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Are Solar Fuels Sustainable?

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Summary

The combined problems of too little fossil fuels to supply the world's future energy needs and the possible negative environmental effects of carbon dioxide emissions which are coupled to their usage has led to the development of fuels based on solar energy. This research aimed at investigating the possibility of sustainably producing solar fuels from CO_2 on a large scale, as a way of meeting part of the global fuel demand and mitigating CO_2-related climate change during the period 2010-2050.

In this report, the CO_2 for the solar fuels was assumed to be derived from carbon capture at large point sources. A short review of carbon capture technology and a comparison with projected transport fuel emissions leads to the conclusion that the carbon capture potential relative to the fuel need was sufficient to make solar fuels a relevant option.

A literature search of solar fuels resulted in 50 articles on CO_2 based solar fuels. The three main methods of producing solar fuels are through thermochemical, electrochemical and photochemical routes. All three methods use catalysts to drive the reaction of carbon dioxide (and water) to fuel or fuel precursors like syngas. Although catalysts are theoretically not consumed in the reaction, in practice they have a limited lifetime. Because some of the catalyst materials used are relatively scarce, the energy output per gram of the least available catalyst metal was determined. Using the production volume of the metal, the fuel production potential of the different routes based on metal availability could be determined. After estimating the cost of the fuel for each route (based on the cost of raw material), eight routes were selected for further analysis.

The eight remaining routes, together with three alternative carbon mitigation options, namely carbon capture and storage, biofuels and electric vehicles, and a Business-As-Usual (BAU) scenario were compared on their impacts upon scaling up. For land use, the thermochemical and electrochemical solar fuel routes performed well compared to the alternatives. For CO_2 emissions, the solar fuels performed about the same as the alternative schemes, but showed an improvement over the BAU scenario. For material impact, cost and ease of implementation the solar fuels generally performed worse than the alternatives. Overall, some of the thermochemical routes and one electrochemical route performed better than carbon capture and storage and it was concluded that they were approaching commercialization.

For further development of solar fuels it is necessary to reduce the cost of the best performing routes, to determine in more detail the material impacts of those routes and to ensure that carbon capture becomes a common practice.

A carbon tax would benefit the implementation of solar fuels, as this would increase the cost of fossil fuels and make carbon capture more attractive. Air travel is an attractive sector for solar fuels in the future, because the sector needs a high quality fuel, which solar fuel technology should be able to provide in sufficient volume.

Nederlandse Samenvatting

Met de alsmaar groeiende wereldbevolking die gemiddeld steeds luxer gaat leven, neemt de vraag naar fossiele brandstoffen nog steeds toe. Omdat fossiele brandstoffen niet hernieuwbaar zijn en hun totale productie dus eindig is, leidt dit op termijn tot problemen. Daarnaast is het gebruik van fossiele brandstoffen gekoppeld aan de uitstoot van CO_2, een broeikasgas. In dit onderzoek werd onderzocht of solar fuels ("zonnebrandstof") een duurzame optie zijn om de uitstoot van CO_2 niet alleen te voorkomen maar deze grondstof met behulp van zonlicht om te zetten in brandstoffen: "Solar fuel".

Om solar fuels te maken zijn katalysatoren nodig. Katalysatoren versnellen reacties zonder daarbij zelf verbruikt te worden. In de praktijk gaan katalysatoren echter op den duur stuk. Omdat katalysatoren soms van zeldzame materialen gemaakt worden, werd in dit onderzoek eerst nagegaan hoe efficiënt de verschillende manieren om solar fuels te maken met hun materiaal omgingen. Daarmee kon worden bepaald welke routes zich op basis van hun materiaalgebruik lenen voor grootschalige toepassing. Ook werd nog een selectie gemaakt op grond van de prijs van de gebruikte materialen en hoeveel brandstof ze naar verhouding produceerden.

Na deze selectieprocedure werden de overgebleven solar fuel routes samen met alternatieve CO_2 uitstoot verminderende routes, namelijk CO_2 opslag, biobrandstof en elektrische auto's, vergeleken op het gebied van opschaling. Als het ging om landgebruik en CO_2 uitstoot waren de solar fuels ongeveer net zo goed als de alternatieven. Bij materiaalgebruik, brandstofkosten en gemak van implementatie bleven de solar fuels achter. Toch zijn er over het geheel genomen een paar solar fuel routes die al dicht tegen commerciële realisatie aanzitten. Ze moeten nog wel wat goedkoper en efficiënter worden. Het gaat dan om de thermochemische (gebruik makend van geconcentreerde zonnehitte) en elektrochemische routes.

Daarnaast werd ook gekeken naar de bron van de CO_2. Ook al is er over de hele wereld CO_2 te vinden afkomstig van auto's, fabrieken en generatoren, zijn alleen de grote bronnen, zoals kolencentrales als CO_2 bron onderzocht. Bij zulke grote bronnen wordt de CO_2 in grote hoeveelheden en relatief grote concentraties uitgestoten, waardoor het gemakkelijk en kosten efficiënt af te vangen is. Hoewel deze afvangtechniek al mogelijk is, wordt deze nog bijna niet toegepast. Om solar fuels toe te kunnen passen, moet dit eerst gebeuren.

Tot slot werd nog gekeken of er een specifieke toepassing is die goed gebruik kan maken van solar fuels. De luchtvaartsector is naar verwachting tegen 2050 de grootste CO_2 uitstoter binnen de transportsector, omdat de luchtvaart niet goed kan overstappen op alternatieve brandstoffen. Solar fuels zouden daarvoor genoeg energie kunnen leveren. De luchtvaartsector en solar fuels zijn dus uitermate geschikt voor elkaar.

Samenvattend: solar fuels zouden in de toekomst een duurzame optie kunnen zijn om CO_2 te voorkomen, maar er moeten nog wel de nodige ontwikkelingen plaatsvinden.

1 Introduction

1.1 Background

The combined problems of too little fossil fuels to supply the world's future energy needs and the possible negative environmental effects of carbon dioxide emissions which are coupled to their usage has led to the development of fuels derived from solar energy.(Roy, 2010) This research aims at determining whether it is possible to produce solar fuels from CO_2 on a large scale, and whether this is a sustainable way of meeting part of the global fuel demand and mitigating CO_2-related climate change.

Global fossil fuel consumption in 2008 was about 350 EJ (IEA, 2011), a figure which is expected to rise with the projected population growth during this century. However, the main energy sources used (the fossil fuels coal, gas and oil), are depletable and will most likely be insufficient to meet the demand in the future, with all three expected to see either a levelling-off or a decline in production in this century. (IEA, 2010) The transport sector, which uses roughly 25% of all fuel consumed, has a need for a high energy density, storable, transportable energy source, which is currently mostly derived from oil. (Jiang, 2010) Replacing the depletable oil-based fuels with a renewable alternative faces the problem that most renewable energy sources have electricity as an output, a form of energy to which the main part of the transport system is currently not adapted.

As mentioned above, relying on the combustion of fossil fuels for energy, has the additional disadvantage that extra CO_2, a greenhouse gas strongly associated with climate change, is emitted into the atmosphere.(IEA, 2010) To limit the amount of CO_2 emitted, one can reduce fossil fuel combustion by using renewable alternatives like wind and solar power. Recently, another mitigation option, capturing the CO_2 from large stationary point sources and storing it permanently underground, has become a much debated subject. (Haszeldine, 2009) While the advantage of this Carbon Capture Storage (CCS) technology is that existing power plants could be retained, there are public concerns about the safety of storage. Rather than storing the captured CO_2, using it as a feedstock for the production of fuels would circumvent the permanent storage concerns and provide a way to supply fuel as well, in which case CCS would turn into carbon capture and reuse, CCR.

Solar fuel is the term for fuels produced by solar power. Generally speaking, the fuels produced are H_2- and CO_2-derivatives, sometimes in combination to produce syngas (H_2 and CO, which can be converted to fuels), although direct routes to hydrocarbons such as methane are also possible. (Roy, 2010) Both thermal solar power, reaching temperatures over 1000^oC and photovoltaic solar power are used. Much research is dedicated to mimic photosystem II found in plants, to generate H_2 from water. However, like the other H_2/H_2O systems, it does not simultaneously address the CO_2 emissions directly. Starting from CO_2, solar fuel routes include biomass conversion, thermochemical conversion with catalysts like ZnO and $CeFe_3$, electrochemical conversion using a range of uncommon and rare metals as catalysts, photochemical conversion with a range of uncommon and rare metals as catalysts or photo catalytic conversion with TiO doped nanotubes. Whilst some of these routes are on the verge of commercial production, like the thermochemical routes(Chueh, 2010), some are still in early development, like the nanotubes. Viability will however not only depend on performance, but also on the possibilities of scale-up.

A lack of mineral resources for an otherwise very promising technology, has already posed problems in the past. For example, Gallium-Arsenide photovoltaic cells, which show very high efficiencies, cannot be implemented worldwide on a large scale because of the low availability of gallium. (Andersson, 2000) For solar fuels from CO_2, some of the photochemical, photo catalytic and electrochemical routes rely on uncommon and hardly available elements, such as platinum, rhodium, gallium and ruthenium. Although thermochemical routes rely on more available metals like cerium and zinc, they have a high rate of loss due to sintering during the thermochemical cycles. (Roy, 2010) Other catalytic routes also suffer from catalyst loss; therefore, long term solar fuel production will probably require vast quantities of catalyst materials, possibly more than readily available.

Aside from mineral availability, the large scale synthesis of any product is bound to have some impact on the environment. For large scale solar fuels production impacts like toxicity of the used minerals, excess heat in thermochemical plants, and building and decommissioning of a plant, are nearly all applicable for the different technologies. Although a study showed that molten-salt concentrated solar power plants have less impact than conventional power plants, the extra conversion step in solar fuels plants significantly lowers the net energy output. (Piemonte, 2011) And when used in small point sources, like vehicles, the combustion of CO_2-derived solar fuels will emit the CO_2 again. Determining the energy output and CO_2 mitigation are therefore important in deciding the merit of the plant as opposed to other fuels and renewable power plants. Aside from energy and CO_2 mitigation merits, the cost and logistical problems of scale up also have to be overcome for a new technology like solar fuels to succeed.

So, while the production of solar fuels could address both the excess emission of CO_2 and the possible fuel shortage problem, large scale production might not be possible or desirable. The aim of the research was to investigate whether or not solar fuel production based on CO_2 emitted from large stationary sources could be scaled up to a significant size, and what the resulting main environmental effects would be.

1.2 Research Aim and Questions

Given the research aim, the main research question was:

Can solar fuel production based on CO_2 emitted from large stationary sources be scaled up significantly and would this be a sustainable option for CO_2 mitigation and fuel production within the period 2010-2050?

This breaks down into the following sub questions:

1) *What is the scope for solar fuels, based on fuels needs and carbon capture usage?*

2) *What is the energy output per unit of catalyst, for the most relevant solar fuel routes?*

3) *Which solar fuel routes can be scaled up?*

4) *How does the energy output and CO_2 mitigation of the scaled up solar fuels compare to other carbon mitigating technologies?*

5) *How do solar fuels perform in terms of land use, cost, material impact and policy implementations compared to other carbon mitigating technologies?*

6) *What application within the transport sector is well suited for solar fuels?*

Because material demands could be a limiting factor, it was determined what these demands would be for the relevant solar fuel routes and what the determining factors of availability are. Based on the fuel needs, carbon capture and material needs, it was determined which solar fuels can be scaled up, and when. For the scaled up technologies, environmental effects and energy needs were researched, although for the environmental effects this was qualitative rather than quantitative. The performance of solar fuels in terms of energy output, CO_2 mitigation and general environmental effects were compared with other carbon mitigating options like CCS and bio-sequestration. Lastly, determining an application within the transport sector would show a practical application for solar fuels.

1.3 Scope

Solar conversion of biomass was not considered, as this is a very different system, and only solar fuels that use CO_2 as a feedstock are taken into account. Although the thermochemical routes and electrochemical routes show the highest energy efficiencies, photochemical routes were also taken into account as they may prove to be beneficial on other aspects, like material use or environmental effects. Because only large stationary point source captured CO_2 was considered, the projected scope, in time, place and volume, of this technology was a vital starting point for scale up. Although CO_2 can theoretically be captured from the air, only CO_2 available from CCS was considered, as this is available in a concentrated form with proven technology. The scope in terms of fuel need is important because the possible environmental benefits and drawbacks are related to whether the amount of solar fuels produced is actually needed. There is no a priori geographical boundary; the global needs and supplies were considered. The time boundary was 2050, as this is the boundary of the International Energy Agency's energy technology perspective.(IEA, 2010)

1.4 Methods

Literature research was the basis for this thesis, unless otherwise noted searches were performed with the Scopus search engine of SciVerse. From literature, calculations were made to analyse and compare different solar fuel technologies and alternatives. Aside from literature research and calculations, expert consultation was used in certain places. Prices are in dollars (April 2012); the price of diesel oil is from 2010 Germany.

Energy output per gram of catalyst

From the articles that contained sufficient information, the energy output per gram of catalyst was determined by using the energy output given in the article and calculating how much this would be for the element in the catalyst with the lowest production volume, as given by the USGS. Most articles gave an amount of moles rather than energy output. So either the heat of combustion for the product of the reaction was used or, in cases where syngas or CO was produced. The equivalent amount of methanol was used for determining the energy output. The assumptions made and data used are further described in section 4.1 and appendix 1.

Combining mineral availability and energy output

With the energy output per gram of catalyst and the mineral production of the element in question determined. The mineral production of the time of writing was used and extrapolated over forty years, with the exception of the few with less than 40 years of known reserves. The latter were extrapolated until the year they are expected to run out. Using 1% of the calculated amount of minerals and multiplying this by the energy output per gram, the energy output per available catalyst element was found.

Material cost based fuel price

Using data mainly by the USGS, the price per gram of catalyst element was calculated. Together with the energy output per gram of catalyst, the energy output per dollar for the catalyst element could be calculated.

Scale up

For several of the scale up factors a rough quantitative analysis was done by extrapolating and processing the data in the literature, while for other factors the analysis was qualitative. In the latter case, each of the items in the factor was given a score, and these scores were added up. By assigning scores to the quantitative results, a cumulative result for scale up was obtained.

Additional considerations

This was done by compiling points of discussion mentioned in the literature and elaborating on it based on the authors gathered knowledge of the field.

1.5 Layout of the report

In chapter 2, an introduction to solar fuels is given, by means of a short history and a summary of the literature search. In chapter 3, a review is given of carbon capture technology and the potential of carbon capture is compared to fuel needs to determine if solar fuels can be scaled up. In chapter 4, routes that were selected in chapter 2 are analysed on energy output and material use. In chapter 5, a further selection of solar fuel routes are compared to other carbon mitigating schemes in terms of land use, CO_2 emissions, material use, cost and policy implications. In chapter 6, some additional considerations to the sustainability and viability of solar fuels are discussed.

2 Solar fuels

This chapter presents a short history of solar fuels; the prevalence in literature is analysed and the selection of routes for further analysis is described.

2.1 History of solar fuels

The term “solar fuel” is first mentioned in 1972 (Scopus). In an article about concentrated solar steam power, it is mentioned that in the future the use of solar heat to drive the production of fuels would be preferential. It is speculated that energy efficiencies as high as 70% could be reached, higher than for electrolysis. Bockris & Handley (1978) discuss the diluteness of solar energy, which many at that time considered too large a hurdle for the implication of solar energy. The authors argue, however, that potential solar fuels could possibly have a larger energy density than fossil fuels.

In both these articles it is suggested that the term “solar fuel” already existed, but perhaps was not used as a term in literature before the 70s. The 1978 article in Science titled “Solar Fuels” certainly changed that, though it is not mentioned who coined the term. (Bolton, 1978) At the time, solar energy was mostly considered as a heat source for power plants and domestic use. Photovoltaic electricity was an upcoming technology at that time. The author saw need for solar energy storage in the future. The aim of the article was to define the kinetic and thermodynamic limits to solar fuel production, and thus provide a basis for future research. In his article, Bolton argues that for thermodynamic reasons, water is the most attractive highly available feedstock, to be used in a process that mimics photosystems I and II. He does mention however, that due to their prevalence in the atmosphere, nitrogen and carbon dioxide could also be candidates.

Searching with the term “solar fuels” also led to a lot of articles in the 70s and 80s on solar/fuel combined power plants, which generate electricity with steam from heating with either concentrated solar power or fossil fuels. This does support the notion by Bolton that photovoltaic solar power was not yet applied at large scales. Aside from power generation, solar power was used for drying purposes on an industrial scale. Solar fuel was and is also occasionally used for bio-ethanol and other plant-derived fuels, as this is also the conversion of sunlight to fuel. (Mathur, 1980)

Even though the earlier in articles mostly photovoltaic solar fuels are mentioned, in the mid-80s articles on “solar fuels” mostly concern thermal conversion. In an 1984 article (Claude, 1984) solar receiver technologies being constructed at the time are reviews and uses for solar fuel and chemical production are recommended. In 1986, in another review of solar thermal technology (Kesselring, 1986), the solar fuel application is seen as a viable option in the long run as highly concentrated solar energy is cheap. The author does note, correctly, that this will not play a major role in the energy systems of the 20th century.

In an 1991 article (Imhof, 1991) a proof of concept with a solar thermal reactor is announced, which initially would be tested with the thermal decomposition of calcite (which actually releases CO_2). The aim was to test the design of the reactor so that in the future it can be used for a variety of purposes.

In 1992, a paper titled “Solar Fuels: Status and Perspectives” (Serpone, 1992) is the first comprehensive review on solar fuels. It clearly outlines the need for solar fuels based on the advantages and drawbacks of conventional fuels and renewable energy and it elaborates on which countries already have programs to implement solar fuels. Estimates of production costs of hydrogen with various proposed routes are made, and it is noted that for fair comparison all externalities should be considered in both hydrogen and fossil fuel production. The authors do not expect solar/hydrogen technology to be available within the next decades from the time of the article, for both economic and political reasons and due to the fact that they expect that research in this field is still in its infancy at the time the article was written.

In a paper from 1993 different strategies for solar fuel generation are discussed (Tributsch, 1993), mostly analyzing different photo-active transition metal catalysts for heterogeneous catalysis of solar fuel production. However, the author notes that the most promising route would be the integration of domestic photovoltaic electricity generation into decentralized electrolytic solar fuel production. He considers both water and carbon dioxide as viable options for this.

In 1999, an article appeared in which for the first time the environmental impacts of solar fuels are described. (Camacho, 1999) In the article an algorithm is presented to determine the minimum thermal impact on the environment due to the thermodynamic losses in transforming atmospheric CO_2 into fuel. However, the article does not focus on an actual technology but aims rather at providing a base for further research.

From the late 90s onwards, the term solar fuels is used ever more frequently, probably due to both the term being more common and more research actually spent on solar fuels. More than 150 articles use the term in the first decade of the 21st century, although this also includes uses of the term in a different way from the one considered in this research.

Although geothermal, hydro and wind power are cheaper than solar power, Jess (2010) notes that the potential for solar power is far greater and the other renewable energy sources are too small to provide the entire world with energy. A plant built in Iceland produces methanol from captured CO_2, powered by geothermal energy.(CRI, 2012) An initiative of Nobel prize winner George Olah, the plant is mostly viable because geothermal energy is abundant in Iceland, and cheap compared to solar energy.

2.2 Article prevalence and selection

The graph below (figure 1) shows the amount of articles published using the term “solar fuel”. It clearly shows that the term started to be popularized around 2000, and that there is a very strong growth in the amount of articles since 2006.

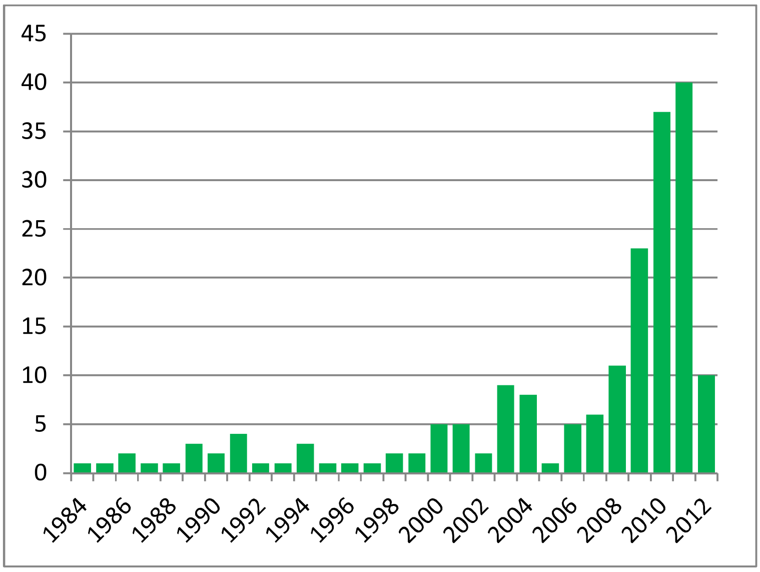

Figure 1: Articles using the term “solar fuel” (after Scopus)

As mentioned in the introduction, the term “solar fuels” is used for more than one concept. As intended in this research, it is the production of fuel from basic molecules such as water and carbon dioxide, powered by solar energy. In searching for solar fuels from 2009 onwards, more than half of the articles describe actual routes and research concerning water-based solar fuels. The search for CO_2-based solar fuels resulted in dozens of different researches, most of them on laboratory scale and focused on the chemistry and physics of the reaction, rather than on the sustainability of the process. Photocatalytic routes were prevalent, with thermochemical and electrocatalytic routes less abundant.

2.3 Solar fuel routes

In the table below, the solar fuel routes are summarized. The routes are a mix of thermochemical, electrochemical and photochemical routes. The first four entries are not further discussed in chapter 4 because their activity is either too low or, in the case of Traynor & Jensen (2002) no catalyst is used. Although the latter could be quite ideal, the route suffers from difficult separation and the data in the article were not sufficient to make it easily comparable to the other routes.

Table 1: Articles describing solar fuel routes after initial selection

	Feedstock	**Product**[f]	**Catalyst**
DeSario 2011	CO_2 and H_2O	Methane	TiO_2 nanocomposites[a]
Fischer & Eisenberg 1980	CO_2 and H_2O	CO and H_2	Ni and Co homogeneous catalysts[a]
Shibata 2008	CO_2 and H_2O	Hydrocarbons up to C_6	Copper based electrodes[a]
Traynor & Jensen 2002	CO_2	CO	None
Ikeue 2002	CO_2 and H_2O	Methane and methanol	Ti on SiO_2 film[b]
Liu 2010	CO_2 and H_2O	Methane	Pt- and Ru-loaded Zn_2GeO_4 nanobelts[b]
Le Gal 2011	CO2	CO (methanol)	Zr-doped CeO[b]
Xi 2011	CO_2 and H_2O	Methane	TiO_2/ZnO[b]
Asi 2011	CO_2 and H_2O	Ethanol	AgBr/TiO_2[b]
Li 2011	CO_2 and H_2O	Methanol	Cu_2O/SiC[b]
Stamatiou 2010	CO_2 and H_2O	syngas (methanol)	FeO[c]
Takeda 2008	CO_2	CO (methanol)	O_3N_3Re[b]
Chueh 2010	CO_2	CO (methanol)	CeO
Abanades & Chambon 2010	CO_2	CO (methanol)	SnO
Abanades 2011	CO_2	CO (methanol)	FeO
Loutzenhiser 2011	CO_2 and H_2O	Syngas (methanol)	Zn
Roy 2010	CO_2 and H_2O	Hydrocarbons	Pt- and Cu-loaded TiO_2 nanotubes[d]
Ampelli 2011	CO_2 and H_2O	Isopropanol	Fe on CNT[e]
Haije & Geerlings 2011	H_2 and CO	FT diesel	zeolite/ZnO/CuO and cobalt
Zhan 2009	H_2O and CO_2	Syngas	Solid oxide electrolysis cell

a) very low activity b) under artificial light c) same group as Loutzenhiser d) under sunlight e) same group as Centi f) between brackets is potential secondary product

3 Carbon Capture and Transport Fuel Needs

The first part of this chapter is a review of carbon capture technology. The different types of carbon capture are discussed, estimates on the volume of future carbon capture are made and the costs and impacts of carbon capture are discussed. In the second part, future transport fuel needs are discussed. The aim of this chapter is to determine whether the projected volume of carbon capture, when uses as a feedstock for solar fuels, is significant compared to the estimated amount of fuel needed.

3.1 Carbon Capture

In order to produce fuel from CO_2, the CO_2 must be available. The CO_2 in the atmosphere is so diluted (roughly 400 parts per million) that it would be impractical for direct use in an industrial process. However, CO_2 is not always released in a dilute form. One third of all anthropogenic CO_2 emissions are from power plants, cement, steel, and aluminium factories and refineries. (Balat, 2009) These industries use fossil fuels, mostly coal, as a source of energy, and thereby produce CO_2 in large quantities and at a high concentration. Because they are an integral part of the global economy, and they are very dependent on coal and other fossil fuels, they play a central role in the mitigation of CO_2. To limit the amount of emissions from these large point sources, they could be fitted with carbon capture technology. When discussing Carbon Capture and Storage (CCS), the captured carbon is often intended to be sequestered in geological formations, which would prevent the captured CO_2 from entering the atmosphere. As this CCS technology would allow for industry and, indeed, mankind to rely on fossil fuels for a longer period of time with less environmental concern, it is an economically favourable option over changing to renewable resources. In fact, the amount of CO_2 produced by the large point sources is expected to grow. So without carbon capture storage any climate change reduction goals are likely to fail. Therefore, the International Energy Agency proposes that 20% of CO_2 mitigation should come from CCS by 2050.

Carbon Capture technology is designed to extract the CO_2 from the point of emission. There are three main technologies: pre-combustion, post-combustion and oxy-fuel combustion.(Haszeldine, 2009) Post-combustion is the most straightforward, and can be fitted to existing plants. The acid oxide CO_2 that is produced by the combustion of, for example, coal is captured at the flume by a basic solvent, like monoethanolamine (MEA). This solvent is then heated to extract the CO_2 and the solvent can be reused thereafter. The add-on to the plant that is necessary for carbon capture will be rather large, however, and the vast quantities of solvent needed pose problems due to emissions to the environment. Pre-combustion technologies gasify the coal, and use the water gas shift reaction to produce H_2 and CO_2, after which the former is used as an energy source and the latter is extracted. The main disadvantage is that this technology in general cannot be implemented in an existing plant; on the other hand, by 2050 most of the current power plants will have been replaced. The oxy-fuel technology burns the fuel with pure oxygen, resulting in a very high CO_2 content in the flue gas. Contrary to pure oxygen combustion, combustion with ambient air results in a low CO_2 concentration in the flue gas (since most of it is N_2), which requires an extra separation step to concentrate the CO_2. The advantage is that no solvent is needed for capture, but the generation of oxygen requires much extra energy.

Pre-combustion technology is considered the most appropriate for future use, although all three methods are being developed.(Haszeldine, 2009) The fact that there are three options being researched and tested simultaneously is also a draw-back, as there is a great need for carbon capture, but the money and means for research are spread out. This means it will take more time before any of the three technologies are ready for a wider scale implementation, thus delaying the point where CCS can become significant in reducing the amount of CO_2 emissions by large point sources. Besides the fact that the money and means for research are spread, the flow of knowledge between different projects is also hampered because of patent laws and general competitiveness.

3.1.1 Emission reduction

The lifetime CO_2 emission reductions that can be achieved by fitting power plants with CCS lie between 65 and 80%. (Balat, 2009, Zhang, 2009) This includes the production of the fuel, plant operation and in some cases construction and dismantling of the plant as well. Differences in system boundaries are the main source of differences between calculated life-time reductions. But with capture rates being around 90%, the energy loss due to CCS is about 20-30% for coal-fired power plants. According to Haszeldine (2009), with more research this loss could be decreased by 20-60%. As the mining and transport of coal caused the largest share of CO_2 emissions in CCS-fitted power plants, research on whether these processes can be improved is lacking.

3.1.2 Capture potential over time

Currently (2010) there are no commercial CCS-fitted plants or factories yet, although there are dozens of pilot plants. The global deployment of CCS on a commercial scale will require at least two learning cycles, after which there needs to be enough incentive to actually build and retrofit plants with CCS. (Haszeldine, 2009) Currently, the political and economic climate does not favour a large scale deployment of CCS, but it is assumed here that the trend will follow the roadmap set by the IEA, as shown in figure 2 (IEA roadmap).

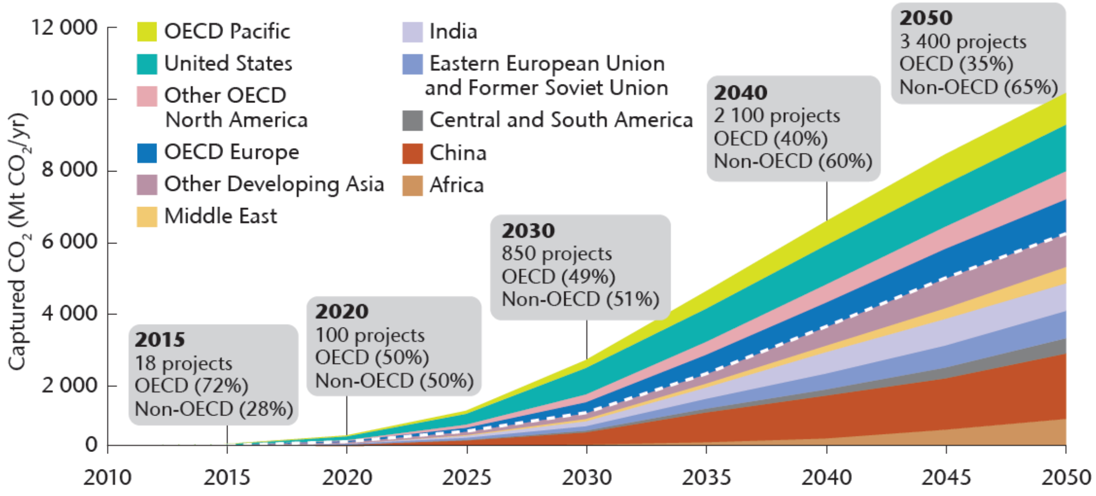

Figure 2: Cumulative carbon capture over time as projected by the IEA (from (IEA, 2009))

Figure 2 shows that the USA is to have the largest share of CCS at first, but it is taken over by China around 2035. It is also evident that CCS is not to be confined to the major economic powers, but that it can take place in all regions. Other schemes on CCS show a similar trend, but tend to have a more rapid increase that levels off slightly towards 2050. In their report, the IEA notes that the shares of industrial and power generation CCS plants differ between regions, but coal-fuelled power plants will be the largest sector overall.

The cumulative CO_2 capture from 2010 to 2050, as presented by several studies, is shown in table 2. Figures vary widely, with Balat *et al.* (2009) being on the high end and Dooley & Calvin (2011) including more pessimistic schemes. It is therefore assumed that the course of the IEA roadmap is followed, both because this is somewhere in between these figures, and because the IEA roadmap includes a wider climate change mitigation policy. It should be noted that the study by Balat *et al.* pointed out that this total potential of 240 Gt CO_2 captured by 2050 will only mean a 37% CO_2 reduction, which is less than the targeted 50%. This emphasizes the need for a mix of CO_2 reduction options.

Table 2: Cumulative carbon capture from 2010-2050

Author	Cumulative CO_2 captured (Gt)	Note
Dooley & Calvin 2011	37.5-187	Dependant on severity of climate policy
Balat 2009	240	Total potential
IEA	145	Part of a roadmap

3.1.3 Costs of capture

Figure 3 shows the investment in carbon capture (*not* transport and storage) needed to achieve the CCS deployment proposed in their road map. The total cost from 2010 until 2050 is over 5 trillion USD, or 125 billion a year on average.(IEA, 2009) Figure 3 shows the expenditure on CCS per region. It is likely that CCS will first be adopted in more affluent countries. But with the high goals set for carbon mitigation, CCS should also be deployed in worldwide. Since heavy industry is located close to the resources, which are located in less wealthy countries too, foreign aid or investment will be necessary to distribute CCS across the globe. An incentive to do this could be the carbon credits of the Kyoto protocol, where countries may offset their own emissions by abatement measures in other countries (Zakkour, 2011).

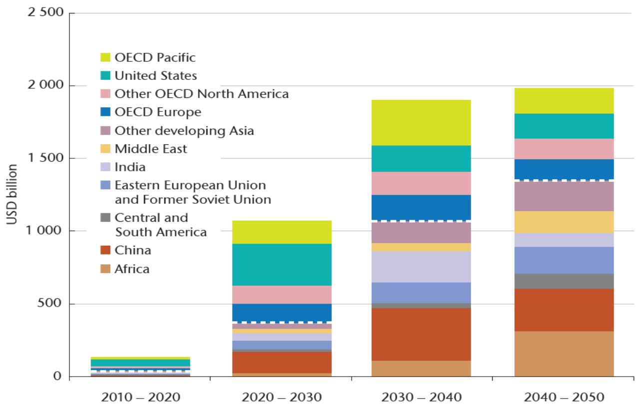

Figure 3: Estimated total cost of CCS (within an optimitic scenario) the coming decades (from (IEA, 2009))

Currently, the costs of CCS are between 35 and 300 $/t, of which capture represents about 75% of the costs. (Balat, 2009) Figure 4 shows the abatement costs per tCO_2 avoided used by the IEA, which shows costs in a similar range.(IEA, 2009) As coal-fired power plants with CCS will have the largest share, the abatement costs will be closer to the 45 USD/tCO_2 avoided mark than in the higher cost ranges represented by biomass and gas in figure 4. It is expected that this figure will decrease with more research and development; but the cost for, for example, electricity will increase with about 10% by 2050 when CCS is deployed on large scale.(Haszeldine, 2009)

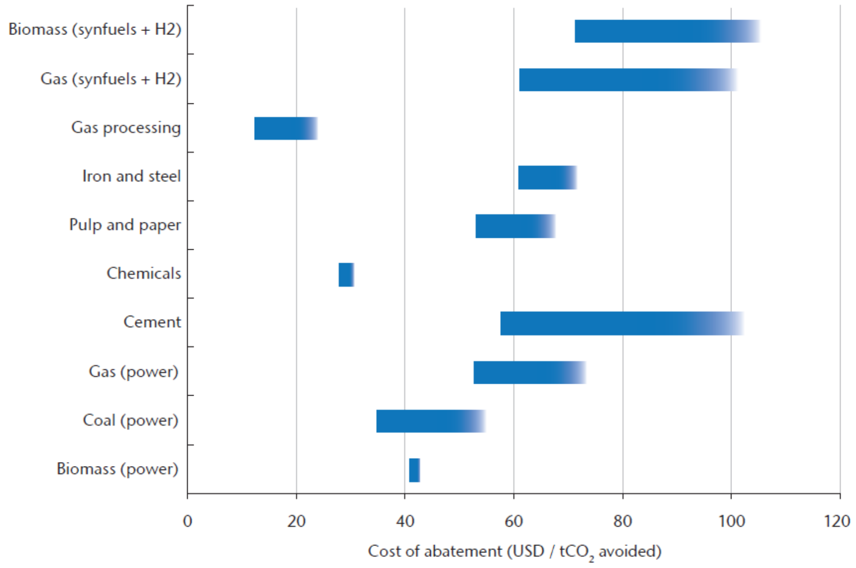

Figure 4: Abatement costs of different kinds of fuel (from (IEA, 2009))

It should be noted that currently, the cost of using CCS for carbon mitigation is lower than renewable energy. (IEA, 2009) For example, if the IEA CO_2 reduction target would be met without CCS, the costs would be 70% higher. Whilst this is an indication that the cost of CCS is within reasonable limits, it does hamper the development of renewable energy technologies.

3.1.4 Additional environmental effects of capture technology

Aside from the monetary cost, there is also an environmental cost of CCS, as capture technologies require energy and materials. As CCS is currently under development, mostly because of its environmental benefit in CO_2 reduction, the environmental cost should not offset this. As noted above, CCS does not reduce the emissions from a plant by 100%, and there is an energy penalty, which further decreases the benefit of having CCS with a plant.

As with the financial cost, the environmental burden results from the capture part of CCS. While from a financial perspective use rather than storage of captured carbon will likely be beneficial (the CO_2 is then feedstock rather than waste), from an environmental perspective the storage will likely be more beneficial because the CO_2 does not end up in the atmosphere.

The environmental effects of capture technology are different for the three main technologies, but limited research has been perforemed in this area. (Koornneef, 2012) A recent review in this area reveals that a full spectrum of emissions to air is not yet available and uncertain, and emissions to water and solid waste streams are lacking, see figure 5. Oxyfuel combustion has lower emissions of NO_x, SO_2 and particulate matter than power plants without CCS. Pre-combustion has particulate matter and NO_x emissions similar to non-fitted power plants. Post-combustion power plants show lower SO_2 emissions than non-fitted power plants, but they have significantly higher NO_x and NH_3 emissions. The biggest concern with pre- and post-combustion technology is the use of large amounts of solvent to capture the CO_2. Furthermore, the effects of the emission of the amines to the atmosphere is not yet known. Zhang *et al.*, in their review of CCS LCAs, found that while acidification and eutrophication potentials increase with 25-40%, indicators predicted an expected overall improvement in health of about 30% due to CCS.(Zhang, 2009)

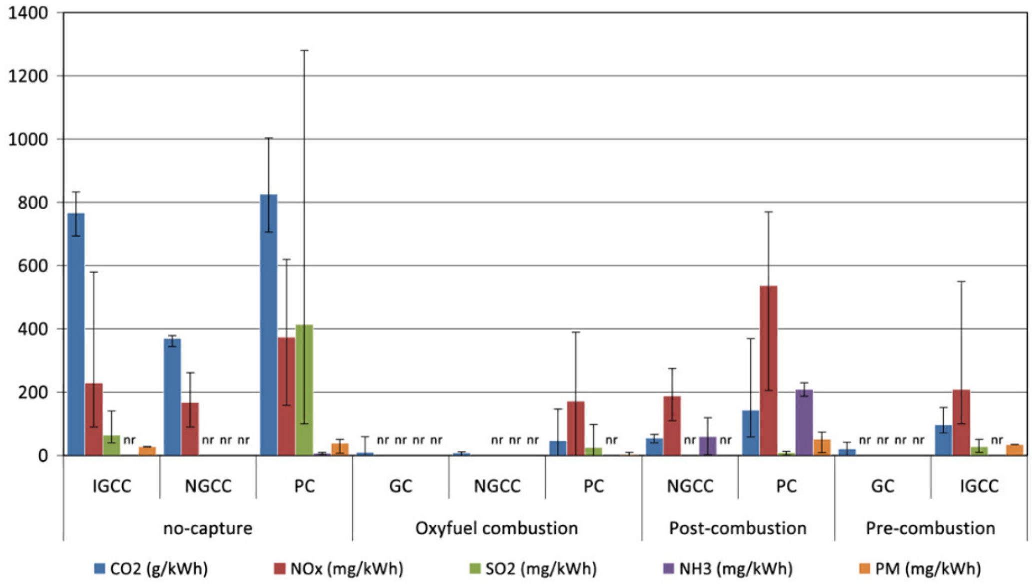

Figure 5: emissions from different CCS technologies, vertical axis legend at the bottom (from (Koornneef, 2012))

3.1.5 Solvent requirements Post-combustion capture

Post-combustion capture is likely to be the first dominant capture method, because it can be applied to existing plants and because it is cheap compared to other methods.(Jones, 2011) But it requires a large amount of solvent (for instance monoethanolamine, MEA), because during operation a small amount of MEA is lost due to degradation. The amount of solvent lost was found to be 0.3 kg MEA per tCO_2. (Moser, 2011) The same pilot plant had a MEA stream of 4000 kg/h for a CO_2 capture rate of 300 kg/h. Thus, per kg of CO_2 captured, 13.3 kg of MEA was necessary. By 2050, estimates of CO_2 capture are between 2 and 12 Gt per year. Assuming that the same MEA/CO_2 ratio is necessary, 3-18 Mt of MEA are needed (based on the hourly global production of CO_2). When the loss of MEA is taken into account, this amounts to 3.6-21.6 Mt of MEA. Production of ethanolamines (including iminodiethanol (DEA), and nitrilotriethanol (TEA)) is 1.3 Mt per year, with a 4% growth annual growth rate. At that rate production would be at 6.2 Mt annually by 2050. For the high carbon capture case (21.6 Mt MEA needed) this would be insufficient, but since it lies within the same order of magnitude and it is not unlikely that the production could be increased to meet the demand of carbon capture. Additionally, it is likely that not all carbon capture will be by post-combustion capture, and the other methods do not require these large amounts of solvent making MEA shortages less of an issue.

3.1.6 Air capture of CO_2

The capture of carbon dioxide from air has been possible since the 1930s (Ranjan & Herzog, 2011), and it would be ideal if large scale deployment would be an option as this would allow societies to develop a negative carbon emission balance. Air capture technologies consist of a wet scrubbing mechanism that captures the CO_2 with basic solutions of NaOH or KOH. The second step regenerates the basic solutions by heating the solutions to liberate the CO_2. The heating step takes up the largest share of energy, although, to get a significant rate of carbon capture, very large volumes of air have to be processed in the first step. Since the CO_2 content of air is only 0.039%, as opposed to the 5-15% from power plants, (Jones, 2011) most of the air that goes through the scrubbing installation goes right through. In order to minimize the costs of the process, the energy supply should come from non-fossil fuels; otherwise the energy supply would give rise to additional CO_2 emissions. Although proponents of air capture estimate the costs to be about \$30-\$1000/tCO_2 (Graves, 2011, Simon, 2011), taking into account more realistic renewable energy prices increases the cost to about \$900-\$4600/tCO_2. Unfortunately, the price is higher than other carbon dioxide mitigation options, which should therefore be preferred. An additional complication is that counting on air capture to be a realistic option within the foreseeable future may lead to carelessness now, if one assumes that any excess of CO_2 can be removed later. Therefore, in my view, carbon capture from air is not a realistic option for the next decades and it is not further considered in this research.

3.2 Fuel needs for transportation

The concept of Solar Fuels is considered in light of both CO_2 emissions excess *and* fuel shortages. In section 3.1, the potential of carbon capture from large point sources was considered. In this part, the future fuel needs up to 2050 are assessed. This is necessary because the comparison between the possible amount that solar fuels can produce and the amount of fuels needed shows whether or not the production of solar fuels is significant. Only the fuel used by the transport sector is considered, both for simplicity reasons (the transport sector is the largest user of oil) and because, as mentioned in the introduction, the transport sector specifically has a need for high density fuels.(IEA, 2010)

The energy required for transport is expected to rise in the first half of the 20th century, the IEA projects this to be 100% more in 2050 compared to 2005.(IEA, 2010) The increase would not only be because of population growth, but also due to increased GDP leading to an increase in the percentage of the population that owns a vehicle. Aside from private transportation, public transport is also expected to increase, although there could be shifts between high speed trains, busses and aviation. As oil production is set to peak within the first half of this century, measures that lower or replace the use of oil products in transport are needed to make the sector more sustainable. Increasing efficiency of engines and transport systems, introducing alternative fuels such as hydrogen and biofuels and increasing the amount of electric vehicles are all options that are under consideration. The IEA considers mixes of these options to decrease CO_2 emissions (transport accounts for 25% of global CO_2 emission) and transfer to a transport system that no longer relies on fossil fuels. In two scenarios, the ACT and BLUE scenarios, they explore different way of implementing the options and compare them to the baseline scenario, which relies mostly on the use of fossil fuels. The ACT scenario aims for cost-effective deployment of more renewable transport technology, whilst the BLUE scenario represents a higher cost, more rapid transfer away from fossil fuels. Both of them will increase the costs of transport, but the measures are considered necessary on the long run. Even with those scenarios, fossil fuels are still present in the transport sector by 2050.

As mentioned before, the amount of fuel needed and the amount of fuel that can be produced with solar fuels are compared in this research. As the solar fuels are based on CO_2 captured from large point sources, the amount of carbon capture (storage) will set a limit to the amount of solar fuels that can be produced. In the previous part, several figures were found for the cumulative potential captured carbons between 2010 and 2050. By comparing this amount with the projected CO_2 emissions from transport in the same period, a maximum value for the share of solar fuels in the total fuels used can be given.

Figure 6 shows the projected CO_2 emissions from transport between 2010 and 2050 for the different IEA scenarios and the amount of CO_2 captured in different CCS scenarios.

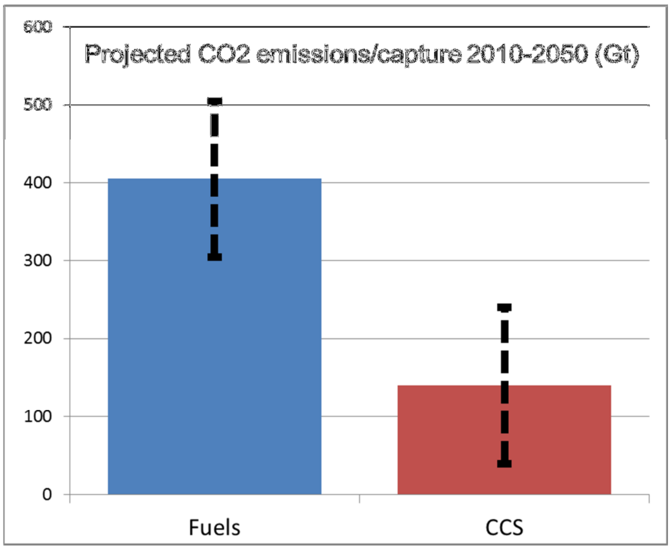

Figure 6: Comparison of fuel emissions and carbon capture, cumulative over the 2010-2050 period. After IEA, 2010, Balat, 2009, Dooley & Calvin, 2009

The data for fuels were acquired by interpolating the projected figures for CO_2 emissions from transport for the different IEA scenarios. For CCS, the lowest and highest estimated potential for the 2010-2050 period were used. The values for fuel use vary greatly, and while it is tempting to take an average, the current trend is still set on the highest fuel-use scenario. As mentioned before, the other two methods of carbon capture still require significant investment and R&D. For the volume of CCS, the same problem exists. However, since CCS increases the sustainability of coal (and other fossil fuels), it is more adapted to current energy use. Furthermore, a policy directed towards large point sources is easier to manage than a policy directed towards small point sources like transport. So, in the “worst case” (for the potential of solar fuels), the amount of CCS is only 7.8% of the amount of emissions from transport; in the “best case”, this is about 80%. With the expected losses in the conversion of captured CO_2 to fuel, the worst case would make solar fuels insignificant, while in the best case solar fuel would ideally be able to supply a large amount of the fuels needed in the world. It should also be noted, however, that the fuels used in the transport sector vary, so a potential solar fuel technology will either be able to supply a range of fuels with acceptable energy efficiency, or suffer a decrease in significance in the fuel market. The question remains whether solar fuels are a sustainable option if their share in the fuel market is between average and ideal.

4 Metal requirements of solar fuel routes

In chapter 3 it was determined that the amount of carbon capture that is projected to take place the next 40 years is within the same order as the amount of carbon released from fuel use in the same period, and that there is thus a potential for carbon-based solar fuels to supply a significant amount of fuel. With that knowledge, the next step is determining whether there are solar fuel routes that are feasible for scale up. Following that, the factors that are important in scale up are assessed.

As mentioned in chapter 2, in order to select routes appropriate for scale up, a selection was first made on availability of data, see appendix 5. For the remaining routes, the energy output per gram of least available catalyst metal was calculated. With that information, and the availability of the metal the total possible amount of energy that can be produced over the 40 year period was calculated. A second criterion was the price of the catalyst metal coupled to its output.

4.1 Energy output per gram of catalyst

Table 3 and figure 7 show the energy output of different kinds of catalyst materials used to convert CO_2 to fuels. Although the materials listed below are catalysts and are thus not formally consumed in the reaction, catalysts do degenerate or get destroyed completely over time.(Rothenberg, 2008) With the (assumed) lifetime of the catalyst and the conversion speed per gram of catalyst, the amount of fuel that can be produced was calculated. With this and the combustion heat for these fuels, the energy equivalent of what a gram of catalyst material can produce during its lifetime could be calculated.

Table 3 description and energy output per gram of catalyst element of solar fuel routes

	Product[d]	**Catalyst**	**Metal used**	Output ($kJ/g_{catelement}$)
Ikeue 2002[a]	Methane and methanol	Ti on SiO_2 film	Ti	0.17
Liu 2010[a]	Methane	Pt- and Ru-loaded Zn_2GeO_4 nanobelts	Ge	0.45
Le Gal 2011[b]	CO (methanol)	Zr-doped CeO	Ce	1.07
Xi 2011[a]	Methane	TiO_2/ZnO	Ti	1.77
Ampelli 2011[a]	Isopropanol	Fe on CNT	Fe	4.9
Asi 2011[a]	Ethanol	AgBr/TiO_2	Ag	10.7
Abanades 2011[b]	CO (methanol)	FeO	Fe	17.5
Li 2011[a]	Methanol	Cu_2O/SiC	Cu	20.3
Stamatiou 2010[a]	Syngas (methanol)	FeO	Fe	30.1
Takeda 2008[b]	CO (methanol)	O_3N_3Re	Re	47.5
Loutzenhiser 2011[a]	Syngas (methanol)	Zn	Zn	57.7
Roy 2010[a]	Hydrocarbons	Pt- and Cu-loaded TiO_2 nanotubes	Pt	99.1
Chueh 2010[b]	CO (methanol)	CeO	Ce	106

Abanades 2010^{b}	CO (methanol)	SnO	Zn	290
Haije & Geerlings 2011^{c}	FT diesel	zeolite/ZnO/CuO and cobalt	Co	1,67 x10^{7}
Zhan 2009^{a}	Syngas	SOEC	Gd	1.08 x10^{8}

a) feedstock: H_2O and CO_2 b) feedstock: CO_2 c) feedstock: H_2 and CO_2 d) between brackets is secondary product, which was used for energy calculations

Details of the calculations and the research of the data can be found in appendix 1. In general, most articles did not give a turnover number or an equivalent for their catalyst, although some authors did perform a catalyst lifetime test. Therefore, lifetimes were estimated by extrapolating graphs given in articles or in cases where only a reaction rate per hour was given, the lifetime was assumed to be one hour. In cases where CO was the product, equivalent amounts of methanol that could be formed by using a portion of the CO in the water-gas-shift reaction were used to determine the energy output. The energy output as seen in the graph is purely the energetic value of the products produced; values are inaccurate because of the need for assumptions. Most of the reactions are currently only on lab scale and not very far developed, so in many of them higher outputs are likely to be possible.

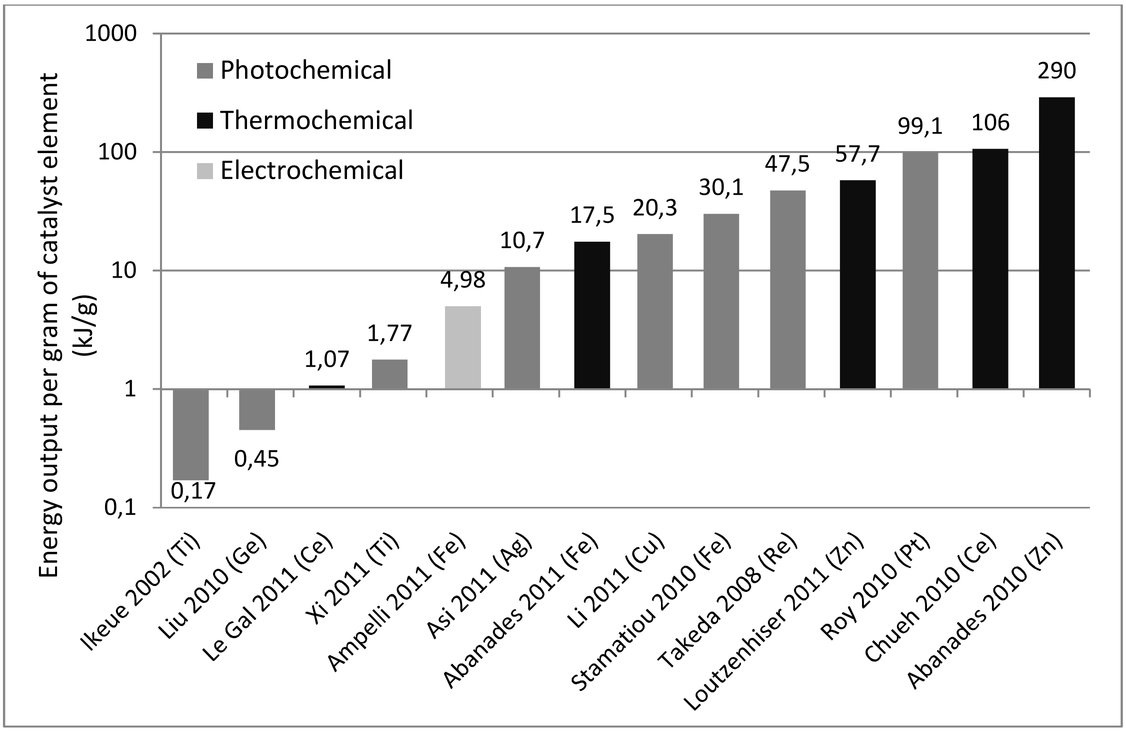

Figure 7: Output per gram of least available element in kJ/g. Note the logarithmic scale. Zhan 2009 and Haije & Geerlings 2011 omitted for clarity

Figure 7 shows that there are large differences between the energy outputs of the different routes. The thermochemical routes perform better on average than the other two types of solar fuel technologies, although the electrochemical routes of Zhan *et al* 2009 and Haije & Geerlings 2011 (not in graph) perform the best.

4.2 Energy output per available catalyst

With the energy outputs per gram of relevant catalyst material calculated in section 4.1, the total possible amount of energy produced can be calculated using the amount of metal available. The table below gives the total production of the different elements, extrapolated over 40 years using the production amounts of 2008.

Table 4: Metal production. After USGS 2011

Element	Production over 40 years (t)	Element	Production over 40 years (t)
Titanium	$3.9x10^6$	Zinc	$5\ x10^8$
Germanium	3200	Platinum	8800
Iron	$4.8x10^{10}$	Silver	$5.1\ x10^5$
Cerium	$2.5x10^6$	Cobalt	$2.8\ x10^6$
Copper	$3x10^8$	Gadolinium	16000
Rhenium	180		

Table 4 is a summary of appendix 2, where the elements that are the base of the catalysis are also assessed on the following:

- Presence in earth's upper crust
- Ease of extraction
- Side effects of extraction
- Annual production
- Current uses
- Outlook on production
- Recyclability

The goal was to use the data from the energy output per gram of catalyst, table 3, and data on the availability of the rarest component of this catalyst to determine which solar fuel routes could have a significant contribution to fuel supply. A 40 year time period was chosen, because the estimates for fuel needs in this period were available through an estimation by the IEA (IEA, 2010), which were roughly 5 ZJ ($5x10^{21}$J).

Figure 8 shows that the output various solar fuel routes could produce in 40 years based on their energy output for a specific element in the catalyst and how much of said element is available. The line shows the estimated fuel needed between 2010 and 2050. The order of the route in the graph is the same as in figure 7, thus showing how low energy output per g catalysts can have more potential than higher output catalysts, because of differences in metal availability.

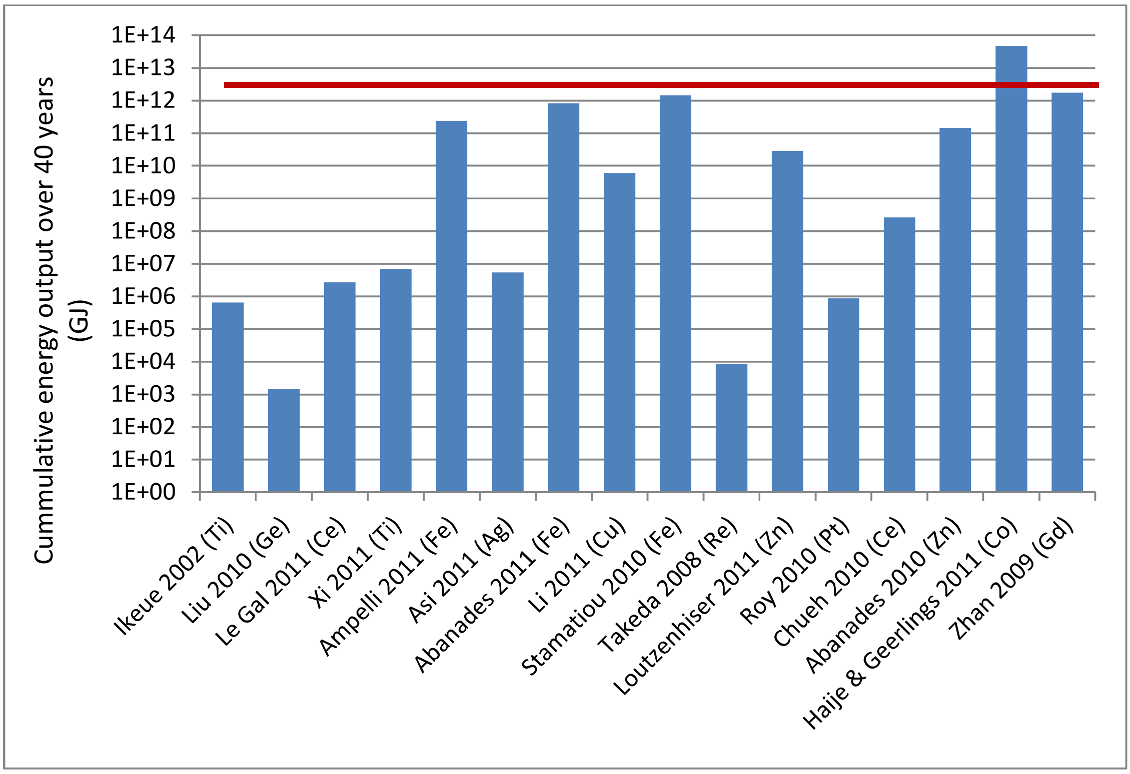

Figure 8: Energy output of the solar fuel routes with metal production

For most of the elements used in the catalysts of the chosen SF routes, reserves are expected to last for longer than this 40 year period, so only part of the reserves were taken into account here. Of course, these elements/catalysts would be available for longer, but for comparison with fuel needs this was negated for the moment. Using 1% of the annual production of these elements and the estimated longevity of the reserves or 40 years, the amount of catalyst available for solar fuel production was estimated. 1% of annual production was used because these elements are used in other processes, and 1% seemed like a relatively non-consequential decrease in availability for the other uses of the elements. Multiplying the resulting amount with the energy output per gram of catalyst, the total amount of energy producible as shown in figure 8 was calculated. It should be noted that for the lower performing routes, like Takeda (2008), a hundred fold increase (representing using 100% of available resources) would not give a significant enough increase.

As is shown in figure 8, routes that rely on available elements like rhenium and platinum with high per-gram-outputs are outperformed by low output routes that use widely available elements like iron and titanium. Some routes, such as Zhan (2009), Haije & Geerlings (2011) and Abanades (2011) come close to or surpass the projected fuel need. While certainly encouraging, it should be noted that these are unrealistic estimates, since most of these routes are still far from actual implementation and large scale fuel production. But the graph does show which routes are and which are not viable, based on material availability.

4.3 Energy output and catalyst price

For another measure of the scale-up possibilities of the different routes, the energy output per dollar was calculated based on the price of the catalyst materials used in the previous sections (4.1 and 4.2), and on the energy output of those materials. Considering the large price differences (see table 5 below) in the catalyst materials, a cheaper but less efficient process may be preferable to a highly efficient but very expensive process.

Table 5: Metal prices, after USGS, 2008 and USGS, 2010

Element	Price($/kg)	Element	Price($/kg)
Iron	0.44	Gadolinium	500
Zinc	2,20	Silver	550
Copper	7.49	Germanium	940
Titanium	8.82	Rhenium	2300
Cobalt	46	Platinum	51400
Cerium	400		

With the calculated energy output per gram of catalyst (table 3) the energy output per dollar for the different routes could be calculated. Figure 9 shows the results of these calculations, in kJ/$. It should be noted that these are not the actual energy production costs of these routes, but merely a rough indication for comparison based on the single catalyst material. Once again, the order of the routes in the graph is the same as in figure 7, to show the difference the price makes in the potential of routes, making some highly active catalysts produce more expensive fuel than cheaper lower active ones.

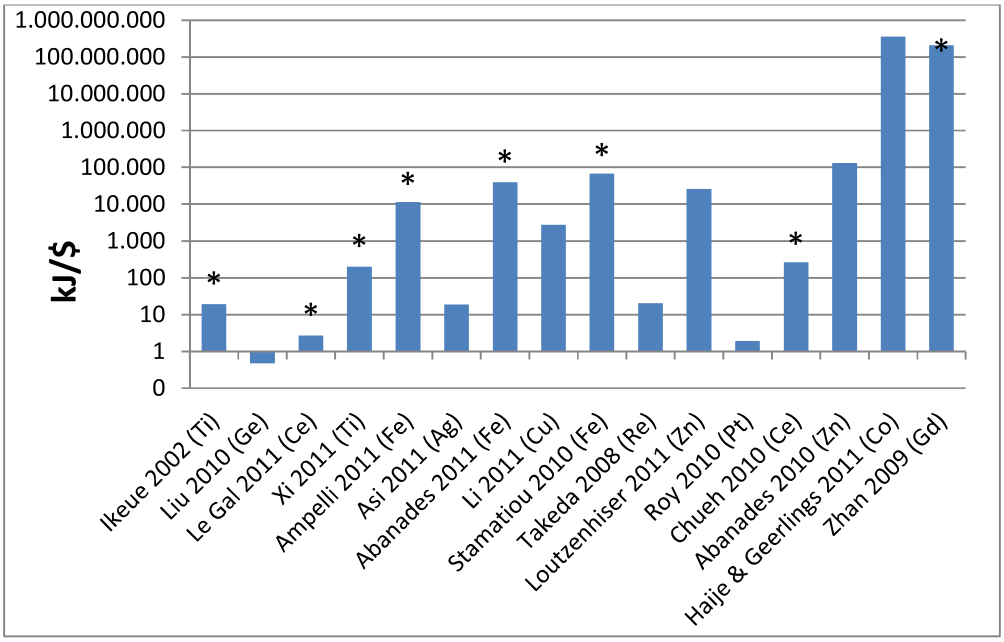

Figure 9: Energy output per dollar. * denotes data from USGS, 2008, the rest is from USGS, 2010

Selected routes

From the calculations presented in figures 8 and 9, four routes were excluded for further calculations, because they are relatively expensive and their material-based energy generating potential is relatively low. Ikeue 2002 was also selected despite not performing very well in the analysis above, but because of the high availability of TiO_2 and the popularity of TiO_2 in nanomaterials, it was still considered for further analysis These routes are:

- Liu 2010
- Le Gal 2011
- Takeda 2008
- Roy 2010 (with platinum)

Most routes discussed are, of course, only still on a lab-scale and may thus prove to be more (or less) efficient with more testing and scale-up. Durability tests were not performed with most catalysts, so they may have higher energy outputs than calculated here. Although the best scoring routes (Zhan, 2009, Haije & Geerlings, 2011) perform far better than others that remain, they are all assessed on other factors in the next chapter, as implementation depends on more than material availability.

5 Scale up Factors

In this chapter a selection of solar fuel routes is being assessed on several factors that are of importance when the routes are scaled-up. In the previous chapter, 4, only their performance in fuel production was considered and whether there were basic material availability problems. But to be able to say whether solar fuels are a viable option for carbon mitigation and/or fuel production, the effects of their use on a large scale must be assessed. The objective of this chapter is to assess which solar fuel routes would face the least problems on scale-up and how the alternative CO_2 mitigation routes perform compared to them. Because some of the routes are described by more than one author, the routes are divided into schemes. First the schemes are looked at individually, but later a broad generalization is given to point out what the major hurdles for the implementation of solar fuels are.

The factors that are examined are: land use, CO_2 mitigation, environmental impact and supply chain impact due to material use, cost and ease of implementation. These factors were chosen to represent the characteristics of the Best Available Technology, as described by the European Union directive (EU, 2012); which states that the best available technique is the one that is cost-effective, acceptable and benefits the environment the most as a whole (appendix 3).

Land use is considered because solar energy is a dispersed form of energy and the utilization of that may take up a lot of space. CO_2 mitigation is important because CO_2 is the primary greenhouse gas and uncoupling transport from it is thus of importance. Environmental impact of material use is important because the production of, for instance, the catalysts for solar fuel production may lead to a large environmental burden that negates the benefit of the solar fuel. Cost is important because fuel is used in such quantities by humans that it is an important part of their expenses, so cost-effectiveness of fuel production is paramount. Ease of implementation is important because the effect of a carbon mitigation route is dependent on its scale, and therefore difficult-to-implement routes will be less effective and maybe not worthwhile. The following solar fuel routes are considered:

Route	Scheme[a]
Zhan *et al.*	SFSOECFT[b]
Abanades *et al.*	SFAbanades
Chueh *et al.*	SFChueh
Xi *et al.*	SFXi
Ampelli *et al.*	SFAmpelli
Roy *et al.*	SFRoy
Haije *et al.*	SFRWGSFT[c]
Loutzenhiser *et al.*	SFLoutzenhiser
Asi *et al.*	SFAsi
Li *et al.*	SFLi
Ikeue *et al.*	SFIkeue

a) for an explanation of the schemes, see below. b) SFSOECFT stands for Solar Fuel route using Solid Oxide Electrochemical Cells followed by Fischer-Tropsch sy thesis. C) SFRWGSFT stands for Solar Fuel routes using Reverse-Water-Gas-Shift followed by Fischer-Tropsch synthesis

Additionally, the following CO_2 mitigation routes were also examined for the same factors:

- Business As Usual
- Carbon sequestration
- Electric vehicles
- Biofuel

The issue with the factors and routes considered is that most of the routes are only on lab scale, while the factors are about large scale implementation, and many of the articles contain little or no information on scale-up. To come to answers on what the effects of scale up are, in some parts values from the articles are extrapolated to large scale, and in other cases rough values are assigned to different attributes for each scheme. The analysis made here is therefore very qualitative.

Scheme description

All the routes considered are used in schemes, because some are proposed by more than one author or have a slight variance between authors. Below is a description of the different schemes.

SFSOECFT- This scheme comprises the routes that use solar energy to make hydrogen, which is then electrolysed at high temperature with CO_2 to make syngas and then processed in a Fischer-Tropsch (FT) reactor to FT-diesel. There are numerous articles on this route which are used here. (Zhan, 2009, Graves, 2011 and Fu, 2010) It is assumed here that the solar electricity is generated with concentrated solar power, because this has the option of continuous production by using, for example, molten salt technology. Continuous production is preferred to improve the longevity of the SOEC stacks. (Graves, 2011) The FT reactor is assumed to use a cobalt catalyst.

SFRWGSFT- This scheme comprises routes that use solar energy to make hydrogen, use this hydrogen in a reverse water-gas-shift reactor with CO_2 to make syngas, and process this syngas in a FT-reactor to make FT-diesel. These routes have been described by Haije and Geerlings (2011) and Jess (2010). The solar energy is here presumed to come from photovoltaics, the reverse water-gas-shift reactor to use a copper on aluminium oxide catalyst and the FT reactor to use a cobalt catalyst.

SFAbanades, SF Loutzenhiser, SF Chueh- These are the schemes of the respective routes Abanades (2010), Loutzenhiser (2011) and Chueh (2010). They are all thermochemical routes that produce syngas, and are grouped together in some sections below as “thermochemical routes”. An article by Kim *et al.* discusses a thermochemical route with methanol production included. (Kim, 2011)

SFAsi- This scheme is the photochemical route by Asi (2011), which uses 32wt% AgBr with TiO_2 nanoparticles to produce a 2:1.5 mixture of methane and methanol.

SFXi- This scheme is the photochemical route by Xi (2011) which uses mesoporous TiO_2/ZnO powder to produce methane.

SFLi- This scheme is the photochemical route by Li (2011) which uses Cu_2O on SiC to produce methanol.

SFAmpelli- This scheme is the photo-electrochemical route as described by Ampelli *et al.* and Centi *et al.* (same group), (Ampelli, 2010, Centi, 2007) which uses a photo-electrochemical cell with TiO_2 nanotubes on the photochemical side to split water and carbon cloth with platinum on the electrochemical side to form isopropanol and other hydrocarbons.

SFIkeue- This scheme is the photochemical route by Ikeue (2002) which uses TiO_2 on porous silica to form methane.

SFRoy- This scheme is the photochemical route by Roy (2010) which uses TiO_2 nanotube arrays with, in this case, a monolayer of copper to produce methane.

BAU- This scheme is the Business As Usual scheme, which is taken from present day or, where indicated, the IEA forecasts, see appendix 6 for a description of the IEA BAU scenario for transport. (IEA, 2010)

CCS- this scheme is carbon capture and sequestration, using the outlook compiled in section 3.1. The fuel use in this scheme is as in the BAU scheme.

EV- This scheme is the implementation of Electric vehicles, as forecasted by the IEA Blue Map scheme (IEA, 2010).

Biofuel- This scheme is the use of biofuel as forecasted by the IEA Blue map scheme, although values are also taken from Fu (2010) and Jess (2011). Only primary biofuels are considered here.

5.1 Land requirement

Since the sun is a relatively dilute source of energy, the essence of harvesting it is to concentrate the energy. Although the total amount of solar energy received by the earth is far greater than what humans require, how much we can use of it depends on our mechanisms of transforming the solar energy into what is needed. As there is also a limit to the amount of space that can be used for harvesting solar energy, the land requirement of the solar fuel routes is an important factor to consider. The land requirement was based on how much land was needed to produce one kJ of energy, based on solar-to-chemical efficiency. So the land used for mining, water supply, transport, storage and such was not considered. Not only time, but also space is important here, as the energy is needed at a certain time. One small solar fuel plant could, given sufficient time, produce the amount of fuel needed in a year, but not at a fast enough speed. Therefore, the land requirement was calculated in m^2/W. Considering that the yearly consumption of transport fuels by 2050 is projected to be about 87 EJ (IEA, 2010), the output of the fuel industry should be at least 2.7×10^{12} W.

Table 6 shows the values that were calculated for the solar fuel routes.

Table 6: Calculated land requirements of the different schemes

Route	m_2/W	For 2.7 x 10^{12} W (x10^{12} m^2)
SFSOECFT	1.6 x 10^{-2}	0.05
SFRWGSFT	5.2 x 10^{-2}	0.14
Thermochemical routes	5.6 x 10^{-2}	0.16
SFRoy	50.6	140
Biofuel	2.0	5.90
Electric Vehicles	1 x 10^{-2}	0.03
BAU	-	-
CCS	-	-

For SFSOECFT, the route that uses high temperature steam electrolysis, a CSP plant was used to calculate the land requirement since this will be the biggest part of the land required, with the reactors and refineries being more concentrated processes. The plant from Burkhardt (2011) needs about 0.01 m^2/W. The efficiency of the process is about 61.7% (minimum values for electrolysis and FT process). Thus the whole process requires 1.62 x 10^{-2} m^2.

For SFRWGSFT, the calculated solar-to-fuel efficiency of 7.7% was used. Considering the sun has an output of 1 kW/m^2 25% of the day, 5.16 x 10^{-2} m^2 is needed per W of output.

For the three thermochemical routes, an article by Kim (2011) was used in which a thermochemical fuel pilot plant is described. The solar-to-methanol efficiency of the process, taking into account the average solar influx, is 7.1%, so 5.60 x 10^{-2} m^2 is needed per W of output.

The photochemical routes all had very different outcomes, but most of the routes are only tested under a lamp instead of sunlight. Since in most of the source articles the actual light influx on the sample is not described, only SFRoy is considered here, as it was tested both under natural sunlight and the data were corrected to a specific influx (1 kW/m^2, global average (Roy, 2010)). Their route gives 7.9 x 10^{-6} W/cm^2, and taking into account that over a whole day this is only 25% of this, this means 50.6 m^2/W.

The CCS scheme is considered to use no land here. Although both fossil fuel production and the storage of carbon take up some land, this is negligible compared to the land needed for solar concentration into fuel. Additionally, the solar fuel routes also take up additional space for plants, transport and storage that was not considered above.

For the biofuel scheme Jess (2011) is used, which gives a solar-to-fuel energy efficiency that results in 2 m^2/W for biofuel. The additional issue with biofuel, aside from its higher land requirement compared to solar fuels, is that the land required also has to be suitable for crop production. Arable land is already a problem, with deforestation, soil degradation and general shortage of how much is available being a problem.

Electric vehicles require land for generation of electricity. We consider here that electric vehicles should run on renewable electricity, with solar power being the most widely available (Jess, 2011). When the charge efficiency of the battery is considered to be 100%, only the solar-to-electricity efficiency is taken into account. Using a CSP plant, the land required is 1 x 10^{-2} m^2/W.

The BAU scheme is considered not to have a land requirement, although there is land needed for refineries and transport, but like the CCS scheme, this is considered negligible.

To put the values obtained into perspective, a comparison can be made with the size of the Sahara, which is not only relatively uninhabited but also located close to the equator, resulting in a high solar influx. The Sahara is about 9.4 x 10^{12} m^2, which means that all the schemes except for SFRoy fit in the area. Of course, not all of the Sahara could be used for solar fuels and biomass for biofuels could not be grown there. And logistically speaking it would be probably be preferable if the solar fuel plants are spread over the world so that the fuel would have to be transported less far.

So, in conclusion, the non-photocatalytic solar fuels perform better than biofuels in terms of land requirement. The only photocatalytic solar fuel that was tested in natural sunlight, SFRoy, performed about 20 times worse than biofuels. Although this is significant, it is imaginable that this gap will be closed in the coming years with more research into these solar fuels.

5.2 CO_2 savings

As mentioned before, solar fuels are a way to both mitigate climate change and provide fuels. In section 4.2, rough quantitative assessments of the different routes were made to see how much fuel they could produce. Here, the amount of CO_2 emissions that are avoided is assessed.

The CO_2 emissions avoided considered here are the part of emissions from coal-powered electricity plants that could be captured and emissions from liquid fossil fuels used in transport. The part of the emissions from coal that can potentially be captured from the flue gas are estimated to be 2 to 12 Gt CO_2 in 2050 (see section 3.1.2). Emissions from transport in 2050, from the estimate by the IEA for the Business As Usual scheme, are 16 Gt CO_2 (IEA, 2010). This 16 Gt CO_2 corresponds to the burning of 160 EJ of fossil fuels by transport (both passenger and freight) in 2050, as also estimated by the IEA in the same report.

The BAU scheme is used as the baseline, from which the other schemes can save emissions by reducing the amount of fossil fuel burnt or by storing coal-based CO_2 emissions. The reason this method was chosen is that it requires less information about the actual CO_2 emissions from each individual route, but does offer a qualitative assessment of the relative CO_2 emissions.

Most of the solar fuels are produced on lab scale, and therefore losses of CO_2 in the process and additional fossil fuel needs are not reported in the literature and thus they are not considered here. Because solar fuel production is limited by carbon capture, fuel can be made from only 2 to 12 Gt CO_2. Because the fuel is produced with the intention of using it in combustion engines, this 2 to 12 Gt CO_2 ends up in the atmosphere again eventually. But there is carbon mitigation as the use of solar fuel avoids the use of an equivalent amount of fossil fuel. It is assumed here that solar fuel can produce the whole spectrum of fuels used in transport, from gasoline to LPG.

To calculate the CO_2 savings, the amount of energy that could be generated per unit of CO_2 was calculated. For SFSOECFT and SFRWGSFT, which both produce FT diesel, it was assumed that FT diesel has the same higher heating value (HHV), 43.1, as normal diesel and the same average carbon chain length, $C_{12}H_{23}$. With the HHV and the amount of carbon per mole, the amount of energy per carbon and thus per transformed CO_2 could be calculated. Appendix 4 shows the results of these calculations, per type of solar fuel.

Table 7 shows the rough estimates of the CO_2 emissions with each route. The coal emissions, as stated above, are only the part that is estimated to be captured by 2050. Fuel emissions are carbon dioxide equivalents of emissions from transport for burning 160 EJ of fossil fuel as estimated by the IEA. The fuel emissions and the total emissions have a range for most schemes. This is because the estimate for carbon capture varies (between 2 and 12 Gt). The lower values in the range correspond to a high carbon capture rate, which means that there is more CO_2 available to make (renewable) fuel from, resulting in less fossil transport fuel needed (and thus less emissions from fossil transport fuel). The higher values in the range correspond to a low carbon capture rate, when more fossil transport fuel is needed.

Table 7: Calculated CO_2 emissions of the different schemes

Scheme	Coal emissions (Gt CO_2)	Fossil transport fuel emissions (Gt CO_2)	Total (Gt CO_2)
Solar fuels (average)	12	0.1-12.9	12.1-24.9
-isopropanol	12	0.4-13.4	12.4-25.4
-Ft diesel	12	0.2-13.4	12.2-25.4
-methanol	12	0-12.9	10-24.9
-methane	12	0-12.2	10-24.2
BAU	12	16	28
Biofuel	12	0-12	12-24
CCS	0-10	16	16-26
Electric vehicles	12	0-14	12-26

The fuel emissions from the different solar fuel routes are determined by the amount of fuel that can be produced from the captured CO_2 from coal plants. The coal plant emissions are kept at 12 Gt because this is the upper limit of the estimations on CCS deployment for 2050. But for the fuel emissions, the lower limit of 2 Gt was also taken into account. To calculate how much emissions for fossil fuel use were left for each solar fuel scheme, the amount of energy produced by each scheme was subtracted from the 160 EJ of fossil fuel that was estimated by the IEA to be needed for transport in 2050. With the remaining amount of energy, from fossil fuels, the amount of CO_2 equivalents that would still be emitted was calculated.

The BAU scheme has the maximum amount of emissions for both coal and fuel emissions, although it should be noted that in the IEA report (2010) there is also a “BAU high” scheme which has higher estimates for fuel use and emissions, but this was not taken into account here because the “normal” BAU scheme is sufficient for the sake of comparison. Adding the “BAU high” would only add a bigger range to all the schemes, but since it would be the same range the results of the comparison would be the same.

Biofuels, like solar fuels, do not permanently store coal emissions, although coal emissions would be partially taken up by the plants that are used for biofuel. The fuel emissions avoidance for biofuel in an ideal case would be 100%, but since there are constraints to biofuels, such as arable land availability, a lower limit was also considered. This lower limit is derived from the IEA Blue map scheme, which assumes that in 2050 a quarter of all the transport energy, equivalent to 42 EJ, originates from biofuel, which results in 12 GT of fossil fuel emissions remaining.

The carbon capture scheme has different values for the coal emissions, as the potential for carbon capture is estimated to be between 2 and 12 Gt in 2050, leaving 0 – 12 Gt of emissions. The emissions from fuel use remain the same as the BAU scheme.

In the electric vehicle scheme the emissions from coal remain unaffected. The values for fuel emissions are between 0 and 14 Gt. In an ideal case all transport could be powered with renewable electricity, but the lower limit for electric vehicles, and thus the higher limit for fuel emissions, is 14 Gt. This is based on the IEA blue map scheme which attributes 12.5% of all the energy used in transport to be electric.

Figure 10 below gives an overview of the different schemes, with higher and lower estimates for the variable ones.

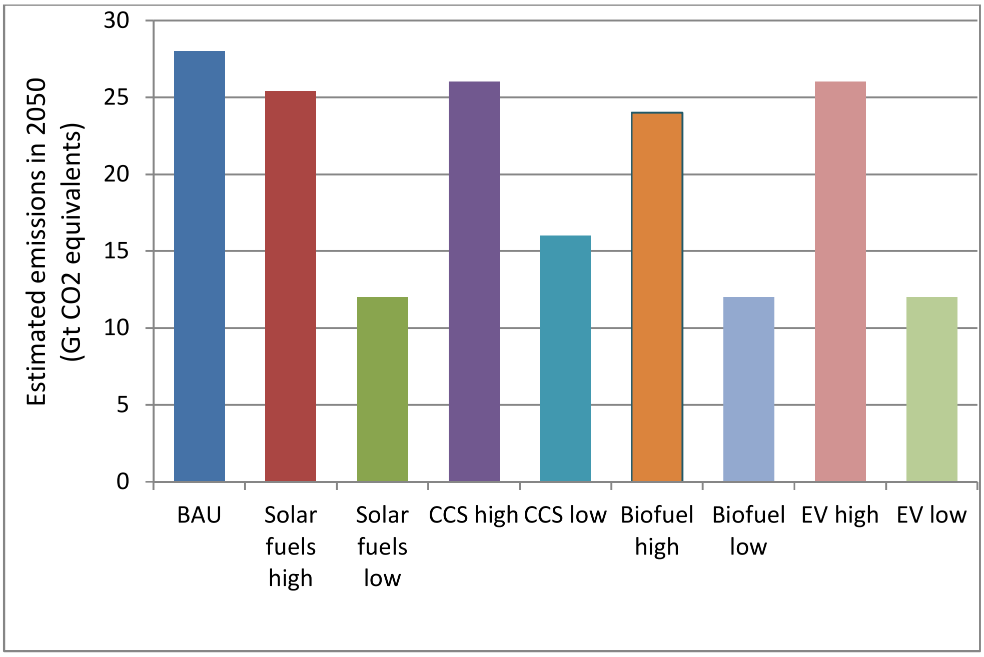

Figure 10: CO_2 emissions of the different schemes

The graph shows that the BAU scheme results in the highest amount of greenhouse gasses, but the high value schemes are not that much lower. In the high schemes, the amount of carbon capture is low, and the coal emissions account for nearly half of the total amount of emissions. Secondly, the high value schemes only offer a small amount of reductions in fossil fuel use. The lower value schemes do make significant impact on the greenhouse gasses emitted, although there is still 12 Gt being emitted in the best cases.

Of course, these calculations are only made to compare the different options. A sustainable future would combine options to get to a better result in terms of greenhouse gas emissions. For example, adding carbon capture and electric vehicles together would ideally result in zero greenhouse gas emissions, from car transportation. In practice, all alternative schemes will show additional losses and other life cycle CO_2 emissions that were not taken into account here.

5.3 Impact of material use

This section elaborates on the use of materials of the different schemes, both from an environmental perspective and a supply chain perspective. As discussed in section 4.2, the material use becomes significant when technologies such as solar fuels are to be deployed on large scale. Whilst in the previous part only a single element from the catalyst material was considered, here more compounds are considered per route and the general impacts of their production on the environment are rated.

The impacts considered here are those by mining produced catalyst materials and the impact of biomass production for biofuel. Although the impacts of mining differ per mine, region and mineral/ore, in general mining gives rise to a range of environmental impacts such as erosion, soil and water pollution, toxic metals that accumulate in the food chain and tailings (leftover minerals) that contain toxic and sometimes radioactive materials.(McKinney, 2007) Biomass production may lead to soil erosion, loss of biodiversity, acidification, eutrophication and pollution when fertilizer is used. For carbon capture, the use of monoethanolamine to capture the CO_2 in large quantities also results in adverse health effects such as an increase in freshwater toxicity (Veltman, 2010).

In this part the BAU scheme is considered the baseline scheme. The other schemes are described qualitatively and it is indicated what their implementation might entail in terms of extra environmental and resource impacts. For the other schemes only the materials that are specific for the scheme are mentioned, such as steel and concrete for production plants, but storage and transportation are left out. As this is a very general overview, only the compounds in the catalyst are mentioned. All the solar fuel routes also require carbon capture facilities and therefore large amounts of amines for capture as well, just as in the carbon capture scheme.

The results of the analysis are in table 8, which shows the three factors “material availability”, “impacts” and “material need”. Details of the different material used are shown in appendix 2.

Methods for determining scores

Material availability is based on the known reserves of the elements or compounds used in the schemes. Reserves of over 100 Mt are considered “high”, reserves of less than 1 Mt are considered “low”, and the rest “medium”. Since for most routes more than one material is used, the least available resource is presented since this is the most likely constraint.

The impacts of the different schemes are determined by the qualitative impacts of the materials. Mining, radioactive waste, fertilizer use and the use of large quantities of MEA are scored 1 (negative) point each; the total score is shown in table 8.

The material need score is based on the values found in section 4.1. Productivities that are higher than 50 kJ/g are considered “high”, less than 5 kJ/g “low”, and values in between “medium”. CCS does not have a score since the fuel production is the same as for the BAU scheme.

SFSOECFT

Although different materials are used for solid oxide electrolysis cells, the Nickel-Yttrium-Zirconium alloy was used by Graves, Fu and Zhang. Yttrium has low known reserves. Additional low available elements such as gadolinium and lanthanum may also be used by some routes. The impacts of the SFSOECFT are from mining, radioactive waste due to rare earth mining and the use of MEA in carbon capture, giving a score of -3. The material need of the route is low, since SOEC’s are highly active catalysts, so the scheme gets a “+” for material need.

SFRWGSFT

This scheme is also based on different researches using different catalysts, especially for the reverse water-gas-shift reaction. But for the Fischer-Tropsch synthesis the consensus among the authors referenced here is the use of a cobalt catalyst. The known reserves for cobalt place it in the medium range for material availability. The impacts of this scheme are due to mining and the use of MEA, giving it a score of -2. The material need is low, since the technologies used are thoroughly researched and applied already.

SFRoy

Depending on whether or not platinum is used in the process, the material availability of this route is low or medium. Since the use of platinum increases the yield, it is considered here. The impacts of this scheme are due to mining and the use of MEA, giving a score of -2. The material need (based on platinum) is low.

SFIkeue

The material availability for this scheme is high, as it uses titanium dioxide on silica. The impacts are due to mining and the use of MEA, giving a score of -2. The material need is high, since the catalyst has poor activity, giving it a “-“ in the table.

SFAmpelli

This scheme has a high material availability, although platinum was used occasionally instead of iron on the electro-catalyst. But since the productivity went down in that case, it is not considered here. The impacts of this scheme are due to mining and the use of MEA for carbon capture, giving a score of -2. The material need is very high, since the catalyst is not very effective.

SFLi

The material availability of this scheme is high, using only Cu_2O and SiC. The impacts are due to mining and the use of MEA giving a score of -2. The material need is medium, giving a score of “0” in the table.

SFXi

The material availability of this scheme is high, using titanium dioxide and zinc oxide. The impacts are due to mining and the use of MEA, giving a score of -2. The material need is high, since the catalyst activity is only 1,7 kJ/g.

SFAsi

The material availability of this scheme is low, since silver has a low amount of known reserves. The impacts are due to mining and the use of MEA, giving a score of -2. The material need is medium, it should be noted that the less available silver is used in relatively large amount (23 wt% AgBr).

SFAbanades

The material availability of this scheme is high. The impacts of this scheme are due to mining and the use of MEA, giving a score of -2. The material need is low, since the catalyst is relatively active.

SFLoutzenhiser

The material availability of this scheme is high. The impacts of this scheme are due to mining and the use of MEA, giving a score of -2. The material need is low, since the catalyst is relatively active.

SFChueh

The material availability of this scheme is medium, as cerium has known reserves of about 2 Mt. The impacts are due to mining, radioactive residues due to mining and the use of MEA, giving a score of -3. The material need is low, since the catalyst is relatively active.

CCS

The material availability of the CCS scheme is high. Impacts are only due to the use of MEA, giving a score of -1. The material need, as mentioned before, is not considered here as the fuel is not provided through CCS.

Biofuel

The material availability for this scheme is high. Environmental impact is due to fertilizer use, giving a score of -1. Biofuel produced from canola needed 100 kg/ha of nitrogen fertilizer and had a net yield of 11,353 MJ/ha, resulting in 113,53 kJ/g of fertilizer. (Fore, 2011) This means the material need is low.

Electric vehicles

The material availability of this scheme is medium, based on both the availability of lithium and the availability of cobalt. The environmental impact is -1, as the cobalt for the batteries needs to be mined (lithium is recovered from brine). Electric vehicles with lithium ion batteries have an energy density of about 200 Wh/kg and a lifetime of 7000 cycles. Thus the lifetime energy density is 5 GJ/kg battery, which is very high compared to the other schemes, the material need for this route is thus low. Of course, this is for energy storage and not production and thus is not entirely comparable.

From table 8 below, it is clear that electric vehicles and biomass perform the best, whilst the solar fuel routes generally perform worse in this analysis. This was to be expected, since the solar fuels use very specific catalyst materials and a relatively inefficient process to make fuel, whilst biomass is essentially its own catalyst. The primary reason that CCS scores relatively well here is that the burden of fossil fuel production is not taken into account. Of course, as mentioned before, this is a only qualitative analysis, more detailed and comprehensive life cycle assessments are needed to give a completer picture of how and to what extent each scheme impacts the environment.

Table 8: Material impacts of the different schemes

Scheme	Material used	Material availability	Impacts	Material need	Total
SFSOECFT	MEA, SOEC (Nickel, zirconium, yttrium, lanthanide, cerium, gadolinium, strontium, cobalt), FT catalyst (cobalt)	-	---	+	**-3**
SFRWGSFT	MEA, RWGS catalyst (Cu (on Al2O3)), FT catalyst (cobalt)	0	--	+	**-1**
SFRoy	MEA, TiO2 nanotubes, copper, platinum	-	--	+	**-2**
SFIkeue	MEA, TiO2 on silica	+	--	-	**-2**
SFAmpelli	MEA, Carbon cloth, nafion, iron, TiO2	+	--	-	**-3**
SFLi	MEA, Cu2O, SiC	+	--	0	**-1**
SFXi	MEA, TiO2, ZnO	+	--	-	**-2**
SFAsi	MEA, AgBr, TiO2	-	--	0	**-3**
SFAbanades	MEA, FeO	+	--	+	**0**
SFLoutzenhiser	MEA, ZnO	+	--	+	**0**
SFChueh	MEA, CeO	0	---	+	**-2**
CCS	MEA	+	-	0	**0**
Biofuel	Fertilizer	+	-	+	**1**
Electric vehicles	EV batteries (LiCoO2, Li compound)	0	-	+	**0**

5.4 Costs and ease of implementation

Aside from its environmental impact, the success of a new technology depends heavily on its cost-effectiveness. This part discusses the cost of fuel in different schemes, as well as the ease of implementation. Fuel cost is a topic of discussion ever since the oil crisis of 1973. Because of the sheer amount of it used throughout society, rising fuel prices substantially affect the economy. The ease of implementation is also an important factor, because if a technology is only feasible if it is applied on a large scale immediately, then the benefits of said technology must outweigh the difficulty of overcoming the application step.

Cost of Fuel

The object of this part is to give an indication of whether or not the different solar fuels are close to being cost-competitive to fossil fuel. The cost of fuel used in the BAU scheme was the untaxed price of diesel in Germany, in 2010. The solar fuels considered are not yet produced commercially and the price of oil is variable and therefore the estimates given here are not representative of what they might be in years to come when solar fouls are/could be commercial. But the estimates do give an indication of how far from commercialization the solar fuels are. The fuel costs were in some cases determined by data given in the articles themselves, and in some cases, the photochemical solar fuels, by estimating the cost of the catalyst.

SFSOECFT - Fu *et al.* put the cost of diesel from this scheme at 1 euro/l. However, they use an electricity price of 50 euro/MW (wind power), whilst for concentrated solar energy the current price is in the range of 150 euro/MW (Gupta, 2012), therefore a value of 2,6 euro/l diesel is used here. With the exchange rate of euros to dollars of 1,3 (april 2012) and the higher heating value of diesel of 35.86 MJ/l, a value of about 100 $/GJ was found.

SFRWGSFT - Jess *et al*. give a value of 2,6 $/l for diesel produced in this scheme. Taking once again the HHV of diesel of 35,86 MJ/l, the SFRWGSFT scheme produces fuel at about 70 $/GJ.

Thermochemical routes - For the thermochemical schemes, SFAbanades, SFLoutzenhiser and SFChueh, the calculations of Kim (2011) were used. They calculate that the methanol produced via the thermochemical route costs 1,22 $/kg, which is higher than the current market price for methanol. With the HHV of methanol of 22,7 MJ/kg, a value of about 50 $/GJ is found.

SFAsi – This scheme uses 23wt% AgBr with TiO_2 powder as a catalyst, with a production of 46,5 kJ/g of catalyst. Since the photocatalyst is the basis of the whole process and further description is lacking, this was used as the base for the cost calculations. From the global trade search engine Alibaba (Alibaba) prices for silver nitrate and titanium dioxide nanoparticles were taken of 0.4 $/g and 0.001 $/g respectively. Per gram of photocatalyst material this is 0.09 $/g. With the catalyst energy production, this means a cost per kJ of produced energy of about 2000 $/GJ.

SFXi - The route of Xi uses TiO_2 nanoparticles which produce 1.77 kJ/g. Like Asi, they are used to calculate the cost of the product. Since TiO_2 nanoparticles are 0.001 $/g (Alibaba), the cost of the fuel comes to about 600 $/GJ.

SFLi - The route of Li uses silicon carbide with Cu_2O, producing 0.611 kJ/g. The cost of the fuel is here assumed to be dependent on the price of the silicon carbide nanoparticles, which cost 0.75 $/kg (Alibaba). The fuel produced thus costs about 1200 $/GJ.

SFAmpelli - For the route of Ampelli, the TiO_2 nanotube arrays and Nafion membrane parts of the reactor were used to determine the cost of the fuel. TiO_2 nanotube array mesh + glass costs about 40 $\$/m^2$ (Wang, 2010), whilst Nafion costs about 1200 $\$/m^2$ (Nafion, 2012). Because of the very low energy output, only 0.1 J/cm^2, the catalyst produces fuel at an astronomical 1.2 billion $/GJ. Although this is still not the completed cell and the running time of the cell could be a thousand fold or so higher, this is still significantly more than the other routes.

SFIkeue - For the route of Ikeue, the photocatalyst consists of porous silica with TiO_2. Tetramethoxysilane (Alibaba) and TiO_2 nanoparticles are both 0.001 $/kg, so with the productivity of the catalyst of 0.18 kJ/g the cost of fuel would be about 5600 $/GJ.

SFRoy - The route of Roy uses TiO_2 nanotube arrays. Although it is topped with a mono layer of other material (copper, platinum or palladium) here only the TiO_2 is taken into account. Since the TiO_2 nanotube layer costs 40 $/m^2 (Wang, 2010) and the output of the catalyst is 0.059 kJ/cm^2, the fuel would cost 70000 $/GJ.

BAU and CCS - For the BAU and CCS schemes, the fuel costs 19.5 $/GJ. This is based on the current price of diesel in Germany without taxes (Jess, 2011).

Biofuel - For biofuel, the value given by Fu (2010) was used, amounting to 30 $/GJ.

Electric Vehicles - For electric vehicles, only the price of charging the vehicle was taken into account here. Since electricity from CSP plants would cost about 15 cents/kWh, per GJ this is 0.04 dollars. The cost of a battery for an electric vehicle is probably substantial.

Table 9: Costs of fuel of the different schemes

Scheme	Dollar per GJ
Solar fuels	
- SFSOECFT	100
- SFRWGSFT	70
- Thermochemical routes	50
- SFAsi	2000
- SFXi	600
- SFLi	1200
- SFAmpelli	1.200.000.000
- SFIkeue	5600
- SFRoy	70000
BAU	19,5
CCS	19,5
Biofuel	30
EV	0,04

All the photochemical solar fuel routes also have additional costs for CO_2 capture, but these are not taken into account here. It is clear that those routes are still far too expensive to be competitive with conventional fuels. The other solar fuel routes are closer to present day fuel costs, and keeping in mind that fossil fuels are likely to increase in price while alternative fuels are more likely to become cheaper, economic competitiveness would be possible in the future.

Ease of implementation

To determine the ease of implementation, four factors are examined: technology readiness level, geographic requirement, scale requirement and policy implications. These four factors were chosen because they represent the time (readiness level), place (geographic requirement) and scale (scale requirement) aspects of a technology, with the last factor (policy implications) being an indicator of any other problems a new technology might face. The technology readiness level is a rough estimate of how far along the learning curve the technology is, whether it is already in place or if a lot more research and innovation is needed for the technology to be implemented. The geographic requirement is an indication of whether there are any requirements to the location for the technology, like arable land for biofuel or enough solar influx for the solar fuel routes. The scale requirement looks at whether or not the technology can be applied at small scale, or whether a larger roll-out is necessary immediately. Some technologies have policy implications attached to them that may halt their implementation.

Technology readiness level- The schemes SFSOECFT, SFRWGSFT, the three thermochemical schemes and the CCS scheme are all at pilot plant scale. Although for the SFSOECFT and SFRWGSFT schemes the pilot plants may not yet be of the whole process, the individual parts of the process are already common practice.

Carbon capture and storage is already operational in a small number of plants, but is not considered a mature technology yet. (Haszeldine, 2009)

The photochemical routes are all at a laboratory scale. Many have not even been tested in sunlight yet ,but only under lamps.

Biofuels and conventional fossil fuels are both mature technologies. Whilst biofuels are not completely implemented around the world, in countries like Brazil biofuel is widely available.

Electric vehicles are already commercially available, but the introduction of charging points is not very advanced yet.

Geographic requirement - All the solar fuel routes are slightly place-bound, since they require solar energy to power the process. As was shown above, economic competitiveness is an issue, so a high solar influx is important to make the whole process more economically viable.

The BAU scheme and electric vehicles are not restricted to specific regions, electricity and fossil fuels are widespread and easily transportable.

CCS and biofuel are place-bound. To store the captured carbon dioxide, appropriate sites need to be found, which is made more difficult by public resistance to the use of such sites. Biofuel needs agricultural land, which, when not in shortage, is in remote areas that have not been cultivated and/or urbanized.

Scale requirement - The schemes SFSOECFT, SFRWGSFT and the three thermochemical schemes are all slightly size-bound because they require multiple plants to make fuel and heliostat/PV fields. Carbon capture storage is also at a fixed scale because whole plants have to be fitted with the technology and because of the safety and societal measures required for storage, smaller scales are less viable. Electric vehicles are size-bound because a problem EVs currently face is that their commercialization is held back by the lack of charging points; a reinforcing loop.

The photochemical and biofuel routes are not size-bound. Because the photochemical routes directly make fuel and can be made on a centimetre scale, one could theoretically place them on domestic roofs, provided there is also a small refining apparatus. Biofuel is already implemented at a small scale with farmers who have small reactors to convert their own waste biomass to fuel for the farm.

Although the Business-As-Usual scheme does not have to be large scale, it is large scale at the moment.

Policy implications- SFSOECFT and SFChueh have some policy implications because they use rare earth metals, which are subject to export/import conflicts. (BBC, 2012) Although rare earth metals are more widespread, the current supply is dominated by China, which is restricting export of rare earth metals to benefit their domestic industry. Biofuel also had some policy implications, since the production of biomass for fuel is in competition with food production, which in turn leads to food shortages due to price increases and the adverse effects of that.

SFRWGSFT and the photochemical schemes have negligible policy implications, as do the other two thermochemical schemes, SFLoutzenhiser and SFAbanades.

The BAU scheme does have political implications, as the largest share of oil comes from the Middle East, which has given rise to significant conflicts throughout the world. CCS also has political implications because of the public resistance to the storage of CO_2 close to populated areas.

Table 10: Ease of implementation of the different schemes

Scheme	Readiness level	Geographic reuirement	Scale requirement	Policy implications	Total
Solar Fuels					
- **SFSOECFT**	-	±	±	±	-1
- **SFRWGSFT**	-	±	±	+	0
- **Thermochemical**	-	±	-	±	-2
- **Photochemical**	--	±	+	+	0
BAU	++	+	±	-	2
CCS	±	-	-	-	-3
Biofuel	++	-	++	±	3
Electric vehicles	+	+	-	+	2

As is evident from table 10, the solar fuel routes are among the more difficult to implement, although carbon capture storage is the hardest in this assessment. As expected, technologies that are already operational score better, although they get most of their points from the fact that they are further up the readiness level scale.

5.5 Cumulative scores scale-up

Table 11 shows the cumulative scores of the different schemes for the scale-up analysis.

Table 11: Cumulative scores of scale-up analysis of the different schemes

Scheme	Land score	Emissions score	Material impact score	Cost score	Implementation score	Total score
SFAmpelli	NV	1	-3	-3	0	**-5**
SFSOECFT	0	1	-3	-1	-1	**-4**
SFRoy	-1	1	-2	-2	0	**-4**
SFAsi	NV	1	-3	-1	0	**-3**
SFChueh	0	1	-2	0	-2	**-3**
SFXi	NV	1	-2	-1	0	**-2**
SFIkeue	NV	1	-2	-1	0	**-2**
CCS	1	0	0	1	-3	**-1**
SFLi	NV	1	-1	-1	0	**-1**
SFAbanades	0	1	0	0	-2	**-1**
SFLoutzenhiser	0	1	0	0	-2	**-1**
SFRWGSFT	0	1	-1	0	0	**0**
BAU	1	-1	NV	1	2	**3**
Biofuel	0	1	1	0	3	**5**
EV	0	1	0	2	2	**5**

NV= no value for this factor in this scheme

To get scores instead of values for the land use, CO_2 emissions and cost factors, the values were assigned a score based on the relative performance of the schemes. For land use, values over 10 m^2/W were assigned -1 points, values between 0 and 10 m^2/W were assigned 0 points, and schemes with no land use were assigned +1 point. For the emissions, the average of the total emissions was used to assign scores. Emissions over 25 Gt CO_2 were assigned -1 point, emissions between 20 and 25 Gt were assigned 0 points, and emissions under 20 Gt were assigned +1 points. For the cost, values below the cost of fuel in the BAU scheme were assigned +2 points, the BAU scheme +1 points, costs between BAU and 100 \$/GJ were assigned 0 points, costs between 100 and 10 000 \$/GJ were assigned -1 point, costs between 10 000 and 100 000 \$/GJ were assigned -2 points and values over 100 000 \$/GJ were assigned -3 points.

5.6 Discussion and conclusion of scale-up

As is apparent from table 11 and figure 11, the solar fuels all score worse than the BAU scheme in the presented scale-up analysis. Fortunately, four solar fuel schemes, SFLi, SFAbanades, SFLoutzenhiser and SFRWGSFT, score equal or better than the CCS scheme.

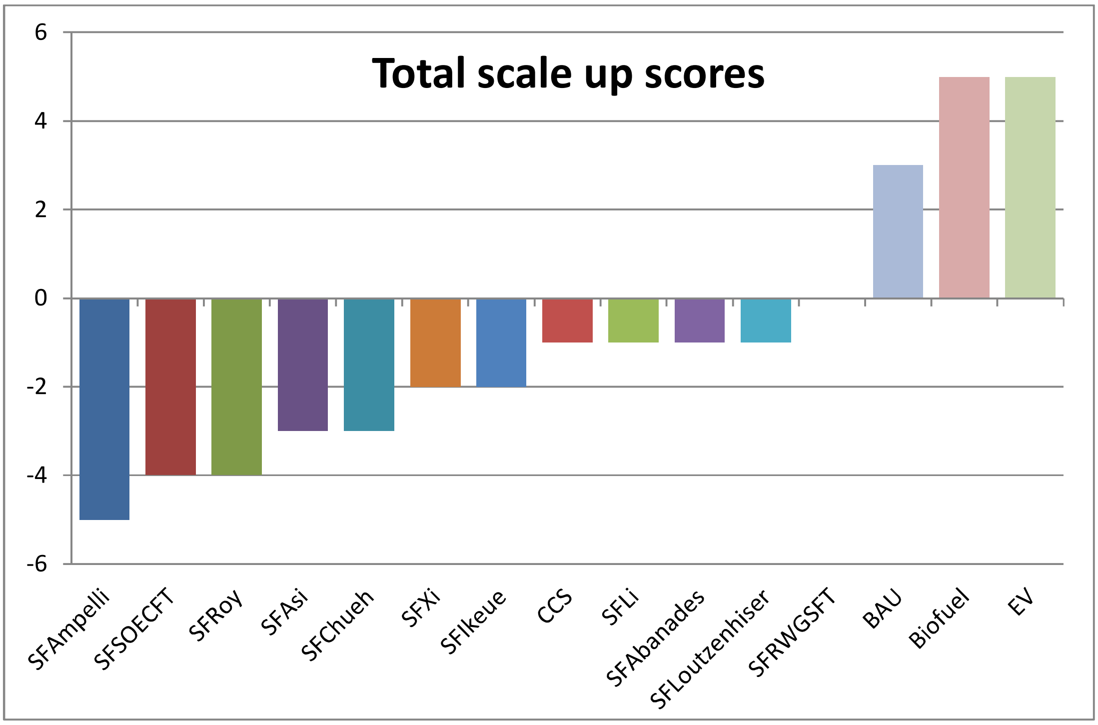

Figure 11: Cumulative scores of the scale-up analysis of the different schemes

In general, the solar fuels score the worst on cost, implementation and material impact compared to the other schemes (BAU, CCS, biofuel and electric vehicles). For the material impact, the accounting was not in favour of the solar fuels, since the separate factors, material availability, impact and material need, all had the same weight in the total score. For the SFSOECFT scheme, which has a very active catalyst and thus very little material is needed, the score was still -3 although the high activity will likely make it a better option, material use wise, than the other solar fuels schemes. As mentioned before, a life cycle analysis will give a better answer on what the impacts of the different schemes are.

The cost score, although also based on rough estimates, is more representative of the actual situation than the material impact score. Although the costs calculated are based on only a few materials, the use of very expensive materials with only a very low catalyst activity and lifetime will result in high-cost fuels. Although the costs are far too high for some routes (like SFAmpelli, SFRoy), for others the costs are within the same order of magnitude as current fuel prices. The schemes could very well become cost-effective with more research, especially if the costs of fossil fuels go up and the demand keeps increasing.

The implementation score also did not favour solar fuels, but this is hardly surprising since they all still need to be implemented, as opposed to existing technologies. Although the factors were equally definable, the scale and geographic requirements being more abstract than readiness level and policy implications, the overall analysis is still valid because the factors themselves were qualitative rather than quantitative.

The emission scores are all rather close together; this is mainly because of the method applied to determining the emissions. Because no life cycle emissions were used, the CO_2 emissions of the whole process were not taken into account and these may be very different for the different schemes.

The land scores, although being rough estimates, are probably correct in the orders of magnitude they represent. Most of the photochemical schemes were not taken into account as they were not tested under natural sunlight, but it is possible that some will have a lower land requirement than SFRoy.

On average, the photochemical routes scored worse than all the other schemes. This is mostly because they show a low output per gram of catalyst, and thus have a high material need and high costs. The thermochemical schemes score better on average, although Chueh lags behind because of the use of the rare earth metal cerium which had a negative influence on the material impact and implementation scores. As mentioned above, SFSOECFT could have performed better if the activity of the catalyst, which is very high, had weighed more. CCS also performed poorly, mostly due to the implementation score.

Biofuel and electric vehicles performed well in this analysis, as they have a low material use, are relatively mature technologies and cost-effective. The BAU scheme also scored well, because it is mature and cost effective, but it would have scored less if the material impact had been taken into consideration.

Overall, it can be concluded from this analysis that compared to biofuel and electric vehicles, solar fuels are not the most sustainable option for carbon mitigation and fuel production yet. But, with more research the price of solar fuels will hopefully go down, which for some, the thermochemical schemes and the two FT schemes, may mean they are cost-competitive in a few decades. And, with a more detailed life cycle analysis, the impacts of solar fuel production can also be specified, which may indicate them to be the more environmentally friendly option as well. However, such a detailed LCA was beyond the scope of this research.

6.0 Additional considerations

In this chapter, some additional considerations regarding the use and future of solar fuels are discussed. These are general points that do not apply specifically to the schemes used in chapter 5, but that are useful in the discussion on the sustainability of solar fuels. Topics are the influence of a carbon tax on the viability of solar fuels, whether methanol or FT-diesel should be produced, whether solar fuels will remain competitive in the future, and the production of electricity or petrochemicals instead of fuels.

6.1 The influence of a carbon tax

The current price of carbon capture, as indicated in section 3.1.3, is between 35 and 300 $/tCO$_2$. Depending on the cost of the rest of the process, this may be a significant share of the cost of fuel. Figure 12 shows the capital and operating costs of the thermal solar methanol fuel plant described by Kim *et al.* (Kim, 2011). They assumed a CO_2 capturing cost of 160 $/tCO$_2$, and the figure shows this is about 12% of the operating costs. Kim *et al.* indicate that changing the cost of CO_2 does not influence the total cost of fuel enough to make it economically competitive, but that the introduction of carbon taxes or emission rights schemes might.

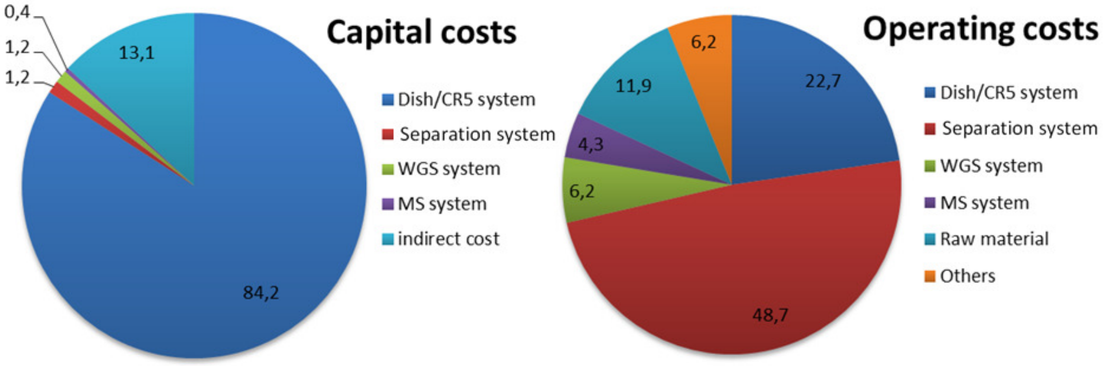

Figure 12: Capital and operating cost of a thermal solar methanol plant. From (Kim, 2011)

A carbon tax could influence the economic competitiveness of solar fuels in several ways. The price of gasoline and diesel could go up, bringing the price closer to those of solar fuels. Considering an untaxed price of 0,7 $/L diesel (Jess, 2011), adding an average current tax of 50% (Rijksoverheid, 2012) would bring the price to 1,05 $/L. To bring the price further up to the 2,6 $/L renewable fuel as estimated by Jess *et al.*, a further 320% tax would have to be added to make the prices level. Aside from a carbon tax, removing subsidies from fossil fuels (Koplow & Dernbach, 2001) would also bring the prices of fossil fuels closer to solar fuels.

Carbon taxes would also likely be instated on coal-fired power plants and other large stationary CO_2 emitters. If the tax would be higher than the price of carbon capture, so at least 35 $/tCO$_2$, the stationary emitters would have an incentive to capture CO_2 and give/sell it on to be stored or processed by secondary users.

An international carbon emissions rights scheme could further benefit solar fuels, as governments would be inclined to steer a course towards more sustainable energy systems. This could lead to solar fuels, instead of normal fuels, being subsidised, and thus becoming more economically competitive.

6.2 Methanol or FT-diesel

The most promising solar fuel schemes, the thermochemical routes, the SOEC-FT and RWGS-FT, all have syngas as an intermediate. In some cases, this is transformed into methanol, and in others Fischer-Tropsch diesel is synthesized. The question arises which of the two is preferable.

Methanol production has the backing of Nobel-prize winner George Olah (Olah, 2011), who, in a review article in 2011, envisioned a manmade carbon cycle with methanol at its base. Aside from use as a fuel, methanol is a starting point for a wide variety of other chemicals, with a yearly methanol consumption of 48 Mt.(Olah, 2011) The downside of methanol is, however, that it has a low gravimetric density and a low volumetric storage density, compared to other liquid energy carriers such as gasoline and diesel.

The Fischer-Tropsch process, although it is not a new technology, is only applied at large scale in recent years in countries such as South Africa that have no crude oil, using it as a way to produce synthetic fuel. Besides diesel, gasoline and other hydrocarbons can also be produced. However, since the process always produces a mixture of products rather than just one, integration into chemical production is less versatile. FT-diesel is expected to rise to 30 Mt/year by 2015 (Jess, 2011). In contrast to methanol, FT-diesel has one of the highest gravimetric and volumetric storage capacities of the commercial energy carriers. Additionally, FT-diesel can be used in conventional diesel engines, whilst methanol requires an adapted gasoline engine to be used.

Determining whether methanol or FT-diesel would be the better choice for future solar fuels lies beyond the scope of this research. But since FT-diesel is more adapted to the current infrastructure, FT-diesel-based solar fuels are likely to be a commercial success sooner than methanol-based solar fuels. However, in both cases the efficiency and cost of the whole process are probably the important factors. In an ideal scenario, methanol produced by solar technology would be used for chemicals production, while solar-produced diesel is used for transport, for which it is more suitable.

6.3 Use as aviation fuel

While a detailed discussion of which applications are most suitable for the use of solar fuels is beyond the scope of this research, a short rationale for its use within air transport is given here.

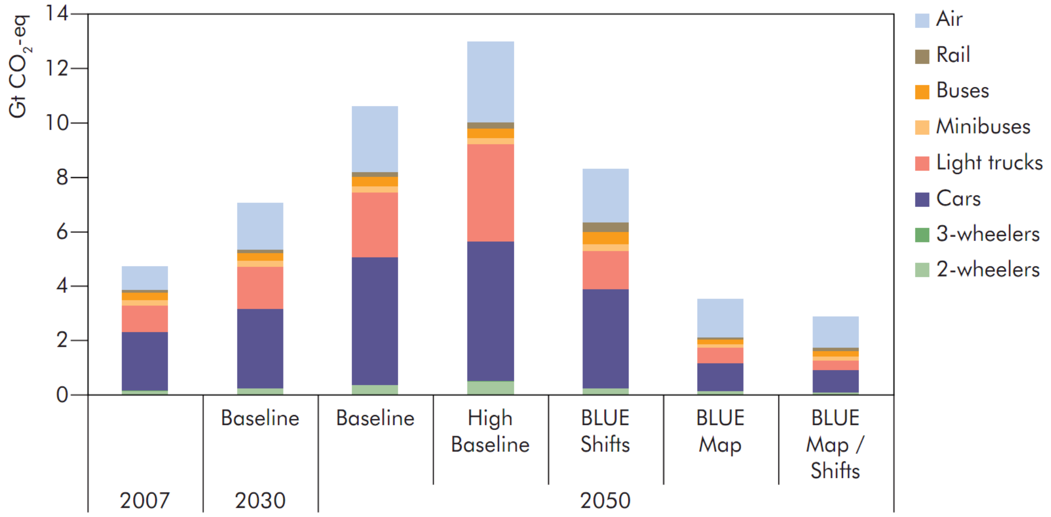

Figure 13: Greenhouse gas emissions per transport mode. From (IEA, 2010)

Of all the transport modes, aviation has the most specific fuel needs.(IEA, 2010) Because aircrafts travel far and need to be as light as possible, a high energy-density fuel is needed. Gas-based fuels, bioethanol, hydrogen and electric vehicles do not have a high enough energy density to be used in the current type of aircrafts. But, as can be seen in figure 13, air travel still accounts for a significant amount of greenhouse gas emissions by 2050. In the baseline scenario it accounts for about 20% of emissions, but in the more sustainable BLUE Map scenario, for almost half of the emissions. So, while other modes of transport emit less greenhouse gas through various means, air transport is restricted due to its need for a high-quality fuel.

Although the solar fuel routes described so far have not produced kerosene, which consists of a mix of C_6 to C_{16} hydrocarbons. This mix of hydrocarbons can be produced by high temperature Fischer-Tropsch synthesis, (Shell, 2012) although some tuning to the process and refining steps are probably necessary. The amount of fuel needed by aviation could, with a high volume of carbon capture, easily be supplied by solar fuels.

The IEA (2010) shows that air travel is projected to use around 500 Mtoe, or 21 EJ, by 2050, with no large differences between scenarios. The main component of kerosene is n-dodecane which has 12 carbons and a higher heating value of about 7500 kJ/mol. Assuming that carbon capture will result in between 2 and 12 Gt CO_2, the amount of kerosene, in terms of energy, that can be produced is between 28 and 170 EJ, which is in both cases more than the projected 21 EJ needed for air travel.

So the large demand for high-quality fuel by the aviation sector, a large greenhouse gas emitter in 2050, could be met by solar fuels.

6.4 Solar petrochemicals

As mentioned in 6.2, solar-produced methanol can also be a starting point for other chemicals instead of just fuel. In a future where crude oil is no longer available, making petrochemicals out of CO_2 would be one of the remaining options, aside from biomass and coal/gas. For the nearer term there are several advantages and disadvantages.

Advantages are that the more complicated compounds have higher market prices than fuel because of the many steps involved in the synthesis. This may make solar chemicals commercially competitive sooner than solar fuels. Furthermore, solar chemicals are a more permanent storage for CO_2, especially when durable plastics are made, in which case the captured CO_2 would end up in the atmosphere at a significantly later time, if at all.

A disadvantage is that the demand is less imminent, because the margins on chemicals are higher than on fuel. While higher fuel prices would affect the economy a lot, prices of chemicals are less dependent on the raw material.

Because there is less pressure to find a cheaper source for petrochemicals, there is less emphasis on solar chemicals. But in my opinion it is likely that in the future they will be produced. Which solar chemical will be the first and the most advantageous is beyond the scope of this research.

6.5 Solar fuel electricity

Aside from producing chemicals and fuels, one could imagine a power plant being powered by them. The carbon would be captured at large point sources, fed to a solar fuel/syngas production facility, after which the fuel is burned in a steam generator to generate electricity. The resulting CO_2 would be looped back to the solar fuel/syngas production facility. The advantage of this is that the CO_2 is not emitted to air, and is thus stored, in a sense. The disadvantage is that it is essentially electricity generation with an extra step, and is thus less efficient than direct electricity generation with solar power. And since each plant, at least theoretically, recycles the same portion of CO_2 over and over, the amount of CO_2 stored would be severely limited by the number of plants. So, the only way this would be a viable process is when there is an excess of solar fuel or when there is suddenly a need for electricity that can only be met by burning pre-made solar fuels (much like gas-fired power plants are currently used, for the top load).

7 Summary, discussion and conclusion

The aim of this research was to find out if solar fuels could be scaled up significantly, and if they would be a sustainable and cost-effective method of CO_2 mitigation and fuel production. The sub-research questions were:

1) *What is the scope for solar fuels, based on fuels needs and carbon capture usage?*
2) *What is the energy output per unit of catalyst, for the most relevant solar fuel routes?*
3) *Which solar fuel routes can be scaled up?*
4) *How does the energy output and CO_2 mitigation of the scaled up solar fuels compare to other carbon mitigating technologies?*
5) *How do solar fuels perform in terms of land use, cost, material impact and policy implementations compared to other carbon mitigating technologies?*
6) *What application within the transport sector is well suited for solar fuels?*

Summary

First, a literature search for solar fuels was performed, resulting in about 50 articles on solar fuels with CO_2 as a feedstock, aside from the many routes based on water. Chapter 3 discussed sub-question one. The potential for carbon capture until 2050 was examined, and costs and constraints were reviewed. In combination with projected transport fuel use emissions for the same period it was determined that the amount of carbon capture was expected to be large enough to be significant in comparison with transport emissions.

From the solar fuel routes found in chapter 2, those routes that were described in literature with enough data were analysed for viability based on materials, to answer sub-question two. First, the fuel production per gram of the least available element in the catalyst was calculated. With this, the total amount of fuel production based on the 40 year production of this catalyst was calculated. Then the amount of energy per dollar was calculated, the cost being the price of the specified element in the catalyst. Based on the total amount producible and the fuel production per dollar, several routes were excluded from further analysis, answering sub-question three.

In chapter 5, the remaining routes were categorised in schemes. Along with alternative schemes, Business As Usual, biofuels, electric vehicles and carbon capture and storage, the schemes were analysed for effects and restraints on their scale up, to discuss sub-questions four and five. It was found that the thermochemical, reverse water-gas shift and solid oxide electrolysis schemes were lower in land use than biofuels, but higher than the alternative schemes. The CO_2 emissions for the solar fuels schemes were lower than the BAU scheme, the CCS scheme and in some case the electric vehicle scheme, but depended on how much carbon capture took place. In material use, the solar fuel schemes scored worse than the alternative schemes on average, although some scored equal to the carbon capture storage scheme. The costs of the solar fuels were higher than the alternative schemes, with some being astronomically high but some also in the same order of magnitude as fossil fuels. The implementation of solar fuels was also more difficult than for the alternative schemes, although the differences were small and largely due to the fact that solar fuels are less mature.

In chapter 6 additional points relating to solar fuels were discussed. A carbon tax would benefit solar fuels through several mechanisms. In the choice between making methanol of FT-diesel, the latter is a more likely candidate for near term transport fuels. Aviation was found to be an attractive application for solar fuels, since it has such specific fuel requirements that other alternative energy carriers are unsuitable. It was estimated that all the energy needed for air travel could be met by solar fuels, providing an answer to sub-question six. And while petrochemicals from carbon dioxide with solar power will likely be made in the future, solar fuel electricity is not beneficial.

Discussion

All in all, it can be concluded that some solar fuels are a relatively sustainable option for carbon mitigation and fuel production in the near future, based on the fact that there are several very efficient routes that require relatively little material input for the plant, that are near cost-competitiveness and that mitigate carbon dioxide in the same range as alternatives whilst using relatively small amounts of land. These findings are in accordance with findings in literature, (Roy 2010, Graves 2011, Jess 2011, Haije & Geerlings 2011), although there is discussion over which routes are the first to be commercialized.

In the literature search on solar fuels, many articles are likely to be missed. Although the fields of carbon mitigation and alternative fuel production are currently very active research areas, they are not very developed yet. In the initial search, “solar fuel(s)” was used as a search term, which gave plenty of results. But later, on searches on terms like “renewable fuel” and “solar carbon dioxide” gave results that were not found before, since the term “solar fuel” is not used universally. But it is unlikely that other researchers obtained results that would greatly differ from the research found here.

To determine which articles were going to be used for further analysis, a selection was made based on available information. It is therefore possible that solar fuel routes were eliminated that were more efficient than some of the remaining, simply for a lack of information in the literature. But it is unlikely that the end result of the research would have differed greatly, since most of the articles concerned photochemical routes which were not among the most efficient routes anyway.

The comparison of potential carbon capture and projected fuel emissions is not entirely correct. First of all, the “CO_2-to-wheel” process will have losses of CO_2 and therefore not all the captured CO_2 will be converted to fuel, even if it is intended to. Secondly, the emissions from fuel are from a whole range of different fuels, each having different carbon-to-energy ratios (as described in section 5.2). And since the emissions are in CO_2 *equivalents*, NO_x and SO_x emissions by solar fuels are not taken into account on the carbon capture side. Although these will likely be lower for solar fuels, carbon dioxide is still the biggest component of the CO_2 equivalents of emissions.

In the calculations on material-based viability, the elements on which the calculations were performed were selected on their annual production. However, because the ratios within the catalyst were not taken into account (except in the case of Zhan *et al.*), other elements in the catalyst may have resulted in a lower total production potential because they are needed in higher quantities in the catalyst. The values for kJ/g of catalyst element found are relatively accurate, although some assumptions were made as indicated in the text. The biggest assumption was the catalyst lifetime, which, when not mentioned was assumed to be only one hour. For many catalysts this is probably longer, but there was no data to support this. Therefore many of the routes will likely perform better than indicated here.

In the calculations on the total amount of fuel producible (based on 1% of the 40 year production of that element) other elements in the catalysts could have given lower results based on the fact that their ratio in the catalyst was higher (as with the calculations of energy output per gram). Still, this gave a good indication of which solar fuel routes came near the amount needed in the 40 year time period.

The calculations on the amount of energy per dollar based on the price of the catalyst element were purely used as an additional selection tool rather than indications of the cost. Because only one element was considered, and not the whole catalyst and process, the resulting costs were not accurate.

The selection of routes for the second analysis was done in such a way that about eight routes remained. Although Ikeue (2002) and Roy (2010) fell outside this selection, Ikeue was reconsidered because they used a highly active TiO_2 catalyst and the copper-doped version of Roy was considered because they tested their catalyst in natural sunlight.

The calculations of the amount of land used by the different schemes were also based on only a few of the contributing factors. But, since the larger contributors were used, the order of magnitude is probably correct. For the photochemical routes that were only tested under artificial light, values for sunlight could have been calculated. But in many cases not all the data necessary were present in the literature and the calculations were beyond the scope of this research.

The calculations of CO_2 were based purely on the amount of carbon in the fuels themselves and on carbon capture. More accurate results would have been found if cradle-to-grave emissions had been calculated. But since a lot of the necessary data were not present in literature and the execution of LCAs takes considerable time, this was beyond the scope of this research. The CO_2 emission values found here do reflect, however, whether solar fuels in principle are better or equal to fossil fuels and other alternative fuels.

For the material impact, a life cycle assessment is even more relevant for more accurate results. Here, only basic data were used, resulting in an indication of which schemes might have a bigger impact. But since the quantities of material used vary so greatly between the different schemes, the actual impacts cannot be predicted by this analysis.

The cost calculations for the schemes were the most accurate for the non-photochemical schemes, since they were based on literature values that took the whole process into account, rather than just the catalyst material. Still, for the photochemical schemes the difference between high cost/low efficiency and low cost/high efficiency schemes clearly showed how much the cost of fuel differed between the schemes.

The ease-of-implementation analysis was also among the more qualitative, but in this case this was sufficient to give a rough estimate of which routes would face difficulties with implementation and which would be deployed more easily.

So, while the individual factors of the scale-up analysis were approached only qualitatively, and in some cases are probably a poor reflection of reality, the cumulative scores of the different factors of the similar schemes combined do show a trend; the photochemical schemes are less suited for scale up and the thermochemical and SFRWGSFT schemes are more ready for scale up.

In the calculations for supplying energy for air travel with solar fuels, losses in the process were not taken into account. It is unlikely that 100% of the captured carbon will end up in an airplane. The lower estimate of 28 EJ of solar kerosene is close to the 21 EJ that is estimated to be needed for air travel, so if carbon capture does not manage to reach even the lower estimates of its volume, solar fuels would fall only slightly short of the energy demand by air travel.

The whole research in general was qualitative; a more quantitative research would have resulted in more conclusive answers. Especially in the scale-up chapter, more detailed studies into life time environmental impacts, carbon emissions and studies into the technical feasibility of large scale solar fuel plants would have given a clearer answer on the sustainability of solar fuels. But because of time constraints this was beyond the scope of the current research.

The choice of the 2010-2050 period for chapters 3-5 is somewhat arbitrary, since this research was started in 2011 and both solar fuels and carbon capture will not be deployed at a large scale until 2020. Aside from the time it will take for carbon capture to be deployed widely, the locations where carbon capture takes place may not be ideal for solar fuels. Solar fuels are ideally situated in places with a high solar influx and they need sufficient room to harvest the relatively dilute power source, so northern crowded industrial areas are less suitable than a single coal-fired power plant in the desert. But CO_2 can be transported through pipelines to a solar fuel suitable location, but this increases the costs and decreases the overall energy efficiency.

Outlook

For the next few decades, solar fuels would be a way of mitigating carbon emissions by replacing part of the emissions from petroleum usage. Saudi-Arabia, Australia, southern Africa and China are very suitable for solar fuels, as they have both high fossil fuel power generation and desert areas with a high intensity solar influx. Although such a use of solar fuels would not provide an entirely renewable fuel, it would provide a means of getting more out of the fossil fuels that are already being used.

When fossil fuels would be phased out entirely solar fuels could still be used, either out of environmental considerations or because supply runs low. Instead of CO_2 from fossil fuel sources, biomass combustion or air capture could provide CO_2, although in the latter case the cost effectiveness should be increased by then.

Conclusion

It can be concluded that solar fuels are likely to be a sustainable option for fuel production and carbon mitigation, despite the remarks in the discussion. For the near future, thermochemical solar fuels, SOECFT and RWGSFT solar fuels are the most viable ones. More research and development is necessary to bring costs down and efficiencies up. Aside from investments in solar fuel technology, to bring carbon capture from its current near mature technology state into a widespread technology is necessary. The implementation of a carbon tax will greatly help to realize of solar fuels since it increases the cost of fossil fuels and makes carbon capture an attractive technology. And while electric vehicles and biofuels outperform solar fuels at the moment, solar fuels have specific advantages over them (like energy density and land use) which will probably lead them to find their own niche within the transport energy system. Aviation is a good candidate for this, since it is projected to be a significant greenhouse gas emitter in 2050 and it has a need for high energy-density fuel, which solar fuel technology should be able to provide, according to calculations.

Recommendations for future research are the execution of LCAs on the best performing solar fuels to give an indication for the environmentally preferable ones. Research into which type of fuel for which part of the transport sector is advantageous on the short term and research into how and where solar fuels can be commercialized.

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9 Appendices

Appendix 1: Calculations for section 4.1

Ikeue 2002

Ikeue *et al.* developed different titanium containing porous silica films, on a laboratory scale. When irradiated with UV radiation, the catalyst converts gaseous CO_2 with water vapour to methane and methanol, at a 7 and 2 µmol/h/g Ti rate respectively. The reaction rate was constant over 6 hours. Assuming that the reaction will run at least 24 hours, one gram of titanium can produce at least 168 µmol of methane and 48 µmol of methanol. With their respective 891 and 630 kJ/mol heats of combustion, the total energy equivalent produced by one gram of titanium is 0.17 kJ.

Liu 2010

Liu *et al.* synthesized single crystal Zn_2GeO_4 nanobelts loaded with RuO_2 and Pt. Under illumination of a xenon arc lamp, the catalyst converts water vapour and CO_2 to methane with a rate of about 10 µmol per gram of catalyst per hour. The catalyst activity decreases over time, producing about 120 µmol of methane per gram of catalyst in 24 hours (extrapolated from 16h of data). The weight fraction of germanium in the catalyst is 24%, which means that for 1 gram of Ge 500 µmol of methane is produced. As methane has a combustion heat of 891 kJ/mol, this amounts to 0.45 kJ being produced per gram of germanium.

Le Gal 2011

Le Gal and co-workers have developed Zr-doped ceria compounds synthesized via different routes for the thermochemical reduction of CO_2. The high temperature needed to reduce Ce_2O_3 back to CeO leads to partial deactivation, doping the CeO allows for a lower reduction temperature and thus less catalyst loss. Zr doped ceria showed a higher catalytic activity at 1000-1200^{o}C and produced 200 µmol of CO per gram of catalyst for three cycles. However, each cycle the amount of catalyst was reduced. It is assumed that the catalyst can have 6 cycles, if 3 of those were to split water, the rate of which is about 400 µmol per gram of catalyst, each gram of catalyst can produce 600 µmol of CO and 1200 µmol of H_2. Assuming that this is equal to 600 µmol of methanol, a gram of cerium (53% of the catalyst mass) can produce 1600 µmol of methanol (heat of combustion 630 kJ per mole), equal to 1.07 kJ.

Xi 2011

Xi *et al.* synthesized mesoporous sticks of TiO_2/ZnO for the photocatalytic reduction of CO_2 to methane in the presence of water. Under a xenon lamp, the catalyst showed stable production of about 55 µmol of CH_4 per hour. Assuming that the catalyst lasts at least 24h, this means that one gram titanium (60% of the catalyst weight) yields 2190 µmol of methane. Taking into account the combustion heat of methane, 891 kJ/mol, one gram of Ti can produce 1.77 kJ.

Asi 2011

Asi *et al.* developed a AgBr/TiO_2 catalyst for the photocatalytic reduction of CO_2 with water to various hydrocarbons. Experiments were performed under a xenon lamp in water for 5 hours. Although AgBr is light-sensitive, the presence of TiO_2 and CO_2 stabilized it, but the catalyst still shows a steady decline in reactivity. The catalyst produces about 590 µmol of methanol, 976 µmol of methane, 1953 µmol of CO and 807 µmol of ethanol per gram of silver (13% of catalyst weight) per 5 hours. Assuming that the catalyst lasts for at least 40 hours (extrapolated from 25h), each gram of silver kan produce 10.7 kJ. Here, the combustion heats of methanol (630 kJ/mol), methane (812 kJ/mol) and ethanol (1196 kJ/mol) have been taken into account, and the CO produced was assumed to be equal to a third amount of methanol.

Li 2011

Li *et al*. have developed a Cu_2O/SiC catalyst for the photocatalytic reduction of CO_2 to methanol. The reaction takes place in water under irradiation of a 200-700 nm xenon lamp. Methanol was produced with 40 µmol/h/g catalyst; the reaction is stable for at least 5 hours. Assuming that the catalyst lifetime is at least 24 hours, this means that 1 gram of Cu (3.12% of the catalyst weight) can produce 32 mmol of methanol. As methanol has a combustion heat of 19.7 kJ/g, this means that each gram of copper can produce 20.3 kJ.

Stamatiou 2010

Stamatiou *et al.*, the same group as Steinfeld, have researched the thermochemical conversion of water vapour and CO_2 to H_2 and CO with FeO as a catalyst. The principal is the same as with the Zn/ZnO cycle. In this article, they varied the fraction of CO_2 in the mixture, to find that the resulting CO fraction in the product seems to be comparable. The reaction of FeO with the gas mixture is complete after about 50 minutes, after which 80% of the gas mixture has been converted. Assuming that after the reaction, 95% of the catalyst can be recovered and the Fe_2O_3 to FeO conversion is about 50%, this means that 1 gram of FeO can be used roughly 10 times. Using the molecular weight of FeO, and the fact that 80% of the CO_2/H_2O was converted, 0.11 mol of H_2/CO is produced by one gram of FeO. Per gram of iron this comes to 30 kJ when the methanol equivalent of the CO is used.

Takeda 2008

Takeda *et al.* have developed a Rhenium (I) complex that photocatalytically converts CO_2 to CO. Under illumination of 365 nm light, about 4 µmol of CO is produced an hour by 2.2 µmol catalyst for at least 16 hours. Assuming that the catalyst lasts for at least 24 h, each gram of rhenium can produce 0.22 mol of CO. Using 2/3 of the CO to produce H_2 (water-gas-shift reaction) and then converting the two to methanol leads to 0.075 mol of methanol. Taking the combustion heat of methanol (630 kJ/mol), one gram of rhenium can produce 47 kJ in the form of methanol.

Chueh 2010

The technology used by Chueh *et al.* is solar thermal dissociation of H_2O and CO_2 catalysed by Ce_2O. They have built a reactor to perform this reaction, in which directly heats the porous ceria, which shows “stable and rapid generation of fuel” for over 500 cycles. They currently have a solar-to-fuel efficiency of about 0.7%, which they consider can be improved with reactor design and system scale. They estimate that they can increase the solar-to-fuel efficiency to 16-19%. The reactor produces about 5 mL of H_2 or CO per gram of ceria per cycle. Assuming that the ceria in the reactor will be stable for 2000 cycles, per gram of ceria 10 L of H_2 or CO is produced. Using the ideal gas law, this means that 0.45 mol is produced, which, when composed of 1 part CO and 2 parts H_2, is converted would be 0.15 mol methanol. The heat of combustion of methanol is 630 kJ/mol, therefore each g of cerium (89% of catalyst weight) can catalyze the production of 106 kJ of energy in the form of methanol. If the solar-to-fuel efficiency was raised to 16%, as the authors deem possible, in the future each gram of ceria could produce 2287 kJ.

Abanades 2010

This group studies the synthesizing by solar means of SnO and Zn nanoparticles, which are then used to split CO_2. The synthesis of SnO and Zn nanoparticles from SnO_2 and ZnO particles respectively takes place in a continuous solar reactor at about 1600°C. By means of a screw, the SnO_2 and ZnO particles are transported into the solar reactor, and swept out of the reactor with Ar gas. The resulting product was 48 wt% Zn or 82 wt% for SnO. The follow-up reaction, splitting of CO_2, was performed in a batch reactor. The conversion efficiency with Zn was 95% at 400°C, for SnO 80% at 800°C. Clearly, higher overall efficiencies would be reached if the Zn and SnO synthesis was more efficient, but since the product is gaseous, this is a problem more researchers encounter, and some deem detrimental. It is assumed that in each cycle both the Zn and unreacted ZnO can be reused, and the recovery rate is 95%. Taking into account that only 48 wt% of this is active, 1 gram of ZnO would then produce about 10 grams of active material (Zn). When 95% of this converts CO_2, 1.4 mole CO is produced. Once again, if this were to be converted to methanol 0.46 mole of methanol or 290 kJ could be produced per gram of Zn.

Abanades 2011

In this article, Abanades *et al.* studied the thermochemical conversion of CO_2 to CO with FeO as the catalyst. Aside from the conversion of CO_2, they tested the Fe_2O_3 reduction to FeO, first to determine the thermodynamics of the reaction, then in a small prototype reactor. At 800°C, 70% of the FeO is converted after 40 minutes, which means about 3.25 mmol CO_2 per gram of FeO per cycle. Assuming a 95% recovery rate, 1 gram of FeO lasts about 20 cycles, or 65 mmol of CO. If the equivalent amount of methanol is used, one gram of Fe (77% of the catalyst weight) can produce 17.5 kJ.

Loutzenhiser 2011

The group of Aldo Steinfeld also works with solar thermal reactors with Zn. They have a 10 kW solar chemical batch reactor that reacts ZnO particles to Zn(g) with 54% efficiency. The Zn can then be further reacted with either H_2O, CO_2 or mixtures of those two. For this, they use a packed bed reactor at about 700K, which resulted in 82.1% conversion of Zn to ZnO (no side products detected). If one assumes a recovery rate of 95% for Zn, one gram of Zn can produce roughly 20 grams of active material, which, at the 82% conversion rate, produces 0.25 mole of either H_2 or CO_2. If the methanol equivalent of this is used, one gram of Zn can produce 57.7 kJ in 20 cycles.

Roy 2010

Roy *et al.* work on photocatalytic conversion of CO_2 with N-doped TiO_2 nanotubes with traces of Pt and Cu. Carbon dioxide gas along with water vapor is reacted on the surface to various hydrocarbons (C2 to C6). It is still very small scale, but the technology works with sunlight. They report a photon-to-chemical energy efficiency of 0.03%, which is low, compared to, for example, photosynthesis. A nanotube array with Pt and Cu coating had a hydrocarbon production of 1.7 $\mu l/cm^2$ of catalyst/h. As no data on reaction time was given, it is assumed that the catalyst is active for 1 hour. Assuming an average hydrocarbon density of 0.7 g/l and 50 kJ/g as the heat of combustion, this amounts to 0.0595 kJ/cm^2. From Lin (2010) the amount of Pt per cm^2 of 0.6 mg was taken, as they use a similar deposition technique on nanotubes. This means that one gram of Pt could produce 99.1 kJ of energy.

Ampelli 2011

Ampelli and Centi *et al*. worked on a photo-electrochemical technology that uses TiO_2 films as a photoanode to split water and carbon nanotube-based electrodes for the gas-phase conversion of CO_2 into liquid fuels. The two systems are split to increase the efficiency; they are separated by a proton-conducting membrane. While this photo-electrochemical cell has not yet been tested as a whole, the separate parts are proven to work. The commercialization of this system is still far off. Fe can also be used on the carbon nanotube cathode, and is considered here because Fe is more available than Pt. On N-doped carbon nanotube cloth with iron particles, among other things, isopropanol is formed at a rate of 0.057 $\mu mol/cm^2/h$. The iron loading on the carbon cloth is 0.5 mg/cm^2, so per gram of iron 114 µmol of isopropanol is produced per hour. Assuming that the catalyst lasts for 24h, one gram of iron can produce 2763 µmol of isopropanol. With the heat of combustion of isopropanol of 30 kJ/g, it was calculated that Fe produces 4.9 kJ/g. It should be noted that this is but half of the total cell, and that there is a lot of room for improvement.

Zhan 2009

Zhan *et al.* use a solid oxide electrochemical cell to produce syngas. The reaction takes place at 700-800^oC, the feedstock is $H_2:CO_2:H_2O$ 1:1:2. The syngas production rate is 7 standard cubic centimetre (scc) per minute per cm^2 of catalyst. The catalyst consist of a Ni-YSZ (YSZ=Y_3O stabilized ZrO_2) cathode and an LSCF-GDC (LaSrCoFe and Gd-doped ceria composite) cathode. As the catalyst is 2.4 cm^2, per catalyst 16.8 scc syngas is produced per minute. Using the ideal gas law, 22 mole of syngas to the litre, 0.3696 mol of syngas is produced per minute, or 2217.6 mol per 100 h. With a H_2:CO ratio of 2:1, 739.2 mol of methanol equivalents are produced. Using the heat of combustion of methanol, 4.6 x10^5 kJ can be produced per catalyst. As the gadolinium content of the catalyst is 4.47 mg, 10.4 x10^7 kJ is produced per gram of Gd.

Haije 2011

Haije *et al.* propose to generate H_2 with electrolysis powered by photovoltaic cells, and use that H_2 to reduce CO_2 in the reverse water-gas-shift reaction. Subsequently, the CO/H_2 gas mixture is to be fed into a Fischer-Tropsch (FT) reactor in the low temperature Fischer-Tropsch process, to produce FT-diesel. The reverse water-gas-shift reaction takes place at moderate heat that can be provided by the excess heat of the exothermic FT-reaction, the RWGS reaction is catalysed by zeolite type catalysts. The low temperature FT synthesis is catalysed by a cobalt catalyst, as this minimizes the formation of CO_2. From Withers (1990) the catalyst productivity of 35 mol FT-diesel/h/kg catalyst was taken, the catalyst activity being that on average for 4000 h. This means that per lifetime of catalyst 140 000 mol of FT-diesel is produced. As cobalt comprises 4.4 wt% of the catalyst, 3 181 818 mol of FT-diesel is produced per kg of Co. From (Withers 1990) it was deduced that the average molecular weight of FT-diesel is 111 g/mol. With the heat of combustion of 47.5 kJ/g (Lilik, 2011), it was calculated that one gram of Co can produce 16 x10^6 kJ.

Appendix 2A: Data on metal availability

Table 12 shows data gathered on the materials used throughout the report, from publications by (USGS). The following factors are described:

Presence on earth (in crust)

Although the presence in the earth's crust is not the same as availability, it does give a maximum value. New extraction methods may change the availability in the future to come closer to the presence in the crust.

Mining method

Describes what the metal is mined from.

Environmental impacts

What are the waste products of the mining process, what is needed to process the ore?

Annual production

Gives an estimate of how common the use of said element/mineral is. This indicates the commercial availability as well, showing whether a decent infrastructure for the extraction of the element is already in place.

Current uses

There may be a more vital process or function of the element in society, or a higher value one.

Outlook on production

How much is the production expected to increase or decrease? Is it almost mined out? As solar fuels are not expected to be commercial in the next few decades, current availability is not the whole story.

Recyclability

Easily recyclable materials should have preference over less easy recyclable ones, in case the sustainability would increase by this. Percentages are the amount of the demand that is met through recycling.

Short descriptions of the gathered data are found in appendix 2B.

Table 12: metal availability

	Presence on earth (ppm)	Mining method	Environmental impacts	Annual production (t)	Reserves	Main current uses	Recycled
Cerium	60	From rare earths	Toxic and radioactive leaking	64 000	40 years	Car catalysts, batteries, polishing	No
Cobalt	30	From Cu and Ni ore	Ar also in ore, acids in extraction	70 000	100 years	Aircraft engines andgas turbines	Yes
Copper	50	Copperore	Sulphur compounds	15 000 000	20 years	Wiring, construction, machinery	yes
Gadolinium	5.2	From rare	Radioactive	400	800+	In phosphors,	No

		earths	tailings, acids and bases		years	MRI imaging	
Germanium	1.5	Byproduct of zinc mining	SO_2	80	-	Optics, catalysts and (solar) electronics	35%
Iron	60000	From iron ore	Sulfur compounds in vast amounts	1 200 000 000	50 years	Construction and manufacturing	Yes
Lanthanum	34	From rare earths	Radioactive tailings, acids and bases	12 500	800+ years	Catalysts, alloys, glass additive	No
Lithium	17	From brine	-	24 000	500+ years	Ceramics, batteries	Yes
Nickel	90	From Ni ore	Sulfur compounds from roasting	1 800 000	45 years	Stainless steel production	Yes
Platinum	0.005	Side product of Ni and Cu mining	-	220	500 years	Car catalysts, jewelry, electronics	Yes
Rhenium	0.0027	From Cu and Mo ore	Extraction with salts	4.5	Low, demand higher than supply	Jet engines, catalyst for petro chemistry	25%
Silicon	270000	From rock	Very high amounts of energy required	1 500 000 (metallurgic grade)	A lot	Semiconductors, integrated circuits	No
Silver	0.08	By product of other mining	-	22 000	23 years	Jewelry, catalysts	Yes
Strontium	360	From minerals	-	380 000	17 years	Glass, ceramics, pyrotechnics	No
Titanium	6000	From minerals	Energy intensive purification, Cl gas	6 700 000	100+ years	Mostly as TiO_2 for pigments	-
Yttrium	29	From rare earths	Radioactive tailings, acids and bases	2 400	200 years	Lasers, TV’s, electrodes	No
Zinc	75	From zinc ore	SO_2, cadmium leaking	12 500 000	About 40 years	Galvanizing and alloys	30%
Zirconium	130	By product of Ti mining	Liquid Mg, Cl gas	1 410 000	40 years	Furnaces. reactors	Yes

Appendix 2B: Descriptions

Carbon Cloth, Nafion, Mono ethyl amine

These three compounds are all carbon-based, crude oil-derived products. Crude oil is produced at 4 000 000 000 t per year and there are 221 000 000 000 t of proved reserves (EIA, 2012).

Nafion is a tetrafluoroethylene-based polymer, with fluorite as the original source of the fluorine. Fluorite has an annual production of 5 400 000 t and 230 000 000 t in known reserves.

Cerium

Cerium is the most common of the rare earth elements, with a crystal abundance of 60 ppm. It is found as a mixture of lanthanides. The extraction process involves several steps to purify the cerium and the other lanthanides. The possibly present thorium and uranium pose a radioactive hazard. The whole purification process makes use of strong acids. Annual production is about 64 000 t, most of this is used as catalytic converters in cars to reduce CO emissions. Although China has the major share in production, their reserves are not exactly known. Based on known reserves in the rest of the world of rare earth metals and the share of cerium of the total rare earth element production, the reserves are about 2 500 000 t. Currently, cerium is not being recycled significantly, although future price increases may drive a transition towards this.

Cobalt

Cobalt is a byproduct of copper and nickel mining; it is extracted from the ore through the formation of different cobalt compounds. Cobalt is mostly used in super alloys, which, due to their thermal stability, are used in jet engines and gas turbines. Other uses include LiCo batteries, catalysis, pigments and radioisotopes. 25% of US-consumed Co is from scrap sources.

Copper

Although copper is a rather abundant element, it is very dispersed. It has been used for over 10 000 years, although not significantly before 1900. Copper ore has an ore grade of about 0.4-1.0% copper, so large amounts of ore need to be mined per amount of copper produced. With production continuing to increase, lower grade ore is being used. Sulphur compounds are a large byproduct of the copper extraction process. Annual production is about 15 Mt, with most going to electrical wiring (60%), followed by construction and machinery (20 an 15%). Recycling of copper is very common, with 80% of all copper still being used today.

Fertilizer

Nitrogen fertilizer is produced at 100 000 000 t per year, using atmospheric nitrogen as the starting product. Although there is a limited amount of nitrogen in the atmosphere, it is in a constant cycle and thus no reserves are reported here.

Gadolinium

Gadolinium is a rare earth element. Its purification is done by treatment with acids and bases, with the radioactive thorium as a side product. Annual production is about 400 t, about 03% of total rare earth metal production. Since global rare earth element reserves are around 110 000 000 t, extrapolating the production share gives gadolinium reserves of about 330 000 t. Gadolinium is used in a wide variety of applications, such as in MRI imaging, alloys, cancer treatment and in phosphors.

Germanium

Although not very rare, germanium is a very dispersed metal. It is mostly recovered as a byproduct from zinc mining, although other ores contain it as well. (US geological survey) Refining it leads to SO_2 as a byproduct. The annual production is about 80 t, most of which is used in fibre and infrared optics and as a catalyst for the PET process. No figures of global reserves are available. About 35% of current demand is met by recycling of germanium from optic cables.

Iron

Iron is the most abundant element in the earth's crust, mostly present in the form of iron ore. Metallic iron is rarely found in nature, as it oxidizes easily. Iron ore has a high iron content, but lower grade ore is being used more and more often. Iron is the most commonly used metal on earth, which the annual production reflects. In the form of steel it is used widely in construction and machinery. Because it easily oxidizes, metallic iron requires protection from air. The currently identified iron ore reserves will last for at least 50 years. Steel is one of the most recycled materials in the world, dating back 150 years.

Lanthanum

Lanthanum is one of the more abundant elements of the rare earth elements. Its purification is achieved by treatment with acids and bases, with the radioactive thorium as a side product. Annual production is about 12 500 t, about 10% of total rare earth production. Since global rare earth reserves are around 110 000 000 t, extrapolating the production share gives lanthanum reserves of about 11 000 000 t. Lanthanum is used in a wide variety of applications, notably as a catalyst and glass additive.

Lithium

Lithium is very abundant in seawater, and although production was originally mostly from ore, production from brine has become dominant. The lithium can be extracted with reverse osmosis, and subsequent electrolysis yields the metallic Li. Annual production is currently 24 000 t, but this is set to increase with the advance of electric vehicles and mobile technology. Reserves are 13 000 000, recycling is on the rise due to the growing demand.

Nickel

Nickel is a relatively abundant metal, found mostly in combination with sulphur and iron. Roasting and reduction of the ore produces 75% pure nickel, which is further purified by reaction with syngas and carbon monoxide at mild to high temperature (40-250° C). The roasting process produces sulphuric acid. Annual production is 1 800 000 t, 43% of this is used in stainless steel production, and about a third for other alloys. Recycling is currently mainly focused on scrap recovery.

Platinum

Platinum is one of the more rare elements. Although occasionally found in metallic form, it is mostly produced as a side product in nickel and copper mining. Purification from the residue of these processes is rather straightforward. Annual production is 220 t, about half of which is used as a catalyst to reduce pollution from cars. Other major applications include jewelry and electronics. Estimated reserves are about 100 kt, recycling from scrap is not uncommon. (USGS)

Rhenium

Rhenium is one of the least abundant elements on earth, mostly found in molybdenum ore. Rhenium crystals are only found in a specific volcanic area. The molybdenum ore is usually extracted from copper ore, the rhenium oxides can be extracted with solutions of specific salts. Annual production is about 4.5 t, mostly from Chile, and until recently also from Kazachstan. 70% of all rhenium is used in alloys for high temperature jet engines, although rhenium catalysts are also a large share, used for generating lead-free high octane gasoline. Because supply is continuing to fall short of demand, the price is rapidly increasing, with it possibly reaching the price of platinum. Rhenium from catalysts is being recovered at about 10t per year.

Silicon

Silicon is, by weight, the second most abundant element on earth, mostly found in the form of silicon dioxide. The production process gets more difficult for higher purity grades, with some application requiring single crystals. Annual production of metallurgic grade silicon is about 1 500 000 t, most of which is used in semiconductors and integrated circuits. Production is increasing; it is possible to recycle solar silicon wafers.

Silver

The precious metal silver is among the more rare elements on earth. Although it is occasionally found in pure nuggets, it is mostly found in copper and zinc ore in combination with other elements like arsenic, sulfur, antimony and chlorine. Annual production is around 22 000 tons worldwide, with 510 000 tons in worldwide reserves. Silver is used in many applications like jewelry, catalysts (cars), photography and it has a wide variety of applications because of its anti-bacterial properties. Silver is recovered on a large scale from old and new scrap.

Strontium

Strontium is the 15th most abundant element in the earth's crust. Found in mineral form, its main applications are in glass, ceramics and pyrotechnics. Annual production is 380 000 t, with known reserves of 6 800 000 t, although the high quality mines are dwindling. There is no recycling of strontium compounds.

Titanium

Titanium occurs in a large number of minerals, but has the highest concentration in ilmenite and rutile. To extract pore titanium dioxide, the minerals are first reduced with carbon, oxidized with chlorine and then re-oxidized with pure oxygen. TiO_2 nanotubes are synthesized from anatase by treating it with sodium hydroxide. Annual production is 99 kt, 95% of used as TiO_2. The metal form has wide applicability, most notably in spacecraft and biomedical uses. TiO_2 is used as a pigment in a very wide range of products and materials. Reserves for titanium are in excess of 600 Mt, and no data on the recycling of TiO_2 were found.

Yttrium

Yttrium is found as a mixture of rare earth elements, purification is achieved by treatment with acids and bases. Annual production is about 2 400 t, with 540 000 t in known reserves. The main application of yttrium is in phosphors, but it is also used in electronics, lasers and superconductors and as a material enhancer. Recycling is not very common.

Zinc

Zinc is the 24th most abundant element, the 4th most used metal on earth. It is mostly mined from the high zinc-containing mineral sphalerite, ZnS. In the production of ZnO, large amounts of sulphur dioxide are created as a side product. Annuals production is about 12 million tonnes, 55% is used to galvanize steel, 21% as alloys, 16% in bronze and brass. The currently identified reserves are about 1.9 tonnes, which are expected to last to about 2027-2055. Zinc is already recycled at a 30% rate.

Zirconium

Zirconium is mainly found in the form of a silicate mineral in titanium ore, most of current production is in Australia and South Africa. The production process entails reduction, treatment with chlorine gas and reduction with liquid magnesium. Annual production is 1 410 000 t, with about 40 years of reserves left. Because zirconium compounds are hard and chemically resistant, the main use is in furnaces and other ceramics. Recycling is mostly focused on recovery of production scrap.

Appendix 3: Description BAT (EU, 2012)

“"best available techniques" shall mean the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent and, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole:

> *- "techniques" shall include both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned,*
>
> *- "available" techniques shall mean those developed on a scale which allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages, whether or not the techniques are used or produced inside the Member State in question, as long as they are reasonably accessible to the operator,*
>
> *- "best" shall mean most effective in achieving a high general level of protection of the environment as a whole.”*

Appendix 4: Energy output calculations of different schemes

Routes	Fuel	HHV (kJ/mol)	kJ/mol$_{CO2}$	Energy with 2 Gt (EJ)	Energy with 12 Gt (EJ)
Ampelli	Isopropanol	1800	600	27.27	163.64
Zhan Haije	FT-diesel	7294	607	27.63	165.77
Li, Abanades, Louzenhiser, Chueh	Methanol	726	726	33.00	198.00
Asi	Methane +methanol	819	819	37.23	223.36
Roy, Ikeue, Xi	Methane	889	889	40.41	242.45

Appendix 5: Solar fuel article selection

The next two tables show the criteria used for selecting which articles to use for the material output analysis (section 4.1) and how the articles score. Each criterion is scored from -2, not present at all, to +2, very present. The second column of the tables shows the weight factor. Multiplying the score on the criterions weight the weight factor and adding them all up gave a score for the article. Articles with a weighed cumulative score of 20 or more were used for the material output analysis.

The articles that have no value are background/qualitative articles on solar fuels and report no experimental data.

	Weight factor	Abanades 2010	Abanades 2011	Ampelli 2010	Ampelli 2011	Angumutho 2010	Asi 2011	Bamberger 1980	Barton 2008	Benson 2008	Blankenschip 2011	Cao 2011	Centi 2007	Centi 2009	Chueh 2010 ceria	Chueh 2010	Desario 2011	Diver 2008	Feng 2011	Fisher 1980	Galzvez 2009	Haije 2011	Hoffman 2011
energy efficiency	0	-1	0	-1	-1	-1	-1		0			-1	-1		0	2	2		-2	-1		2	
quantum efficiency	0	-1	0	-1	-1	1	-1		2			1	-1		0	-1	-1		-2	1		-1	
future perspective	2	-1	0	-1	-1	-1	-1		-1			-1	-1		0	1	-1		-2	-1		2	
thermodynamic maximum	0	-1	1	-1	-1	-1	-1		-1			-1	-1		0	2	-1		-2	-1		0	
solvents	0	2	2	2	2	2	2		0			2	2		2	2	2		2	1		-1	
other materials	0	0	2	2	1	2	2		-1			0	1		2	0	0		2	-1		-1	
CO2 emissions	0	-1	-1	-1	-1	-1	-1		-1			-1	-1		0	1	-1		-1	-1		-1	
heat emissions	0	-1	-1	-1	-1	-1	-1		-1			-1	-1		0	1	-1	2	2	-1		1	
feedstok qualitative	0	2	2	2	2	2	2		1			2	2		0	2	2		1	2		2	
feedstok quantitative	2	2	2	2	1	-1	2		-1			1	2		0	0	0		1	2		-1	
concentration feedstock	2	2	2	2	1	-1	2		-1			1	2		0	2	2		2	2		1	
composition catalyst	0	2	2	2	1	2	2		1			1	2		2	2	2		2	2		-1	
amount of catalyst	5	2	2	2	0	-1	2		-1			1	1		2	1	1		1	2		-1	
lifetime catalyst	5	-1	-1	1	-1	-1	1		-1			-1	1		2	1	1		-2	0		-1	
product qualitiative	0	2	2	2	2	2	2		2			2	2		2	2	2		1	2		1	
product quantitative	5	1	2	2	1	0	2		-1			-1	2		2	1	1		1	2		-1	
product ratio	1	1	2	2	2	2	2		-1			1	2		2	1	0		-1	0		-1	
product concentration	2	1	0	2	-1	-1	0		-1			0	1		2	1	0		0	-1		-1	
product phase	0	2	2	2	2	2	2		1			-1	1		2	2	2		2	1		2	
reaction speed	2	2	2	2	1	2	0		-1			-1	1		2	2	0		1	2		-1	
product selectivity	0	1	0	2	0	0	1		-1			-1	0		0	1	-1		-1	0		0	
Reaction temperature	0	2	2	2	0	2	2		0			1	2		2	2	2		2	2		1	
Reaction pressurs	0	0	1	2	0	2	2		0			1	2		2	0	2		2	2		0	
overpotential	0	2	2	2	2	2	2		2			2	2		2	2	2		2	2		-1	
reaction phase	0	2	2	2	1	2	2		-1			2	2		2	2	2		2	2		1	
Costs of product	0	-1	-1	-1	-1	-1	-1		-1			-1	-1		2	-1	-1		-1	-1		-1	
Produced energy	10	1	1	2	0	-1	1		-1			-1	1		2	1	1		1	1		1	
Total		21	29	32	10	13	26	0	-8	0	0	6	24	0	34	32	19	2	13	20	0	0	0

	Weight factor	Hori 2005	Ikkue 2002	Indrahanti 2009	Kodama 2003	Le Gal 2011	Li 2011	Liang 2011	Liu 2010	Loutzenhiser 2009	Loutzenhiser 2011	Noda 1990	Olah 2009	Ordorica-Garcia 2011	Pan 2011	Rajeshwar 2011	Roeb 2011	Roy 2010	Sanchez 2001	Sato 2011	Schunk 2009	Shi 2011	Shibata 2008	Stamatiou 2010	Takeda 2008	Traynor 2002	Usubranata 2006	Zhan 2009	Xi 2011
energy efficiency	0		-1			-1	-1	-1	-1		-1	-1		!!!!!!!!!	1			2	-1	2		-1	-1	-1	-1	2		0	-1
quantum efficiency	0		2			-1	-1	-1	-1		-1	-1			1			2	1	-1		-1	1	-1	2	-1		0	-1
future perspective	2		-1			-1	-1	-1	-1		-1	-1			-2			-1	-1	-1		-1	-1	-1	-1	2		2	-1
thermodynamic maximum	0		-1			1	-1	-1	-1		0	-1			-2			2	-1	-1		-1	-1	2	-1	2		2	-1
solvents	0		2			2	2	-1	2		2	2			-2			2	2	2		2	2	2	2	2		1	2
other materials	0		0			0	2	1	-1		1	-1			-2			1	-1	2		2	1	1	2	1		1	2
CO2 emissions	0		-1			-1	-1	-1	-1		-1	-1			-2			-1	-1	-1		-1	-1	-1	-1	-1		-1	-1
heat emissions	0		-1			-1	-1	-1	-1		-1	-1			-2			-1	-1	-1		-1	-1	-1	-1	2		-1	-1
feedstok qualitative	0		2			2	2	2	2		2	2			1			2	1	1		2	2	2	2	2		2	2
feedstok quantitative	2		2			2	1	-1	-1		1	-1			-2			-1	-1	-1		-1	0	1	2	0		1	2
concentration feedstock	2		-1			2	1	-1	-1		2	1			-2			-1	-1	0		-1	1	2	2	0		1	1
composition catalyst	0		2			2	2	2	2		2	2			2			2	2	1		2	2	2	2	0		2	2
amount of catalyst	5		2			2	2	0	-1		1	1			1			1	-1	0		2	0	1	1	1		1	2
lifetime catalyst	5		1			0	1	-1	1		-1	-1			-2			1	-1	1		1	1	-1	1	1		0	0
product qualitiative	0		2			2	2	2	2		2	2			1			2	2	2		2	2	2	2	2		2	2
product quantitative	5		2			2	1	1	1		1	0			1			1	-1	1		0	1	2	1	0		1	2
product ratio	1		2			-1	0	-1	1		1	1			-2			2	-1	1		0	2	2	0	1		2	-1
product concentration	2		-1			2	0	-1	-1		2	-1			0			1	-1	1		1	1	2	-1	2		1	2
product phase	0		2			2	0	-1	2		2	-1			1			2	2	1		1	2	2	1	2		1	2
reaction speed	2		2			2	1	1	1		2	-1			-1			2	-1	1		-1	0	1	1	1		1	2
product selectivity	0		1			0	1	-1	1		2	1			-1			1	-1	2		-1	2	1	-1	2		1	-1
Reaction temperature	0		2			2	1	-1	1		2	2			-1			2	2	1		0	2	2	2	2		2	2
Reaction pressure	0		1			0	1	-1	1		0	2			-1			0	2	2		0	2	2	2	0		0	2
overpotential	0		2			2	1	0	2		2	2			-1			2	2	2		2	1	2	2	2		2	2
reaction phase	0		2			2	2	-1	2		2	2			-1			2	2	2		1	2	2	2	2		1	2
Costs of product	0		-1			-1	-1	-1	-1		-1	-1			-1			-1	-1	-1		-1	-1	-1	2	-1		1	-1
Produced energy	10		1			-1	1	0	1		1	1			0			1	-1	0		-1	1	1	1	1		1	1
Total		0	24	0	0	21	17	-9	10	0	23	8	0	0	-18	0	0	27	1	18	0	6	22	27	25	29	0	27	23

Appendix 6: Explanation IEA ETP baseline scenario

From (IEA, 2010), p263

***“Baseline:** In this scenario, vehicle ownership and travel per vehicle for LDVs, trucks and other modes are consistent with IEA (2009c) and a world oil price rising to USD 120/bbl by 2050. This scenario assumes greater urbanisation in developing countries and lower suburbanisation than in OECD countries, greater income disparities between the wealthy and the poor in non-OECD countries, and limits on the capacity of non-OECD countries to develop the infrastructure needed to support large numbers of vehicles. As a result, passenger LDV ownership is somewhat lower in the developing world at a given level of income than has occurred historically in many OECD countries. This scenario also assumes that the decoupling of freight travel growth from GDP growth that has clearly begun in OECD countries continues and that it spreads also to non-OECD countries.”*