable process design is not to create additional burden on the CO₂ management problem by releasing more CO₂ than necessary. That is, process synthesis-design alternatives are to be determined that either reduces the energy demand significantly through retrofit design (providing a very good solution to “curing” the problem); generates alternative

fuels-chemicals through renewable sources (providing a very good solution to “curing” or “preventing” the problem); and integrated and sustainable CCU process synthesis-design that “prevents” the problem through zero or net negative CO₂ emission. In all cases, non-tradeoff solutions are sought with respect to economic, environmental and energy indicators.

4.1 Energy versus sustainability

Energy (demand and supply) is directly related to the sustainability of any chemical or biochemical process. Energy consumption increases as energy demand for running the process increases. As energy consumption increases, the carbon-footprint as well as the cost of operation increases. It is possible therefore to obtain non-tradeoff process designs for many chemical and biochemical processes.

Distillation is one of the most widely used separation techniques in the chemical process industry. As a separation technique, it is also one of the most energy intensive, while from an efficiency point of view, it is among the processes having the least thermal efficiency (Pellegrino, et al. 2004). Thermal efficiency is defined as the ratio of the net work to the heat supplied by combusted fuel. Even though distillation is ranked among the processes with the least thermal efficiency, nearly 80% of all vapor-liquid separations in chemical process industries are performed by distillation (Wankat, 2007). According to the US Department of Energy, separation technologies from all the manufacturing industries used nearly 150 million kW in 2005 (Angelini, et al. 2005), out of which, distillation (49%), drying (20%) and evaporation (11%) accounted for more than 90% of the total energy consumption. It is estimated that the United States alone has more than 40,000 distillation units operating in more than 200 different processes (Angelini et al., 2005), which clearly points to distillation as a significant contributor to the overall energy consumption. Therefore, design of new vapor-liquid separation systems or retrofitting existing systems must be considered for more energy efficient options and sustainable solutions. One such option is to use hybrid separation systems, which combine one or more low energy consuming separation techniques with the higher energy consuming distillation in such a way that a target separation can be achieved at significantly lower energy consumption. Hybrid schemes involving membrane-based separation with distillation have been proposed by many. For example, Stephan et al. (1995), Pettersen et al. (1996), Davis et al. (1993), Moganti et al. (1994) and Caballero et al. (2009) proposed hybrid schemes for recovery of olefins. Also, Rautenbach and Albrecht (1985) highlighted the application of hybrid schemes for separation of an azeotropic mixture of benzene-cyclohexane, while Goldblatt and Gooding (1988) highlighted the application of hybrid schemes to separate an azeotropic mixture of ethanol-water. The main questions, however, are when such hybrid schemes should be applied, what characteristics the separation problem should have, what the configuration should be and how much improvement could be expected?

Tula et al (2017) recently proposed a general method for synthesis-design of hybrid distillation-membrane based separation schemes taking into account the mixture to be separated, the difficulties of using only distillation or membrane-based operations to achieve the desired

separation, the optimal distillation-membrane based hybrid scheme, the potential for energy saving without compromising the product specifications, and the capital and operating costs. For several test cases, Tula et al. (2017) showed substantial decreases in energy consumptions while matching the same product purity specifications.

4.2 Environmental impact versus sustainability

Solvent based separations are widely used in process industries to extract components from different mixtures, including valuables from waste, API's, and fine chemicals. In addition to the aqueous phase extraction, organic solvents such as alcohols, ketones, volatile organic compounds (VOCs), aldehydes and some esters are the most frequently used solvents in industries. To replace the toxic organic solvents and enhance sustainability in separation processes, research is focused on synthesis and use of green solvents such as bio-derived solvents (Li, et al. 2016), supercritical fluid CO₂ (Ramsey, et al. 2009), ionic liquids and eutectic mixture (Penn-pereria and Namiesnik, 2014). Gani, et al. 2006 proposed model based methods and tools for selection of solvents, considering process performance, economics and environmental aspects. This methodology avoids most of the experimental burden on selection of the solvent. Mitrofanov, et al. (2012) presented a framework for solvent selection and design. The framework consists of several modules which can handle different aspects of solvent extraction processes. Carvalho et al. (2013) and Garcia et al. (2016) showed that selection of the appropriate solvent not only reduces the environmental impact, but also increases profit through reduced energy consumption and therefore, also reduced carbon foot-print. Papadakis, et al. (2016) proposed a systematic methodology for solvent selection to execute solvent swap task in pharmaceutical processes. The method incorporates a pharmaceutical solvent database, tools for calculating properties of solvents and the process models of batch distillation and crystallization to perform the swap task.

4.3 Achieving sustainability through process intensification

Process intensification is development of a process/equipment that leads to improvement of reaction kinetics/energy efficiency/process safety and/or reduction in equipment size/waste generation/product cost (Stankiewicz and Moulijn, 2000; Reay, et al. 2008; Ponce-Ortega, 2012; Lutze et al, 2013). Process intensification can be applied at different scales in process system engineering (Lutze et al. 2013): unit operations scale (equipment used in process flowheet to represent the operations performed in the processing route), task scale (different tasks performed, for example, reaction and separation tasks) and phenomena scale (the phenomena involved within a task that needs to be performed). Process intensification in these three scales and interlinking to each other, with the overall improvement of the process as an objective, has the potential to generate new and innovative more sustainable process alternatives compared to a “base case” design. Babi, et al. (2014) reported several highly improved non-tradeoff solutions with respect to energy consumption, carbon footprint, profit as well as other performance (sustainability) factors for methyl acetate and dimethyl carbonate processes.

Process intensification also accounts for process integration, which can be applied at process level in the following form: heat integration (Yu, et al. 2017), mass integration (Klemes, et al. 2013), scheduling and supply chain management (Verderame and Floudas, 2009).

4.4 Sustainable process design for prevention

For synthesis and design of CO₂ utilization processes, Roh, et al. 2016a presented a methodology, containing three stages. In process synthesis stage, a network of CO₂ utilization processes are developed using superstructure optimization approach; setting of targets for process improvement, and identifying new process design alternatives that “prevent” the CO₂ emission problem.

Use of optimization-based techniques during process synthesis and design allows to consider simultaneously multiple issues and to obtain optimal matches of raw material, processing technologies and product, hence leading to processing routes that not only are economically attractive, but also ensure an efficient use of raw materials and minimized waste and emissions. Bertran, et al. (2017) proposed a generic methodology for sustainable synthesis and design of processing routes. This consists of three stages: In stage-1, super structure optimization is performed to find the optimal processing route using data related to process, compounds, economics and environmental issues. A computer aided tool Super-O (Bertran, et al. 2016) is developed to guide the user with data management and data transfer to GAMS (Corporation, 2013) software for execution. In stage-2, the detailed design of optimal process path is performed along with identification of bottle necks of the process and scope for innovations. In stage-3, process intensification methodology is proposed to come up with unique, innovative and more sustainable process designs.

This 3-stages sustainable process design has been applied for biorefinery network synthesis (Bertran et al. 2017); net CO₂ emission based CCU process design for value added chemicals (dimethyl carbonate, methanol, dimethyl ether, succinic acid) production (Frauzem et al. 2017) as well as chemical process design and wastewater network optimization. All these solutions point to “prevention” of the CO₂ emission problem rather than curing it afterwards.

5. Application Examples

In this section, four examples of sustainable chemical process design are given to highlight the issues of energy-sustainable design, energy-CO₂ neutral design, energy-retrofit design, and energy-process intensification. In all cases it was possible to obtain non-tradeoff solutions. In all examples, the objectives are to reduce energy consumption, carbon foot-print (indirectly and directly reducing CO₂ emission) and production costs without affecting negatively any other performance indices. The solution approach used in all cases is the extended 3-stage framework for sustainable process design (Bertran et al., 2017).

5.1 Energy-sustainable process design

A relevant example for the transition from oil- to biomass-based fuel is ethanol. Whereas it can be used as fuel on its own, it can also be blended with gasoline, which is currently done in various countries to promote sustainability and as a transition towards more renewable transportation fuels (Renu, et al. 2016; Mofijur, et al. 2016). The case of conversion of biomass to useful products, including energy is highlighted in this example. An important aspect towards the shift from fossil-based sources to renewables for energy is the appropriate selection of feedstock, processing route and products by considering all the relevant aspects (economics, limited biomass availability at different locations, given energy demand, technology maturity, etc.). Figure 9 highlights a biorefinery network for multiple biomass sources and multiple products that has been created based on known information on biomass pretreatment, conversion steps, and separation steps. The vertical columns indicate processing steps and the boxes within each step indicate the known technologies that may be applied. The boxes on the left represent the different biomass available and the boxes on the right indicate products that may be obtained. That is, the sources are linked to multiple processing technologies classified in terms of alternatives available within the processing steps. By solving the profit optimization problem, a processing route (feedstock-process-product) is obtained, which converts available material to desired products, satisfies supply-demand constraints, has higher profit and lower environmental impact. Therefore, once a network (superstructure) is created, different problems can be formulated and solved.

[Insert Figure 9 here]

The application of the superstructure optimization based technique for processing route synthesis is highlighted here for multiple biomass feed-stocks (wheat straw, corn stover, sugarcane bagasse, switch grass, hardwood chips, and cassava rhizome) available at different geographic locations for the production of ethanol. Note that network (see Figure 10) considered for this problem is a subset of the network of Figure 9. The method employed allows the consideration of different feed-stocks, processing steps, process technologies available for each processing step and the products and by-products, as highlighted in Figure 10. The method allows the simultaneous consideration of different aspects (location, feed-stock availability, CAPEX, OPEX, operational limitations, etc.) involved in the design, therefore leading to sustainable solutions ensuring a profitable process, efficient raw material use, minimal waste and reduced emissions. Therefore, through assisting the decision making involved in design with a systematic optimization-based methodology, sustainable solutions can be obtained. The resulting MINLP or MILP problem is formulated and solved through Super-O, which employs GAMS as the numerical solver. Super-O allows the generation of different versions of the synthesis problem evaluating different scenarios for synthesis, design, operation, and manufacturing objectives. That is, given the data and performance criteria (objective function), the best processing route for a given scenario can be determined.

[Insert Figure 10 here]

Bertran et al (2017) highlights several optimal scenarios in terms of the optimal biomass (together with the location of the biomass availability) for the cheapest production costs (including annualized capital cost). The combination of sugarcane bagasse (feedstock), no limits on feed-stock availability and Thailand (production location) gives the cheapest dehydrated ethanol (fuel grade). Table 3 summarizes the results for different location scenarios studied.

[Insert Table 3 here]

A new case, considering limits on feedstock availability, feedstock location, transportation costs for multi-location production, however, gives interesting new results. A selection of these new results is given in Table 4. In this case, the processing route is fixed and optimization is used to determine the choice of raw material(s) and allocation of raw material purchase, product sale, and process allocation, where the process has been divided into two sections, pretreatment (pre-fermentation) and processing (fermentation to purified product), which can be allocated to different geographical locations. It is observed that, since transportation costs are taken into account, changes in the feedstock availability and product demand greatly affect the selection of raw materials and locations, which are reflected in the overall economic profit (used as objective function). The optimal solution from Table 3 is no longer feasible (because of the limit on feed-stock availability). Information related to the processing route data for the optimal solutions corresponding to various scenarios studied can be obtained from the authors.

[Insert Table 4 here]

5.2 Energy-CO₂ neutral designs

The 3-stages framework for sustainable process design has been adopted for sustainable design of CCU processes by Bertran et al. (2017). Figure 11 highlights a superstructure of alternative processing routes for captured CO₂ as the feedstock and various products, such as methanol, dimethyl ether, dimethyl carbonate, ethylene glycol and propylene glycol. The optimal processing route together with the product that maximizes the profit and provides a net CO₂ negative emission is also highlighted in Figure 11 (Frauzem et al., 2017): the route to produce dimethyl carbonate is shown through the shaded boxes. The optimal processing routes for each value added product has also been determined in order to determine the total reduction of net CO₂ emissions. Considering all the conversion processes available within the superstructure, the net CO₂ emission would reduce the equivalent of around 60 power plants (considering an average power-plant as an 150 MW coal-fired power plant emitting 1.5 million tons of carbon dioxide, as well as the current demand of the value-added products). Figure 12 highlights this result where the y-axis indicates the number of power plants, in this case 150 MW coal-fired power plants is considered, whose emissions can be avoided and the x-axis indicates the optimal route for a certain product.

[Insert Figure 11 here]

Insert Figure 12 here]

The processing route for one of the value added chemicals, dimethyl carbonate is further investigated in this paper. The production of dimethyl carbonate (DMC) from carbon dioxide via ethylene carbonate is found to be the optimal processing route. This route is then designed and analyzed in detail (stage-2 of the 3-stage methodology), as depicted by the flow diagram in Figure 13. The capture process has been optimized to reduce the energy requirement of the desorption process to make it more sustainable. Information related to the detailed design for the integrated DMC process together with the processing route data can be obtained from the authors. Note that the purity of the carbon dioxide product is reduced to 97 mol% resulting in almost 10 fold reduction of utility requirement and costs. Producing dimethyl carbonate via CO₂ conversion according to the optimal processing route, gives a net carbon dioxide reduction of CO₂ emissions by 0.09 tons per ton of dimethyl carbonate, considering the direct and indirect CO₂ emissions of the capture process as well as the conversion process. A net reduction of 1.37 tons of carbon dioxide per ton of dimethyl carbonate is obtained when compared with a DMC production process not utilizing captured CO₂. If world-wide production of DMC were thus replaced by this optimal processing route, a net CO₂ emission reduction by about 1.5 million tons per year would be achieved. Disappointingly, this represents the CO₂ emissions of only one 150 MW coal-fired power plant (IPCC, 2005). Therefore, it is necessary to consider a network of processes to produce various products from conversion in conjunction with other energy saving technologies.

[Insert Figure 13 here]

5.3 Energy-hybrid separations

In this paper, the method of Tula et al (2017) is extended to a series of aqueous separations (water plus a second compound that may or may not form azeotrope with water.). The results for methanol-water separation are given in Table 5. These types of separations are particularly interesting when the water needs to be removed to obtain a high purity product. Clearly, as shown by Tula et al (2017), separation by distillation is not very energy efficient after certain product purity. Therefore, a hybrid scheme where distillation is performed until a cut-off point and then another separation technique (for example, membrane) that can perform the remaining separation at low energy consumption is employed. In the case of methanol-water separation, an actual membrane able to perform the separation and with reasonable permeability and selectivity has been found.

[Insert Table 5 here]

5.4 Energy versus process intensification

Applying the 3-stages sustainable design methodology (Babi et al. 2015), several new, innovative and more sustainable process designs have been reported recently: Anantasaran et al. (2017) for toluene methylation; Landero et al. (2017) for dioxolane production and Wisatwattanna et al. (2017) for ethylene glycol production. Table 6 gives details of the

intensified processes for three well-known cases involving methyl acetate production; dimethyl carbonate production and biodiesel production.

[Insert Table 6 here]

6. Conclusions

The review of the data and its analysis point to the need for greater use of renewable, green and nuclear energy sources to meet the future demand of 815 quadrillion Btu in 2040, if the level GHG emissions are to be restricted to the established targeted limits. This would indeed be a “preventive” measure as these energy sources will release negligible amounts of GHG. However, continued use of fossil fuel sources, although unavoidable due to price, availability and established utilization techniques, should be reduced to a level such that the “curing” measures such as CCS, CCU or their combination can have a significant impact. For the industrial sector, and in particular, the energy intensive chemical and biochemical sector, sustainable process synthesis-design-intensification has shown that it is possible to obtain non-tradeoff solutions where profit is increased while at the same time, reducing energy consumption and CO₂ emissions as well as improving other sustainability factors. This is a truly “predictive” measure as substantial reductions in energy consumption are possible to achieve without any negative effects on economy and/or environment. Also, in the case of retrofit design, new and innovative sustainable solutions are possible to obtain where the additional capital costs are minor and can quickly be covered through the increased profit without any negative impact on other sustainability factors. While some technologies are already available and many more will need to be developed, planned development where energy source, energy consumption together with their impacts need to be investigated to develop more sustainable solutions. Retrofit re-design of current energy intensive operations that significantly reduce the energy consumption is necessary and hybrid-operations (separations) as well as process intensification need to be employed. The problems to be solved need to include many inter-related factors and therefore improved and systematic methods and tools are needed to manage this complexity. Process systems engineering can play a very important role here by providing and further developing the needed methods and tools. Finally, more effort and focus is needed at “preventive measures” instead of “curing measures” with respect to energy consumption and CO₂ concentration management.

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Table 1: Energy resource availability and utilization statistics in 2015 year

Energy	Availability/ capacity	Utilization	Remarks
Fossil fuels Oil Coal Natural gas	1656 Bb 891.531 Bt 186874.7 Bcm	9.542 Bb/Day 7.8 Bt/year 3538.6 Bcm/year	Oil, coal and natural gas accounts for 32.9%, 30% and 24% of global primary energy consumption respectively. They account 4.1%, 39.3% and 22.9% of required electricity, respectively. In recent years, the global coal production rate has been decreasing while power generation from natural gas and other renewable & green sources has been increasing. With an average decrease of 1% per year in the coal consumption, 50% of the present coal reserves will be exhausted by 2100.
Nuclear	382.9 GW	2441331 GWh	Accounts for 11% of the total electricity required.
Hydro power	1212.3 GW	3969115 GWh	Accounts for 16.4% of the total electricity required. From 2005 to 2015, 39% of growth is reported in installed capacity.
Electricity from solar	227.101 GW	253000 GWh	Accounts for 1% of the total electricity required. To increase this electricity share, the capacity has to be expanded. With the present technology this is not economical and sustainable.
Wind power	431.948 GW	841231 GWh	Wind power accounts for 7% of total global power generation capacity, which accounts for 4 % of the total electricity required.

Data Source: World Energy Resources, 2016. The International Energy Outlook, 2016. Units: Bb-Billion barrels, Bt-Billion Tons, Bcm- Billion cubic meter, GW- Giga Watt

Table 2: Perspectives on CO₂ management in 2DS to 2050

Issues	CO₂ emission/ handling capacity	Target value	Remarks
Total CO ₂ emission	34 Gt / year (2015)	14 Gt / year (2050)	Energy related CO ₂ emissions need to be zero by 2090.
CO ₂ capture, storage and utilization	0.120 Gt /year (2015)	90 Gt*	10 ³ to 10 ⁴ Gt of CO ₂ sequestration capacities are necessary.
CO ₂ emission reduction technologies	Not reported	277 Gt*	By introducing energy efficient technologies this target need to be achieved. Chemical Industry, transportation and building sectors are having high scope to reduce the CO ₂ .

Data source: IPCC, 2005; EIA 2015; * Cumulative CO₂ reductions by 2050

Table 3: Optimal topology and objective function value (million USD) for each considered location – excluding capital costs (Bertran et al. 2017)

Location	RM	WADD	PRET	HYD	FERM	BIOR	SEP1	SEP2	PROD	Profit
Brazil	SB	ARP	ARP	NREL	ETOH	CENTR	BEER	BMIM	ETOH	11.38
Canada	WS	-	STEX	NREL	ETOH	CENTR	BEER	BMIM	ETOH	-28.78
China	SB	DILAC	DILAC	NREL	ETOH	CENTR	BEER	BMIM	ETOH	37.86
India	SB	DILAC	DILAC	NREL	ETOH	CENTR	BEER	BMIM	ETOH	82.13
Mexico	WS	-	STEX	NREL	ETOH	CENTR	BEER	BMIM	ETOH	-4.46
Thailand	CR	-	STEX	DILAC	ETOH	CENTR	BEER	BMIM	ETOH	116.03
USA	HWC	-	STEX	CONCA	ETOH	CENTR	BEER	BMIM	ETOH	47.63

Abbreviations

RM: raw material (CR: cassava rhizome, HWC: hardwood chips, SB: sugarcane bagasse, WS: wheat straw); WADD: water addition (ARP: ammonia recycled percolation, DILAC: dilute acid); PRET: pretreatment (ARP: ammonia recycled percolation, DILAC: dilute acid, STEX: steam explosion), HYD: hydrolysis (CONCA: concentrated acid, DILAC: dilute acid, NREL: enzymatic with NREL enzyme); FERM: fermentation (ETOH: ethanol fermentation); BIOR: biomass removal (CENTR: centrifuge); SEP1: separation step 1 (BEER: beer distillation); SEP2: separation step-2 (BMIM: extraction with ionic liquid BMIM-Cl); PROD: product (ETOH: fuel grade ethanol).

Table 4: Optimal feedstock/location selection and objective function value (million USD) for various scenarios – including transportation, multi-location options and capital costs

Scenario			RM		Location				PROD	OF
EtOH rate (kt/y)	RM AV (kt/y)	PROD DEM (kt/y)	Type	Rate (kt/y)	RM	PRET	PROC	PROD	Rate (kt/y)	Profit
150	No limit*	No limit*	WS	703	IN	IN	IN	MX	150	95.30
150	500	150	WS / CS	500 / 203	IN / IN	IN	IN	MX	150	94.28
150	700	75	WS	700	CA	CA	CA	MX / US	75 / 75	90.94
150	Country limit*	Country limit*	WS	700	CA	MX	MX	US / MX	145 / 5	85.34

* “No limit” cases use a fictitious infinite availability of all feedstocks in all locations; when a value is stated, that value is used for all locations (even though it might exceed the maximum in the given location); “Country limit” cases use the maximum availability/demand in each location as constraint.

Abbreviations

EtOH: ethanol, RM: raw material, PROD: product, AV: availability, DEM: demand, PRET: pretreatment, PROC: process, OF: objective function, CS: corn stover, WS: wheat straw. Countries (CA: Canada; CN: China; IN: India; MX: Mexico; US: USA)

Table 5: Comparison of separation by distillation versus hybrid scheme for methanol-water mixture

Comparison factors	Distillation		Hybrid scheme	Percentage reduction
Product purity	90%	99.5%	99.5%	No change
Energy required (KJ/h)	2.98×10^6	6.7497×10^6	$2.98 \times 10^6 + 105$	55%
Carbon footprint (tons)		0.94	0.52	44%

Table 6: Summary of improvements through process intensification

Comparison factors	Base case	Intensified process (alternatives)		Remarks
		1	2	
Number of UOPs	11	4	1	Methyl acetate production*
Energy Usage/kg product	21.88	19.12	2.225	
Utility Cost/kg product	0.10	0.08	0.01	
RM Cost/kg product	0.88	0.87	0.87	
Profit/kg product (Fobj)	2.06	2.09	2.16	
Number of UOPs	5	3	1	Dimethyl carbonate production*
Energy Usage/kg product	78.65	10.44	38.17	
Utility Cost/kg product	0.36	0.05	0.16	
RM Cost/kg product	2.03	2.03	2.03	
Profit/kg product (Fobj)	0.27	0.58	0.47	
Number of UOPs	19	12		Biodiesel production*
Energy Usage/kg product	119.16	73.10		
Utility Cost/kg product	7.79	4.66		
Product/raw material (ratio)	0.94	0.94		
Total carbon footprint (kg CO ₂ equivalent)	0.183	0.143		

* Detailed results producing the numbers in this table can be obtained from the authors

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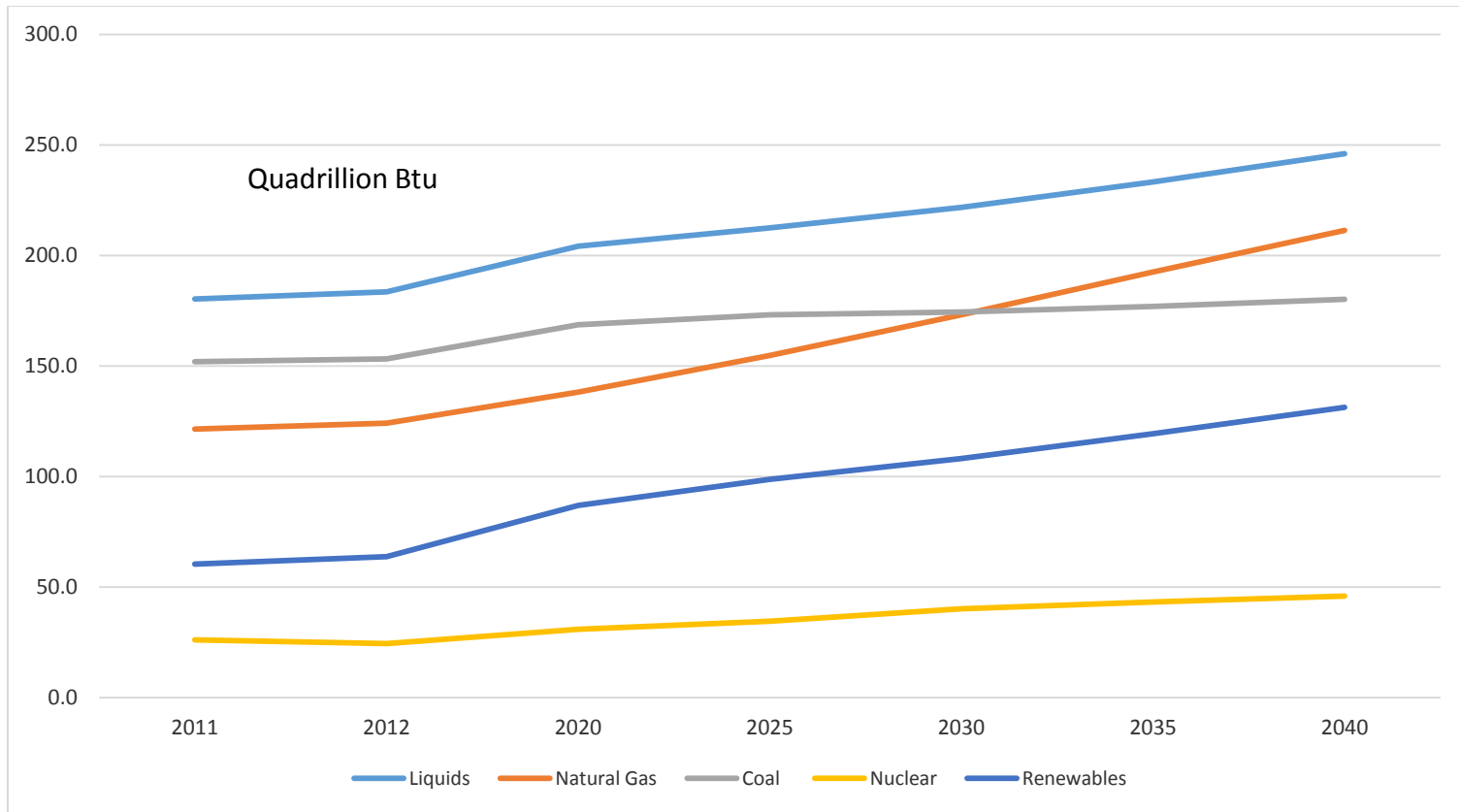


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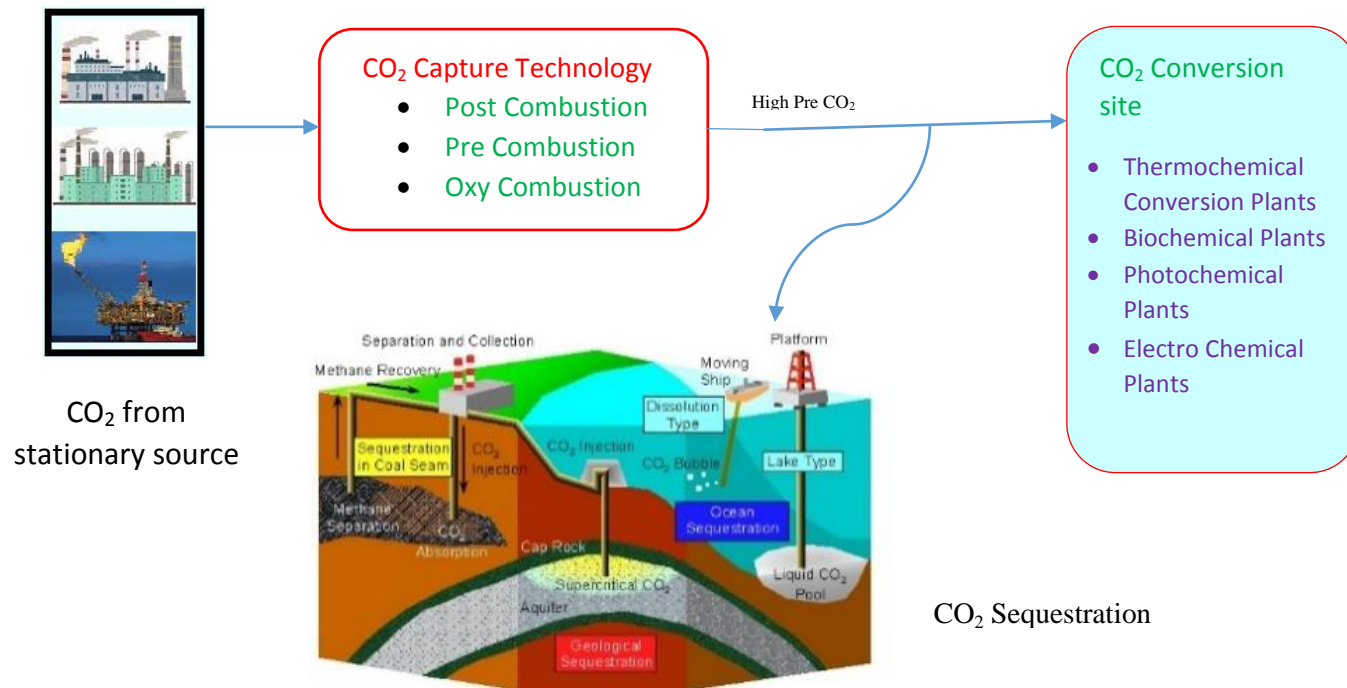
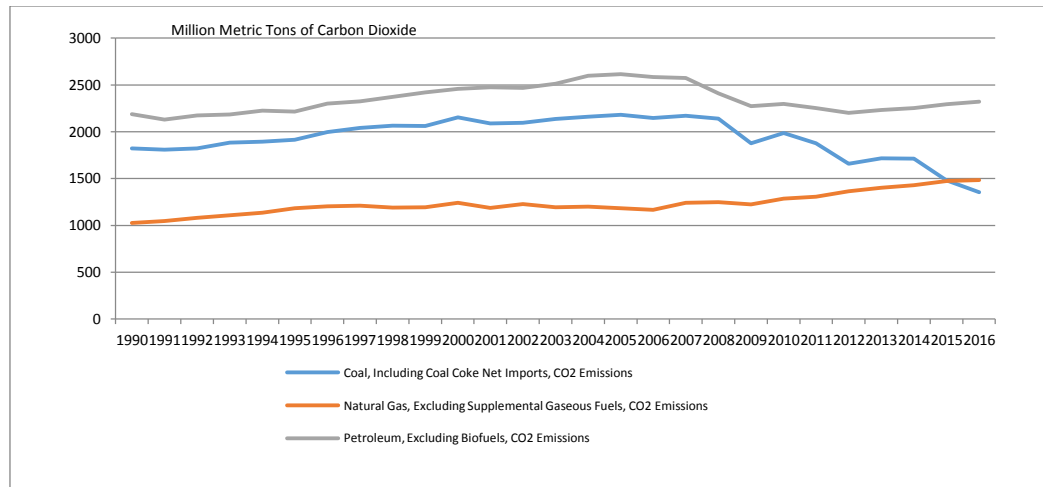
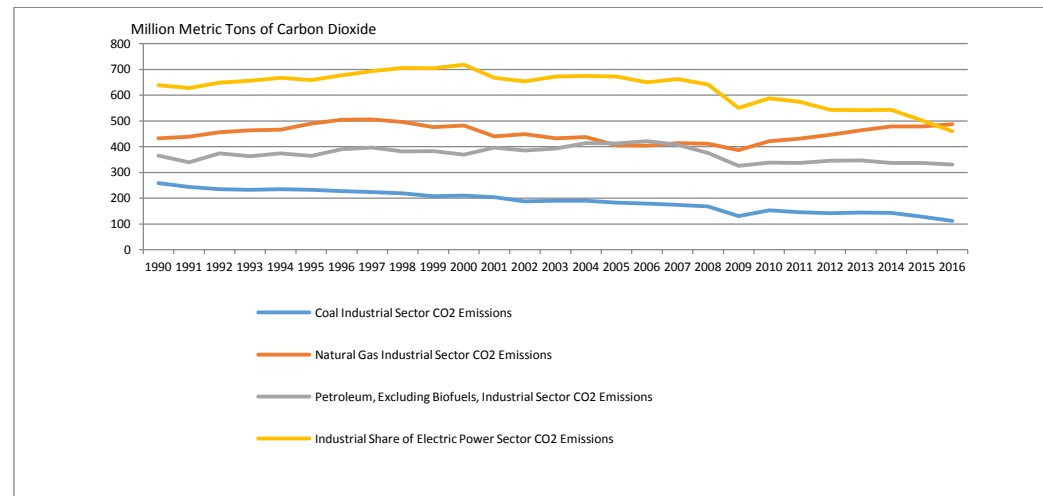


Figure 2: CO₂ capture, sequestration and conversion steps.



3a



3b

Figure 3: CO2 emissions from use of fossil fuels (a) Use in all sectors including industrial, domestic and transport (b) Use only in industrial sector (Data Source: EIA 2016).

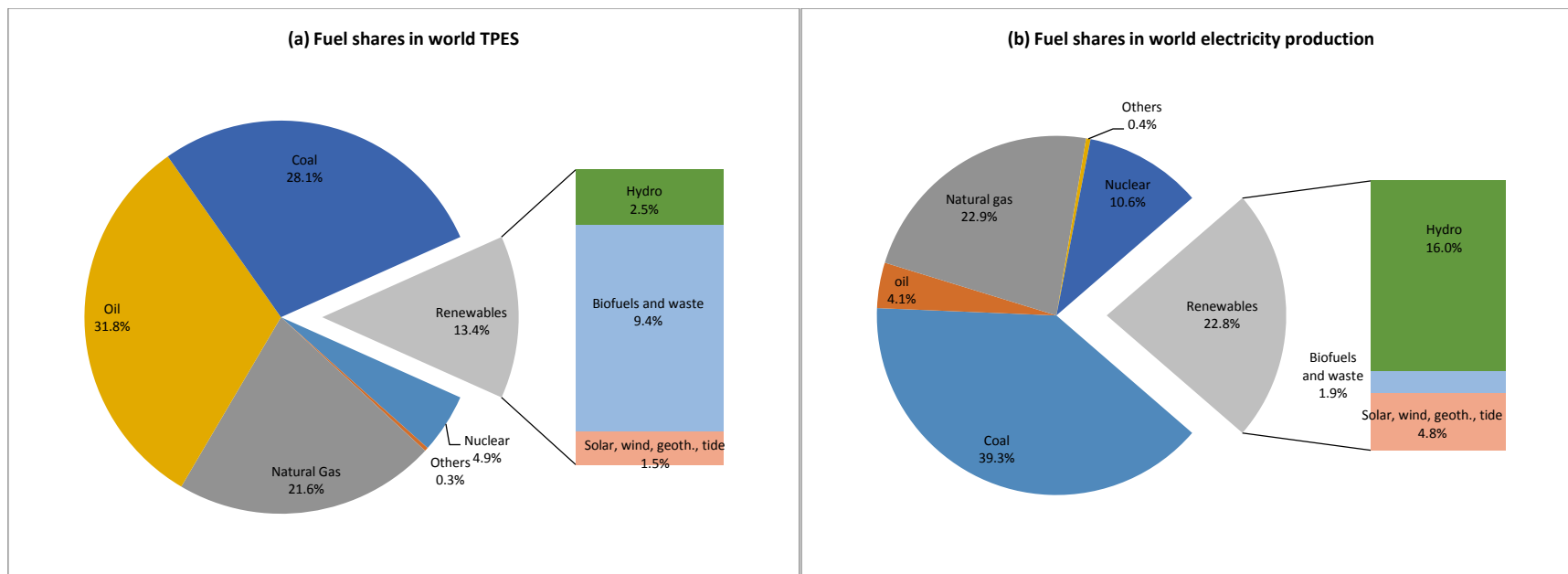


Figure 4: Fuel usage statistics in year 2015 (Data Source: Renewables information: Overview, IEA-2017).

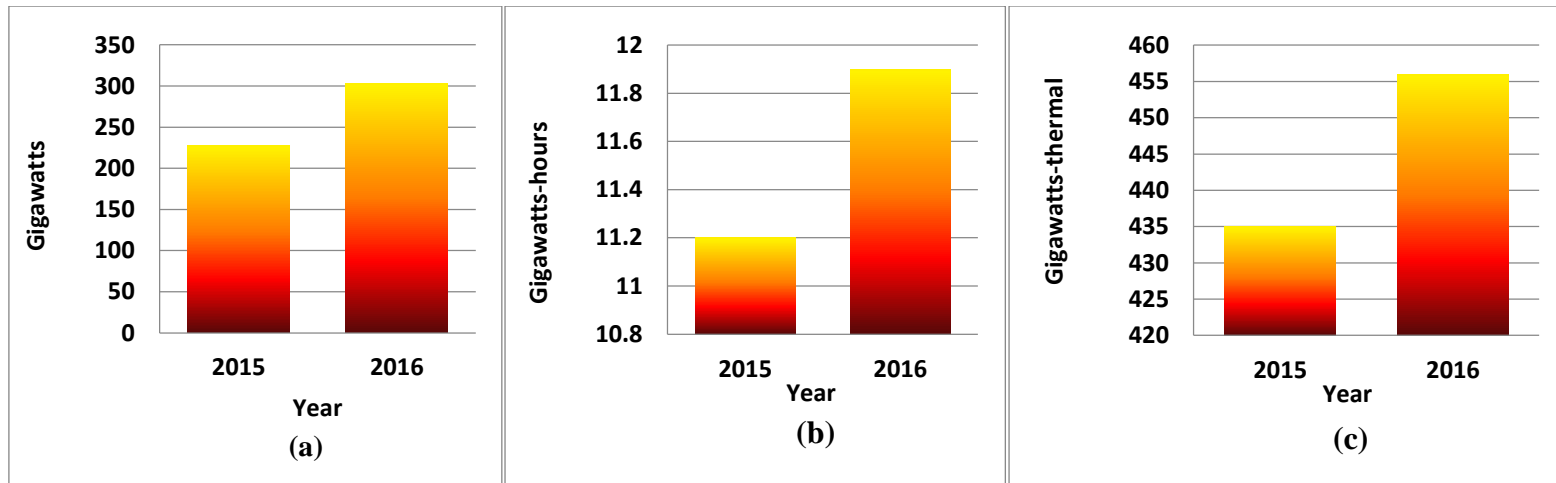


Figure 5: Global capacity of Solar energy production in (a) Solar PV (b) CSP and (c) Solar water heating in the year 2015 and 2016 (Source: REN21, 2017).

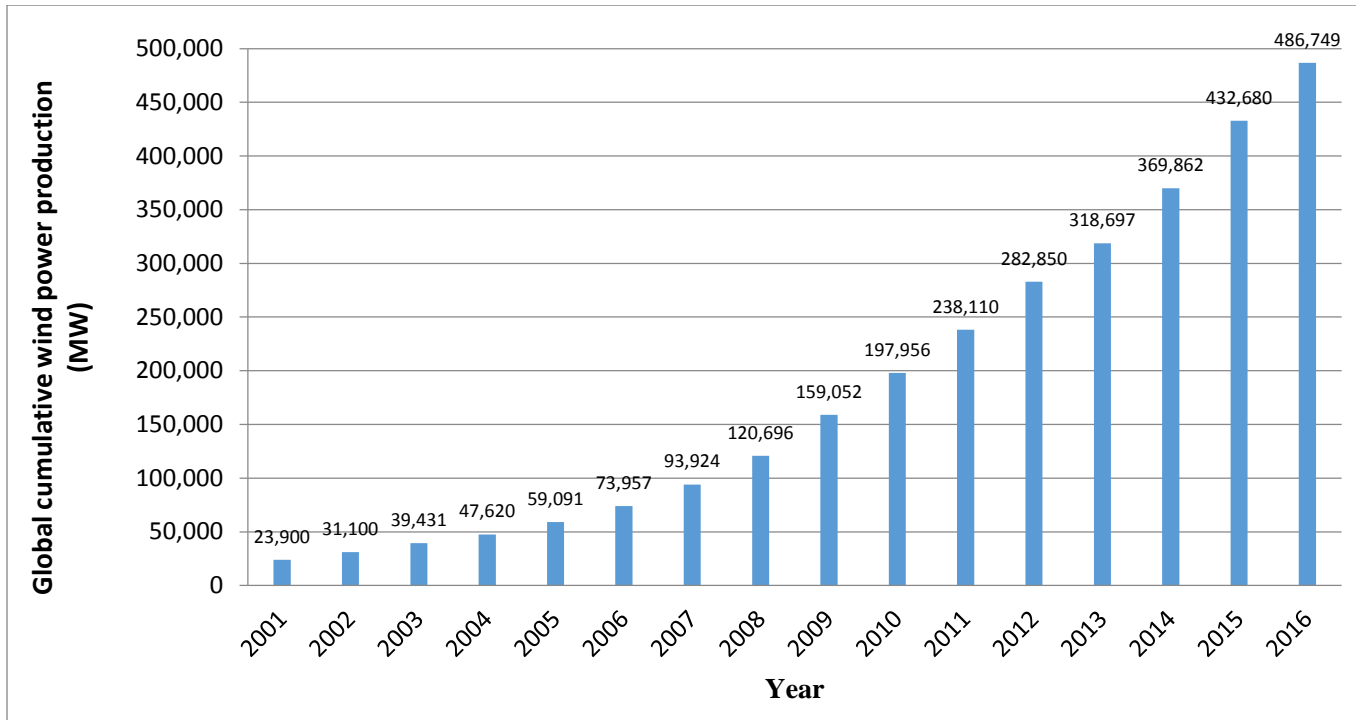


Figure 6: Global cumulative installed wind capacity from 2001 to 2016 (Source: GWEC, 2016).

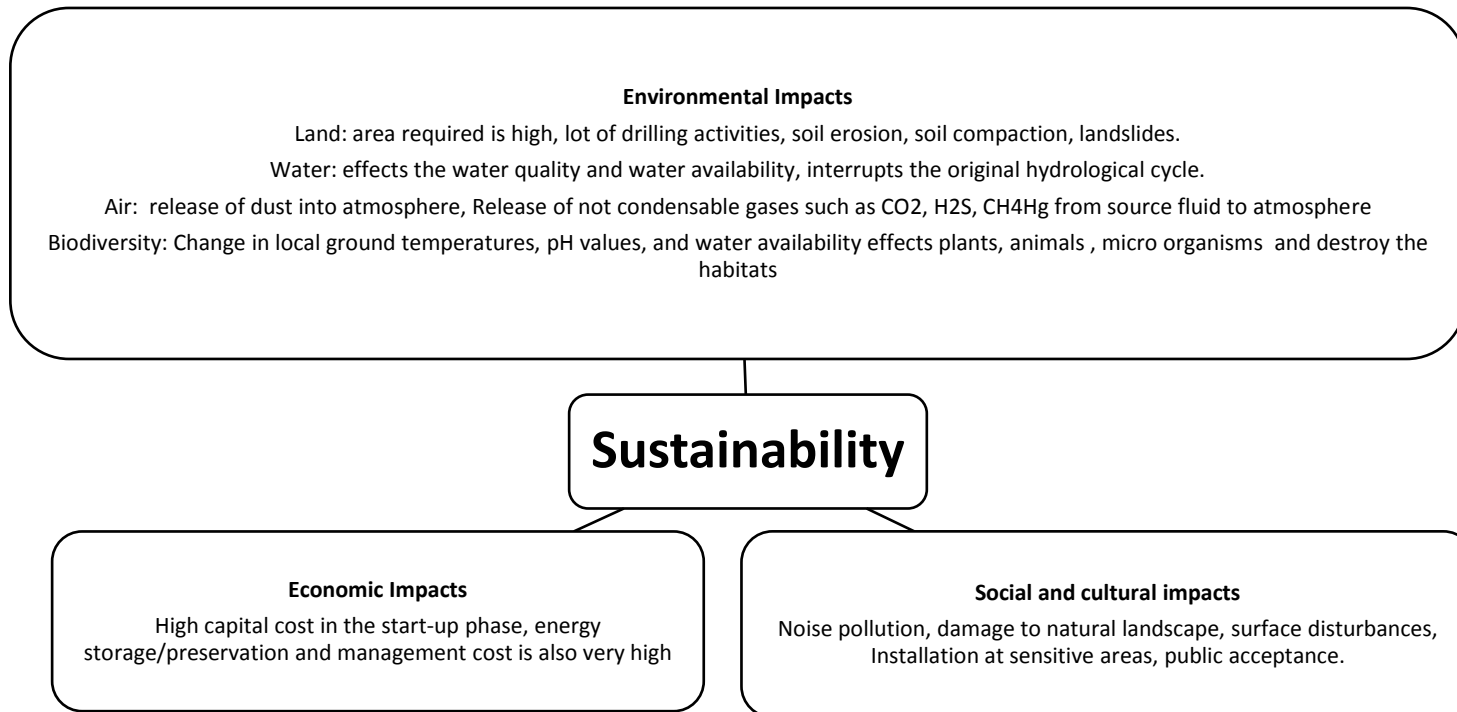


Figure 7: Sustainability challenges in geothermal energy production.

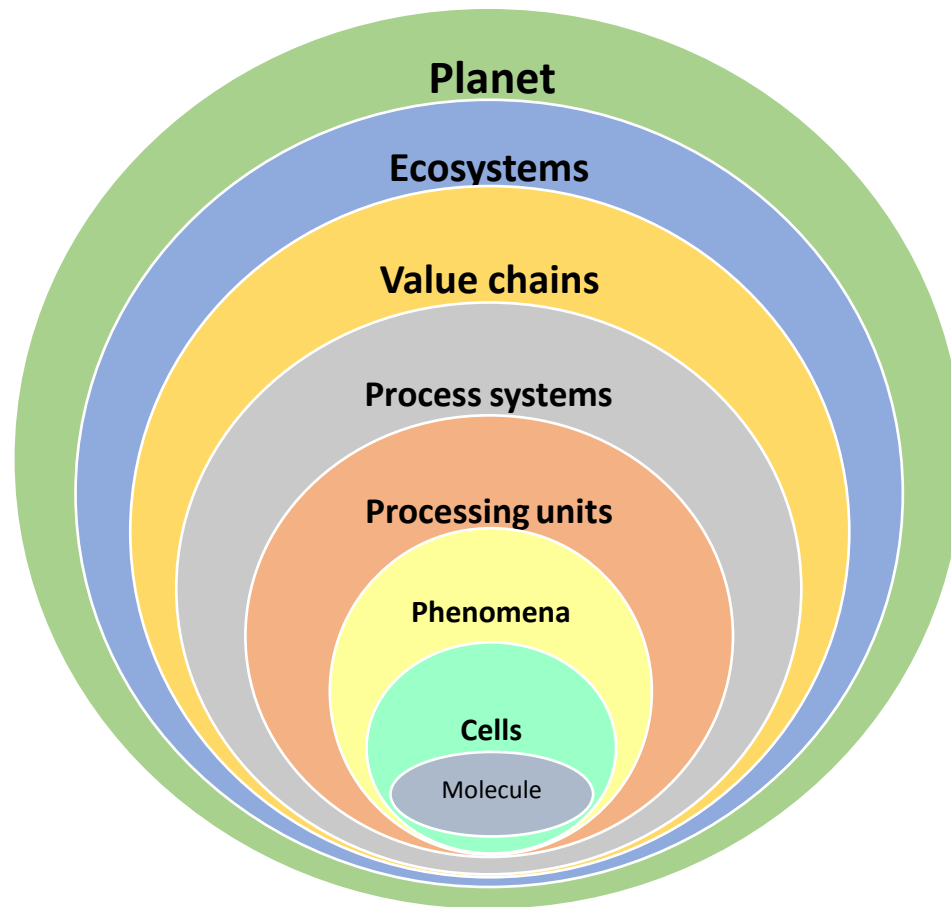


Figure 8: Boundaries in Process design (Hernandez, 2017).

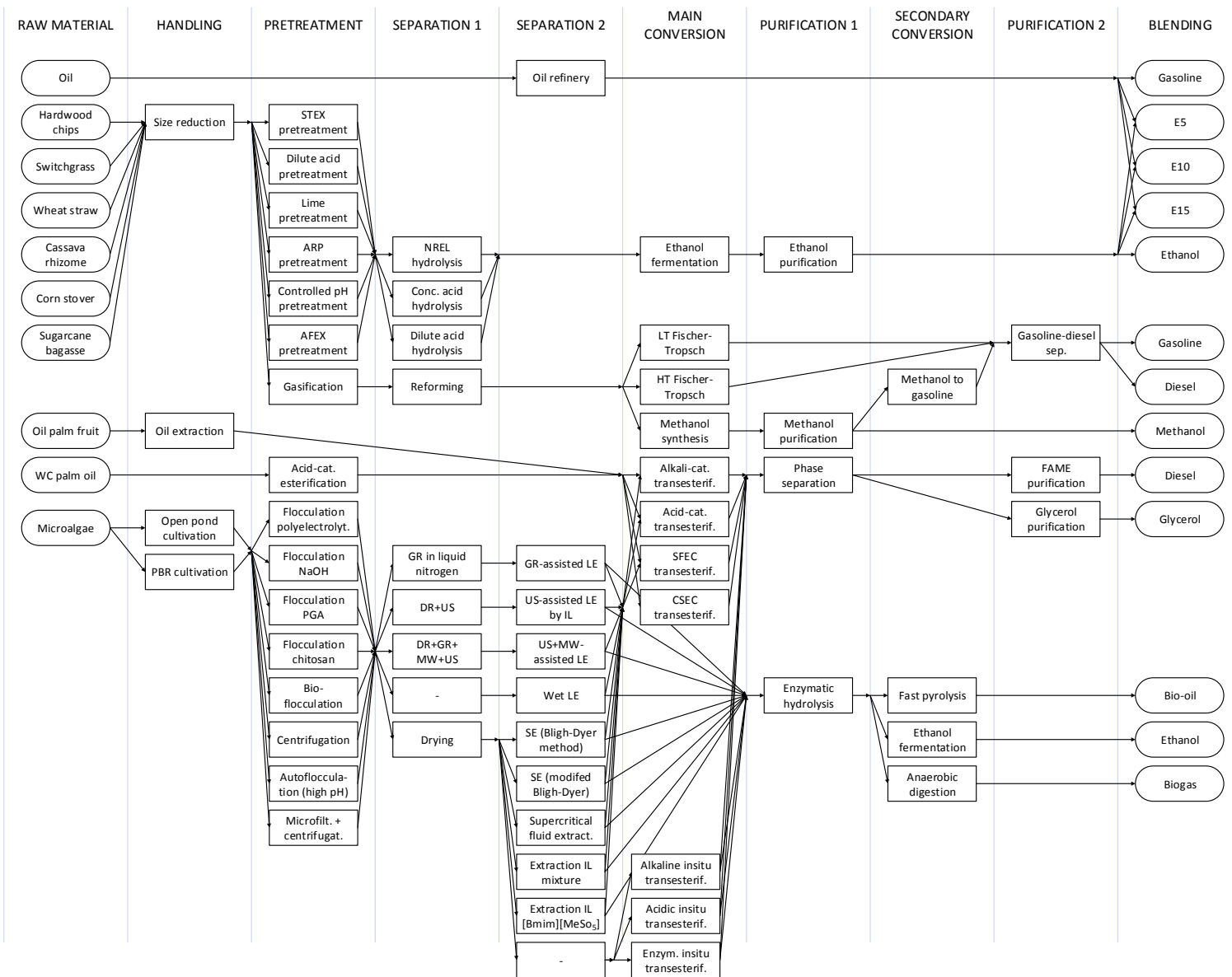


Figure 9: Superstructure of alternative feedstocks, processing technologies and products for biomass-to-energy processes.

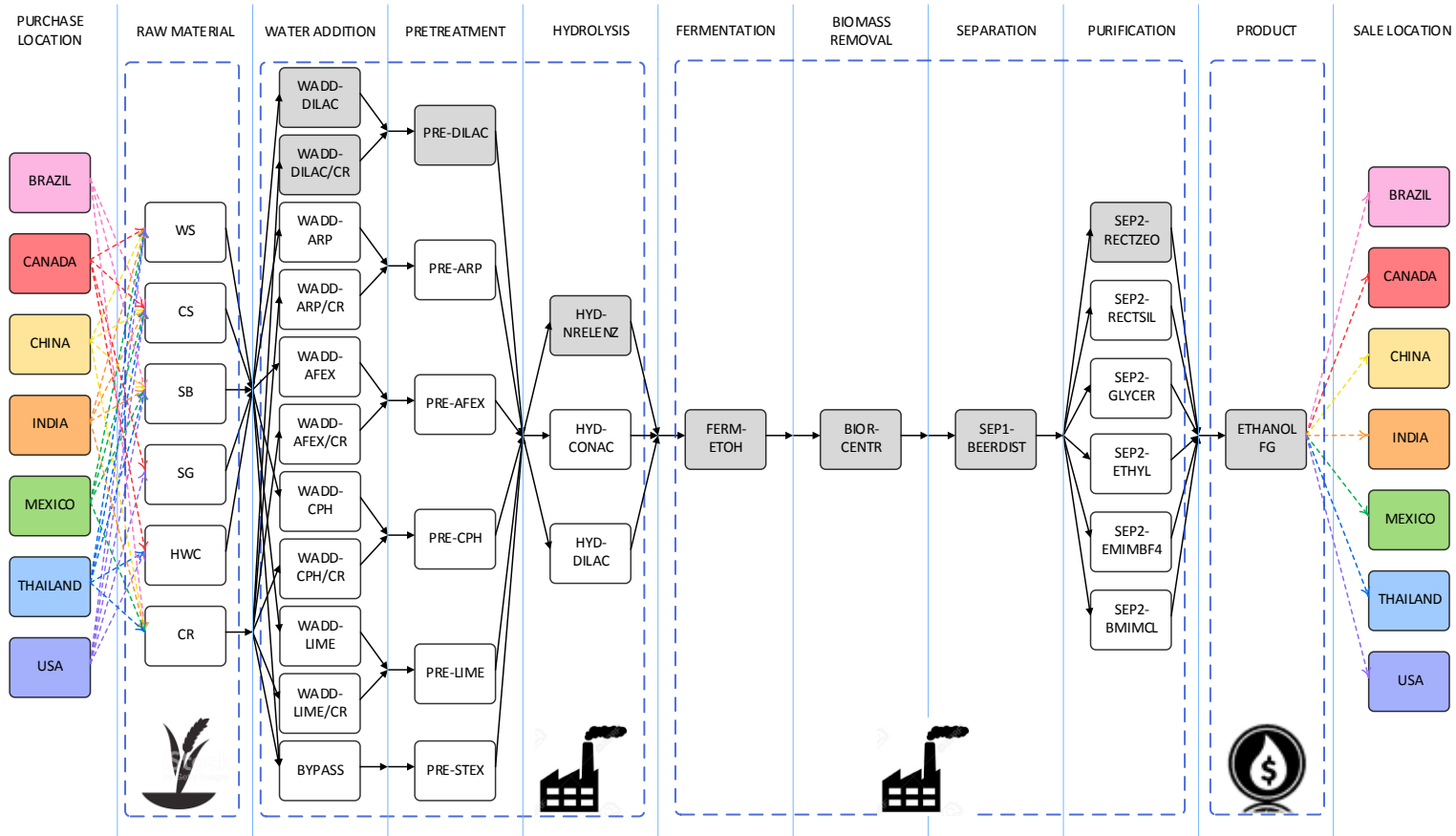


Figure 10: Biomass-to-ethanol superstructure with sections for allocation and fixed processing route highlighted.

Abbreviations - Raw materials (WS: wheat straw, CS: corn stover, SB: sugarcane bagasse, SG: switch grass, HWC: hardwood chips, CR: cassava rhizome); WADD: water addition (DILAC: for dilute acid, ARP: for ammonia recycled percolation, AFEX: for ammonia fiber expansion, CPH: for controlled pH, LIME: for lime pretreatment); PRE: pretreatment (DILAC: dilute acid, ARP: ammonia recycled percolation, AFEX: ammonia fiber expansion, CPH: controlled pH, LIME: lime pretreatment); HYD: hydrolysis (NRELENZ: enzymatic with NREL enzyme, CONAC: concentrated acid, DILAC: dilute acid); FERM: fermentation (ETOH: ethanol fermentation); BIOR: biomass removal (CENTR: centrifugation); SEP1: separation step 1 (BEERDIST: beer distillation); SEP2: separation step 2 (RECTZEO: rectification column followed by zeolite membrane, RECTSIL: rectification column followed by silica membrane, GLYCER: extractive distillation with glycerol as solvent, ETHYL: extractive distillation with ethylene glycol as solvent, EMIMBF4: extraction with ionic liquid EMIM-BF₄, BMIMCL: extraction with ionic liquid BMIM-Cl); Products (ETHANOL FG: fuel grade ethanol).

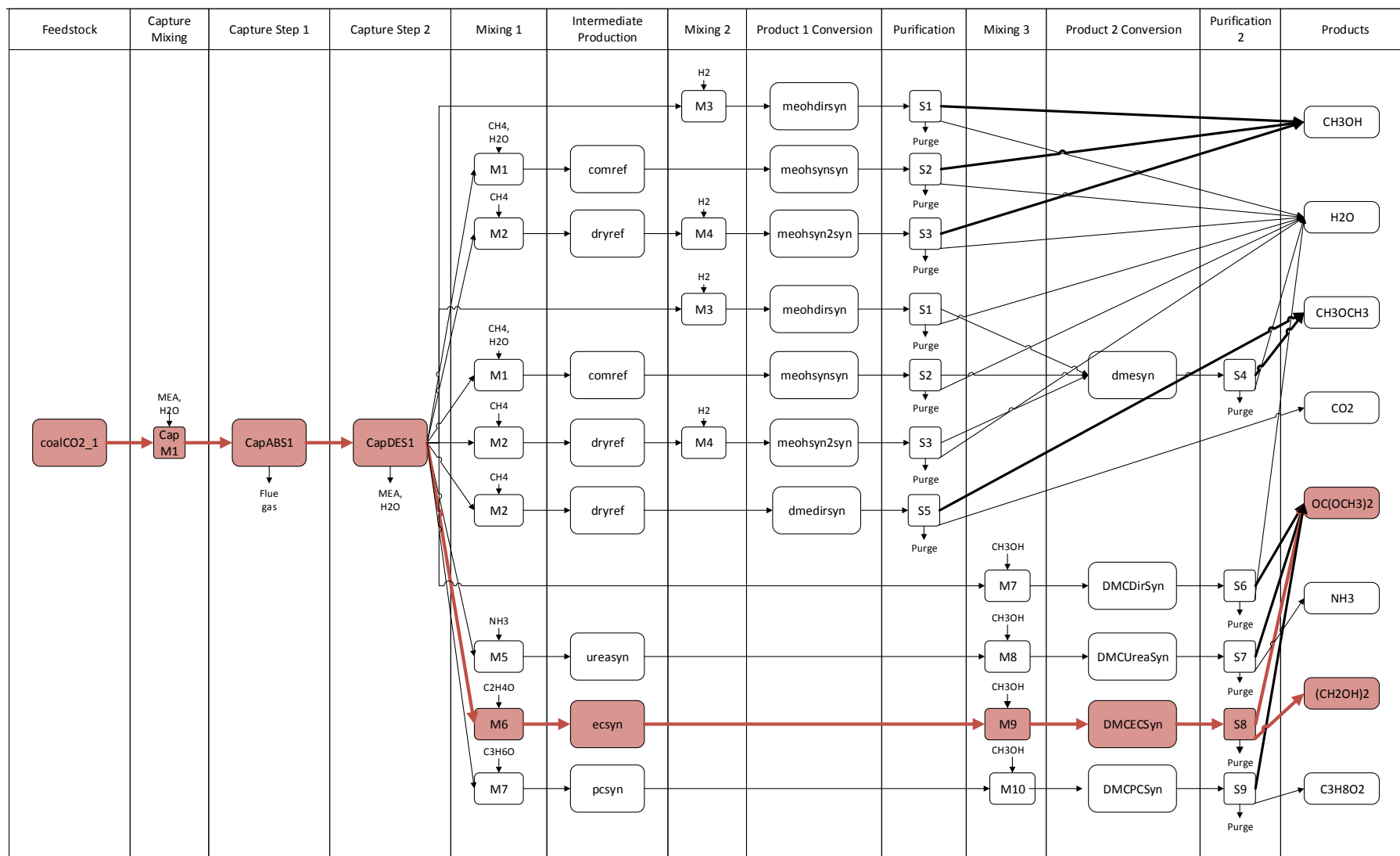


Figure 11: CO2 conversion network to produce methanol, dimethyl ether, dimethyl carbonate, ethylene glycol, propylene glycol

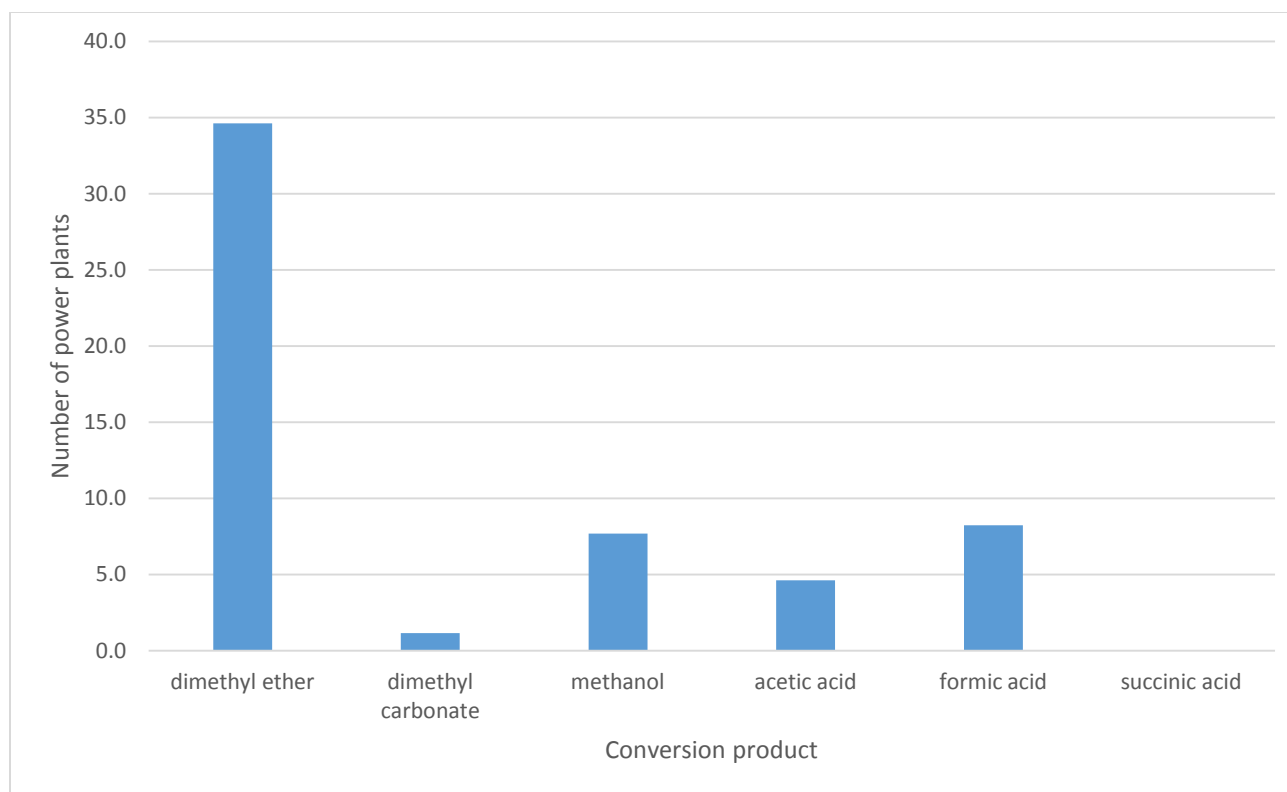


Figure 12: The number of power plants whose emissions can be reduced by the production of these products via carbon dioxide conversion processes. Note: this considers an average power plant as a 150MW coal-fired power plant.

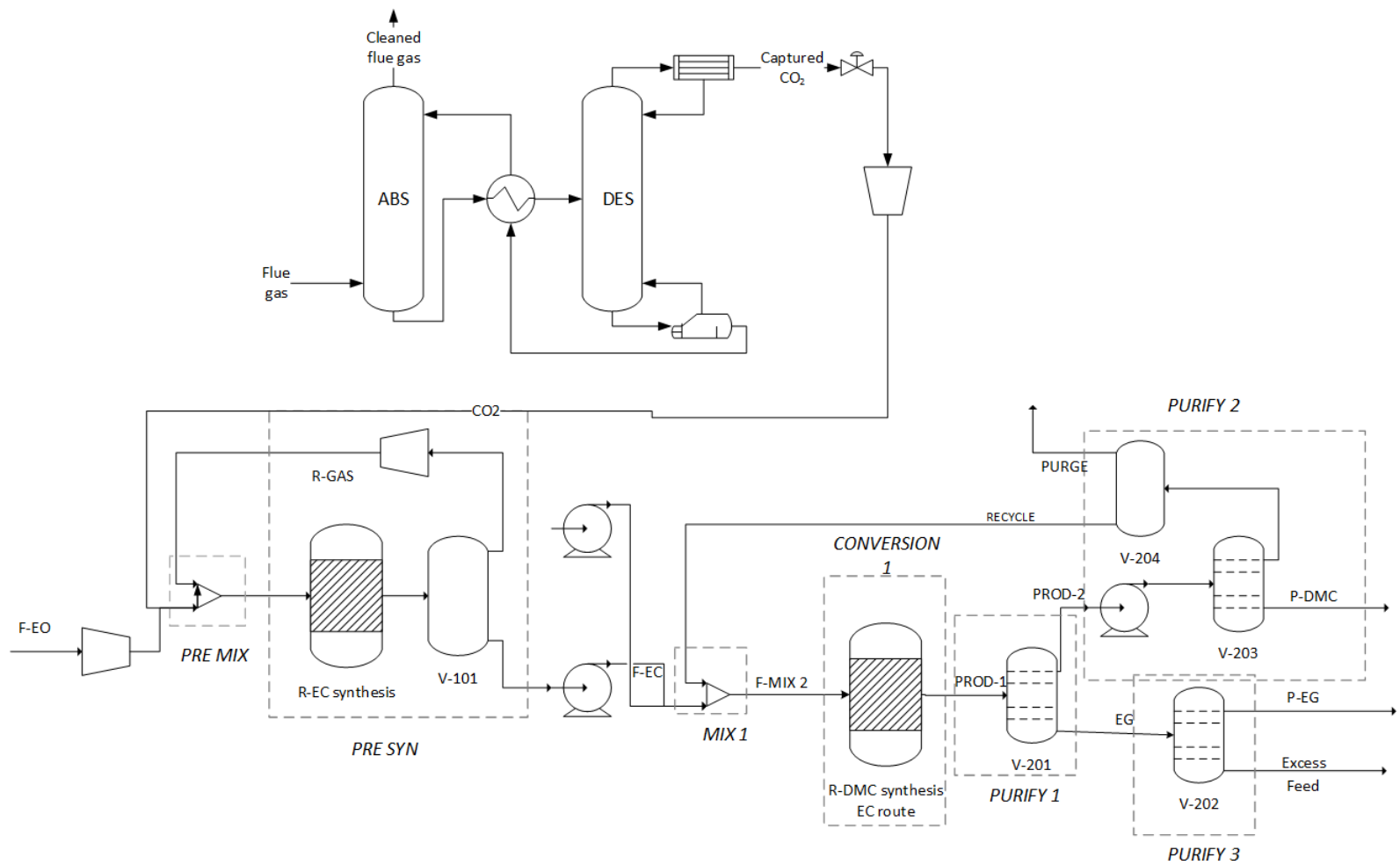


Figure 13: The process flow diagram for the carbon dioxide capture and conversion to dimethyl carbonate via ethylene carbonate production.

