

UNIVERSITY OF ZAGREB  
FACULTY OF MECHANICAL ENGINEERING  
AND NAVAL ARCHITECTURE

# **MASTER'S THESIS**

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UNIVERSITY OF ZAGREB  
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AND NAVAL ARCHITECTURE

# **THE FEASIBILITY OF SYNTHETIC FUELS IN RENEWABLE ENERGY SYSTEMS**

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*I hereby declare that this thesis is entirely the result of my own work except where otherwise indicated. I have fully cited all used sources and I have only used the ones given in the list of references.*

Zagreb, January 2012

Iva Ridjan

*Unless you try to do something beyond what you have already mastered, you will never grow.*

*Ronald E. Osborn*

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## NOMENCLATURE

### Materials, substances and fuels

|  |  |
|--|--|
| CO <sub>2</sub>                                | Carbon dioxide                                     |
| CO   | Carbon monoxide                                    |
| H <sub>2</sub> O                               | Water  |
| H <sub>2</sub>                                 | Hydrogen   |
| OH <sup>-</sup>                                | Hydroxide  |
| H <sup>+</sup>                                 | Hydrogen ion                                       |
| O <sub>2</sub>                                 | Oxygen   |
| O <sup>2-</sup>                                | Oxygen ion   |
| SO <sub>x</sub>                                | Sulphur oxides                                     |
| NO <sub>x</sub>                                | Nitrogen oxides                                    |
| NH <sub>3</sub>                                | Ammonia  |
| C <sub>6</sub> (H <sub>2</sub> O) <sub>5</sub> | Biomass  |
| MeOH   | Methanol (CH <sub>3</sub> OH)                      |
| DME  | Dimethyl-ether (CH <sub>3</sub> OCH <sub>3</sub> ) |
| GHG  | Greenhouse gas emissions                           |

### Energy units etc.

|     |                               |
|-----|-------------------------------|
| kJ  | Kilojoule                     |
| MJ  | Megajoule                     |
| PJ  | Petajoule (1 billion MJ)      |
| EJ  | Exajoule (10 <sup>18</sup> J) |
| MW  | Mega watt (1,000 kW)          |
| kWh | Kilo watt hour (3.6 MJ)       |
| kt  | Kilo ton                      |
| Mt  | Mega ton                      |
| ha  | Hectare                       |

### Economy

|     |                                 |
|-----|---------------------------------|
| €   | Euro                            |
| O&M | Operation and maintenance costs |
| \$  | US Dollar                       |

### Electrolysers and fuel cells

|      |                                  |
|------|----------------------------------|
| SOEC | Solid Oxide Electrolyser cells   |
| PEM  | Proton Exchange Membrane         |
| RWGS | Reverse Water Gas Shift Reaction |

### Abbreviations

|      |  |
|------|--|
| CCR  | Carbon capture and recycling           |
| RES  | Intermittent renewable energy sources  |
| PES  | Primary energy supply                  |
| CEEP | Critical Excess Electricity Production |
| R&D  | Research and development               |

## ABSTRACT

This thesis is intended at answering the question: What is the feasibility of using synthetic fuels for reaching a 100% renewable transport sector? To answer this question an energy system analysis was carried out and two pathways for producing synthetic fuels were created with a specific focus on solid oxide electrolyser cells (SOEC) which are combined with the recycling of CO<sub>2</sub>. The first pathway entails *co-electrolysis of steam and CO<sub>2</sub>* and the second one includes *hydrogenation of CO<sub>2</sub>*. These scenarios have been compared in terms of primary energy supply, biomass consumption, flexibility of system and socio-economic costs with two pathways that have direct usage of biomass in the production process of liquid fuels - *hydrogenation of biomass* and *conventional biodiesel* pathway. The scenarios provide all liquid fuels that cannot be replaced by direct electrification which has the first priority.

The reason for this analysis lies in the fact that at present, the transport sector is the only sector in which there have been no significant renewable energy penetrations and it is heavily dependent on oil with rapid growth in the last decades. Moreover, it is challenging to obviate the oil dependence due to the wide variety of modes and needs in the sector. Nowadays, biofuels are proposed as one of the main options for replacing fossil fuels in the transport sector, along with electricity. The main reasons for avoiding the direct usage of biomass in the transport sector, i.e. producing biomass derived fuels, are land use shortage, limited biomass availability, interference with food supplies, and other impacts on environment and biosphere. Hence, it is essential to do a detailed analysis of the transport sector in order to match the demand and to meet the criteria of a 100% renewable energy system in 2050. The analysis was carried out for Danish system, because the most developed 100% renewable energy system is available from the CEESA project, which includes a wide variety of transport and other energy system measures.

The analysis showed that the synthetic fuel scenarios increase the system flexibility and this is essential for the conversion of the energy system into a 100% renewable system. The costs of synthetic fuel scenarios are more expensive, but biomass savings associated with this make the additional costs worthwhile due to the scarcity of biomass for the energy system. With feasible technological development and mass production of the Solid Oxide Electrolyser Cells, synthetic fuels could be competitive and have market advantage over biomass derived fuels based on their supply related issues, land use shortage, limited biomass availability, etc.

## SAŽETAK

Svrha ovog rada je pružiti odgovor na pitanje: Kolika je opravdanost korištenja sintetičkih goriva u svrhu postizanja 100% obnovljivog prometnog sektora? Stoga je provedena analiza energetskeg sustava te su osmišljena dva scenarija za proizvodnju sintetičkih goriva, scenarij koji obuhvaća elektrolizu vode i CO<sub>2</sub> (*eng. co-electrolysis*) i hidrogenizacija CO<sub>2</sub> (*eng. CO<sub>2</sub> hydrogenation*), s posebnim fokusom na elektrolizatore s elektrolitom od krutih oksida (SOEC) u kombinaciji s recikliranjem CO<sub>2</sub>. Usporedba, s dva scenarija sa izravnom upotrebom biomase za proizvodnju goriva - hidrogenizacija biomase (*eng. hydrogenation of biomass*) i scenarij s konvencionalno proizvedenim biodizelom, je provedena u pogledu opskrbe primarnom energijom, potrošnje biomase, fleksibilnosti sustava te društveno-ekonomskih troškova. Scenariji osiguravaju potrebe za tekućim gorivima koja ne mogu biti zamijenjena prvim prioritetom - izravnom elektrifikacijom sektora.

Razlog analize jest činjenica da je prometni sektor trenutno jedini sektor u kojem nije bilo značajnih penetracija obnovljivih izvora energije, u potpunosti je ovisan o nafti, te ima brzi porast potražnje u posljednjih nekoliko desetljeća. Nadalje, veliki je izazov otkloniti ovisnost o nafti zbog različitih oblika i potreba prometnog sektora. Biogoriva, odmah nakon elektrifikacije, predstavljaju glavnu zamjenu tekućim fosilnim gorivima u sektoru. Glavni razlozi za izbjegavanje izravne uporabe biomase u sektoru prometa, tj. proizvodnji biogoriva, su problemi vezani za nedostatak dostupnog zemljišta, ograničenost resursa, utjecaj na opskrbu hranom te drugi utjecaji na okoliš i biosferu. Stoga je neophodno napraviti detaljnu analizu prometnog sektora kako bi se namirile potrebe te zadovoljili kriteriji 100% obnovljivog energetskeg sustava u 2050-toj. Analiziran je danski sustav, najrazvijeniji 100% obnovljivi energetski sustav dostupan u CEESA projektu, koji uključuje široku raznolikost mjera u prometnom kao i ostalim energetskeg sustavima.

Analiza je pokazala da scenariji za proizvodnju sintetičkih goriva potvrđuju poboljšanja fleksibilnosti sustava što je ključno za pretvorbu energetskeg sustava u 100% obnovljivi sustav. Scenariji za proizvodnju sintetičkih goriva su skuplji, no dodatni troškovi se isplate zbog ušteda na biomasi, čija je količina ograničena u energetskeg sustavu. S mogućim tehnološkim razvojem i masovnom proizvodnjom SOEC-a, sintetička goriva mogla bi postati konkurentna i imati tržišnu prednost u odnosu na biogoriva, s obzirom na sigurnost opskrbe, nedostatka zemljišta, ograničenost resursa itd.

## PROŠIRENI SAŽETAK

Postizanje globalne održivosti važna je stavka današnjeg društva kako bi se spriječilo ugrožavanje potreba budućih generacija. Diljem svijeta, energetske opskrbljivači suočavaju se s ključnim izazovima održivog razvoja. Povećanje sigurnosti opskrbe, smanjenje emisija ugljičnog dioksida i ostalih zagađivača u svrhu zaustavljanja klimatskih promjena te povećanja kvalitete života građana i njihovog zdravlja, glavni su inicijatori odmicanja od fosilnih goriva te korištenja obnovljivih izvora energije. Općeprihvaćeni pravac ka održivom razvoju jest upravo korištenje intermitentnih obnovljivih izvora energije i biomase.

Prometni sektor jedan je od najbitnijih sektora našeg vremena, pa tako i značajan nosač te okosnica gospodarskog i društvenog razvoja svake zemlje. Prometni sektor u potpunosti ovisi o nafti, odgovoran je za 19% svjetske potrošnje energije i 23% emisija ugljičnog dioksida. Prema sadašnjim trendovima, predviđa se porast potrošnje energije i CO<sub>2</sub> emisija u sektoru za otprilike 50% do 2030, a ta brojka bi mogla porasti iznad 80% do 2050.

Zamjena nafte s ostalim gorivima u sektoru bit će težak proces. Benzin, dizel i ostali naftni derivati predstavljaju primarni izvor energije u prometnom sektoru više od stoljeća. Razlog zbog kojeg su naftni derivati vladali sektorom bez premca, jest njihova visoka energetska gustoća i jednostavnost rukovanja. Štoviše, gotovo sva prometna infrastruktura je prilagođena tekućim ugljikovodicima, a trajna potreba za tim gorivima zahtjeva održivu proizvodnju istih.

Smanjenje potrošnje nafte u prometnom sektoru je ključni korak prema društvu bez ugljičnih emisija. Dok je većina ostalih sektora primjenjivala mjere za smanjenje CO<sub>2</sub> emisija i polako prelazila na obnovljive izvore energije, udio štetnih emisija prometnog sektora se polako povećavao. Jedino gorivo koje trenutno može namiriti potražnju je - nafta. Ipak, smanjenje ovisnosti o nafti i naftnim derivatima u prometnom sektoru je zastrašujuć izazov. Danas, nafta i naftni derivati predstavljaju dominantna goriva u ovom sektoru s preko 96% zastupljenosti. Poticanje snažne dekarbonizacije prometa moglo bi rezultirati energetsom sigurnošću, kao važnog cilja održivosti.

Biomasa se može koristiti kao obnovljivi izvor svih oblika korisne energije - toplinske, električne i mehaničke (biogoriva). Upravo zbog te činjenice, ima rastuću potražnju u gotovo

svim sektorima, uključujući i prometni sektor. Biogoriva, odmah nakon elektrifikacije, predstavljaju glavnu zamjenu tekućim fosilnim gorivima u prometnom sektoru. Problem ovakvog pristupa jest u potencijalu biomase i korištenju zemljišta, te odnos s potrebom za biogorivima. Biomasa bi mogla predstavljati ozbiljno „usko grlo“ u društvu bez fosilnih izvora pri čemu, promatrajući iz dugoročne perspektive, zamjena fosilnih goriva u prometu s biogorivima možda nije najbolje rješenje.

Konvencionalna biogoriva su na prekretnici zbog socijalnih i ekoloških izazova, uglavnom zbog upotrebe prehrambenih usijeva u procesu proizvodnje, što bi moglo dovesti do povećanja cijena hrane i moguće neizravne promjene korištenja zemljišta. Napredna biogoriva predstavljaju moguće rješenje navedenih socijalnih rizika, korištenja zemljišta i zaštite okoliša, s obzirom na upitna smanjena emisija stakleničkih plinova korištenjem konvencionalnih goriva. S obzirom da njihov proizvodni proces koristi organski otpad, ostatke drvenih ili travnatih biljaka i alge daje im prednost pred konvencionalnim biogorivima. Ipak, proizvodnja biogoriva može samo djelomično pokriti potrebe, čak i unutar prometnog sektora.

U budućnim energetske sustavima, intermitentni izvori, kao što su vjetroturbine, fotonaponske ćelije i solarna termalna energija, uz učinkovite tehnologije za pretvorbu i skladištenje energije, predstavljaju ključne tehnologije. Kako bi se omogućio dugoročan prodor distribuiranih energetske izvora, potrebno je suočiti se s glavnim problemima vezanim za integraciju ovakvih izvora u postojeće i buduće energetske sustave. Jedan od glavnih izazova budućnosti jest integracija fluktuacija u proizvodnji električne energije iz obnovljivih izvora. Primjena intermitentnih izvora energije, zbog svojih karakteristika zahtjeva dodatne potrebe u pogledu upravljanja i rada sustava, kapaciteta rezervi te pojačanja mreže na potrebnim mjestima. Fleksibilnost tehnologija budućih energetske sustava bit će presudna za uravnoteženje obnovljivih izvora.

S vrlo malim lokalnim utjecajima na okoliš te većim učinkovitostima od konvencionalnih tehnologija, gorivni članci i elektrolizatori mogli bi dobiti na važnosti. Razlog za primjenu elektrolizatora nije samo u pronalasku alternative fosilnim gorivima koja ne bi emitirala emisije ugljičnog dioksida u prometnom sektoru, već i mogućnost reguliranja snage u elektroenergetskom sustavu. Stoga, elektrolizatori predstavljaju važnu opciju koja bi se morala uzeti u obzir pri planiranju održivih energetske sustava s velikim udjelom intermitentnih izvora energije jer čine sustav fleksibilnim.

Središnja tema ovog rada su sintetička goriva, koja u svom proizvodnom procesu ne uključuju korištenje fosilnih goriva kao ni izravno korištenje biomase, te omogućavaju potencijalnu geografsku neovisnost i sigurnost opskrbe, inače karakterističnih problema konvencionalnih goriva. Glavni razlozi za izbjegavanje izravne uporabe biomase u sektoru prometa, tj. proizvodnji biogoriva, su problemi vezani za korištenje zemljišta, dostupnost resursa, utjecaj na opskrbu hranom te drugi utjecaji na okoliš i biosferu. Korištenje sintetičkih goriva moglo bi biti rješenje ne samo za smanjenje emisija CO<sub>2</sub>, već i za pružanje geografske neovisnost i rješavanje problema opskrbe konvencionalnih goriva i biogoriva.

Iako je elektrifikacija prometnog sektora prioritet, nije moguće elektrificirati sve vrste prijevoza te postoji potreba za tekućim gorivima. Pretvorba električne energije u sintetičko gorivo mogla bi biti važna stavka u prometnom sektoru budućnosti. Glavna prednost elektrolize u procesu proizvodnje sintetičkih goriva jest što omogućava proizvodnju različitih vrsta goriva poput, metana, metanola, dimetil etera itd. putem kemijske sinteze goriva iz sintetičkog plina nastalog kao produkt tijekom procesa. Sintetička goriva predstavljaju iskorak nad biogorivima i problemima vezanim za njih pri čemu u njihovoj proizvodnji nema direktnog korištenja biomase.

U svrhu analiziranja potrebnih koraka za postizanje 100% obnovljivog prometnog sektora u 2050-toj, kreirana su četiri scenarija. Svi modelirani scenariji predstavljaju ekstremne slučajeve zamjene svih tekućih goriva u prometnom sektoru sa sintetičkim, bio-gorivima ili bio-dizelom.

Dva glavna scenarija usmjerena su na sintetička goriva: su-elektroliza (*eng. co-electrolysis*) i hidrogenizacija CO<sub>2</sub> (*eng. CO<sub>2</sub> hydrogenation*). Su-elektroliza je kombinirani proces elektrolize vode i CO<sub>2</sub>. Hidrogenacija CO<sub>2</sub> uključuje elektrolizu vode i naknadnu reakciju proizvedenog vodika s recikliranim ugljikovim dioksidom. Plinske mješavine nastale ovim procesima mogu se katalizirati u sintetička goriva. Scenariji su podijeljeni u ciklus od tri koraka: izvor ugljika i energije, disocijacija oksida i sinteza goriva. Osnova sintetičkih goriva je ugljikov dioksid te su za potrebe rada razmatrana dva izvora CO<sub>2</sub>: izdvajanje i recikliranje ugljikovog dioksida (*eng. Carbon capture and recycling – CCR*) te izdvajanje ugljikovog dioksida iz zraka (*eng. Air capturing*) kao perspektivna tehnologija koja će omogućiti zatvoreni CO<sub>2</sub> neutralni gorivni ciklus.

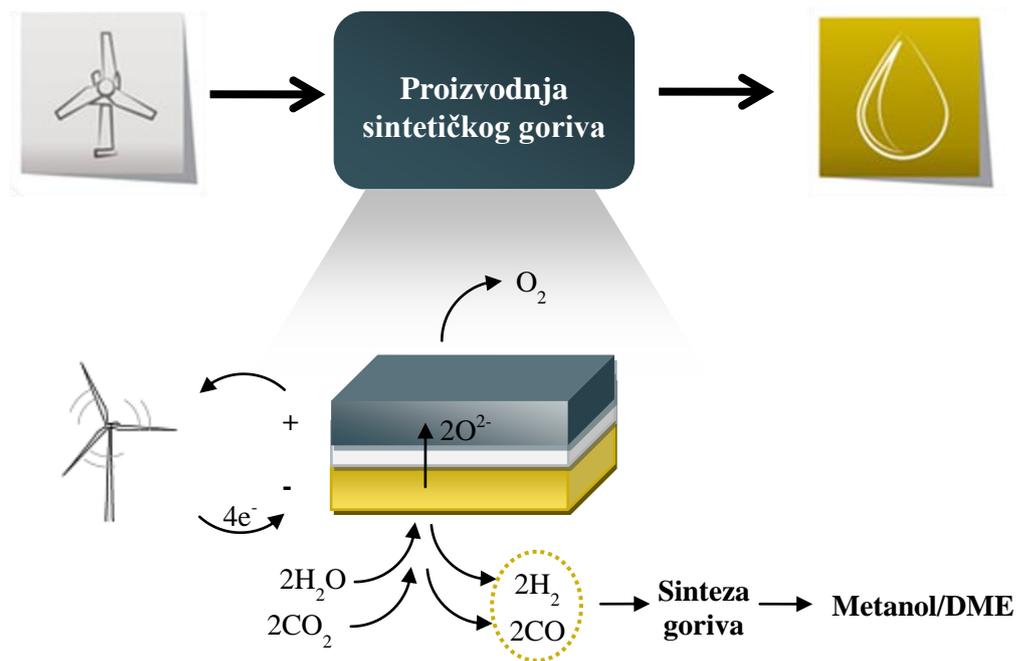


Figure 1. Proizvodnja sintetičkog goriva

Iako je moguće proizvesti razne vrste goriva, metanol i DME (dimetil eter) su odabrani za analizu kao obećavajuća goriva, primarno zbog dobro znane kemijske sinteze za proizvodnju ovih goriva kao i mogućnost njihove skoro izravne primjene u postojećim motorima s unutarnjim izgaranjem.

Kako bi se kompletirala analiza, formirana su dva usporedna scenarija s biogorivima koji uključuju izravnu upotrebu biomase za proizvodnju goriva: hidrogenizacija biomase (*eng. hydrogenation of biomass*) i scenarij s konvencionalno proizvedenim biodizelom. Hidrogenizacija biomase je poznat proces s kojim se podiže energetska sadržaj i energetska gustoća biomase s vodikom. Hidrogenizacija biomase uključuje rasplinjavanje biomase u sintetički plin te naknadnu reakciju vodika proizvedenog elektrolizom sa sintetičkim plinom. Konvencionalna proizvodnja biodizela je jedini scenarij koji ne uključuje elektrolizatore u proizvodni proces.

### Istraživačko pitanje

Istraživačko pitanje ovog rada jest:

“Kolika je opravdanost korištenja sintetičkih goriva u svrhu postizanja 100% obnovljivog prometnog sektora?”

Glavna svrha ovog rada je identificirati potencijalne scenarije za proizvodnju sintetičkih goriva s posebnim fokusom na elektrolizatore s elektrolitom od krutih oksida – SOEC u kombinaciji s recikliranjem CO<sub>2</sub>. Kako bi se izvršila studija izvedivosti, analiza energetskog sektora je provedena u EnergyPLAN modelu. Scenariji su procjenjivani na temelju sljedećih kriterija:

- 1) Potrošnja goriva koja ukazuje koji je scenarij najučinkovitiji sa stajališta goriva
- 2) Uravnoteženje proizvodnje električne energije iz vjetra kao pokazatelj fleksibilnost sustava
- 3) Ukupna potrošnja biomase u odnosu na problem korištenje zemljišta konvencionalnih biogoriva i potencijala biomase, s obzirom da se biomasa iskorištava i u drugim sektorima
- 4) Društveno-ekonomski troškovi koji mogu pružiti relevantne informacije u smislu određivanja koji sustav ima prednosti u odnosu na potrošnju goriva, pogon i godišnje troškove ulaganja.

Analiza je provedena za prometni sektor koji je dio danskog 100% obnovljivog energetskog sustava u 2050-toj koji je predstavljen u projektu “Coherent Energy and Environmental System Analysis” poznatom pod kraticom CEESA. Izabrani referentni scenarij na kojem je temeljena analiza jest *Recommendable scenario CEESA 2050*.

Ukratko, ova teza istražuje ukupan učinak korištenja elektrolize za proizvodnju sintetičkih goriva u prometnom sektoru i potencijal elektrolizatora za integriranje intermitentnih obnovljivih izvora energije u drugim sektorima.

## 1. INTRODUCTION

*“We've embarked on the beginning of the last days of the age of oil. Embrace the future and recognize the growing demand for a wide range of fuels or ignore reality and slowly—but surely—be left behind.”*

Mike Bowlin, chairman and CEO of ARCO (now BP), 1999

For reaching the global sustainability it is important to reduce the dependence on fossil fuels and raise the usage of alternative fuels to reduce carbon dioxide emissions. The incentives for sustain drive towards renewable energy are climate change, security of supply and job creation. From a world aspect, there are two inevitable challenges for achieving a sustainable future: improving security of supply by reducing fossil fuel dependence and reducing greenhouse gas emissions by mitigation of climate change. A 100% renewable energy system is not achievable without combining all energy sectors.

The transport sector is one of the most important sectors of our time, as well as a significant carrier and the backbone of economic and social development of each country. The transport sector is heavily dependent on oil. Transport accounts for about 19% of global energy use and for 23% of energy-related carbon dioxide emissions. Given current trends, transport energy use and CO<sub>2</sub> emissions are projected to increase by nearly 50% by 2030 and more than 80% by 2050 [1].

The reduction of oil consumption in this sector is one of the key steps towards zero carbon society. While most sectors have been taking measures to reduce CO<sub>2</sub> emissions and shifting to renewable energy sources, the emission share for transportation has been steadily increasing. At present, oil is the only fuel that can meet the demand. Reducing reliance on oil and oil products in the transport sector is a daunting challenge. At the moment, oil and oil products cover more than 96% of energy needs in transportation. Encouraging the strong decarbonisation of transport could lead to energy security which is an important goal for sustainability.

It should be stressed that in order to achieve Europe's targeted 80% reduction of greenhouse gas emission by 2050, compared to the 1990 levels, the consumption of oil in this sector must drop by 70% from today's rates [2].

This directly implies that it is by no means an overreaction to state there is a need for a revolution in transport fuels and ways of travelling. Regardless of technical progress, potential for energy efficiency improvements and policy efforts, since the first big oil crisis 40 years ago, the transport system has not fundamentally changed.

There are also 40 years left until 2050; the current situation and trends must be changed within the next five to ten years to get transport on a sustainable road within this timeframe. “Growing out of oil” will not be possible just by relying on a single technological solution. There is need for a cluster of new technologies as well as a more sustainable behaviour [3].

A preferred alternative to fossil fuels in many sectors is biomass, with a growing demand not just for heat and power services but also for transportation fuels. Biofuels are proposed as the main option for replacing fossil fuels in the transport sector, along with electricity. The problem lies in biomass potential and land use issues, as well as their correlation with the demand for biofuels. Biomass may be a severe bottleneck of the fossil free society, and replacing fossil fuels in the transport sector with biomass liquid fuels may not be the best solution from a long term perspective. Furthermore, there are some concerns that direct conversion of biomass into transport fuels may not be better than using the biomass for heat and power [4]. Even if electricity based energy carriers partially replaced liquid fossil fuels, there would still be a great need for hydrocarbon fuels.

### **1.1. Advantages of electrolysers**

Fuel can be produced from biomass resources, but that will cover the need only partly, even within the transport sector. The conversion of electricity to fuel is beneficial for future energy systems. Fuel cells and electrolysers have very low local environmental effects and they have potentially better efficiencies than conventional technologies [5]. The flexibility of technologies in future energy systems is going to be essential for balancing renewable systems. The usage of intermittent renewable energy sources and biomass are widely accepted as a path to sustainable future. Due to its characteristics, the application of intermittent energy sources entails additional requirements regarding system operation and management, capacity reserves and network reinforcements in weak grid areas.

The reason for implementing electrolysers is not just to find an alternative to fossil fuels in the transport sector which would not imply the release of carbon dioxide emission, but also to regulate the power shaving through electricity system. Therefore, electrolysers provide a

possible good solution in this kind of systems with high shares of intermittent renewable energy.

## **1.2. Synthetic and biomass based fuels**

The production of synthetic hydrocarbon fuels in future energy systems is a possible solution for reducing oil consumption and carbon dioxide emissions. The advantage of synthetic liquid fuels over hydrogen lies in their similarity to the currently used fossil fuels, so there is no need for the modification of the existing infrastructure. The basis for producing synthetic hydrocarbon fuels is the synthesis gas, which is traditionally produced through processes that consume fossil fuels and emit greenhouse gases such as coal gasification or steam reforming of natural gas. Recycling CO<sub>2</sub> into synthetic fuels would open the door to renewable energy in the transport sector, which was previously not accessible in form of liquid fuels, with the exception of using biomass for producing biofuels.

The focus of this thesis is on synthetic fuels, because of the production process that does not include the usage of fossil fuels or the direct usage of biomass, as well as the potential independence from the geographical and supply related issues of conventional fuels. The main reasons for avoiding the direct usage of biomass in the transport sector, i.e. producing biomass derived fuels, are land use problem, resource use, interference with food supplies, and other impacts on environment and biosphere. With captured CO<sub>2</sub> from atmosphere, the proposed production process of synthetic fuels could enable a closed-loop carbon-neutral fuel cycle.

## **1.3. Analyses of potential applications of electrolyzers**

At present, the transport sector is the only sector in which there have been no significant renewable energy penetrations. It is clear that transport cannot develop along the same path in the future. Hence, the key research question in this thesis is:

“What is the feasibility of using synthetic fuels for reaching a 100% renewable transport sector?”

The main purpose of this thesis is to identify potential pathways for producing synthetic fuels, with a specific focus on solid oxide electrolyser cells which are combined with the recycling of CO<sub>2</sub> to produce synthetic fuels. Two pathways are proposed as potential future solutions for reaching a 100% renewable transport sector. The first pathway entails co-electrolysis of steam and CO<sub>2</sub> and the second one includes hydrogenation of CO<sub>2</sub>. Co-electrolysis is a

combined process of steam and CO<sub>2</sub> electrolysis. Hydrogenation of CO<sub>2</sub> involves steam electrolysis that produces hydrogen which later reacts with recycled CO<sub>2</sub>. The gas mixture products of these processes can then be catalysed into synthetic fuel. Two sources of CO<sub>2</sub>, which is the basis for hydrocarbon fuels, were also considered: carbon capture and recycling as an established technology and air capturing as a perspective future technology which will enable closed-loop CO<sub>2</sub>-neutral fuel cycle.

To complete the feasibility study, an energy system analysis was carried out, which measured the following for each scenario:

- 1) Fuel consumption that indicates which scenario represents the most fuel-efficient solution
- 2) Balancing wind production as an indicator of the system flexibility
- 3) Overall biomass use regarding the land use issue connected with the production of conventional biofuels and the biomass potential, given that biomass is exploited in energy sectors
- 4) Socio-economic costs which can provide relevant information in terms of defining which system has advantages in terms of fuel, operation and annual investment costs.

Analysis is carried out for the transport sector in the Danish 100% renewable energy system for 2050, projected as a part of “Coherent Energy and Environmental System Analysis” known as CEESA project [6]. The chosen reference system for this thesis is Recommendable scenario CEESA 2050.

To conclude, this thesis investigates the overall effect of using electrolysis for the production of synthetic fuels in the transport sector and its potential for integrating fluctuating renewable energy sources in other sectors.

## 2. FEASIBILITY STUDIES

The purpose of this chapter is to explain the principles of feasibility studies and why they are conducted in the first place, furthermore it will provide more about theoretical background and framework for development of these kinds of studies. The chapter is based on literature review [8-10]. There are many different approaches to feasibility studies, but this specific methodology is defined by the Sustainable Energy Planning Research group at Aalborg University [7].

The feasibility study should give an answer to the question: Which alternative is the most feasible for solving a given problem? [9] The results of feasibility studies conducted on the same problem can have different conclusions based on varied premises. There are three main steps in feasibility analysis [Figure 2]. The first step deals with what, for whom and why something should be studied – the so called www-analysis, the second step takes a detailed design of the content of the study and the third step copes with the feasibility study itself and it is the major part of the process.

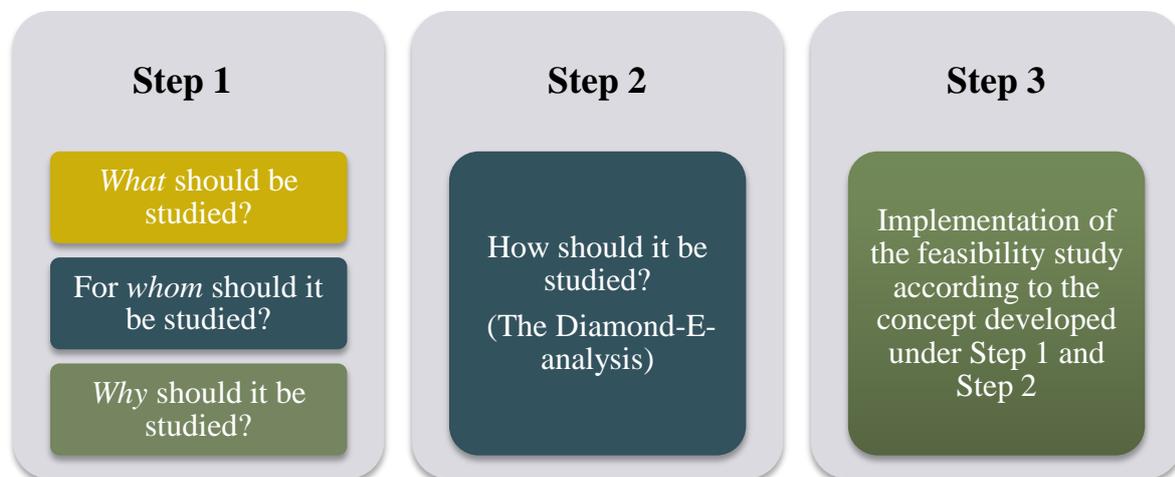


Figure 2. The main steps in a feasibility analysis

Feasibility studies can be applied in both private and public decision making. Two kinds of feasibility studies should be distinguished – the socio economic and the business ones. Socio economic feasibility studies cope with the question whether project is feasible for the society as a whole, while business feasibility studies analyse project from a company side only. However one does not exclude the other, many companies include socioeconomic studies when their project is going to reflect on the society itself.

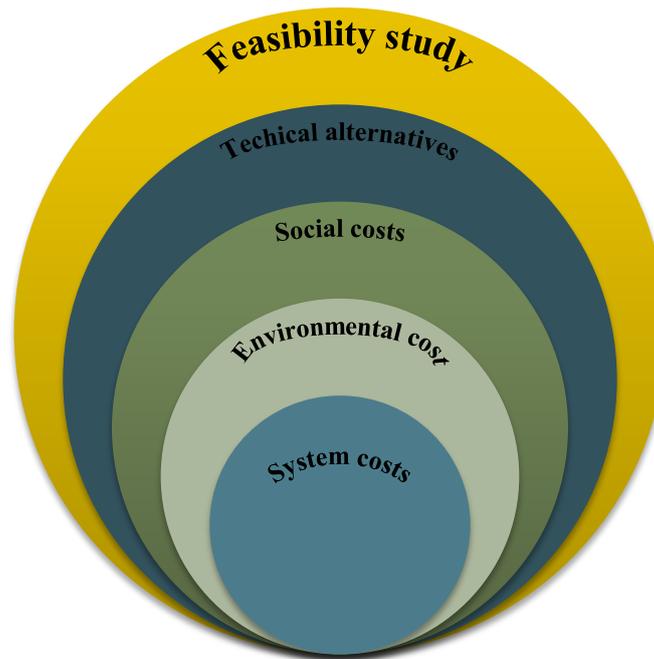


Figure 3. What feasibility study includes

The existing energy system before large implementation of renewable energy sources is characterized by large electricity and heat supply companies along with many different consumers such as households, public and private enterprises.

#### Existing supply system

- Single purpose companies, i.e. production and/or sale of energy services
- Division: heat, electrical, natural gas systems, etc.
- Having investments that are capital intensive and almost 100% asset specific
- Investments in equipment with a very long technical lifetime, often 20-40 years
- Often being organisationally linked to fossil fuel-based systems
- Being consolidated from a capital point of view.
- Being consolidated from a political point of view

The implementation of radical technological changes cannot be based on the solution such as rebuilding the existing energy system by building better power plants or pollution abatement measures. However, it is important to integrate new solutions to existing energy system.

## **2.1. Choice of awareness theory**

The Choice Awareness theory has significance for the implementation of a radical technological change. Radical technological change can be defined as a change of more than one of four elements of technology – technique, knowledge, organization and products.

The theory is strongly connected to a word choice as it can be seen from the name itself. It is important to make a distinction between a true and a false choice. A true choice is a choice between two or more real options, while a false choice can be described as some sort of choice illusion, or in other words no real choice at all. The most famous false choice examples are a Catch-22, Hobson's choice, Morton's fork, Sophie's choice and Dilemma.

The Choice Awareness theory points out that many cases lead to a situation of no choice. This is often present in terms of technological change, which is related to this thesis by implementing renewable technologies in the existing energy system. The theory deals with the societal level. The huge barrier in implementing renewable energy solutions in the first place was the fact that the public was not aware that there was a choice. The state in which an individual, later observed at a collective level, has the feeling or perception that he/she has no choice can lead to fatal consequences. The experience is that if a person has a choice which includes a possibility to say “no”, he/she will be able to think of even better and constructive alternatives.

The collective can be manipulated by individuals or organisations if they convince the society in general that there is no certain alternative or, in other words, if the society has a false choice. Many examples can be seen in the power sector – deciding for building a new power plant. This can be seen as “power” acting, in which an organisation or an institution that needs to make a decision offers no choice - “This power station or none!” This can lead to a collective perception of no choice; although in principle society has a choice at a higher level. The construction of the collective perception of no choice has an important role when making major societal decisions on energy planning. Choice Awareness is therefore crucial for implementing radical technological changes.

The existing institutional setup in many countries may favour established technologies at many levels. The technological solutions differ from country to country and along with the implementation of new technologies there is a need for new types of organisations. A radical technological change to a renewable energy system implies substantial changes and poses a

threat to existing organisations depending on the technologies to be replaced or diminished. Such organisations will not by themselves create and promote the alternatives required to implement this change. It is probable that the existing organisations will use power to protect their interest and respond to threat. The first logical response is the elimination of choice in the public debate and collective perception.

Choice-eliminating activities have been executed at many levels and in various forms. Power theory can be used to identify a systematic way of analyzing the different levels at which such activities are practiced. Definition of power: “Power is seen as the possibilities of actors to attend to their interests in relation to the allocation of goods and burdens in society (material as well as immaterial).” [10] Power can be categorized into four levels: direct power, indirect power, mind-controlling power, and structural power [Figure 4].

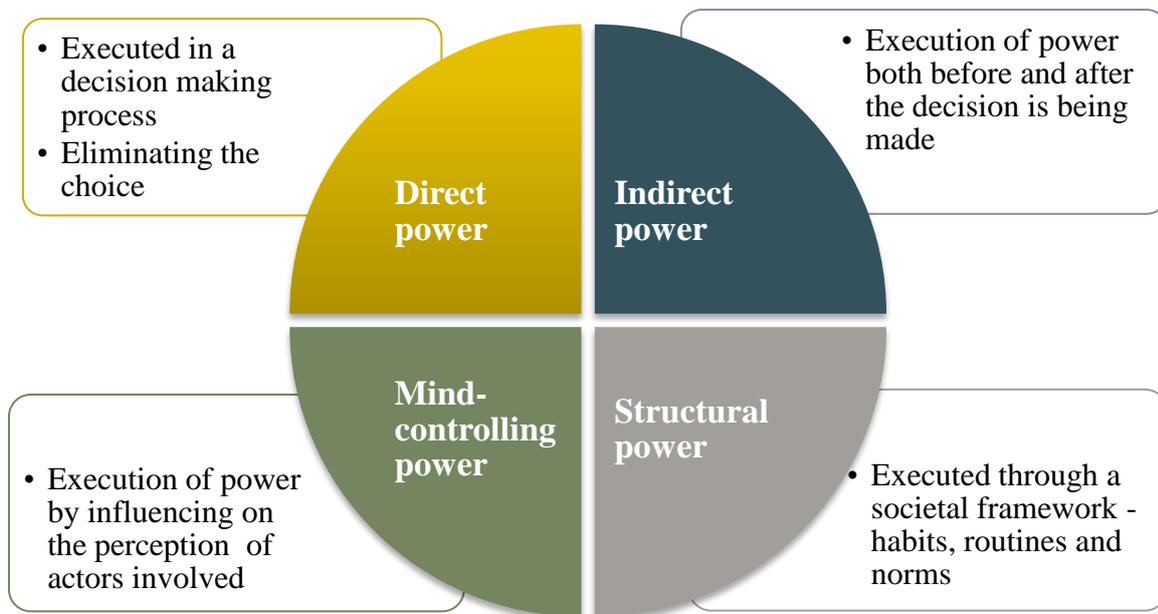


Figure 4. Categorization of power [8]

However, the existing organisations can create certain alternatives, whereas other alternatives are out of their perception. Even if they wished to promote alternatives they would often not be able to implement them within the existing institutional setup. The technological change can be seen as a change from undifferentiated solutions implemented by few single-purpose organisations to differentiated solutions implemented by many multipurpose organisations [10].

### **2.1.1. Two theses**

The concept of Choice Awareness theory includes two theses. The first thesis is based on the observation that often when major societal decisions on energy planning are discussed, society has a perception of no choice. This thesis puts emphasis on the fact that the existing organizations will influence the perception of the society and affect the implementation of radical technological change sought by society. This will hold back the development of new technologies and even eliminate certain solutions while creating a state of no choice from society's perspective but to implement technologies that will save and constitute existing organisations. Usually in these scenarios feasibility studies are designed in a way that new technologies are assessed as not being economically feasible to the society. This is based on an applied neoclassical perception that the existing institutional and technological setup is defined by market. Market, by definition, functions on a principle of identifying and implementing the best solution. This however is constrained on the economical point of view.

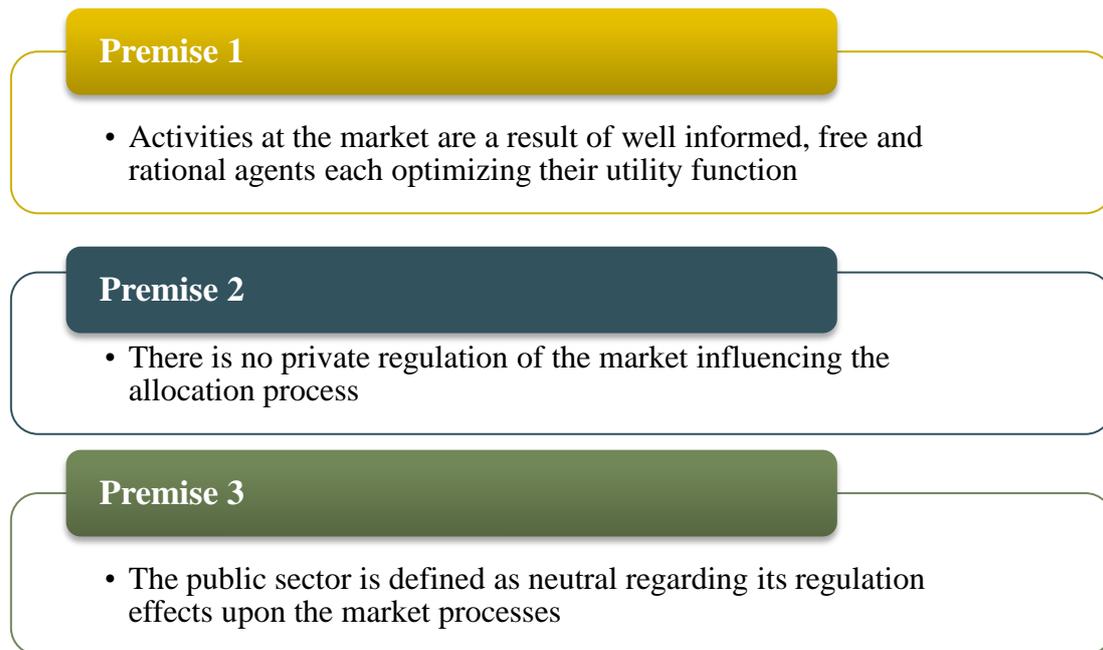
The second thesis of the Choice Awareness theory argues that in such the situation that is explained in the first thesis, society can benefit by raising the awareness that alternatives do exist and that it is possible to make a choice. Awareness can be promoted by debates and decisions on new plans and projects at all levels, by promoting methodologies of feasibility studies that include political objectives and promotions of public regulation measures to advance technologies.

## **2.2. Market economy**

Market economy is formed by a number of market institutions. In Neoclassical economy market institutions are often considered as static and non changeable. When implementing technological change, changes in market institutions are needed.

Neoclassical economy is based on the concept of a free market. The "free market" was described by Adam Smith in *The Wealth of Nations* [11]. The "free market" is not a market without public intervention, but a market where the public regulation in some decisive way acts to establish and maintain the institutional preconditions of the free market [8].

Characteristics of Neoclassical economy are based on three premises [Figure 5]. The combination of these premises has as its consequence that the production at a given point of time can be regarded as optimal [10].



**Figure 5. Premises of Neoclassical economy**

Macro economists are using an optimality premise for energy planning purposes as a precondition of the econometric models. This premise basically assumes that we are living in the best of all worlds and that any change away from this optimum represents socioeconomic costs for society.

This premise is wrong [8]. The reason for this lies in the fact that in econometric models, the economic process eliminates the possibility of systematic institutional mistake. It is therefore important to see the economy as an institutional economy, with a big probability that from socioeconomic aspect it is not optimal at all. Instead of taking the neoclassical economic optimum for planning, public regulation should begin with very concrete analyses of the institutional context, which would result in finding projects which are both economically and environmentally feasible. It should be pointed out that this is not an easy task.

There is an essential difference between a “free market” and a “real market” at a given place and a given time. In a “real market”, “free market” ideology is often used to argue for no public regulation which mainly manifests itself by an argument “let the free market decide”. This argument can be interpreted by the sentence “let us decide”, whereby "us" stands for the largest energy supply companies with only few suppliers. Thereby, feasibility studies and public regulation of “real market” are often influenced by the interests of established energy supply giants. This results in the fact that public planning favours short term solutions that are conservative and support the existing companies.

### 2.3. The procedure of performing feasibility studies

The above conclusions have the following consequences on forming feasibility studies. Economic feasibility studies were explained in detailed in [10].

Socioeconomic feasibility studies should:

- Perform analysis with a very long time horizon in order to find the best solutions relatively independent of existing technical systems.
- Analyse the bindings of existing technical systems. This is especially important under conditions of overcapacity in the energy system
- Analyse the links between the economy of a project, and the future changes of the technical energy system.
- Analyse the links between the economy of the project and the legislation which is necessary for the feasibility of the project.
- Analyse the links between the above institutional sensibility analysis and the political process.

#### 2.3.1. The *www*-analysis

When designing a feasibility study, three steps should be followed [Figure 2] The first step, known as *www*-analysis, answers the questions important for starting a feasibility analysis – *what* should be studied, for *whom* and *why* [8]. It is important to place these questions in context, where the time horizon and time priority in the feasibility is decided upon.

The time horizon is the period within which calculations are made. When dealing with single investments the time horizon is often equivalent to the expected technical life time of the investment. When dealing with energy systems and energy scenario developments the time horizon is chosen in accordance with the specific purpose of the study. When dealing with long time horizons, characteristic of feasibility studies, it is necessary to analyse a broad spectrum of socioeconomic consequences of different energy scenarios.

The following are the steps of *www*-analysis:

**What** - The most frequently conducted studies are single project analyses (power plants, energy conservation measures in an apartment complex, etc.) or energy system analyses. The single project analyses at present are carried out as isolated cases, without

systematic discussion concerning the effect of the projects on future energy scenarios. Single case projects analyses are no longer sufficient, neither when making business nor socioeconomic feasibility studies. Thus it is emphasized that feasibility studies of single projects should include studies regarding the feasibility of the specific investment in relation to scenarios of technical changes in the energy system of which it is going to be a part.

**For Whom and Why** - Feasibility studies can be made for the national government, municipalities, energy supply companies, private companies, etc. The direct purpose of feasibility studies may be a demonstration of the necessary documentation, when deciding which investment to choose among technical alternatives and which implementation strategy to choose among implementation alternatives or when applying for loans.

Figure 6 illustrates the relationship between business economy, socio-economy and public regulation for capital intensive technologies with a long technical lifetime. There are two Situations that can occur in implementing new technologies. In Situation I there are specific conditions in the market and a specific legislation (Public regulation I ). Under these conditions there might be economic conditions favouring the existing technologies based upon extensive use of fossil fuel and the economy in energy conservation might be bad from a business point of view (Business economy I).

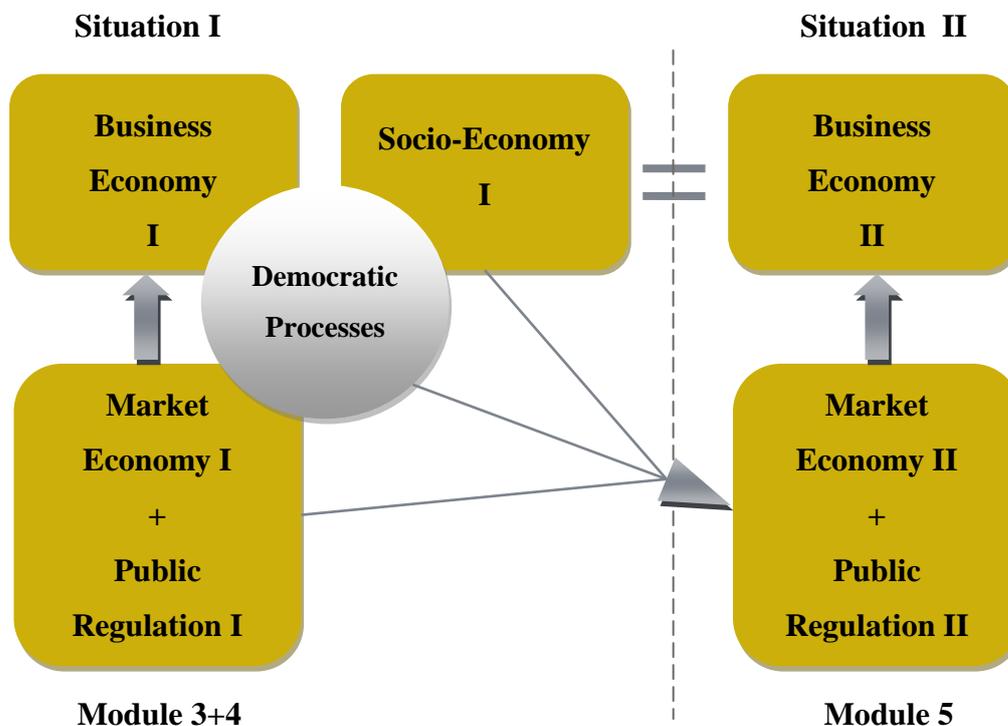


Figure 6. Relationship between business economy, socio-economy and public regulation

However, socioeconomic feasibility studies (Socio-economy I) can show that developing and investing in new technologies could be feasible from society's point of view. This situation can be explained as a situation where what is good for society is not good for business. Situation is then discussed in a democratic process and "Public regulation II" is developed and implemented. This public regulation should assure that what is best from the society's point of view is also best for business (Business Economy II). Situation II represents an ideal situation, where the market companies will act in accordance with what is best for society.

### 2.3.2. *The Diamond-E analysis*

After Step 1, the www-analysis explained above, follows Step 2 i.e. how such analyses should be carried out. A way of systematizing this analysis is to use the Diamond-E framework described in [Figure 7]. The discussion regarding the exact design of feasibility studies may pass through an analysis of each of the areas that are part of framework.



Figure 7. The Diamond-E framework

Third Step is to conduct the calculations of the feasibility study which includes collecting necessary data and information - Socioeconomic analysis. Details about the Diamond-E analysis and Socioeconomic analysis can be found in [8].

## 2.4. Feasibility study of synthetic fuels

The aim of this feasibility study is to enhance the knowledge of the electrolysers as a technology for producing liquid fuels to meet the need for a 100% renewable transport system and to analyse the economic consequences for the society. This thesis is based on the Danish

Government's objective that Denmark must use 100% renewable energy in 2050. It is essential to do a detailed analysis of the transport sector in order to match the demand and to meet the criteria of a 100% renewable energy system in 2050. The purpose of applying this feasibility study is to create alternatives for supplying transport liquid fuels in the future by measuring: primary energy supply, biomass consumption, system flexibility and socio-economic costs.

The methodology for analysing synthetic fuel implementation can be divided into three steps: data collecting, technology and fuel review, energy system analysis and, finally, feasibility study.

Input data for the analysis has been gathered by literature reviewing and by interviewing relevant people for this subject matter. There is very little literature relating to the energy system in this particular area, given that it mostly focuses on materials, performance, and durability of the electrolysis cells as well as the modelling of SOEC stacks.

After collecting all the needed data, possible scenarios were proposed as well as comparable ones. This was followed by reviewing individual stages of the production cycle of synthetic fuels. Mass and energy balances are formed based on chemical reactions of fuel production. A separate energy/mass flow diagram is formed for each pathway outlining the electricity, biomass, CO<sub>2</sub> and water needed for producing 100 PJ of the primary fuel.

Energy system analysis is performed by the use of the freeware model EnergyPLAN. The feasibility study is divided into two analyses – technical and socioeconomic analyses which are both conducted from the perspective of the whole energy system. Fuel consumption is evaluated, the wind capacity integrated in the system in comparison to electrolyser's capacity is determined, as well as biomass consumption. CO<sub>2</sub> emissions are negligible because the system is 100% renewable and this is proven through analysis.

The thesis proposes to evaluate the socio-economic feasibility of implementing synthetic fuels in the transport sector. It is going to be done by calculating socio-economic costs that include costs of fuel, operation and maintenance costs and investment costs in the transport system.

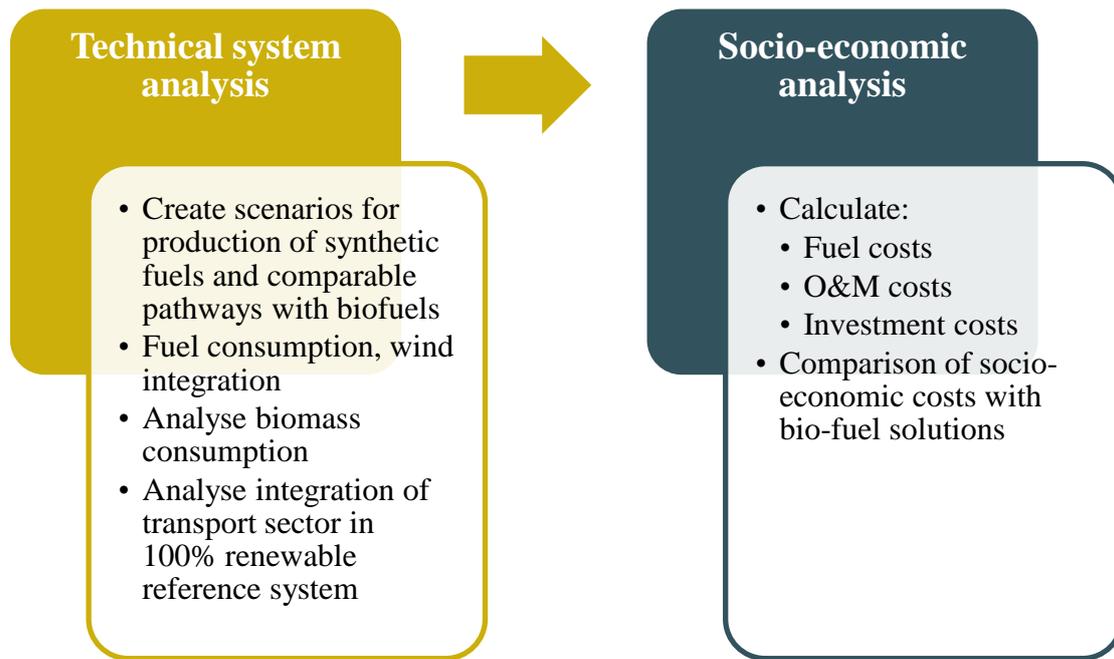


Figure 8. Structure of analysis

Active energy and transport policy is needed for implementing such radical technological change, but the Public regulation part of feasibility study is not included in this thesis.

## 2.5. Limitations

This section describes the broad limitations to the scope of the thesis and limitations in the methodology of the actual research.

Due to the fact that there is very little literature relating to the energy system in this particular area, this caused limitations to input data for modelling. To date, the report “*Technology data for future high temperature solid oxide electrolyser and current alkali electrolysers*” by Mathiesen published as appendix in IDA’s Climate Plan 2050 gives the most comprehensive data for our area of interest. [12]

Related to scenarios, compared to *Biodiesel* scenario which is the most accurate one, due to well-known technology already commercially available, predictions of scenarios that include SOEC that are still on research and development level are based on literature review, today’s predictions on technology development and efficiencies achieved in laboratories.

Due to some uncertainties regarding chemical synthesis, an additional 5% loss is subtracted from electrolyser’s efficiency to account for storage and chemical synthesis losses in case of synthetic fuels scenarios.

As no mass and energy flows existed at the moment of writing this thesis, all mass and energy balances were formed based on the personal knowledge later confirmed during interviews.

Regarding energy system analysis, due to limitations of implementing the production of these kinds of fuels, referring to synthetic fuels, in Transport tab of EnergyPLAN model, detailed explanations are provided in Section 8.1.

### 3. SHIFTING FROM FOSSIL FUELS TO SYTHETIC FUELS

Transport sector energy use is almost entirely depended on oil. Oil is, along with water and gas, one of the three fluids of modern life. Oil is used in virtually every means of transport - road transport, aviation, maritime etc. The amount of oil is limited and the demand continues to increase. Transport sector energy use and CO<sub>2</sub> emissions are strongly linked with the increasing population, as well as the industrial and economic progress.

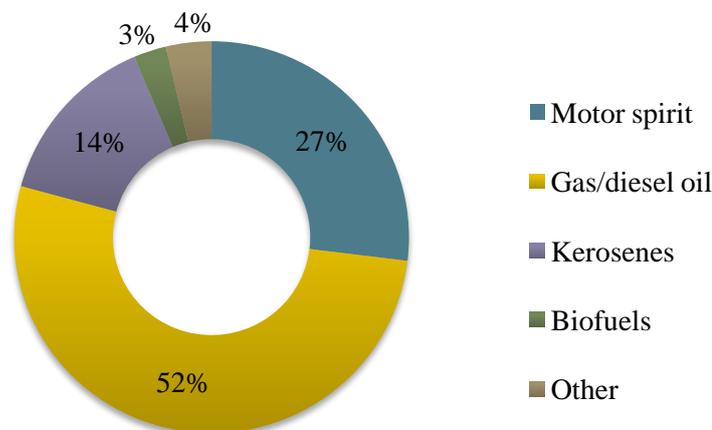


Figure 9. Final energy consumption in transport sector 2008 for the EU-27 [13]

Although oil is pumped in 123 countries, the 20 largest producers provide over 83% of total world production [14]. Reserves are reviewed periodically according to the information obtained during the extraction, the local geology, the available technology, the price of oil etc. Total proven<sup>1</sup> world oil reserves in 2010 were 1383.2 thousand million barrels [15]. Oil consumption is unevenly distributed around the world. Rich, developed countries and those with large oil reserves have the highest consumption rates. Moreover, there is a strong connection between oil prices and global economy; any disturbance in the oil supply results in increasing its price [16]. From 1971 to 2007, global transport energy use rose steadily by between 2% and 2.5% a year, closely paralleling growth in economic activity around the world. Transport energy use has more than doubled since 1971, and has been dominated by road transport [17].

<sup>1</sup> Proven reserves are those reserves claimed to have at least 90% confidence of being recoverable under existing economic and political conditions, with existing technology.

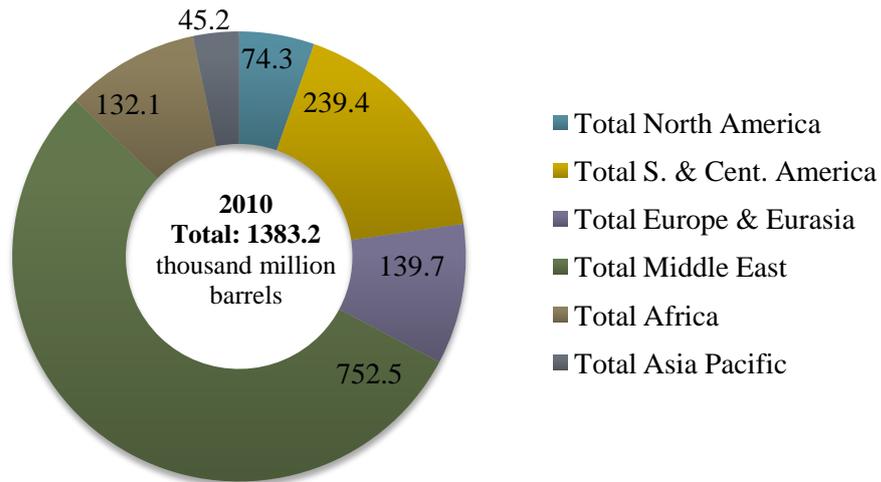


Figure 10. Proven oil reserves in world [15]

Shifting from oil to other transport fuels is going to be a difficult process. Gasoline, diesel and other petroleum products have provided energy for the transport sector for over a century. The reasons for this lie in their high energy density and ease of handling. All transport infrastructures are adjusted for liquid hydrocarbons. The continued need for hydrocarbons production calls for their sustainable production. In 2005 CO<sub>2</sub> emissions in the transport sector were 23.3% and there are strong indicators that this rising trend is going to continue due to the fact that transport is the only sector that has had steadily rising emission shares. From 1980 to 2004 a rise in global CO<sub>2</sub> emissions was 95% just in road transport [18].

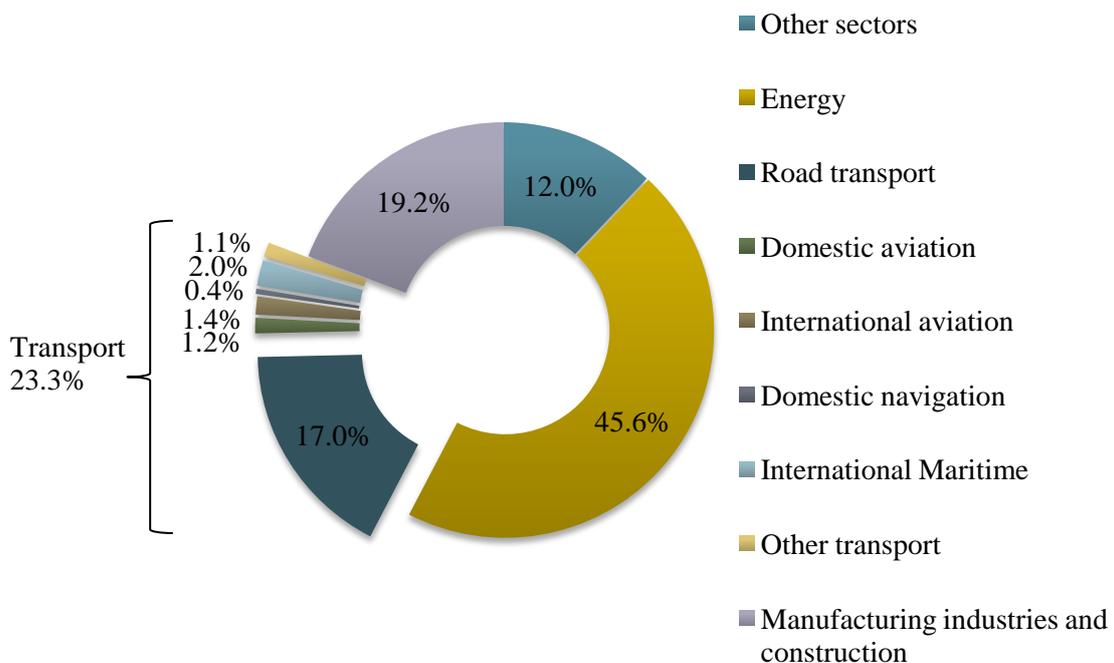


Figure 11. Global CO<sub>2</sub> emissions from fuel combustion, 2005 [18]

Shifting from oil to other fuels is not just desirable, it is necessary for a number of reasons: resources are limited, geographic distributions are uneven and the greenhouse gas emissions must be reduced. With a rapidly growing demand in the last decades, the infrastructure relied on liquid fuels and different kinds of modes and needs; the transport sector represents a challenge for implementing renewable energy sources.

As stated above, the motive for choosing synthetic fuels as the focus of this thesis lies in the advantages of the production process. The term 'synthetic fuel' is defined in many different ways and it may include different types of fuels. Regarding that, it is important to point out from the start what is meant by 'synthetic fuels' in this thesis. Here, the word synthetic relates to fuel which is made by using electrolysis as a base process and a source of carbon to produce liquid hydrocarbon 'synthetic' fuels. Even though biomass is not a direct fuel source, by using carbon capture and recycling at a biomass power plant, carbon source is provided for electrolysis.

Using this kind of fuels could be a solution not just for lowering the CO<sub>2</sub> emissions, but for providing geographical independence and solving supply related issues of conventional fuels and biofuels. With captured CO<sub>2</sub> from the atmosphere, the proposed production process of synthetic fuels could enable a closed-loop carbon-neutral fuel cycle.

### **3.1. Synthetic fuels vs. biofuels**

Biomass is a preferable replacement for fossil fuels not only in the transport sector but also in heat and power services. Biomass use became more competitive due to the rising prices of fossil fuels. The reason why biomass is interesting for the transport sector is that it can be converted to high density fuels and it is seen as a carbon feedstock source. Along with electricity, biofuels are proposed as a long term solution in this sector [3, 19]. The potential demand for biomass is relatively high compared to the amount of biomass that can be used sustainably. Biomass requires one to two orders of magnitude more land than other energy sources to provide a given amount of energy.

Due to the set up goals for 2020, followed with ambitious government policies and many subsidies for this kind of fuels, biofuel<sup>2</sup> production rose in the last 10 years. The largest

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<sup>2</sup> The term biofuel refers to liquid and gaseous fuels produced from biomass, including the technologies for hydrogenation of biomass.

biofuel producers are Brazil and the United States, and the dominant biofuel product is ethanol. Biofuels account for only around 2% of the total transport fuel today [19].

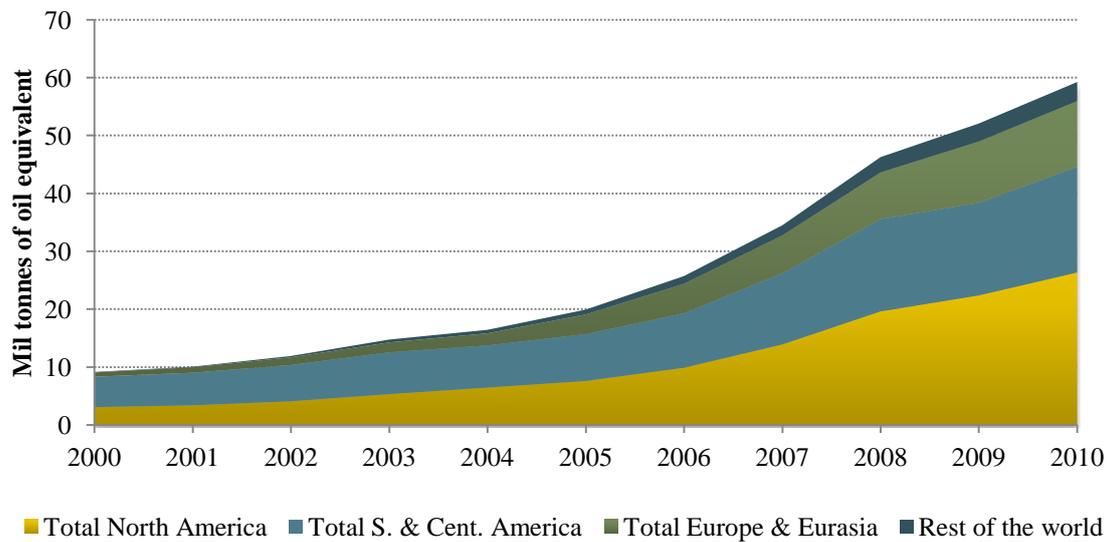


Figure 12. Biofuels production in world [15]

The main trigger for the growing production of biofuels was the concern about global greenhouse gas emission levels as well as energy security, because of the transport sector's dependence on oil. There were some concerns about the extent to which biofuels really influence emission reductions.

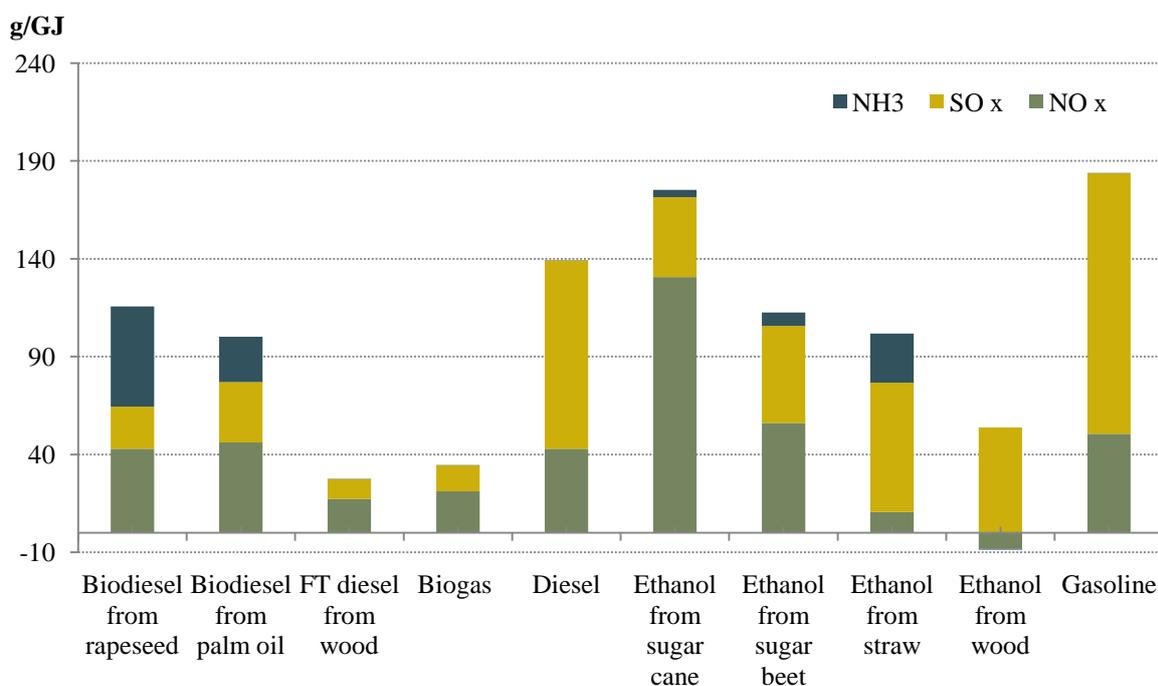


Figure 13. 2020 emission for diesel and gasoline replacers and their fossil reference [20]

Air pollution effects from biofuels supply chains [Figure 13] were recently analysed in the 'BOLK II' study [21]. It can be seen that all biodiesel chains, including biogas, have in general lower  $\text{SO}_x$  emissions than the fossil diesel. On the other hand, biodiesel chains have worse  $\text{NH}_3$  emissions than fossil diesel, particularly those produced from rapeseed, because of the use of fertilisers. The Fischer-Tropsch diesel and biogas reduce all stated emissions in relation to conventional diesel. In the case of bioethanol, ethanol from sugar cane and sugar beet has higher  $\text{NO}_x$  and  $\text{NH}_3$  emissions than the fossil reference. Even though the  $\text{NH}_3$  emissions for sugar cane and sugar beet are considerably lower than the ones for biodiesel from rapeseed and palm, they are higher in comparison to gasoline.  $\text{NO}_x$  emissions for ethanol produced from sugar cane and sugar beet are significantly higher than all biodiesel chains, including fossil diesel and gasoline. Ethanol from wood chips has lower emissions than reference gasoline. Negative emissions are caused by excess electricity generated in the ethanol conversion process, which replaces electricity from the grid.

Concerns about emission reductions of biofuels are mainly caused by direct and indirect land-use changes for conventional biofuel production in correlation with emissions [22-24]. This was followed by a public debate over whether conventional biofuels can harm food security and this still remains a critical topic for making biofuel policies.

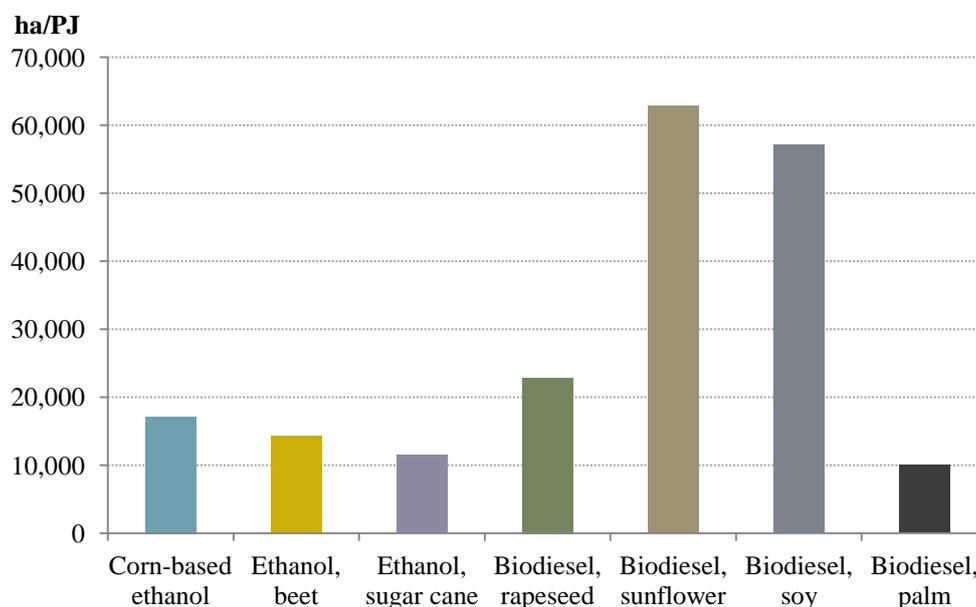


Figure 14. Land-use for different kind of biofuels [17]

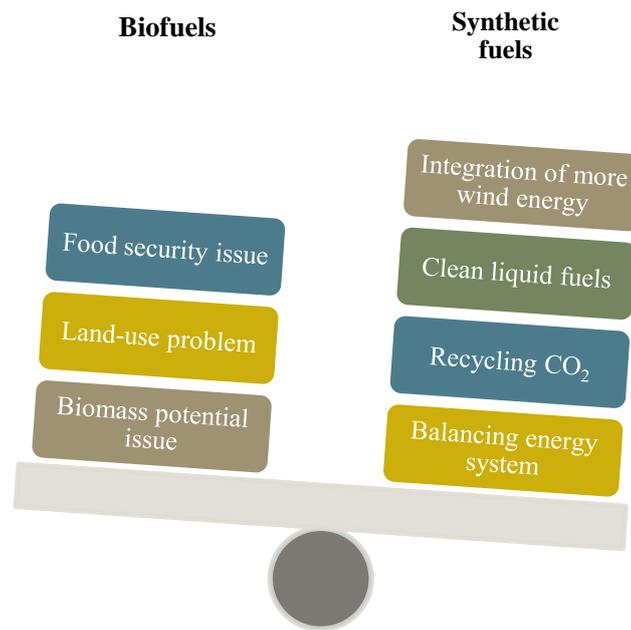
Conventional biofuels are facing social and environmental challenges, mainly because of the use of food crops in their production, which could lead to an increase in food prices and

possibly to indirect land-use change. The potential influences of biomass on food prices emerged during the food crisis in 2007 and 2008, when market prices of food and feed crops almost doubled [4]. In combination with a higher energy price, an increase in fertilizer prices and transport costs, followed by dollar weakness, food prices rose by about 35-40% from January 2002 until June 2008. The latter caused 25 to 30% of this food price growth, and the remaining 70 to 75% were caused by biofuels and the related consequences of low grain stocks, large land use shifts etc. [25]

Advanced biofuels could be seen as a solution to these social risks, land use and environmental issues, due to questionable reductions in greenhouse gas emissions by using conventional biofuels. The advantage of advanced biofuels is that their production processes rely on non-food biomass such as organic waste, forestry residues, grass energy crops and algae. The most promising advanced biofuel is the one that uses algae as feedstock.

Recent studies show large differences in biomass potential, with the potential interval ranging from 75 - 1500 EJ/year from the most pessimistic to the most optimistic assessments [26]. It should be emphasized that all of these studies concern the maximum potential independent of any barriers for harvesting the potential. Studies that include market and economic oriented consideration report lower biomass potential in the interval from 75 - 150 EJ/year. Studies that consider only biomass residue part, i.e. the biomass potential not in competition with food production, reported the interval from 15 to 100 EJ/year, which corresponds to around 2–15% fossil substitution in 2030.

Considering the latter, biomass is not likely to be a sustainable energy source at a large scale production, with the possible exception of algae and the hydrogenation of biomass. Future energy systems will require an efficient use of land and resources, low impacts on environment. In order to step out from the closed loop of un-sustainability, it is necessary to plan ahead.



**Figure 15. Synthetic fuels vs. biofuels**

Synthetic fuels, together with the electrification of the transport sector, could be seen as a way for the future transport sector to avoid the direct usage of biomass and to step out of fossil fuel dependence. The implementation of electrolyzers in the transport sector does not only provide synthetic fuels for transportation, it also provides an option for regulating the energy system. Therefore, electrolyzers could be a good solution for balancing a system with high shares of renewable sources, which is important due to their intermittency.

## 4. TYPES OF ELECTROLYSERS

Electrolysers are powered by electricity that forces electrochemical process in which substances are decomposed by current that is passing through them. Fundamentals of electrolysis were discovered in the 1800s but it continued to expand till present time. During the last twenty years electrolysers are in a phase of more intensive research. The chlorine-alkaline electrolysis, which is worldwide the largest source of electrolytic produced hydrogen, has been in commercial use for about 100 years.

The most important scientists in the history of this specific area are William Nicholson and Anthony Carlisle. They accidentally discovered electrolysis in 1800 by replicating Volta's battery experiment [27]. Electrolysis would not have been discovered if a few years earlier, more precisely in 1783, Galvani had not discovered the physiological action of electricity and demonstrated the existence of natural electric current in animal tissue. Galvani used the term "animal electricity" because he believed that the activation of muscles of his specimens was generated by an electrical fluid that is carried to the muscles by the nerves. As Galvani's peer and intellectual adversary, Volta disproves his associate's theory on the galvanism phenomenon. Volta, essentially, objected to Galvani's conclusions about "animal electric fluid", but the two scientists disagreed respectfully and Volta coined the term "galvanism" for a direct current of electricity produced by chemical action. In 1800, Volta announced a new electrical device, the Voltaic Pile, an early form of battery, and demonstrated that metals and chemicals in contact produce electrical current. William Nicholson and Anthony Carlisle decided to replicate Volta's experiment a few weeks later, and in order to overcome a problem they added a drop of water to the circle. They were surprised to note the appearance of a gas soon shown to be hydrogen. They discovered electrolysis.

All electrolysers consist of a core cell with two electrodes - anode and cathode separated by electrolyte. The electrolyte closes the electrical circuit by enabling protons to cross between the anode and the cathode while creating voltage. While protons move between the electrodes, electrons cross to the anode section in an external circuit to avoid a short circuit inside the cell. Specific reactions in electrolysers depend on the type of fuel cells. Different types of fuel cells have different electrodes as well as electrolyte. Electrolyte can be a liquid - alkaline or acid, or a solid - polymer electrolyte or solid oxide. An electrolysis cell dissociates water

and/or carbon dioxide using electricity in a single step, and the products are released separately in the anode and cathode compartments of the cell.

**Table 1. Electrolysis cells**

| Type of electrolysis cells | Alkaline                      | Acid                         | Polymer electrolyte                       | Solid oxide                       |
|----------------------------|-------------------------------|------------------------------|---|-----------------------------------|
| Charge carrier             | OH <sup>-</sup>               | H <sup>+</sup>               | H <sup>+</sup>                            | O <sup>2-</sup>                   |
| Reactant                   | Water                         | Water                        | Water                                     | Water/CO <sub>2</sub>             |
| Electrolyte                | Sodium or Potassium hydroxide | Sulphuric or Phosphoric acid | Polymer                                   | Ceramic                           |
| Electrodes                 | Nickel                        | Graphite with Pt, polymer    | Graphite with Pt, polymer                 | Nickel, ceramics                  |
| Temperature                | 80°                           | 150°                         | 80°                                       | 850°                              |
| Produced fuel(s)           | Perfectly pure H <sub>2</sub> | Pure H <sub>2</sub>          | Pure H <sub>2</sub> or CH <sub>3</sub> OH | H <sub>2</sub> , CO, hydrocarbons |

The alkaline electrolysis is well established technology already available on a large scale. The reason why these types of electrolyzers are not the one of interest is because of their lower efficiency compared to solid oxide electrolyser cells, along with the fact that they can only be used for steam electrolysis. However, the alkaline electrolyzers could be a possible transition solution because solid oxide electrolyser cells, which are the only electrolyser technology consider in this thesis, are still not commercially available.

#### **4.1. Solid Oxide Cells and Solid Oxide Electrolyser Cells (SOEC)**

This section provides a brief introduction to high temperature electrolysis and solid oxide electrolyser cells, as the use of this kind of electrolyzers is a specific subject of the thesis.

Solid oxide cells can operate reversibly as a fuel cell or as an electrolyser. The ability to operate reversibly depends only on cell geometry and has nothing to do with electrochemistry. The difference between the two modes of operating is that in a fuel cell mode, cell converts the chemical energy from a fuel into electricity through a chemical reaction and in electrolysis

mode; cell produces fuels such as  $H_2$  and  $CO$ . The topic of interest in this thesis is the electrolysis mode.

In the electrolysis mode there is need for a reactant for just one electrode, which can be steam and/or carbon dioxide, but sweep gas of air or oxygen is often supplied to the other electrode. Voltage is applied across the cell. The electrode at which the reduction of reactants or intermediates takes place is called the cathode. The anode is the electrode at which the oxidation of reactants or intermediates takes place [27]. The voltage drives the electrolysis of the  $H_2O$  and/or  $CO_2$  by removing an oxygen atom from these oxides at cathode, which is then transported by electrolyte as an oxygen ion to the anode, where the oxide ions recombine to produce gaseous oxygen. As a result,  $H_2$  and/or  $CO$  are produced. A gas mixture that contains varying amounts of carbon monoxide and hydrogen is called synthetic gas or shortly syngas. Syngas can be reformed into other fuels, such as methane or different kinds of liquid hydrocarbons. The process that combines steam and  $CO_2$  electrolysis is called co-electrolysis.

The advantage of solid oxide electrolyte is that it conducts oxide ions, so it can oxidize  $CO$  and reduce  $CO_2$  in addition to  $H_2/H_2O$ . This cannot be done with other types of cells, like proton exchange membrane (PEM) or alkaline cells, because their electrolytes conduct protons ( $H^+$ ) and hydroxide ions ( $OH^-$ ) respectively.

High temperature electrolysis has both a thermodynamic advantage and an advantage in reaction rates. One of the benefits of the high temperature electrolysis is that part of the energy required for splitting reactants is obtained in the form of high temperature heat which enables the electrolysis to occur with lower electricity consumption. The electrolysis process is endothermic e.g. it consumes heat. High temperature electrolysis thus produces almost no waste heat, resulting in very high efficiency, significantly higher than that of low-temperature electrolysis. High temperature results in faster reaction kinetics, which reduces the need for expensive catalyst materials. Thus, in comparison with low temperature electrolysis, which uses precious materials, high temperature electrolysis enables relatively cheap electrode and electrolyte materials.

Carbon dioxide and water electrolysis, as well as co-electrolysis of  $CO_2$  and  $H_2O$  using solid oxide cells, was first demonstrated in the 1960s under NASA contracts. Studies were carried out for reclaiming oxygen from expired carbon dioxide during prolonged space missions. The first high temperature electrolysis project which was not related to space investigation was the

HOT ELLY project in Germany, initiated in 1975 [28]. In the early 1980s, Dönitz and Isenberg reported on solid oxide electrolysis cells that used basically the same electrolyte and electrode materials that are still used for the state-of-the-art SOECs [29].

There are several current research and development projects on SOEC in Europe, and the main research centres for SOEC are located in Denmark [30, 31]. While water electrolysis was highly investigated, electrolysis of CO<sub>2</sub> was reported on a smaller scale [32].

If steam and CO<sub>2</sub> electrolyses are combined in a process called co-electrolysis, the produced synthesis gas can be catalyzed into various types of synthetic fuel. Co-electrolysis is relevant for the production of CO<sub>2</sub> neutral synthetic fuel. High operating temperature and high pressure, which provides further efficiency improvement, enables the integration of catalysis of the synthetic gas to synthetic fuel. The heat generated in the catalysis reaction can be utilized for steam generation, which means the heat reservoir becomes more or less superfluous [27].

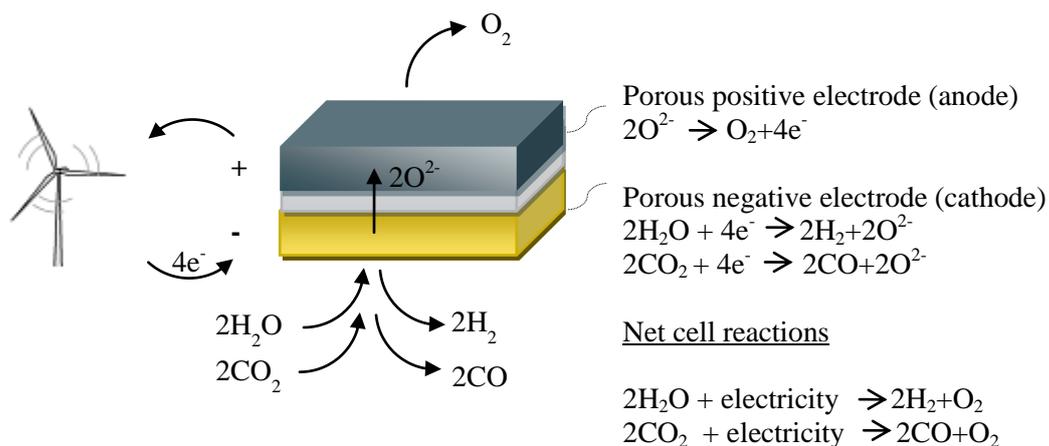


Figure 16. Electrolysis reactions

The advantages of solid oxide electrolyser cells are the potential for great fuel production rates at high efficiency, low material costs and the possibility of co-electrolysis of H<sub>2</sub>O and CO<sub>2</sub>. The main disadvantage of SOECs is the durability of the cell - durable performances at high current densities remain to be proven.

## 5. PRODUCTION CYCLE OF SYNTHETIC FUELS

Chapter 3 indicated the advantages of synthetic fuels in comparison to biofuels and identified synthetic fuels as a promising sustainable carrier which can be used in the existing infrastructure with minor changes. Different energy carriers for transportation require different primary energy consumption and have diverse technology requirements for their implementation. Fuels have been prioritised according to the above characteristics. After identifying preferable fuels, individual stages of the production cycle of synthetic fuels are reviewed, including details about the individual steps of the full production cycle.

### 5.1. Prioritisation of fuels

Direct electrification is the most energy efficient form of transport. Electrification can provide energy security, as it can be generated by a wide variety of means. Electrical vehicles are significantly more energy efficient than petrol or diesel vehicles. More precisely, an electrical motor is 4 to 5 times more energy efficient than a conventional internal combustion engine. This means that even if the electricity source is generated from fossil fuels, electrical vehicles provide a reduction in overall energy consumption over conventional vehicles. Moreover, this means that electrical vehicles can overcome the much greater energy losses that occur during electricity generation. The high efficiency of the electrification, therefore, results in a higher net energy balance and lower life-cycle GHG emissions than the other energy carriers for the transport sector. An electrical engine is also quieter than internal combustion engines and, thus, the noises in the transport sector could be reduced.

With the decarbonisation of the power sector by shifting away from fossil-based power stations and moving more towards renewable energy sources, electrical vehicles will, in the future, provide a further increase in energy efficiency. Unfortunately, many transport subsectors are not suitable for electrification and will continue to rely on liquid fuels as a result of limited energy storage, power and weight issues e.g. long distance transportation, such as trucks, aviation and maritime transport [33].

Apart from electrification, the only other proposed solution for achieving a 100% renewable transport sector has so far been the use of biofuels that can cover subsectors that are not suitable for electrification. As it can be seen from the Danish case, bioenergy potential is much lower than wind potential [Figure 17].

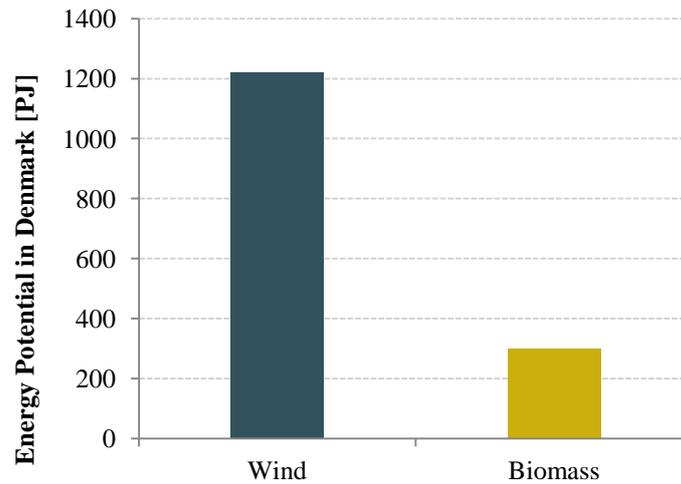


Figure 17. Wind and biomass potential in Denmark [34]

Biofuels production represents a great concern in renewable energy systems, mainly due to the land use problem which was elaborated before. Even though the land use problem is obvious, many biofuels technologies are well established on the market, primarily because they can be used directly or with slight changes in the existing combustion engines that are available on the market. Many fuels are subsidized in order to achieve the set up goals of 10% of biofuels in the transport sector by 2020 in the European Union. All EU members have either quota obligation and/or tax exemption for implementing biofuels [20]. Moreover, related  $\text{NO}_x$  and  $\text{NH}_3$  emissions of biofuels are not lower for all types of biofuels in comparison to those of reference fossil fuels. As it can be seen from Figure 18, in comparison to wind average biofuel production requires approximately 30 times more land area for producing the same energy [6].

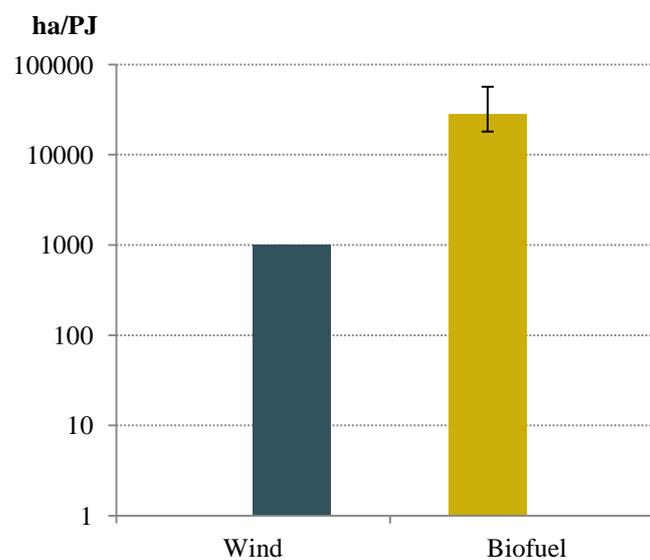


Figure 18. Required land use per 1 PJ of produced fuel

Even though electrification has the priority, it cannot be used for all kinds of transport and there is a need for liquid fuels. The conversion of electricity into fuel in the form of synthetic fuels could be beneficial in the future transport sector. The main advantage of electrolysis in the production of synthetic fuels lies in the fact that output gas can be catalyzed into various types of fuels. Synthetic fuels overcome land-use problems and are not interfering with food supply issues. Moreover, in their production there is no direct usage of biomass at all. Furthermore, the production of synthetic fuels relies on electricity for driving the electrolysis process in electrolyzers that can be used to balance intermittent energy production from renewable sources.

In this thesis, methanol and DME are chosen as the most promising types of fuels, primarily due to well know chemical synthesis for producing these kinds of fuels and the possibility of their almost direct application into existing internal combustion engines. Although methane is often considered as an easiest fuel to convert from syngas, it is not included in the thesis, because it is assumed that the application of methane is too expensive as a result of the fact that the existing infrastructure is utilised for liquid fuels [6].

### **5.1.1. Methanol**

Methanol is well known fuel and the purpose of this subsection is to provide a condensed overview of the most important facts about methanol [35-46].

Methanol is the simplest and lightest of alcohols, with the lowest carbon content and highest hydrogen content of any liquid fuel (chemical formula  $\text{CH}_3\text{OH}$ ). It is a colourless, tasteless and poisonous fluid. At ambient conditions methanol is in liquid phase. The primary source for producing methanol is synthesis gas and it is nowadays based on the process of steam reforming of natural gas. In terms of its chemical formula, methanol is extremely useful as a hydrogen carrier fuel, since it is packed with hydrogen and has no carbon to carbon chemical bonds; it is easy to break down for obtaining energy [35].

Methanol is most suitable for application as a petrol substitute in Otto engines due to its high octane rating. Methanol's volumetric energy density is about half of petrol's and it is not completely compatible with engine materials, and this needs to be taken into account. Methanol has a higher flame speed than gasoline, resulting in higher efficiency as well as a higher latent heat of vaporization.

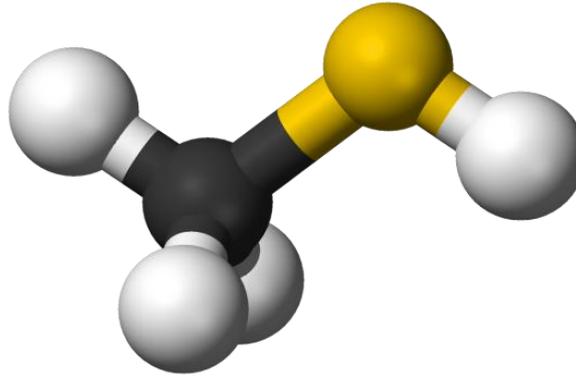


Figure 19. Methanol molecule (black-carbon, yellow-oxygen, white-hydrogen)

Methanol can be blended with petrol up to 10-20% without the need for engine or infrastructure modification [35]. Methanol burns with an invisible flame; it is poisonous and, consequently, additional safety measures need to be taken for handling this fuel. The problem with blending it with gasoline is water presence; even 0.1-0.2% of water can cause a separation of the methanol and gasoline mixture into gasoline and water-alcohol phases.

Another issue related to using methanol is methanol's corrosivity to some metals, particularly aluminium. Although it is a weak acid, methanol attacks the oxide coating that normally protects aluminium from corrosion. This represents a problem due to the fact that nowadays modern engines contain large amounts of aluminium.

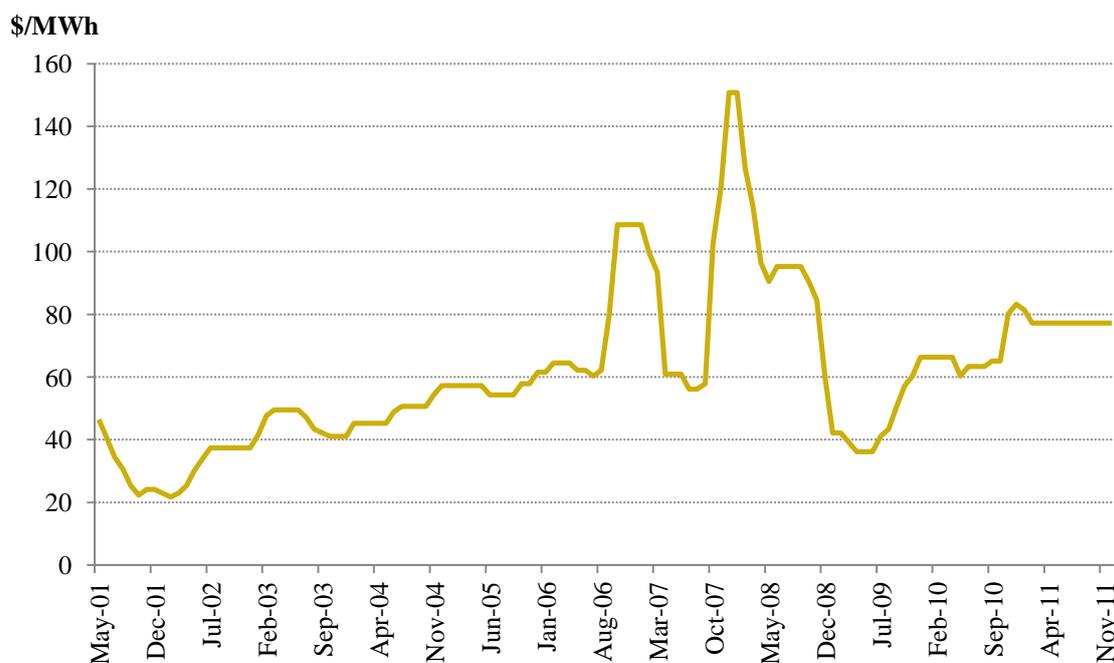


Figure 20. Methanol prices [37]

Burning methanol as a transportation fuels reduces the emission of nitrogen oxides and volatile organic compounds that form “smog”. The only toxic component of the methanol burning is formaldehyde, which means that methanol has lower reactivity than gasoline in the atmosphere. Methanol fuel also does not contain highly carcinogenic BTEX additives that can be found in gasoline. Compared to gasoline, methanol is a safer and more environmentally friendly fuel. Methanol is safer than gasoline in terms of fire security. Methanol burns 75% slower than gasoline, and methanol fires release heat at only one-eighth the rate of gasoline. Methanol vapours must be four times more concentrated in air than gasoline to ignite [38].

Methanol flexible fuel vehicles were available in the United States from the mid-1980s to the late 1990s [39]. These types of vehicles were capable of running on any combination of methanol and gasoline in the same tank, up to a blend of 85% methanol and 15% unleaded gasoline, shortly known as M-85. These vehicles can be used as a substitute for petrol vehicles in the transition period to pure methanol vehicles. The advantage of these vehicles is the fact that they can be operated by conventional petrol or any mixture between M85 and pure petrol [43]. Presently, there is no production of methanol-capable vehicles in the United States.

China is currently the leader in using methanol for transportation. In 2007, China's Committee on Standardization requested three methanol standards [41]. Presently, five different methanol gasoline mixtures are available on the market - M5, M10, M15, M85 and M100 [39]. In Europe, the implementation of methanol fuels has been limited to light blends. The world's first commercial biomass to methanol plant, VärmlandsMetanol AB, is going to be built in Hagfors, Sweden. Methanol will be produced there by the conversion of the syngas which results from gasified forest biomass residues. The planned start of production is 2014/2015 [46].

Compared to fossil petrol, methanol's performances can be summarized in following benefits:

- Lower exhaust emissions
- Safer in terms of fire security
- Lower emissions of nitrogen oxides and volatile organic compounds
- Low CO<sub>2</sub> emissions
- Low engine noise
- Lowest carbon content
- High octane rating

### 5.1.2. DME – dimethyl ether

The purpose of this subsection is to provide a condensed overview of literature about DME which is relevant for this thesis [44, 47-51].

Dimethyl ether, shortly DME, is a clean energy carrier with low environmental impact as a result of the combustion that does not generate sulphur oxide or soot. DME is a liquefied gas with similar characteristics to those of liquefied petroleum gas so it can be used as a domestic sector fuel or transportation fuel. DME is in the gaseous state at standard atmospheric conditions but at higher pressures it condenses to liquid phase. Gaseous DME is denser than air, while liquid DME has a density two thirds that of water [47].

DME is often characterized as one of the most promising alternative automotive fuel solutions among the various renewable and low-carbon fuels as it is an environment-friendly fuel that does not produce much pollution during combustion. DME is a substitute to diesel fuel due to its high cetane number 55 – 60 (fossil-derived diesel has around 45) and good auto ignition qualities [48]. Therefore, DME presents an ideal fuel for the highly efficient diesel process as it can be used in diesel engines with only few modifications.

DME has high oxygen content without C-C bonds in the molecular structure; along with low auto-ignition temperature and almost instantaneous vaporisation, this enables almost smoke-free combustion. DME also has ultra low exhaust emission, nearly no NO<sub>x</sub> emissions and low CO<sub>2</sub> emission as a result of using lubrication oil. A demonstration showed that engines running on 100% DME have smoke free combustion, while engines using a DME/diesel blend exhibit a significant reduction of soot [48].

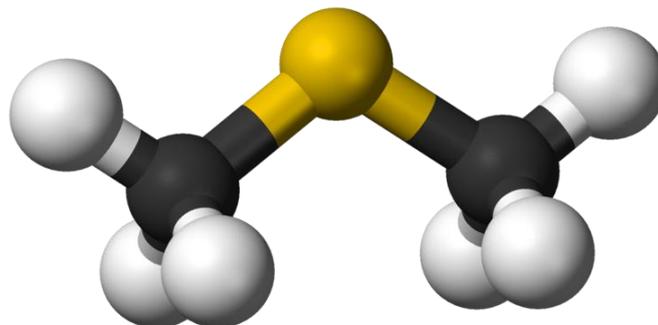
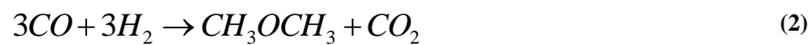


Figure 21. Di-methyl ether molecule (black-carbon, yellow-oxygen, white-hydrogen)

The production process of DME is very similar to that of methanol. DME can be produced from pure methanol in a process called catalytic dehydration, which separates the water from methanol (1) or by direct production from synthesis gas (2).



In contrast to methanol, DME is not corrosive to metals and it is not poisonous, but it is not compatible with most elastomers. DME is favoured more than methanol mainly because it is a replacement for diesel fuel, so it can be used in the highly efficient diesel process. DME has low viscosity and, therefore, it needs a lubricity improver to insure normal service to the injection system.

The first DME fuelled heavy vehicle was developed by Volvo as a part of the development project in the period of 1996-1998. The aim of the project was to demonstrate the low emissions and high efficiency of using DME in diesel engines. In 2005 Volvo launched the second generation of DME trucks fired by DME gas. These engines are characterized by a low-pressure, common rail system, with an injection pressure less than 20% that of an equivalent diesel engine [49]. The technology is also available on a bus scale in the European Union, Japan and China.

In Sweden, significant efforts are put into the production of bioDME and biomethanol. The hub of the BioDME project is the energy technology company Chemrec's pilot plant for DME production in Piteå, inaugurated in 2010. The first bioDME and biomethanol were produced in July 2011 [50]. As part of the same project, Chemrec is building another plant in Domsjö, with a plan to start the production in 2015.

Compared to fossil derived diesel, DME's performances can be summarized in following benefits:

- Higher cetane rating
- Smokeless combustion, low CO<sub>2</sub> and 90% reduction of NO<sub>x</sub> emissions
- Aftertreatment devices are unnecessary
- Low engine noise
- Ignition characteristics equivalent to diesel engine performance

## 5.2. Production of synthetic fuels

This section will explain individual stages of the production cycle of synthetic fuels, including details about the individual steps of the full production cycle.

Concepts of carbon recycled liquid fuels are not novel. They were first mentioned during the oil crisis in the 1970s by Steinberg and Dang [52-56] that have proposed a pathway for CO<sub>2</sub> free synthetic fuel that involved ambient air capturing, water electrolysis and synthesis of fuel. All energy needed for this system is supplied by nuclear fission or fusion. Many different concepts were explained in different publications during the last decades, but it appears that returning to the beginnings is going to be the probable future solution.

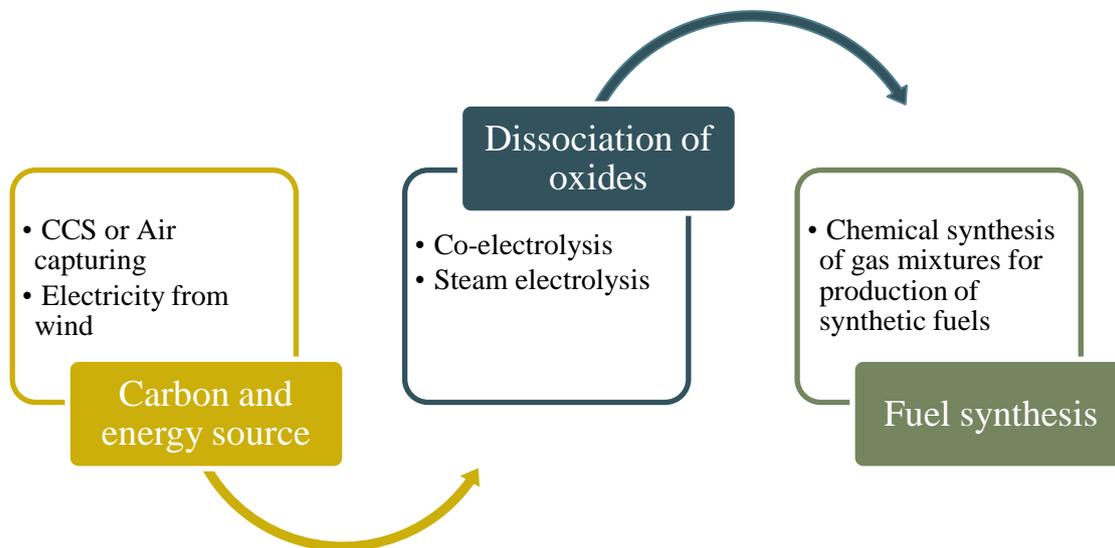


Figure 22. Production of synthetic fuels

The concept of carbon capturing and recycling is important not just because of the issue of global warming, but also in order to achieve 100% renewable systems. This concept enables the production of sustainable fuels that can be used in transport sector. Two carbon sources are proposed - CCR from energy sector or air capturing as a promising future technology.

Pathways are divided into three steps [Figure 22]. Energy source drives dissociation of oxides, either H<sub>2</sub>O or both H<sub>2</sub>O and CO<sub>2</sub>, which results in gas mixtures that are in the last step catalyzed to fuels.

### 5.3. Carbon and energy source

#### 5.3.1. Carbon source

The production of hydrocarbon liquid fuels, as its name suggests, requires a carbon source. Carbon can be provided from carbon capture and storage options or from ambient air. There are currently three known methods for carbon capture from the existing power plants or industrial processes [57]:

- post-combustion
- pre-combustion
- oxy-fuel

*Post-combustion capture* stands for removing the CO<sub>2</sub> from flue gases produced in the combustion process just before releasing them into the atmosphere. This capturing technique uses a chemical solvent that can be recycled after releasing CO<sub>2</sub> for compression and transportation.

*Pre-combustion capture* is a concept which refers to extracting carbon from fuel before burning. This method uses a gasification process which will, as an outcome, produce a mixture of hydrogen and carbon monoxide (syngas). CO<sub>2</sub> is then separated to yield a hydrogen fuel gas.

*Oxy-fuel combustion* is the combustion of fossil fuels in almost pure oxygen. Oxygen is provided from air by removing nitrogen and other gases. Combustion in pure oxygen produces a CO<sub>2</sub> rich gas that can be then separated relatively easily.

Carbon capture system energy demand for operating the system reduces the overall efficiency of power generation or other processes; as a consequence this increases fuel requirements, solid wastes and environmental impacts relative to the same type of base plant without capture. This will not be the case with more efficient plants that will become available in the future and their net impact will be lower.

In this thesis, an analysis with CCR was conducted with post-combustion process, due to the fact that this method is more established for CO<sub>2</sub> capture than the others. Oxy-fuel combustion is at a large development stage at present. The main problem with this method is the step of separating oxygen from the air. The reason why pre-combustion is totally excluded

from this thesis lies in the process itself. In the pre-combustion capture, hydrocarbon fuel, normally methane or gasified coal is converted into hydrogen and carbon monoxide; then the carbon monoxide is converted into CO<sub>2</sub> by a shift conversion and, finally, CO<sub>2</sub> is separated from the hydrogen. This process for carbon capturing is not applicable in pathways analysed in this thesis because it interferes with other steps proposed in those pathways.

Removing carbon from air has been practiced for decades in the context of producing CO<sub>2</sub>-free air by scrubbing [58]. Despite the low concentration of only 0.038% of carbon dioxide in the air, the capture of CO<sub>2</sub> directly from the ambient air is possible and has been demonstrated [59]. Carbon dioxide is a gas with the fourth largest concentration in the atmospheric air, following nitrogen, oxygen and argon. Even though, in terms of concentration, carbon dioxide is very dilute, in terms of its energy equivalent, CO<sub>2</sub> content of air is large. After capture, CO<sub>2</sub> is recovered from the sorbent by desorption, through heating, applying vacuum, or electrochemically [40].

At present 70% of the cost of the device is accounted for by the resin and the regeneration chambers. A reduction by a factor of ten in these parts of the equipment would make the compressors and pumps the largest capital expenditure. It is expected that the first prototypes could break even at \$200/ton of CO<sub>2</sub> [58].

An important difference between air capture and CCS is that this process enables a CO<sub>2</sub> closed loop. This process is not connected to any specific carbon source and is, thus, more flexible than CCS technologies. In addition, air capturing can be used to collect emissions from mobile sources like airplanes and vehicles. This technology could play an important role in 100% renewable energy systems because air capture can keep up with the entire world emissions, and could even be used to reduce the CO<sub>2</sub> content of the atmosphere. It is expected that artificial carbon trees could be a thousand times faster in removing carbon dioxide than real trees [60]. Single air collector that can extract a ton of CO<sub>2</sub> a day and fits in a standard shipping container would roughly match agricultural rate biomass production that take up a hectare of land [58].

### **5.3.2. Energy source**

The electricity which enables the electrolysis process is provided by wind turbines. This option is chosen not only because wind energy is a renewable source, but also due to the fact that the integration of electrolyzers in the transport sector enables the integration of wind

turbines and the balancing of the system. Moreover, Denmark is a leader in modern wind energy, with 19% of electricity produced from wind in 2009 [Figure 23].

Like many European countries, Denmark has limited conventional energy resources. This fact drove policy makers to investigate alternative energy options in order to reduce reliance on imported fossil fuels. Wind power is one of the most raising renewable sources in Denmark, due to country's climate that is characterized by wind conditions that are favourable for electricity production.

Wind energy research and development started in Denmark in the late 1970s, which resulted in developing a technology standard based on a three-bladed wind turbine for wind energy generation [61]. Furthermore, in 1991 Denmark became the first country in the world that installed wind turbines in the sea [62].

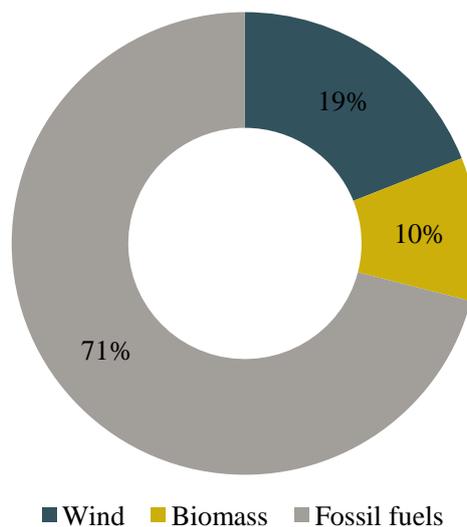


Figure 23. Electricity production in Denmark by energy source for 2009 [34]

As it can be seen from [Figure 24], after a great increase in the second half of the 1990s, in 2000 wind energy had an almost 15% share in electricity production. In 2010, the share of wind power reached approximately 21%, with installed capacities exceeding 3,500 MW produced by about 5,000 wind turbines.

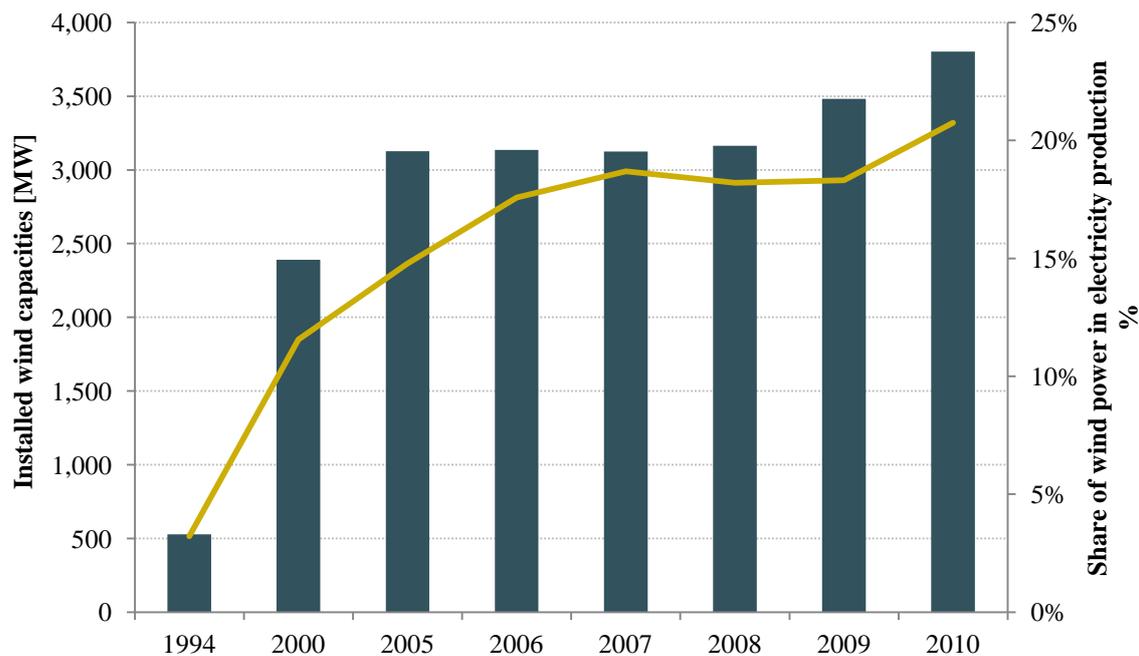


Figure 24. Installed wind capacities (columns) and share of wind power in electricity generation (line) for period 1994-2010 [63]

Further expansion of wind capacities, especially off shore due to limited onshore locations, will play an important role in renewable energy systems even though production costs are higher. Calculations have shown that there is a need for at least 10,000 MW, and up to 18,500 MW wind power in 2050 [64]. The installation of these capacities requires a flexible system which must be able to deal with peak-load periods due to the fluctuating nature of wind. Thus, electrolyzers for the production of liquid fuels are proposed to be a solution in 2050 to facilitate wind power integration.

#### 5.4. Dissociation of oxides

Dissociation of oxides –  $H_2O$  or a mixture of  $H_2O$  and  $CO_2$ , can be conducted with steam or co-electrolysis. These processes use electricity to drive dissociation. As it was mentioned in the previous section, electricity is provided by wind energy. This is the main step in the proposed pathways. Moreover, this process has the largest energy conversion, because this is where electricity is converted to fuel or fuel precursors. Electrolysis performs the dissociation in a single step.

Dissociation can also be powered by heat; however, this process is more difficult and requires expensive materials that are stable at very high temperatures or a complicated multiple-step process that needs careful material handling and heat management [32]. Water dissociation has been researched more than  $CO_2$  dissociation or dissociation of both water and  $CO_2$ .

Water electrolysis is a well-known technology available on a commercial scale with alkaline electrolysis. Water electrolysis with SOEC is experimentally confirmed in laboratories. Electricity to fuel efficiency used in this thesis for energy system analysis for H<sub>2</sub>O electrolysis is 73% [12].

Water splits into hydrogen and oxygen, according to equation (3). For splitting water, the electric current applied to stack must exceed the minimum value of decomposition voltage.



The following are the reactions at the cathode and anode:



Water dissociation results in hydrogen gas and oxygen ions (4). The hydrogen gas diffuses to the surface and gets collected, the oxygen ions are transported through the electrolyte to the anode, where they are oxidized to oxygen gas (5) and thus release electrons [65].

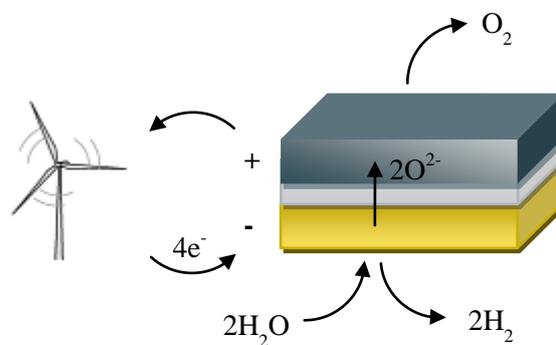


Figure 25. Solid oxide cell water electrolysis

The total energy demand as well for water electrolysis increases slightly with temperature, while the required electrical energy decreases [Figure 26]. The total energy demand ( $\Delta H$ ) for hydrogen production is calculated according to equation (6).

$$\Delta H = \Delta G + T\Delta S \quad (6)$$

Where  $\Delta G$  is the electrical energy demand and  $T\Delta S$  is the thermal energy demand.

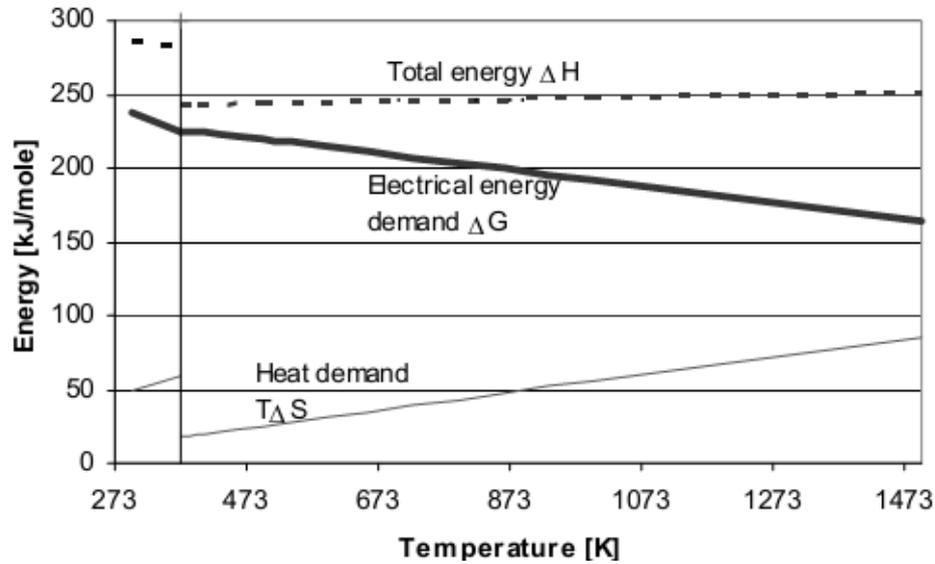


Figure 26. Thermodynamic data for H<sub>2</sub>O electrolysis [66]

The chemistry of co-electrolysis of H<sub>2</sub>O and CO<sub>2</sub> is more complicated than that of steam electrolysis. Solid oxide electrolysis cells are the only technology being reported as practical for co-electrolysis.

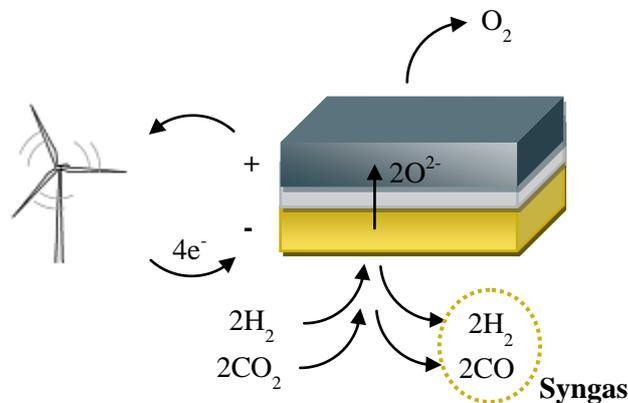


Figure 27. Solid oxide cell co-electrolysis

The overall reaction for the co-electrolysis is:



Three main reactions occur simultaneously, the electrolysis of CO<sub>2</sub> to CO, the electrolysis of water and the reverse water gas shift reaction (RWGS). The following reactions occur at the cathode (8), (9), (10) and anode (11):



However, there is a possibility that one further electrolytic reaction occur if the cell potential is high enough – conversion of CO to carbon. This needs to be avoided since carbon can damage cell performance, but the risk of this occurring is lower than in CO<sub>2</sub> electrolysis. In the co-electrolysis, the reverse gas shift reaction is responsible for most of the CO production and therefore the overall electrical requirement is less.

The co-electrolysis of H<sub>2</sub>O and CO<sub>2</sub> has higher electricity to fuel efficiency than steam electrolysis. The latter is the result of a higher, 86% efficiency of CO<sub>2</sub> electrolysis, compared to a 73% efficiency of steam electrolysis [12]. Electricity to fuel efficiency used in this thesis for energy system analysis for co-electrolysis is 78% [67]. It should be stated that the SOEC technology is still in the early development stage.

Co-electrolysis of CO<sub>2</sub> and H<sub>2</sub>O is researched at:

- Risø National Laboratory, Denmark
- Northwestern University, USA
- Idaho National Laboratory, USA

It is expected that commercial SOEC plants will be available from 2020.

## 5.5. Fuel synthesis

This section briefly explains methanol and DME synthesis according to the following sources [30, 40, 42, 44, 47, 68], because these fuels are the topic of our interest.

Methanol synthesis has been a commercial process for about 80 years [30]. At present there are four catalyst suppliers and six companies' complete proprietary processes for methanol synthesis: ICI, Lurgi, Topsøe, Mitsubishi, M.W. Kellogg and Uhde.

The methanol synthesis is a widely studied process. The process is exothermic and the maximum conversion is obtained at low temperature and high pressure. Methanol synthesis is

the second largest process, after ammonia synthesis, which uses catalysts at high pressure. Even though maximum conversion is obtained at high pressure, some methanol plants are operated at low pressure due to economical and operational benefits. Low pressure methanol synthesis is one of the most mature technologies existing in the field of chemical industry and production. Thermodynamics, reaction mechanism, kinetics, and catalyst properties are discussed in [68].

If CO and hydrogen are used as feed gases, the main reaction is the CO hydrogenation (12). The second reaction is the reverse water gas shift reaction, which proceeds in the reverse direction (14). It should also be noted that the first reaction of the methanol synthesis is exothermic, while the second reaction of RWGS is endothermic. According to this mechanism, via the reduction of carbon dioxide in the RWGS reaction, more reactant carbon monoxide is produced to boost the synthesis of methanol [68].

If mainly CO<sub>2</sub> and H<sub>2</sub> are present, the predominant reactions are the CO<sub>2</sub> hydrogenation to methanol (13) and the reverse water gas shift reaction (14). Methanol produced from CO<sub>2</sub> hydrogenation has significantly high water content as both dominant reactions in this process (13), (14) are accompanied by the formation of water. The water content is strongly dependent on the CO<sub>2</sub> as well as on the activity of the catalyst towards the (reverse) water gas shift reaction [44].



Raw methanol is a mixture of methanol, a small amount of water, dissolved gases, and traces of by-products. By-products of methanol synthesis like DME; higher alcohols e.g. are thermodynamically more favoured than methanol. Despite this fact the methanol synthesis catalyst and process are highly selective up to 99.9% [42]. Methanol synthesis gas is characterised by the stoichiometric ratio M=2 (15) and H<sub>2</sub>/CO ratio of 2.17.

$$M = \frac{H_2 - CO_2}{CO + CO_2} \quad (15)$$

The capital investment for a methanol plant using CO<sub>2</sub> and H<sub>2</sub> is estimated to be about the same as that of a conventional syngas based plant [40]

As it was mentioned before, the production process of DME closely resembles that of methanol. DME can be produced by two methods [47]:

- Catalytic dehydration of methanol (1)
- Direct conversion from synthesis gas (2)

Currently, most DME is produced by the dehydrogenation of methanol using alumina- or zeolite-based catalysts from syngas. The direct conversion of syngas to DME, syngas to methanol conversion and methanol dehydrogenation can occur simultaneously in one reactor using appropriate catalysts.

## 6. PATHWAYS FOR PRODUCING SYNTHETIC FUELS

This chapter examines the possible pathways that can be used for the production of synthetic fuels outlining the energy and mass balances necessary for analysing these in energy-systems-analysis tools. The chapter also includes an explanation of methodology steps taken for analyzing possible pathways that can be used for the production of synthetic fuels. Based on the chemical reactions during electrolysis and chemical synthesis for producing certain fuels, the energy and mass flow balances are calculated. Finally, pathways are developed which outline how these fuels could be produced in future renewable energy systems.

After identifying cycle steps needed for the production of synthetic fuels in the previous chapter, two pathways are proposed with four variations that can be chosen [Figure 28]. The first pathway is co-electrolysis of steam and CO<sub>2</sub> and the second one is hydrogenation of CO<sub>2</sub>. Co-electrolysis as it was explained in Section 4.1. is a combined process of steam and CO<sub>2</sub> electrolysis. Hydrogenation of CO<sub>2</sub> involves steam electrolysis and then a reaction of hydrogen with recycled CO<sub>2</sub>. Gas mixtures products of these processes can be catalyzed into synthetic fuel.

Pathways are divided into three cycle steps identified in the previous chapter: carbon and energy source, dissociation of oxides and fuel synthesis.

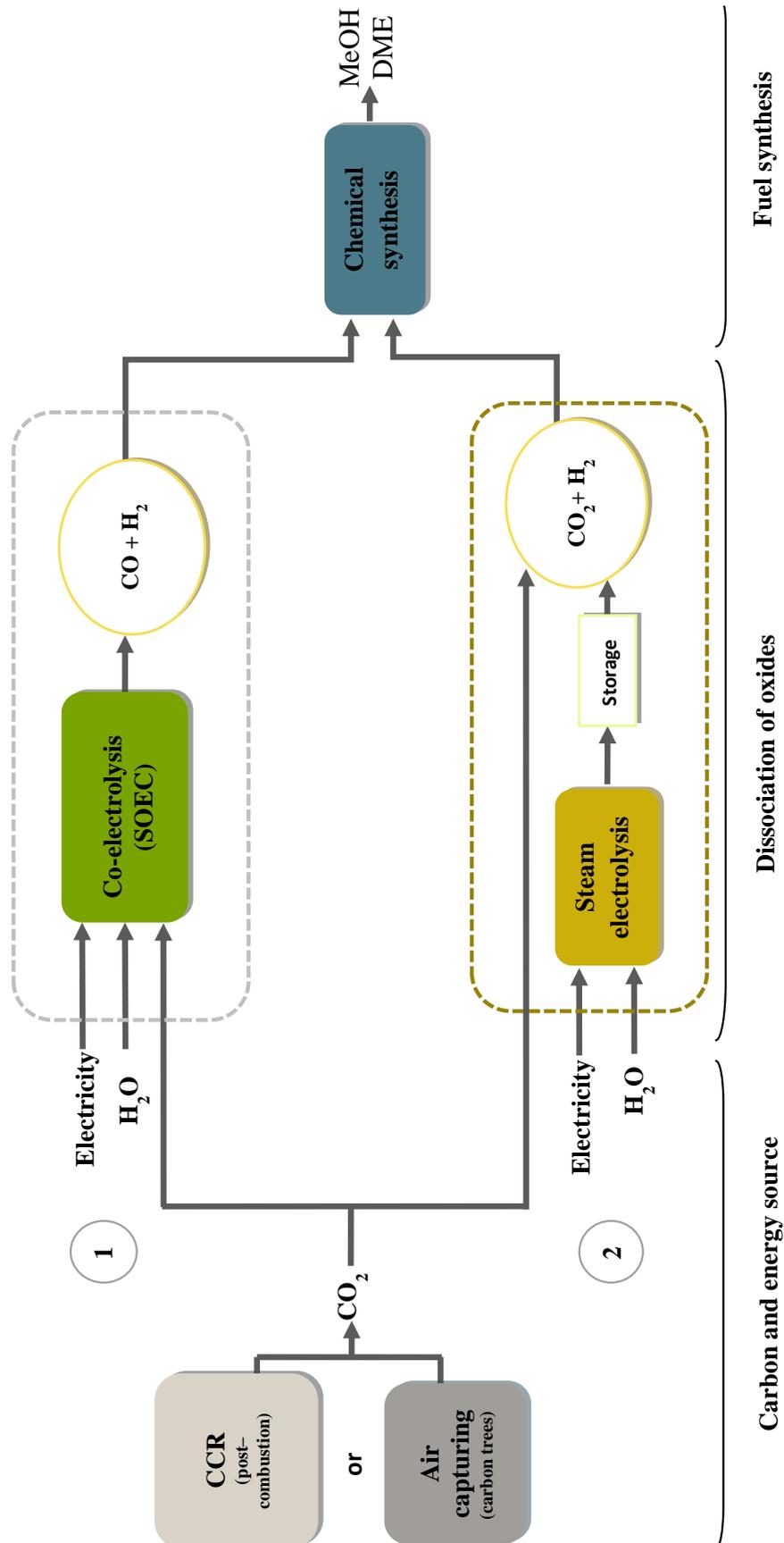


Figure 28. Pathways for production synthetic methanol or DME, first *co-electrolysis*, second  $\text{CO}_2$  *hydrogenation*

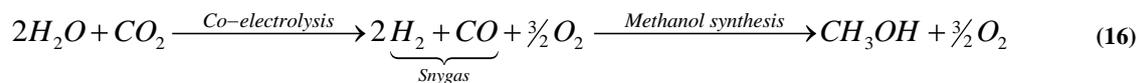
## 6.1. Identifying mass and energy balance for methanol/DME production

The chemical reactions for methanol/DME production are constructed. From these, the energy and mass flow balances are calculated. In order to simplify the calculations, methanol and DME are treated the same. As DME is produced from methanol, the efficiency lost when comparing with methanol is gained through higher efficiency of diesel engines suitable for DME compared to petrol engines suitable for methanol.

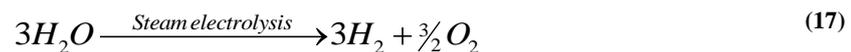
In the co-electrolysis pathway water and CO<sub>2</sub> are dissociated into hydrogen and carbon monoxide. This mixture is known as syngas. Syngas is later catalyzed into methanol (16). Hydrogenation of CO<sub>2</sub> involves steam electrolysis (17) and then a reaction of hydrogen with recycled CO<sub>2</sub> (18).

### Chemical reactions

In order to write a correct chemical equation, we must balance all of the atoms on the left side of the reaction with the atoms on the right side.



Surplus oxygen from co-electrolysis is not used for methanol production, it is in the reaction just for balancing the equation.



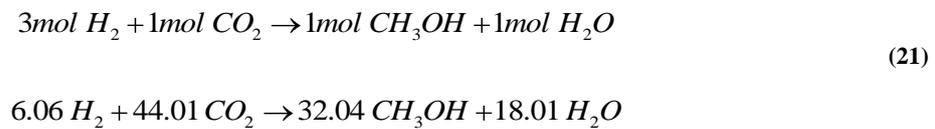
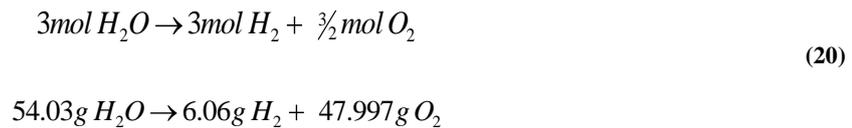
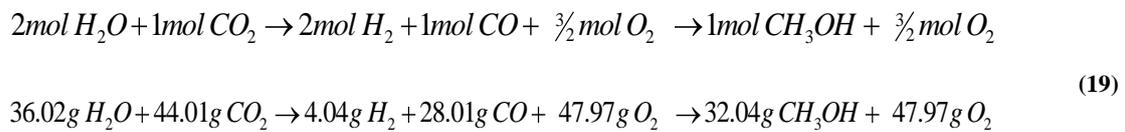
### Mass balance

The law of conservation of matter states that matter is neither lost nor gained in traditional chemical reactions; it simply changes form. Therefore, if we have a certain number of atoms of an element on the left side of an equation, we have to have the same number on the right side. For forming mass balance, molar mass of reactants and products needs to be known.

**Table 2. Molar masses for reactants and products**

| Reactants/Products | Molar mass<br>[g/mol] |
|--------------------|-----------------------|
| CO <sub>2</sub>    | 44.01                 |
| H <sub>2</sub> O   | 18.01                 |
| H <sub>2</sub>     | 2.02                  |
| CO                 | 28.01                 |
| O                  | 15.999                |
| CH <sub>3</sub> OH | 32.04                 |

According to this mass balances for co-electrolysis (19) and for hydrogenation of CO<sub>2</sub> (20), (21) are formed.

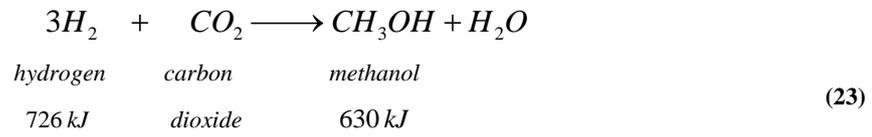
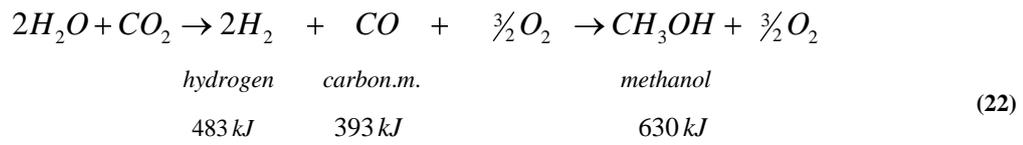


### Energy balance

Energy balances are calculated from formulated mass balances according to energy densities of reactants and products. According to this energy balances for co-electrolysis (22) and for the hydrogenation of CO<sub>2</sub> (23) are formed. Under the equation is given the energy content of the inputs to and the outputs from the reaction in terms of the lower heat value of the substances.

**Table 3. Energy content of reactants and products**

| Reactants/Products | Energy density<br>[MJ/kg] |
|--------------------|---------------------------|
| CO <sub>2</sub>    | -                         |
| H <sub>2</sub> O   | -                         |
| H <sub>2</sub>     | 120.05                    |
| CO                 | 14.03                     |
| O                  | -                         |
| CH <sub>3</sub> OH | 19.65                     |



The resulting energy and mass flow diagram for both pathways is outlined in Figure 29.

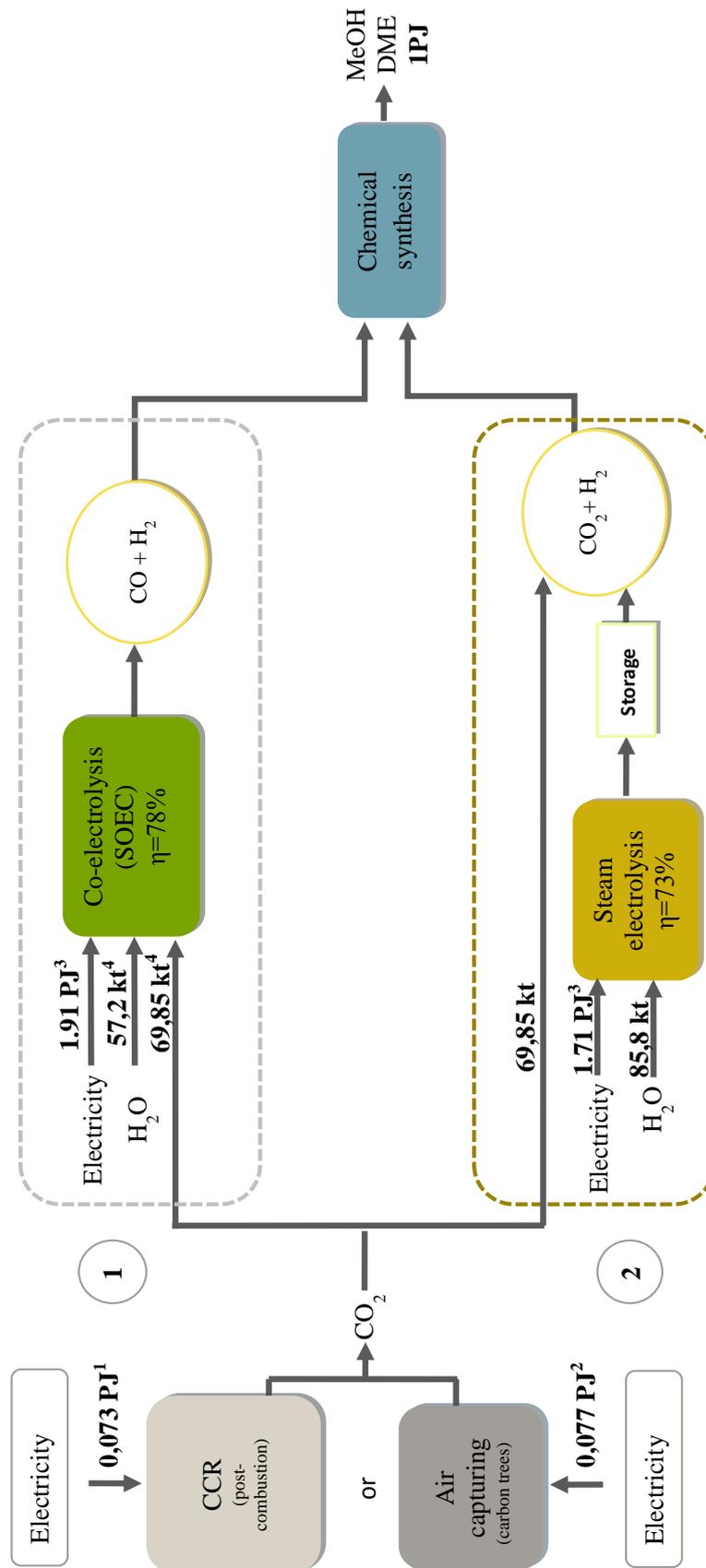


Figure 29. Methanol/DME synthesis from carbon capture and recycling/Air capturing. <sup>1</sup>Energy required for extracting 69.85 kt CO<sub>2</sub> calculated from [69]. <sup>2</sup>Energy required calculated according to [58]. <sup>3</sup>Electricity needed for both electrolysis processes is calculated according to efficiency and methanol/hydrogen ratio. <sup>4</sup>Water and CO<sub>2</sub> masses are calculated from mass balances for 1 PJ of methanol.

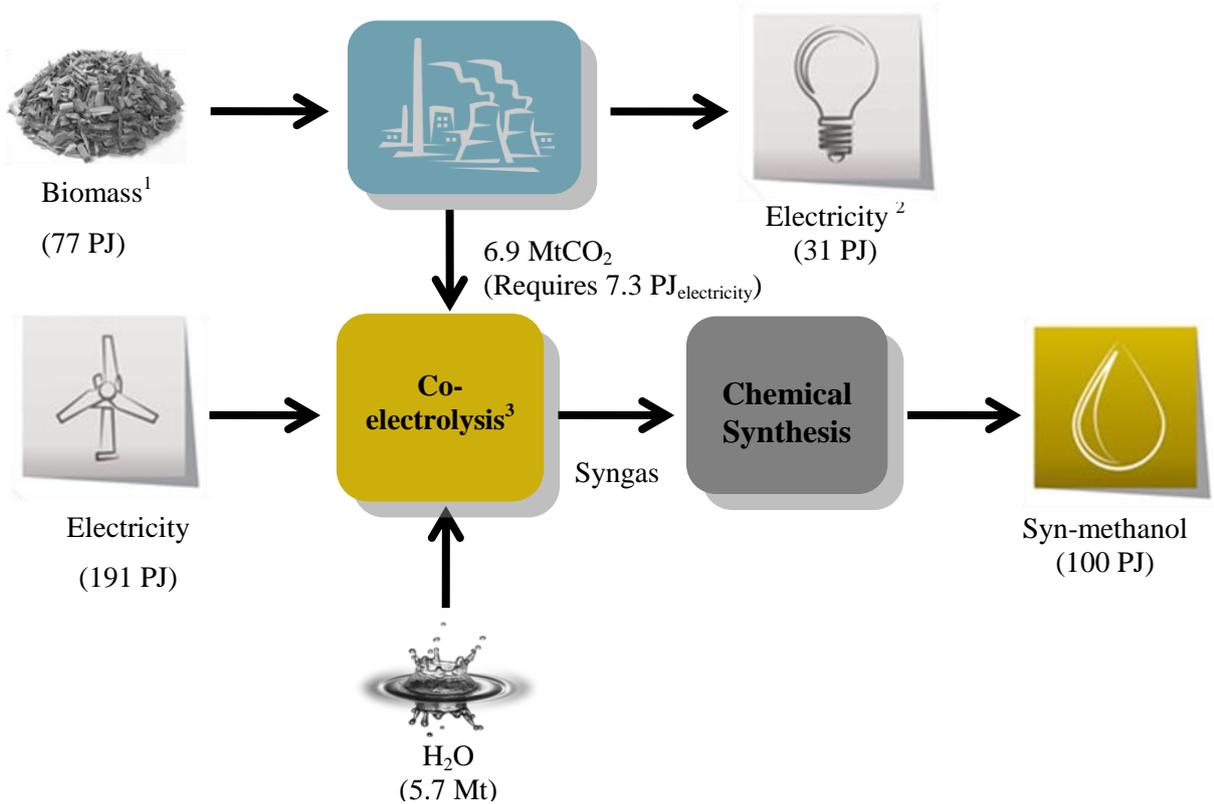


Figure 30. Co-electrolysis scenario. <sup>1</sup>Based on dry willow biomass. <sup>2</sup>Assumed an electricity generation efficiency of 40%. <sup>3</sup>Assumed an electrolyser efficiency of 78% [67], minus 5% account for storage and chemical synthesis losses.

Both pathways for producing synthetic fuels exclude direct biomass input for fuel production. However, these pathways are in strong connection with power and heat sector that uses biomass. As it can be seen from flow charts [Figure 30, Figure 31] the same amount of carbon dioxide for the production of fuel is needed so it is reflected as the same amount of electricity needed for the carbon capturing and recycling system. Air capturing was excluded from the analysis because it would require approximately 5% more electricity which would not cause significant variation in the results of the whole system. In the case of air capturing, all sectors are not connected and there is not even indirect biomass input.

Assumed electrolyser efficiencies are reduced by 5% accounting for storage and chemical synthesis losses. In the hydrogenation of CO<sub>2</sub> pathway, synthesis of methanol has excess water production which can be recycled. Calculations for both pathways were carried out with dry willow biomass fired power plant with assumed electricity generation efficiency of 40%.

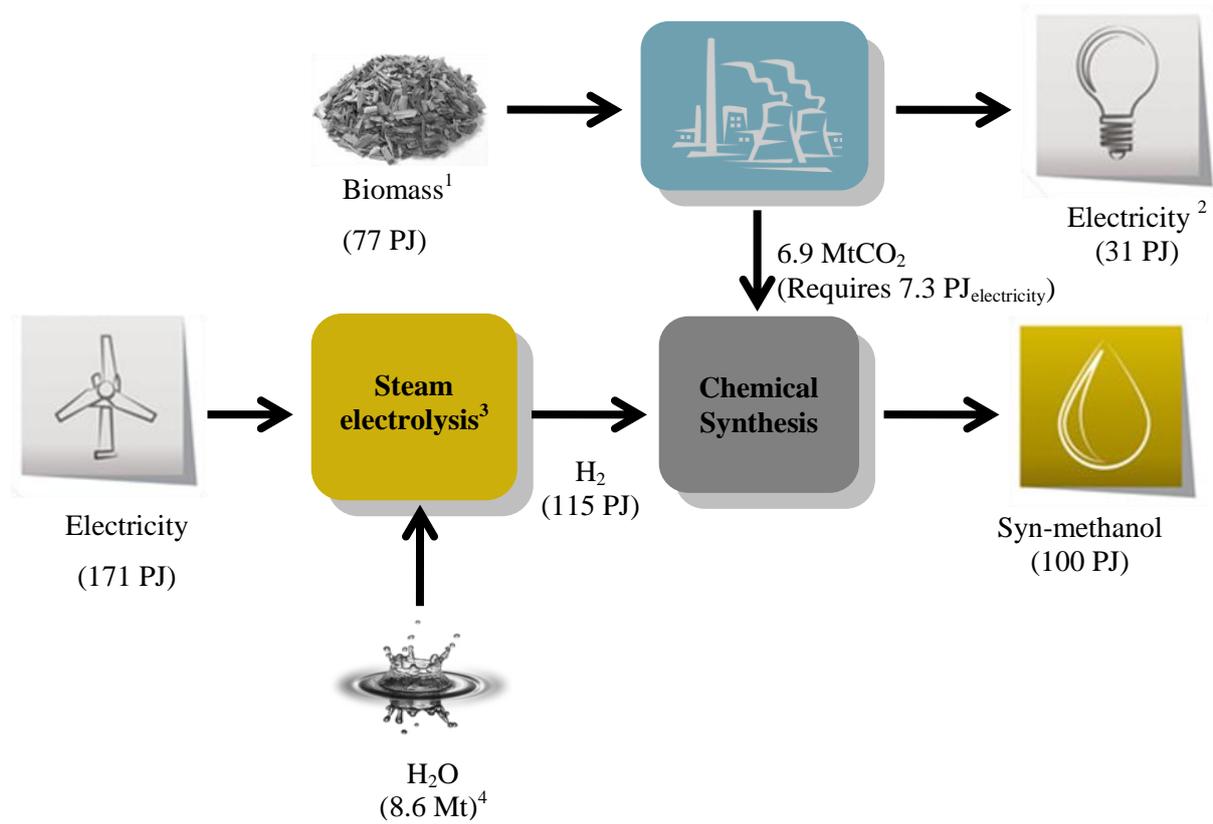


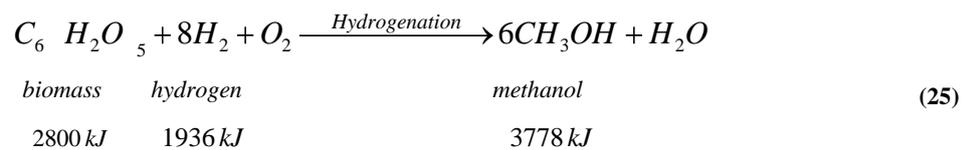
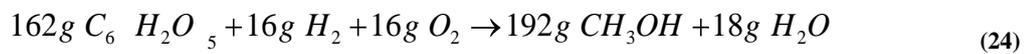
Figure 31. <sup>1</sup>Based on dry willow biomass. <sup>2</sup>Assumed an electricity generation efficiency of 40%. <sup>3</sup>Assumed an electrolyser efficiency of 73% [12], minus 5% account for storage and chemical synthesis losses. <sup>4</sup>This does not include the excess water which can be recycled from the hydrogenation process.

## 7. ALTERNATIVES TO ELECTROLYSERS

### 7.1. Hydrogenation of biomass path

Hydrogenation of biomass is a well-known process of upgrading the energy content and energy density of biomass with hydrogen. Hydrogenation of biomass involves gasifying the biomass into a syngas and then reacting hydrogen with this gas.

The mass (24) and energy balances (25) for the hydrogenation of biomass into methanol are given below. Under the equation, there is the energy content of the reactants and products from the reaction in terms of the lower heat value of the substances.



The reaction of hydrogenation is exothermic, meaning that chemical energy from the biomass and hydrogen is released as heat during the reaction helping to run the reaction itself. It is also evident from the equation that the energy content of methanol is much higher than of biomass. Moreover, the quality and usefulness of the energy is higher, which means that methanol is a better energy carrier than biomass. By the hydrogenation alone, the energy content of biomass can be increased by 35% in the case of methanol production.

The hydrogenation of biomass with 40 PJ of hydrogen results in saving 60 PJ of biomass [4]. The hydrogenation of biomass enables the production of hydrocarbons with much higher energy content and energy density compared to direct biomass conversion to bio fuels.

The hydrogenation of biomass is a path for producing liquid fuels that involves direct input of biomass. It is more preferable than the conventional production of biofuels due to the fact that it consumes less biomass and allows the integration of more wind in the system.

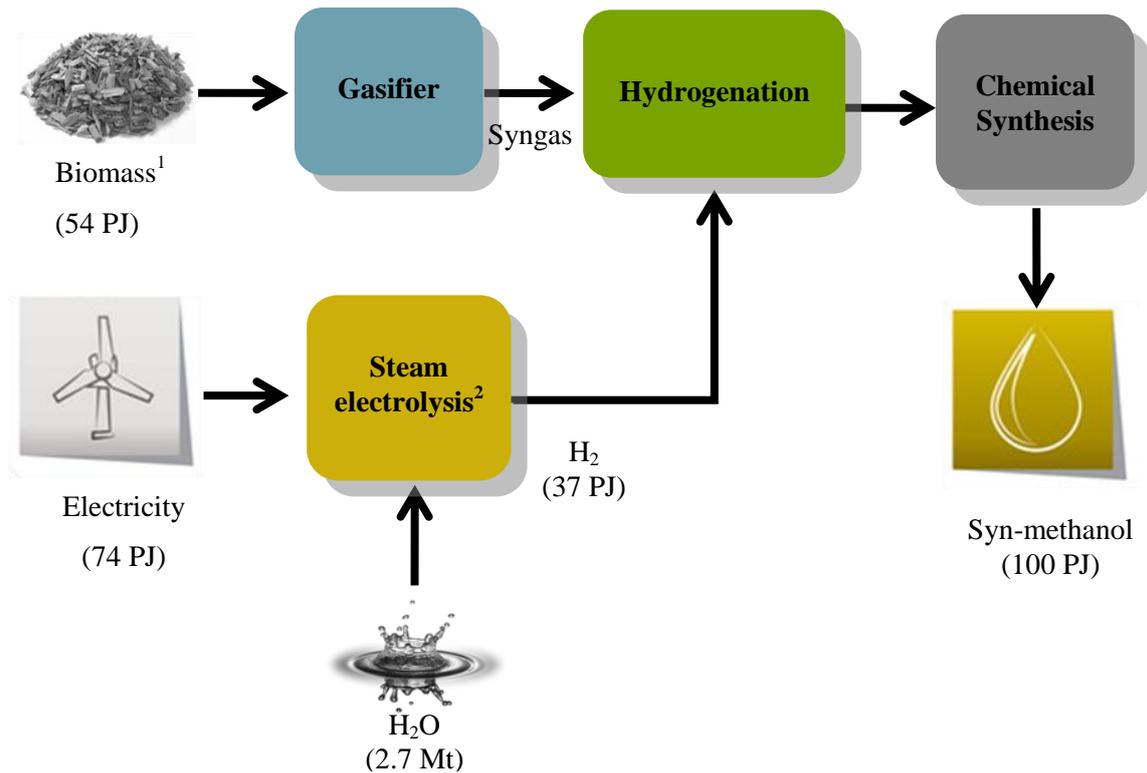


Figure 32. Gasification of biomass. <sup>1</sup>Based on straw/wood chips. <sup>2</sup>Assumed an electrolyser efficiency of 73% [12], minus 5% account for storage and chemical synthesis losses.

### 7.1.1. Biomass gasification

Biomass gasification is a high-temperature process (500 to 1400°C) for converting complex hydrocarbons of biomass into a combustible gas mixture primarily consisting of hydrogen and carbon monoxide, known as syngas. However, in practice some carbon dioxide, water and other hydrocarbons can be formed as well. The gasification of biomass breaks biomass into combustible gas mixture in the presence of gasification agents. The agent may be oxygen, air, steam or a combination of them [70].

Gasification can handle a wide range of biomass feedstocks, ranging from woody residues and agricultural residues to dedicated crops without major changes in the basic process. A system can be designed to handle a variety of feeds.

Biomass gasification is an emerging commercial technology evolving out of intensive research and development in the 1970's and 1980's, although its developmental roots in small-scale biomass gasifier and coal gasification date from the early 20th century. Biomass gasification systems from small to large are commercially available. Many technology developers are in the prototype and first commercial demonstration stage [71].

A variety of biomass gasifier types have been developed. They can be divided into four major classifications:

- fixed-bed updraft
- fixed-bed downdraft
- bubbling fluidized-bed
- circulating fluidized bed

Differentiation is based on the means of supporting the biomass in the reactor vessel, the direction of flow of both biomass and oxidant, and the way heat is supplied to the reactor [72].

## 7.2. Biodiesel path

This pathway is a response to Technology Roadmap - Biofuels for Transport [19] published this year based on the Energy Technology Perspectives 2010 [17], BLUE Map Scenario, which sets out cost effective strategies for reducing greenhouse-gas emissions by half by 2050. The scenario suggests that a considerable share of the required volume will come from advanced biofuel technologies that are not yet commercially deployed.

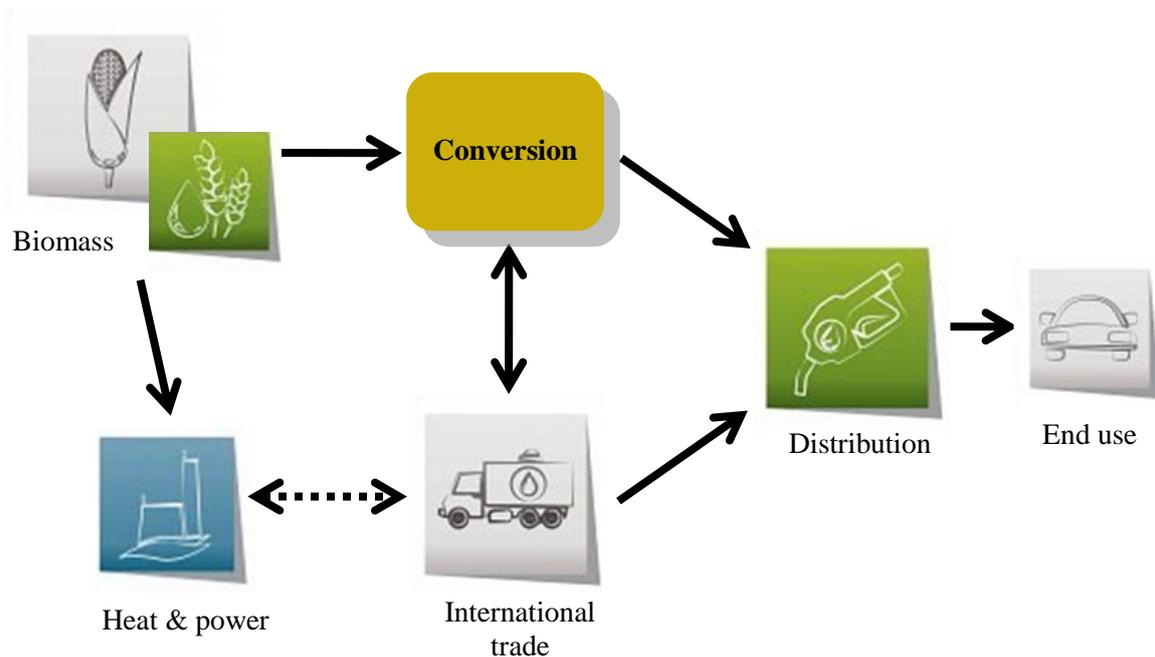


Figure 33. Common future scenario for bioenergy – using biomass in all sectors

Biomass is a preferred alternative in many sectors, with a growing demand for the heat and power service, for transportation fuels and as feedstock for chemicals and materials [See Figure 33].

However, the biodiesel path analysed in this thesis is an extreme case of the conventional production [Figure 34] of biodiesel in 2050. Biodiesel production is based on the transesterification of vegetable oils and fats through the addition of methanol (or other alcohols) and a catalyst, with glycerol as a co-product. Feedstocks for producing biodiesel include soy seeds, rapeseeds, mustard seed, palm oil, jatropha, waste vegetable oils, and animal fats. The hydrotreating of oils and fats is a new process on the market that produces a biodiesel that can be blended with fossil diesel up to 50% without any engine modifications [73].

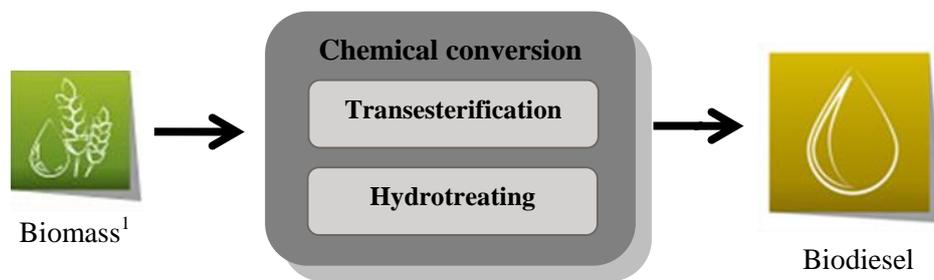


Figure 34. Biodiesel production

Biodiesel is used in standard diesel engines and can be used alone or mixed with diesel. Biodiesel can be mix together with diesel up to a fraction of 20% without the need to adapt the vehicle engine. If higher proportions of biodiesel are applied in mixtures with diesel, a number of relatively minor changes are required, such as the use of alternative materials due to the chemical aggressiveness of biofuels towards metallic materials, rubber seals, coatings and elastomers that are used in vehicle engines [36]. Its high cetane number enables an improved combustion in diesel engines and low emissions of sulphur and particulates.

## 8. ENERGY SYSTEM ANALYSIS

### 8.1. Tool for analysis - EnergyPLAN

There is a wide variety of tools for analysing the integration of renewable energy into various energy systems [74]. Energy system analysis is performed by the use of the freeware model EnergyPLAN [7].

The EnergyPLAN model is a deterministic mathematical model for national or regional energy system analyses according to inputs defined by the user. The model was developed in 1999 and has expanded on a continuous basis since then. It is based on analytical programming which makes the calculations direct and the model very fast when performing calculations. EnergyPLAN takes into account three primary sectors of any energy system: electricity, heat and transport sector.

The model has an input/output user-friendly interface with a wide-range of inputs, such as energy demands, production capacities, renewable energy sources and efficiency of systems. Outputs include energy balances and resulting annual productions, fuel consumption, import/export of electricity, and total costs including income from the exchange of electricity. Model can be used for three types of energy system analysis: technical analysis, market exchange analysis and feasibility study. The advantage of this model is that it is based on an hourly approach for a one-year period as opposed to scenario models that analyse a series of years. This approach enables precise modelling of hourly fluctuations in demand and supply as well as the influence of the intermittency of renewable energy sources on the system. The EnergyPLAN model has been used and applied for various energy system analyses [75].

The modelling of the transport sector in EnergyPLAN is outlined in the following flow chart [Figure 36] EnergyPLAN model generally consider total fuel demand, not all details about fuel production are in the main Transport Tab [Figure 37], so transport needs to be modelled by using Biomass conversion Tab and Electrolysers and Energy storage Tab as it is explained later.

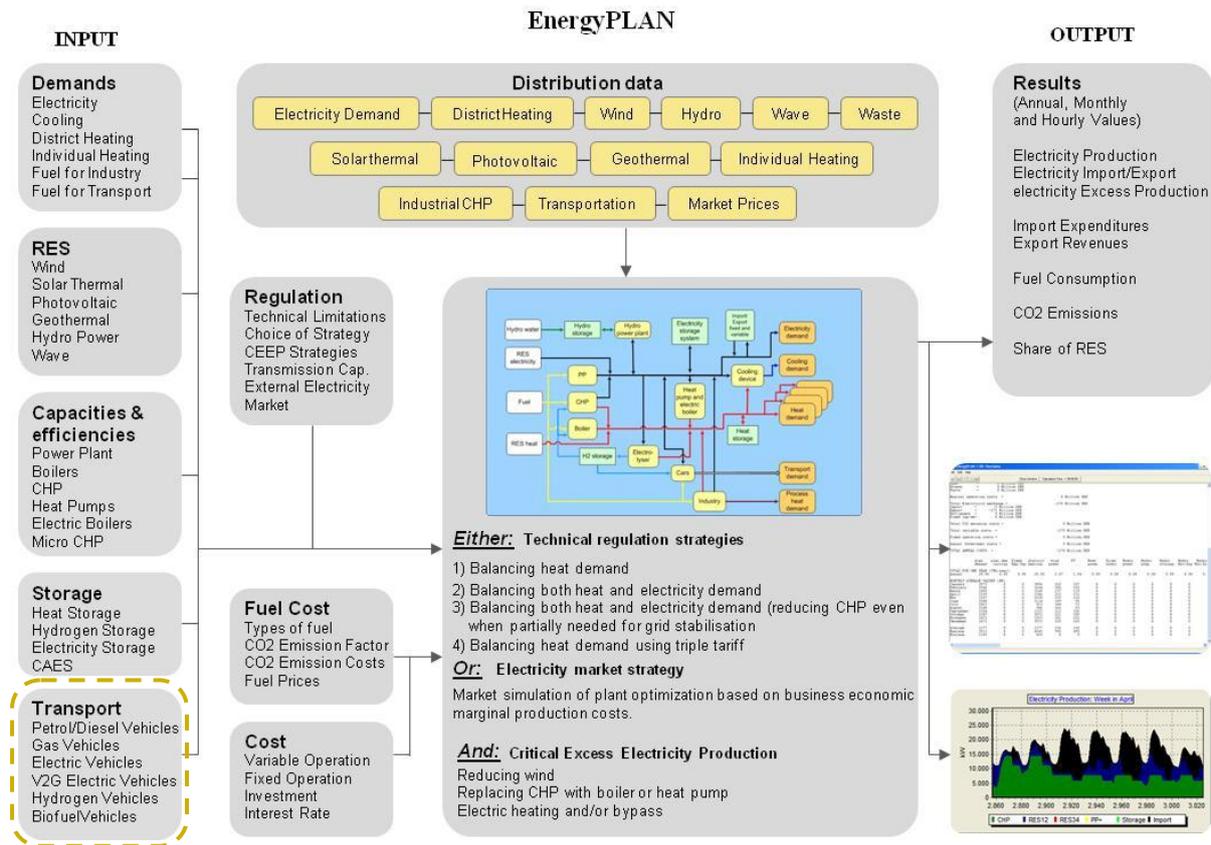


Figure 35. EnergyPlan model [76]

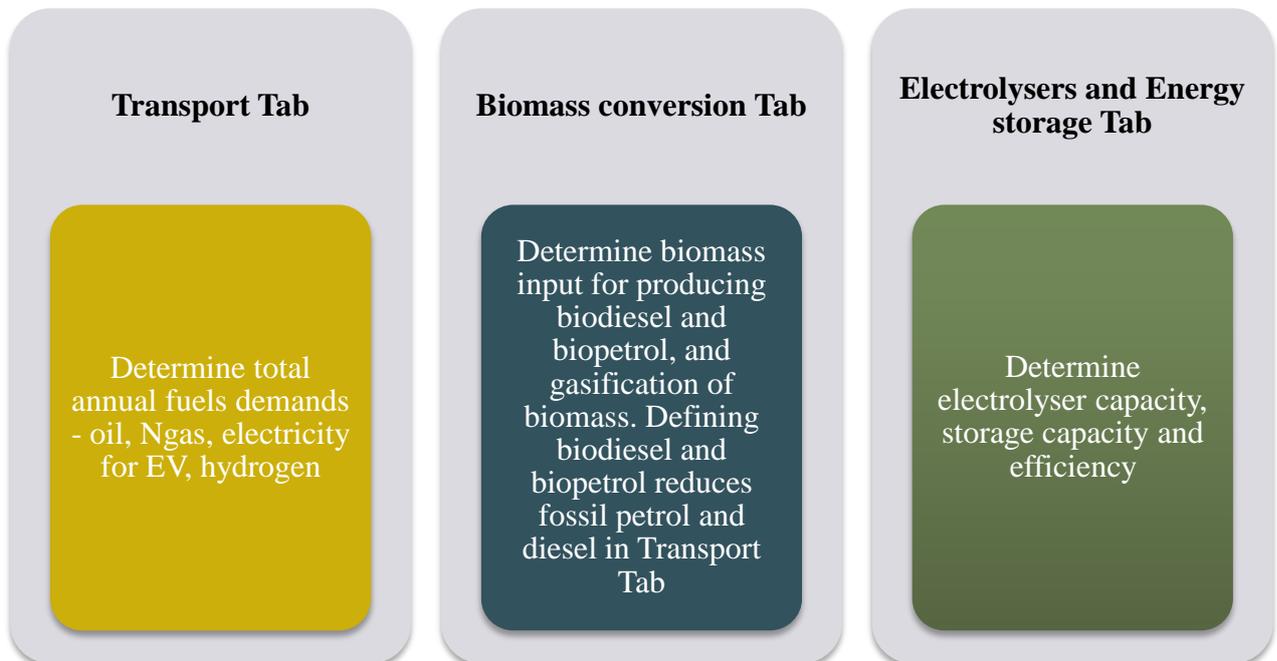


Figure 36. Transport balancing methodology

The key inputs required for Transport Tab are the total annual fuels demands including jet fuel, diesel, petrol, natural gas, liquid petroleum gas (LPG), biofuels, and electricity.

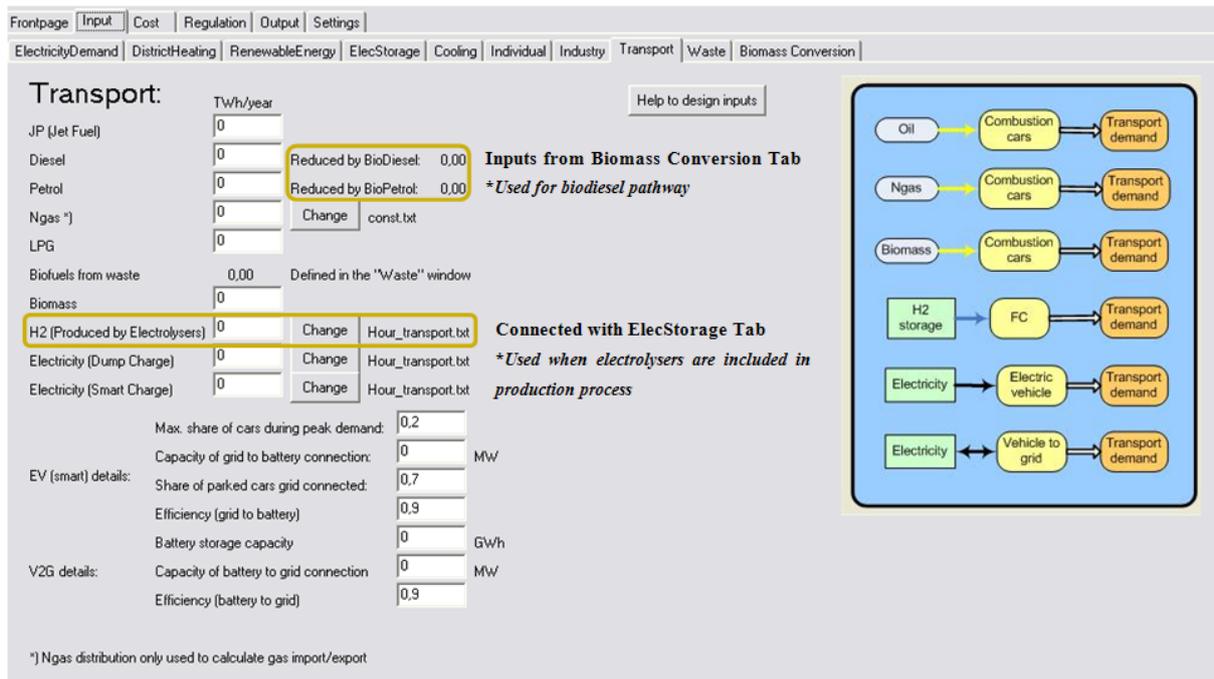


Figure 37. Transport tab in EnergyPLAN

Since pathways for producing synthetic fuels include electrolysers in the production process, their capacities are determined in the Electrolysers and electricity storage systems tab as outlined in Figure 38.

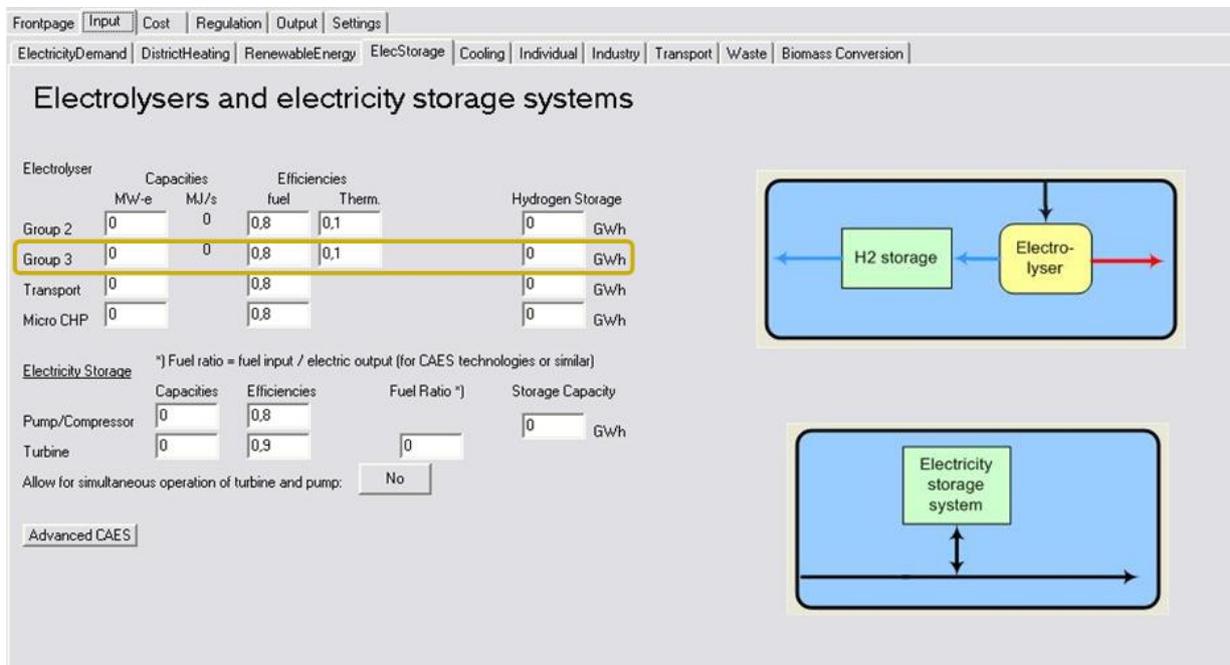


Figure 38. Electrolysers and electricity storage systems Tab in EnergyPLAN

Although Transport tab has direct biomass for transportation, this tab is not used for modelling biofuels. Instead, biofuels are modelled in Biomass Conversion tab [Figure 39]

where biomass input for producing biodiesel and biopetrol can be determined. By defining biodiesel and biopetrol demand, fossil petrol and diesel are reduced in the Transport tab to balance non fossil fuel input.

The screenshot displays the 'Biomass conversion plants' section in EnergyPLAN. It includes several sub-sections with input fields and tables:

- Biogas Plant:** Includes fields for Input (Dry/Wet Biomass), Electricity, DH gr.1-3, Output (Biogas), Upgrade to grid Efficiency, and Input to Gas Grid. A 'Change distribution' button is present.
- Gasification Plant:** Includes fields for Biomass, Electricity, Steam, Coldgas, Gas Output Capacity (Average/Max Cap), DH gr.3, Output (Syngas), Upgrade to grid Efficiency, and Input to Gas Grid. A 'Change distribution' button is present.
- BioDiesel Plant:** Includes fields for Dry Biomass, Electricity, BioDiesel, Biomass, and Output (BioDiesel). A 'Change distribution' button is present.
- BioPetrol Plant:** Includes fields for Biomass, Electricity, Steam, BioPetrol, Food bi-product, DH gr.3, Output (BioPetrol/Food), and Food value. A 'Change distribution' button is present.

A flow diagram on the right shows 'Biomass conversion' leading to 'Gas storage', which then leads to 'Import/Export gas'.

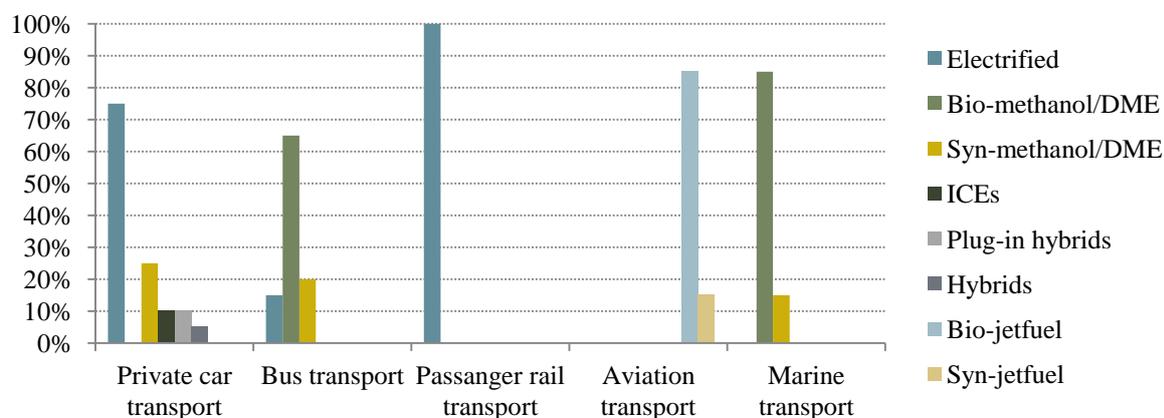
Figure 39. Biomass Conversion Tab in EnergyPLAN

## 8.2. The reference energy system

The reference energy system is taken from a 100% renewable Danish energy system for 2050 which was completed as part of the CEESA project [6]. In CEESA three different energy system scenarios have been modelled in EnergyPLAN: Conservative, Ideal and Recommendable. The chosen reference system for this thesis is Recommendable CEESA 2050, described as “realistic and recommendable” with realistic and achievable technology improvements. Production of liquid fuels for the transport sector was modelled by the hydrogenation of CO<sub>2</sub> and the hydrogenation of biomass. In addition to that, this scenario has included both synthetic fuels and biofuels in transportation. The main priority in the reference scenario, as in all the scenarios analysed in the thesis, is the direct electrification of the transport sector.

Biofuels supply 44% of the liquid fuels that are not covered by electrification while synthetic fuels supply the rest of the remaining fuels. Even though 34% of the liquid fuels are supplied

by synthetic fuels, biofuel demand of 62 PJ/year is now in line with available biofuels resource of 60 PJ/year in Denmark [6].



**Figure 40. Reference model of transport sector according to type of fuels and type of vehicles in case of private car transport**

“CEESA modelling is not completely comparable to other publications due to the fact that the international transport demand was included in projections” [6]. International transport was calculated by assuming that 50% of the demand was assigned to Denmark and 50% was assigned to the other country of origin. As follows, both countries share responsibility for the transport demand created between them. In all scenarios transport is accounted for national/international demands and both passengers and freight [6].

**Table 4. 100 % renewable reference energy system**

| <b>Renewable energy and conversion technologies</b> |   |
|---|---|
| Wind power  | 14,150 MW   |
| • On shore wind                                     | 4,454 MW  |
| • Off shore wind                                    | 9,710 MW  |
| Photo Voltaic                                       | 5,000 MW  |
| Wave Power  | 300 MW  |
| Small Combined Heat and Power                       | Engines/Fuel Cells/Gas turbines                         |
| Large Combined Heat and Power                       | Combined cycle/Large Fuel Cell<br>Combined Cycle CHP/PP |
| Gasification for electricity and power production   | Yes   |
| <b>Transport</b>                                    |   |
| Direct electricity                                  | 21%   |
| Bio-Methanol/DME                                    | 45%   |
| Syn-Methanol/DME                                    | 33%   |
| Bio-Methanol/DME plants                             | Yes   |
| Electrolysers for Bio-Methanol/DME plants           | Yes   |
| Electrolysers for Syn-Methanol/DME plants           | Yes   |

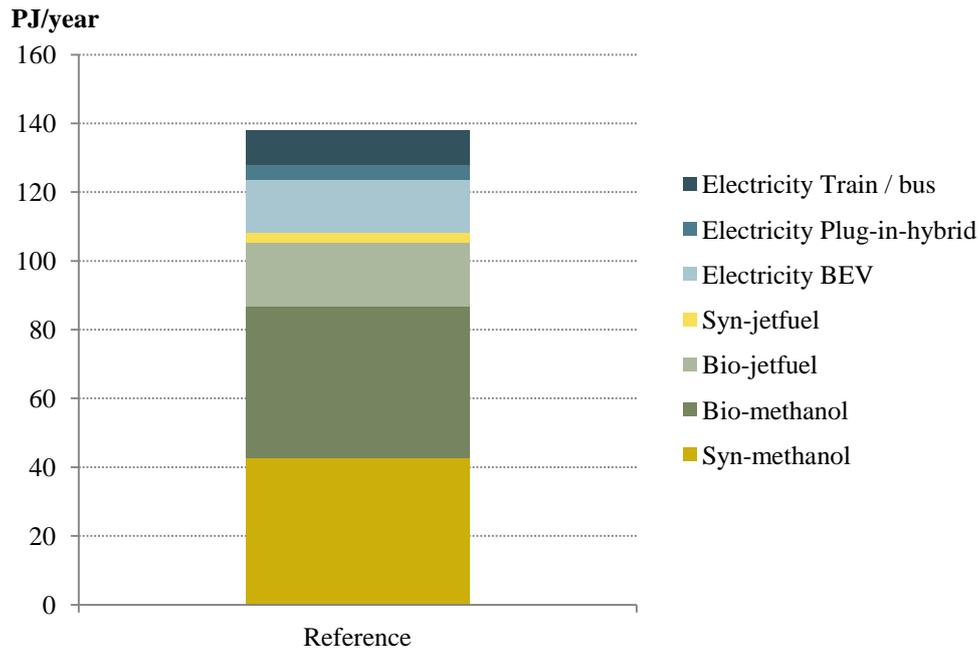


Figure 41. Energy consumed by fuel type in 2050 for the reference scenario

Total fuel demand in 2050 is 138 PJ/year which is equal to 38 TWh/year. Pathways modelled for this thesis represent extreme cases of replacing total liquid fuel demand with synthetic, bio fuels or bio-diesel. Total fuel demand is kept the same in all scenarios while fuel mix is changed. Moreover, as only the transport sector is analysed, renewable energy and conversion technologies are not changed except for the wind capacities.

### 8.3. Evaluation of scenarios

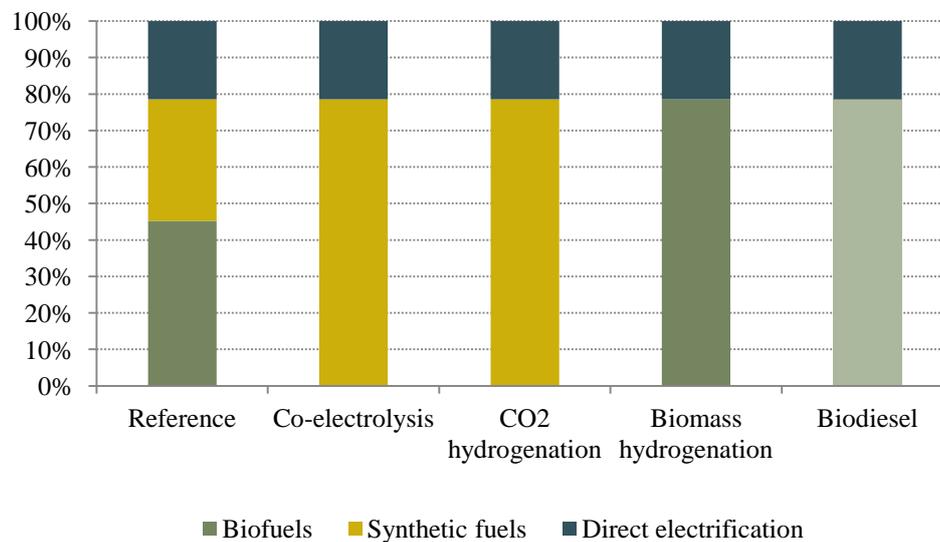
One of the main problems in the transition to a 100% renewable transport sector is limited biomass resources that are used both for providing heat and electricity. Considering high wind potential in Denmark due to country's climate, the focus is put on maximizing the use of electricity and replacing liquid fossil fuels with renewable fuels.

In order to analyse the steps needed for achieving a 100% renewable transport sector in 2050 and to analyse the different key elements for establishing latter, four scenarios have been created as it was explained in Sections 6 and 7 [Table 5]. Two main pathways are focused on synthetic fuels for providing all liquid fuels that cannot be replaced by direct electrification - *Co-electrolysis* and *CO<sub>2</sub> hydrogenation*. Two biofuels scenarios that have direct usage of biomass for producing liquid fuels are included in the analysis: *Hydrogenation of biomass* and *Conventional biodiesel* pathway. Conventional biodiesel production is the only scenario that does not include electrolyzers in the production process.

**Table 5. Pathways for producing liquid fuels in 2050**

| Pathways                      | Description   |
|-------------------------------|---|
| Co-electrolysis               | Production of liquid fuel by a combined process of steam and CO <sub>2</sub> electrolysis. Carbon source is CCR cycle from biomass power plant. No direct biomass usage.              |
| CO <sub>2</sub> Hydrogenation | Hydrogenation of CO <sub>2</sub> involves steam electrolysis and afterwards the reaction of hydrogen with recycled CO <sub>2</sub> from biomass power plant. No direct biomass usage. |
| Hydrogenation of biomass      | Hydrogenation of biomass involves gasifying the biomass into a syngas and then reacting hydrogen from steam electrolysis with this gas  |
| Conventional Biodiesel        | Conventional biodiesel production by transesterification of vegetable oils and fats   |

These pathways are principally extreme cases of replacing total liquid fuel demand in 2050 with synthetic or biofuels [Figure 42]. While Reference scenario includes liquid fuel mix, all other scenarios have one type of liquid fuels that cover 79%, while the rest of the transport energy demand is met by electrification. In terms of transport demand is even more significant.

**Figure 42. Share of different types of fuels in scenarios**

To meet the 138 PJ demand for liquid fuels scenarios implement different fuel mixes. Even aviation fuel is covered by the same type of fuel without mixing bio and syn-fuels. Due to specific requirements for aviation fuels the same kind of fuels that can be used for other transport modes are not suitable for this application so additional losses of 10% were added in calculations. Moreover, there is no aviation fuel identified as a good future solution.

Energy system analysis is carried out by focusing on four criteria for measuring feasibility of implementing these scenarios: primary energy supply, system flexibility, biomass use, socio-economic costs.

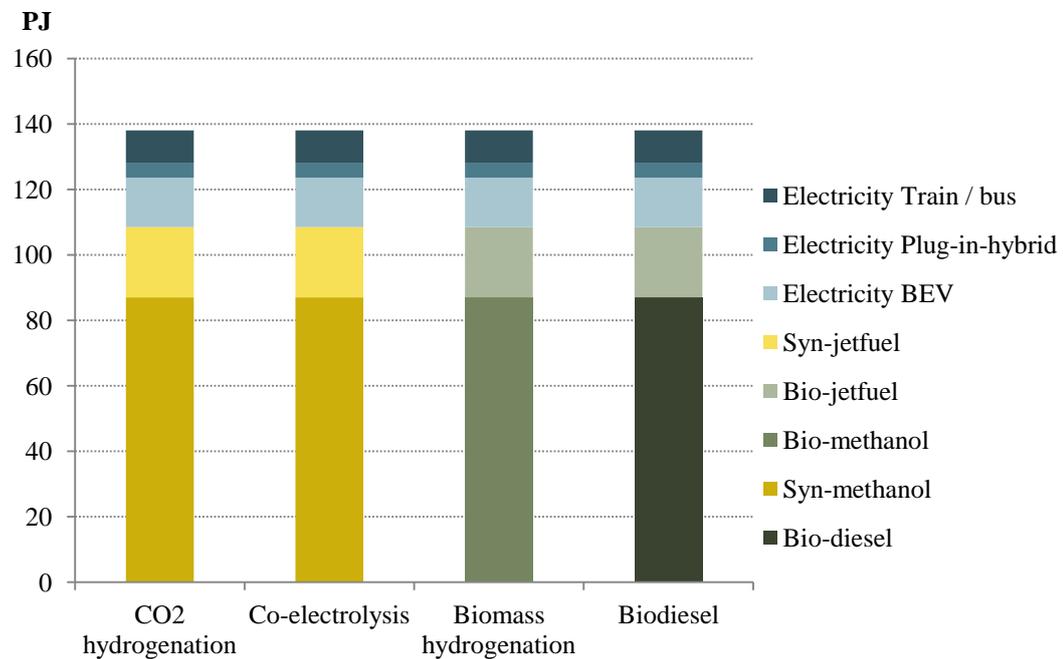


Figure 43. Energy consumed by fuel type for the proposed pathways

Due to uncertainty of fuel prices in a long-term planning three fuel price assumptions are used:

- 1) A low fuel price development corresponding to an oil price of \$65/barrel.
- 2) A medium price level corresponding to an oil price of \$85/barrel.
- 3) A high price level corresponding to an oil price of \$125/barrel.

The price of CO<sub>2</sub> included in marginal production prices is 50 \$/ton for 2050.

Table 6. Fuel prices used in analysis [6]

| €/GJ               | Straw / Wood chips | Energy Crops |
|--------------------|--------------------|--------------|
| Low price level    | 4.04               | 5.52         |
| Medium price level | 5.52               | 7.40         |
| High price level   | 8.34               | 11.84        |

All future prices of fuel and investment costs for new technologies and units have been taken from EnergyPLAN data used in the reference scenario [6].

## 9. RESULTS OF MODELLING IN ENERGYPLAN

All scenarios represent 100% renewable scenarios for 2050, without any fossil fuel input. In general, 21% consumption is met by the electrification of the transport sector, with different types of electric vehicles and electrically powered trains, while the rest is covered by different kinds of liquid fuel depending on scenarios.

The main idea in creating scenarios was to keep biomass consumption as low as possible in the transport sector, so it can be used in other sectors and priority for liquid fuels is given to methanol/DME. This approach resulted in synthetic fuel scenarios that allow the integration of more wind turbines into the energy system. For integrating a large share of electrolyzers, which is the main characteristic of synthetic fuels scenarios, it is important to have a smart energy system. The term – smart energy system is a more extensive term than smart electricity grids, which is in fact just one part of it. Scenarios for synthetic fuels production enable the transport sector to become an important part of the smart energy system.

Two kinds of studies can be carried out in EnergyPLAN: Technical and Market Optimisation. Technical Optimisation was used in this thesis, which is based on the technical abilities of the components within the energy system. Only in the case that the power producing units are not able to meet demand, power is imported from the external market, and in the case of excess energy production, energy is exported to the external markets [77]. The analysis used technical optimisation - Balancing Both Heat and Electricity Demands (Reducing CHP also when partly needed for grid stabilisation). This optimisation ensures that the energy system operates with the largest efficiency possible.

Technical optimisation of the system is carried out with minimum Critical Excess Electricity Production (CEEP). The socio-economic study in EnergyPLAN is designed to minimise the costs to the society and it represents costs associated with the Technical optimisation. This enables the optimization of the energy system performances without the restrictions imposed by economic infrastructure [77]. Socio-economic costs are calculated as annual expenses and do not include taxes. Costs are categorised under the fuel cost, investment and operation and maintenance costs divided into: energy system and transport sector costs. A real interest rate of 3% is used.

All results shown, if it is not specified under the diagrams, are calculated for medium fuel price level.

Once the scenarios were defined and integrated in EnergyPLAN, the feasibility study was completed with a focus on four criteria [Figure 44]. Results will be explained following the order of the criteria.

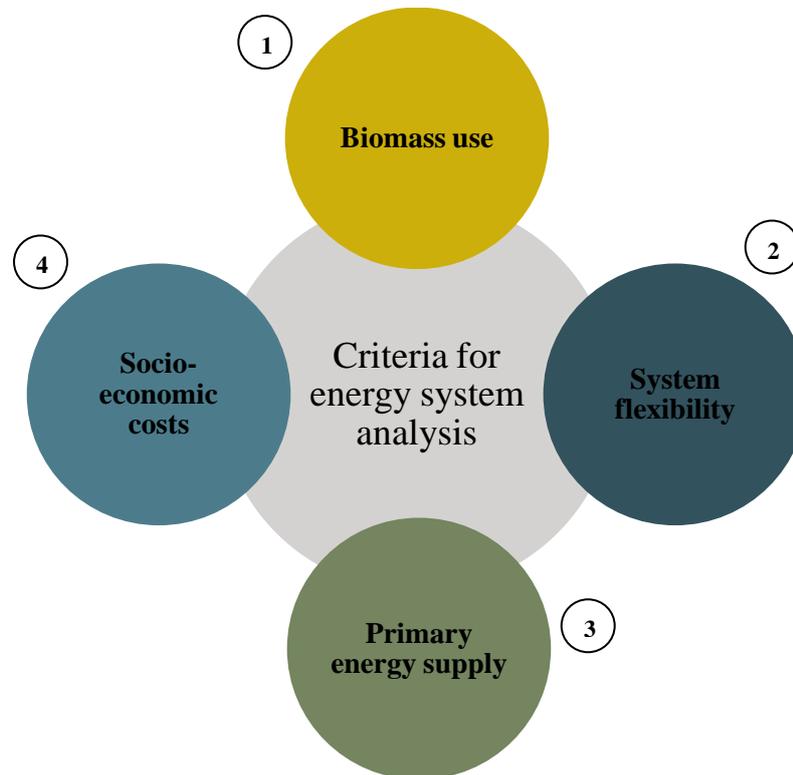


Figure 44. Criteria for measuring feasibility of implementing scenarios

Biomass issues and its potential were explained in detail throughout the thesis. It is considered that biomass along with wind, is a strong base for a non-fossil energy system. However it is really important to carefully distribute biomass use, taking into account the fact that biomass resources and land area are limited.

The biomass consumption for the whole energy system is illustrated in Figure 45. The assumed biomass feedstocks, used for the production of biofuels in transport, are energy crops (willow) and straw/wood chips for the *Hydrogenation of biomass* scenario. It can be seen that the *Co-electrolysis* scenario uses the least biomass possible - 193.2 PJ while in the *Biodiesel* scenario consumption is almost 280 PJ on a system level, On the transport level, this ratio is even worse at the expense of the *Biodiesel* scenario, due to the fact that *CO<sub>2</sub> Hydrogenation* and *Co-electrolysis* have no direct biomass input in the transport sector.

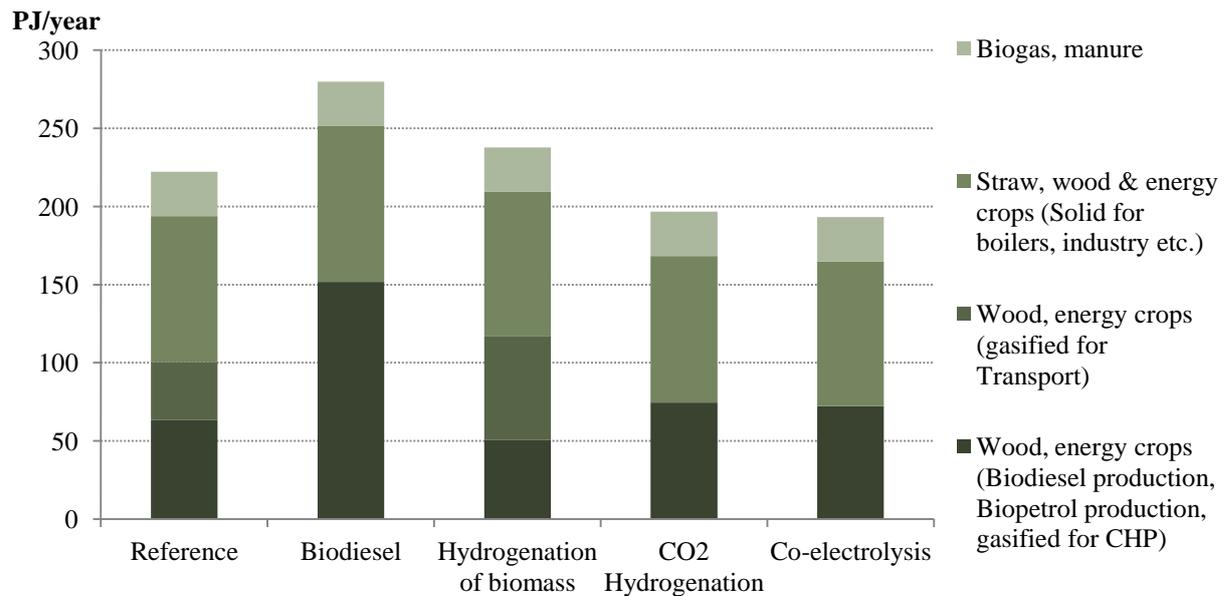


Figure 45. Biomass use in overall energy system

Flexibility of the system was measured by the integration of wind capacities with a focus on offshore capacities, while on shore capacities were fixed for all scenarios so that systems can be compared. Installed on shore capacities are 4,454 MW. From the energy system perspective, 20-25% of the wind power can be integrated without significant changes to the system, while integrating more than this implies the installation of large storages like heat pumps. To balance the energy system with more than 40-45% of wind power which will probably be indispensable for establishing a 100% renewable system, transport sector will have to implement technologies that could facilitate wind power integration [6].

CEEP (Critical Excess Electricity Production) is the difference between the total electricity production and the demand. The CEEP diagrams serve as an illustration of the ability of a system to integrate fluctuating RES which differ from one year to another. These kinds of diagrams can be used for comparing radically different systems. A rise in CEEP indicates an existing lack of flexibility in the system. Integrated offshore wind capacities in scenarios are adjusted so the CEEP for all scenarios is 0.5 TWh/year. As it is presented in Figure 46, the contribution of electrolyser capacity is enviable in different systems for further integration of wind energy. It can be seen that, as it was expected, the *Biodiesel* scenario is the least flexible one, followed by the *Hydrogenation of biomass*. The integration of more than calculated wind capacities results in an increase of CEEP. Such increase in the storage capacity, provided by electrolyzers, significantly reduces excess production.

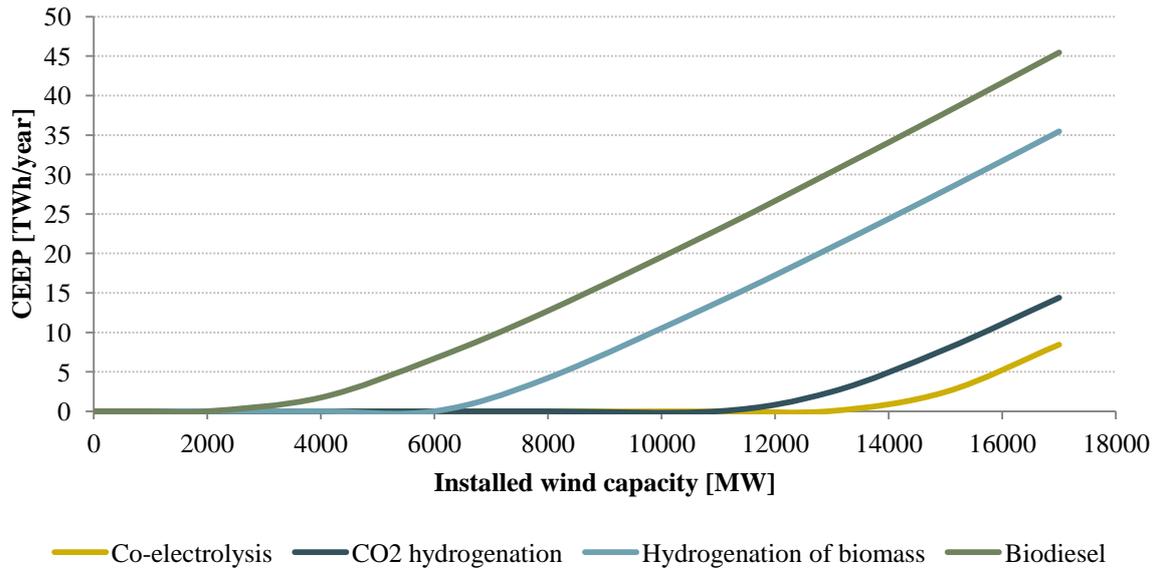


Figure 46. Increasing wind integration by different scenarios

Installed wind capacities are strongly connected with the integrated electrolyser in the system [see Figure 47]. The implementation of electrolysers in the system enables a flexible and efficient integration of larger amounts of renewable energy into the transport sector. Large amounts of fluctuating electricity production increase the need for system balancing, which can be regulated by electrolysers. As it was expected, the *Co-electrolysis* pathway represents the most flexible scenario with 14,203 MW integrated off-shore wind turbines. It is evident from the results that the *Biodiesel* scenario can utilise very little wind energy compared to the rest of the scenarios. In total, the *Biodiesel* scenario has approximately four times less off-shore wind capacities (3,444 MW) than the *Co-electrolysis* scenario. This is due to the much larger electricity demands and energy storage capacities available in the scenarios that include electrolysers.

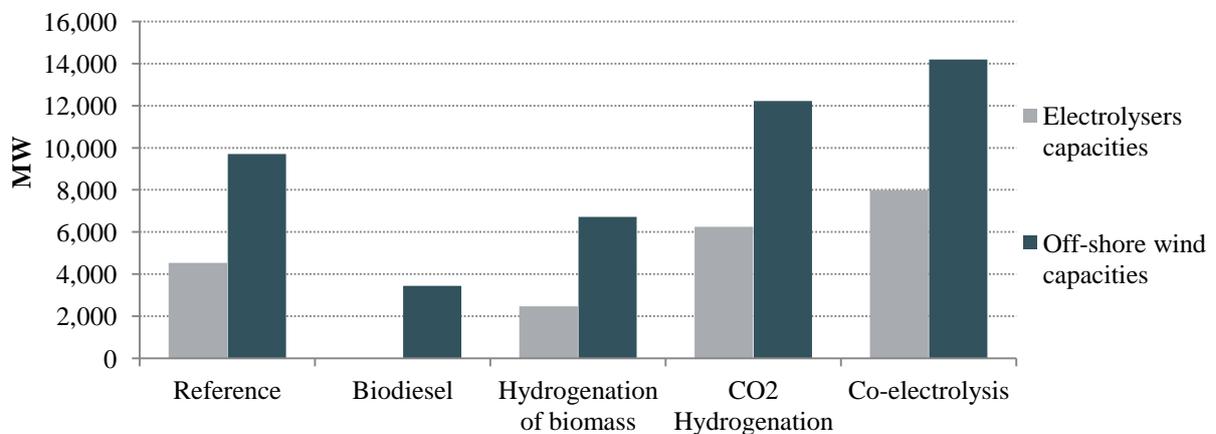


Figure 47. Installed electrolysers and off-shore wind capacities

“In a normal wind year, Danish wind turbines generate the equivalent of approx. 20 % of the Danish electricity demand” [6]. All scenarios that implemented electrolyzers have higher wind shares in primary energy supply (up to 49%), than the *Biodiesel* scenario with 21%. However, as these scenarios are part of a 100% renewable system, significant fraction of electricity is generated from wind power. The wind share of the projected electricity demand varies from 107% to 260% of the projected conventional electricity demand [see Figure 48]. High shares of wind, which are characteristic of the proposed scenarios, dramatically increase the need for system balancing in response to prediction errors and short-term fluctuations.

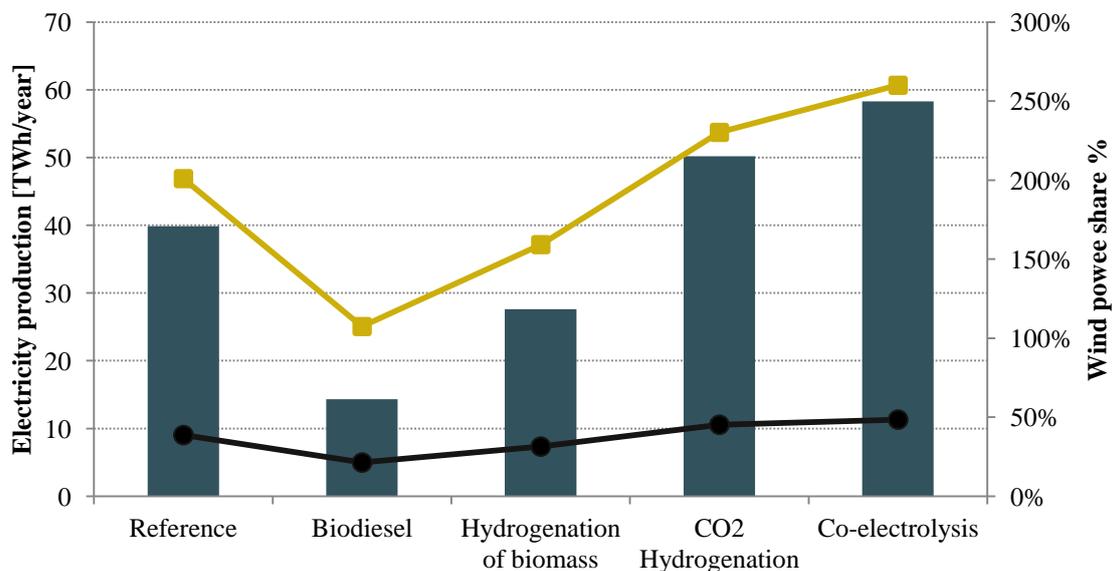


Figure 48. Off-shore electricity production (columns, TWh/year) with according share of total wind power in primary energy supply (black line, %) and wind share of projected electricity demand (yellow line, %)

The primary energy supply is outlined in Figure 49. The scenarios differ only in their utilisation of biomass and offshore wind power, while the use of the rest of renewable energy sources is identical. The more wind is integrated in the system, the higher the primary energy supply is. It is obvious that the technologies implemented in different scenarios are crucial for the biomass consumption.

Even though the *Biodiesel* scenario overall has the lowest primary energy supply among all analysed scenarios, including the *Reference* scenario, with 454.5 PJ compared to 526.2 PJ in the *Co-electrolysis* pathway, this system has the lowest wind integration and the lowest flexibility. Moreover, as it was previous outlined it has the highest biomass use. In other scenarios, electricity produced with wind replaces the demand for biomass while electrolyzers stabilize the grid.

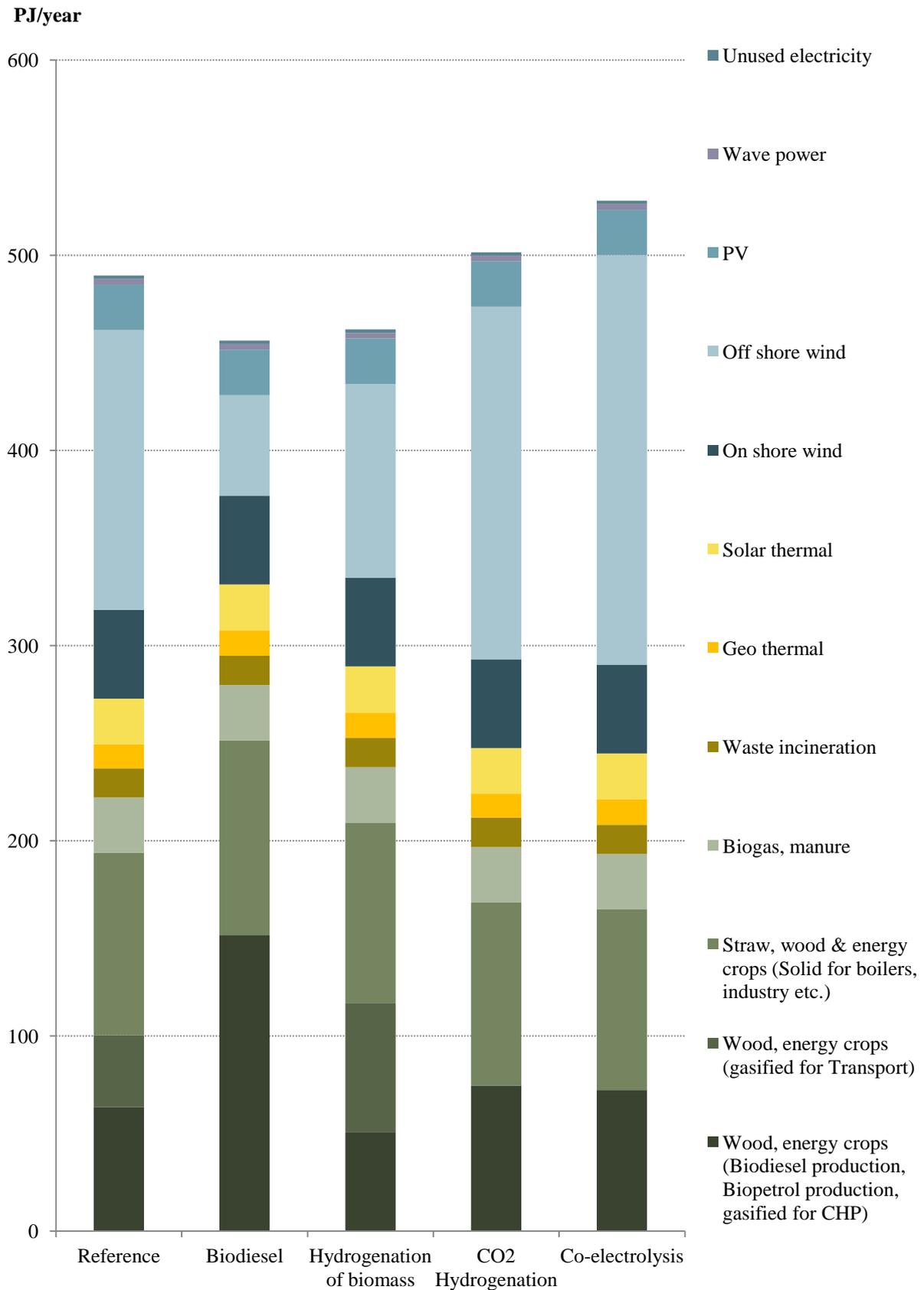


Figure 49. Primary energy supply in the 2050 reference energy system and analysed scenarios

Figure 50 illustrates the annual primary energy supply excluding renewable energy sources. The advantage of presenting PES excluding renewable energy sources is the fact that such results can reveal the ability of the technology to utilise RES, in this case offshore wind power. In our system, this basically represents the biomass fuel consumption.

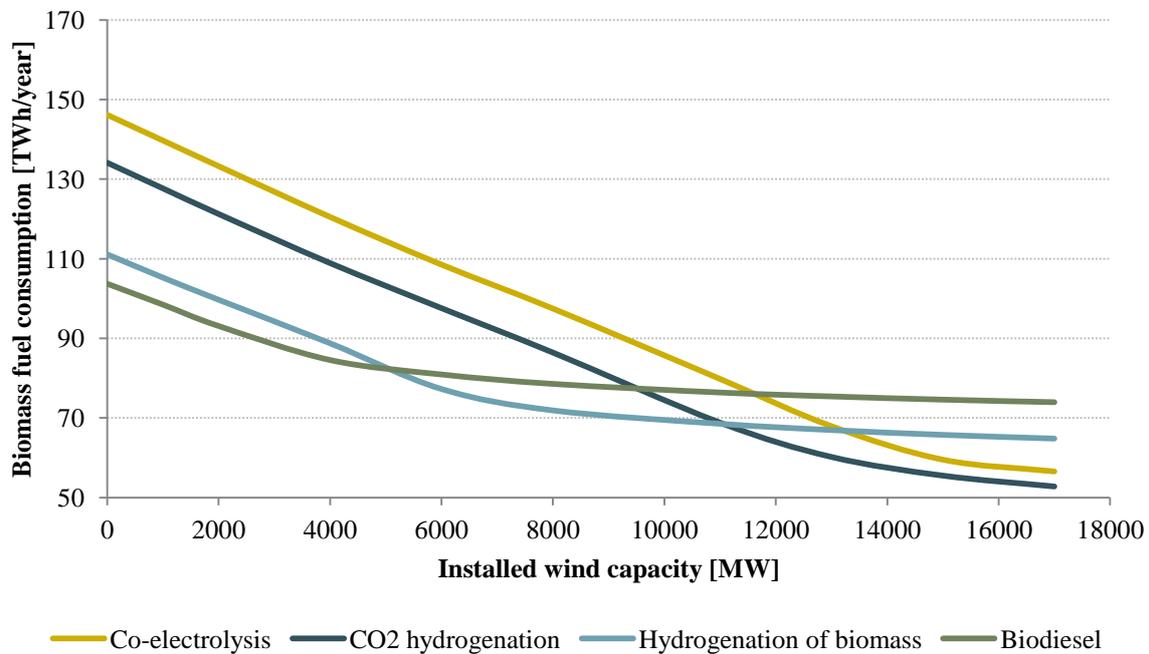


Figure 50. Biomass fuel consumption for all scenarios

The specified electricity demand for installed electrolyzers cannot be met by the capacity of power plants in combination with import on the transmission line which results in higher primary energy supply in case of *Co-electrolysis* and *Hydrogenation of CO<sub>2</sub>*. After reaching a certain capacity of wind power in the system, in case of *Biodiesel* and *Hydrogenation of biomass*, flexibility of their systems becomes lower than those with larger integration of electrolyzers, and system's biomass fuel consumption stays almost the same while CEEP continues to rise.

The socio-economic costs are shown in Figure 51. The scenarios differ in energy system and fuel costs. Due to the implementation of new technologies, scenarios with electrolyzers have higher investment costs followed by lower fuel costs. The investment costs of SOEC are assumed to be 0.25 M€/MW for grid connected electrolyzers with a 20 year lifetime and 2 per cent fixed O&M costs [12].

In terms of the overall system, a 100% renewable system is not so fuel price sensitive because the energy system is constructed not to be fuel dependent.

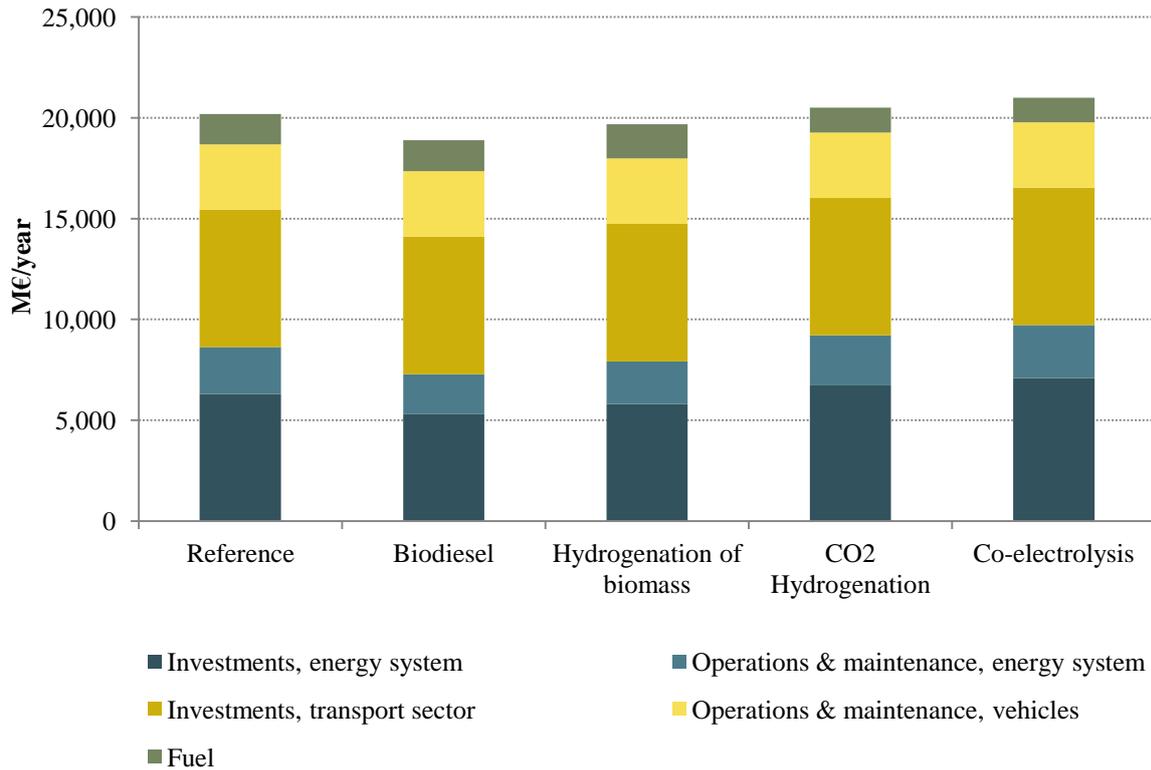


Figure 51. Socio-economic costs of system for all scenarios according to different fuel price level

However, in terms of the transport sector alone, since the fuel costs are the key difference between scenarios, scenarios were analysed with three different price levels, as outlined in Figure 52. The middle price level that is used in all calculations corresponds to an oil price of \$85/barrel. The high price level corresponds to an oil price of 125\$/barrel, and the low price corresponds to an oil price of 65\$/barrel.

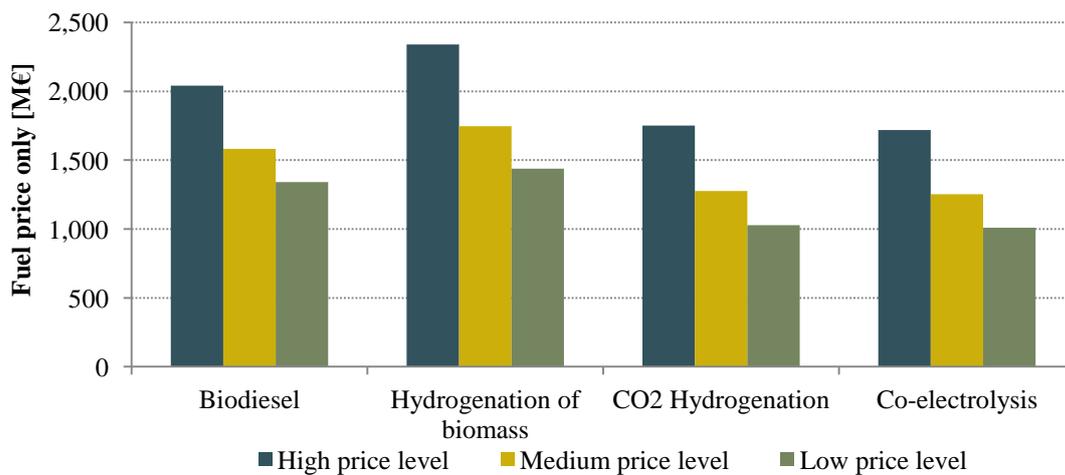


Figure 52. Total fuel costs according to low, medium and high price level

As displayed in Figure 53, the fuel/energy costs were calculated based on fuel, investment, and operational and maintenance costs. It can be seen that the fuel/energy component of synthetic fuel scenarios has large investment costs, since a large proportion of their transport demand was met by electricity from wind turbines and electrolysers. It is obvious that the *Biodiesel* scenario has the lowest investment costs because its transport demand was met by conventional biodiesel, which is a well-established technology. As scenarios are more fuel efficient, due to implementing new more efficient technologies, their investment costs are higher because of the new expensive technologies. It can be seen that the *Hydrogenation of biomass* scenario has the highest fuel costs, followed by *Biodiesel*. It is therefore important to implement scenarios that are less dependent on fuels, because it is reasonable to consider that fluctuating fuel prices are going to continue in the future.

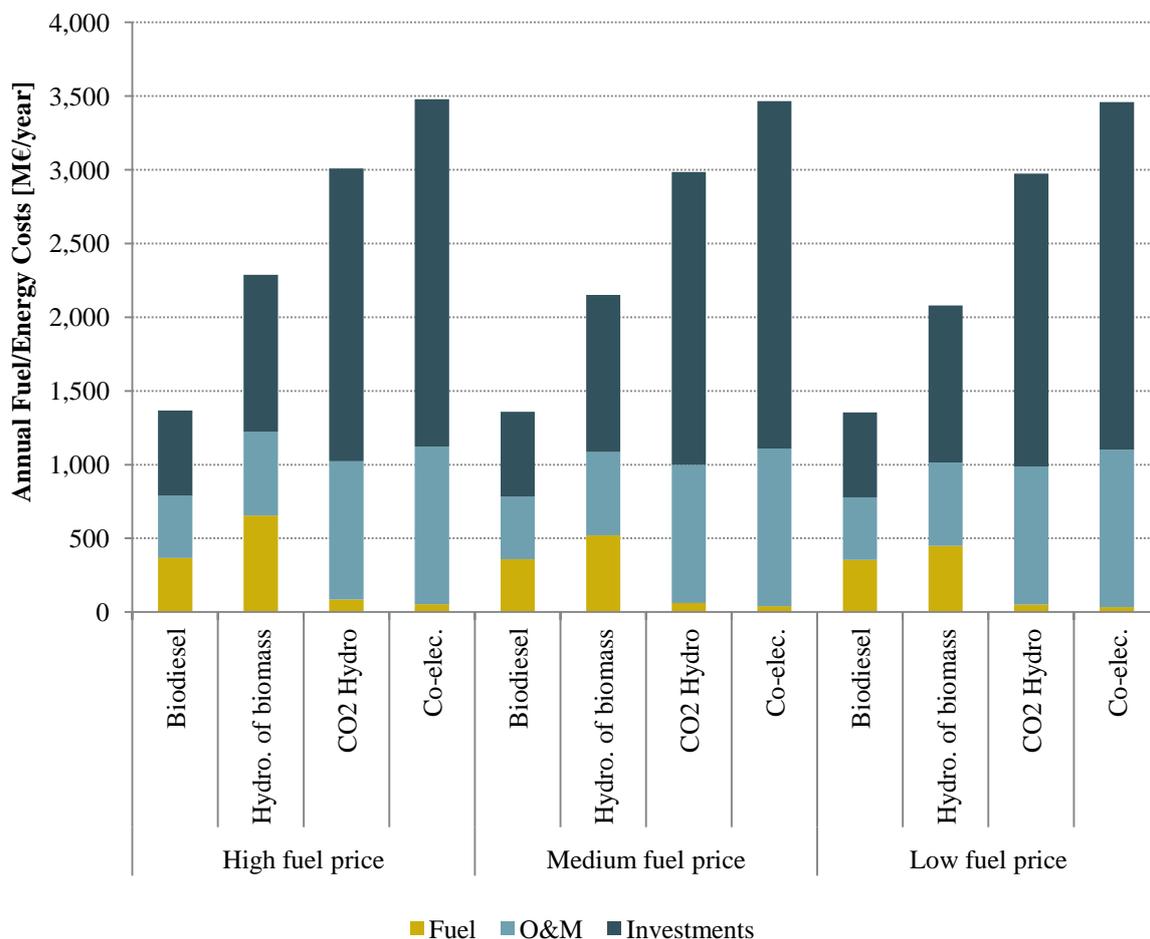


Figure 53. Annual fuel/energy costs for all scenarios for medium price level in the transport demand

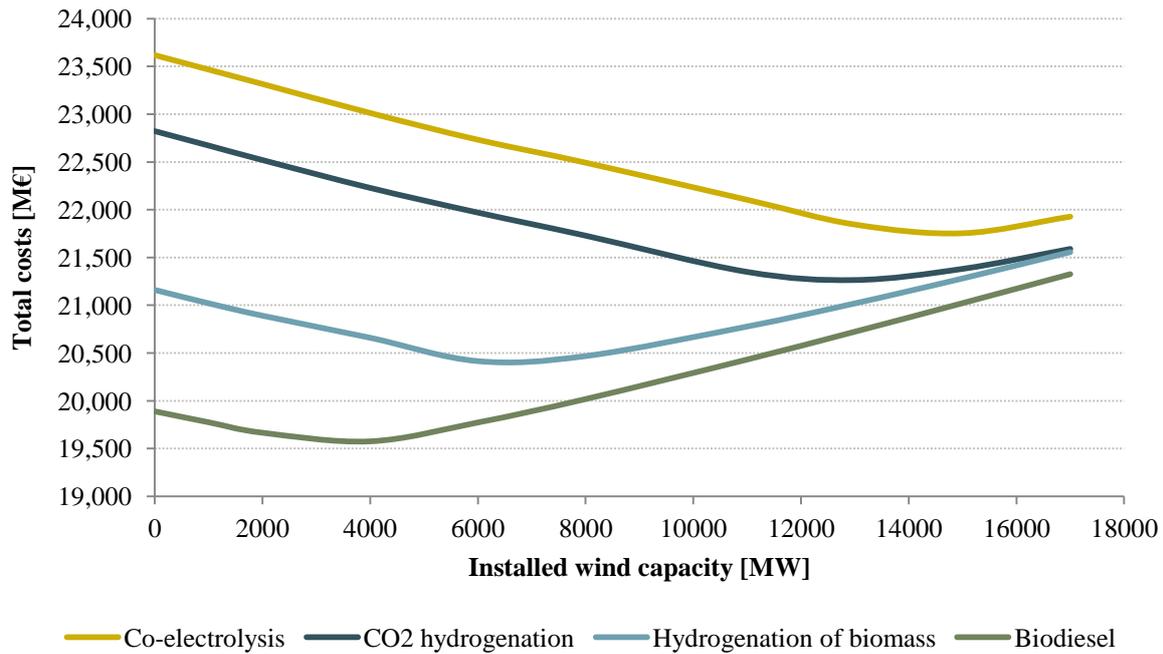


Figure 54. Total energy system costs for all scenarios

As it was expected [see Figure 54], the *Biodiesel* scenario has the lowest total energy system costs, which is due to using today's well-established technology that is cheaper than integrating big capacities of electrolyzers in the system. It is interesting to see that the *Hydrogenation of biomass* and the *Hydrogenation of CO<sub>2</sub>* system costs are almost equalized with integrating 17,000 MW of offshore wind capacities; however, as it was seen from CEEP diagram, *Hydrogenation of biomass* is less flexible.

## 10. CONCLUSION

This thesis presents new technologies for achieving non fossil reliable transport systems, which is necessary for establishing a 100% renewable energy system. The shift to a 100% renewable energy system will imply a raise in intermittent renewable energy sources led by wind and solar. To balance the energy system with more than 40-45% of wind power, which will be indispensable for establishing that kind of system, the transport sector will have to implement technologies that could facilitate wind power integration. However, transport is a very complex sector for transitioning to renewable energy because it has many different modes and needs. To meet all the needs, considering the high wind potential in Denmark which is due to country's climate, the focus is put on maximizing the use of electricity and replacing liquid fossil fuels with renewable fuels by minimising the use of biomass due to its limitation.

The two proposed pathways are focused on synthetic fuels for providing all liquid fuels that cannot be replaced by direct electrification - *Co-electrolysis* and *CO<sub>2</sub> hydrogenation*. Two biofuels scenarios that have direct usage of biomass for producing liquid fuels are included in the analysis: the *Hydrogenation of biomass* and the *Conventional biodiesel* pathway. The analysis of the scenarios showed that the *Biodiesel* scenario has the highest biomass demand, that it is least flexible but its overall energy system costs are the lowest. These results were expected as this scenario is the only scenario that uses absolutely well-known, established, commercially available technology. Results for *Hydrogenation of biomass* showed that this scenario is the most fuel price sensitive one, because it has the highest fuel costs due to its production process which relies on wood gasification. *Co-electrolysis* and *CO<sub>2</sub> hydrogenation* have proved to be the most flexible alternatives, with high share of wind energy and with lowest fuel consumption. However, synthetic fuel scenarios have large investment costs, since great proportion of their transport demand was met by electricity from wind turbines and electrolyzers.

The production of synthetic fuels has many advantages, it combines the heat and power sector with the transport sector, it uses CO<sub>2</sub> for its production, and by using electrolyzers it helps balancing the grid, facilitates wind power integration and it represents smart energy system solutions. By combining electricity and electrolyzers for transport it becomes possible to relocate the electricity consumption and to replace inefficient technologies. The synthetic fuel

scenarios showed improvements of system flexibility and this is essential to the conversion of the energy system into a 100 per cent renewable system. Moreover, the advantage of synthetic fuels scenarios is that processes finish with chemical synthesis, meaning the choice of fuel production is very flexible, because syngas can be transformed to many different fuels depending on different catalysts. However, as synthetic fuel scenarios were based on technologies that are still in R&D level, the ultimate decision on which scenario is the best for the future transport system will depend on the technological development and demonstration of proposed facilities on a large scale. Overall, the costs of synthetic fuel scenarios are more expensive, but biomass savings associated with this make the additional costs worthwhile due to the scarcity of biomass for the energy system. With feasible technological development and mass production of the Solid Oxide Electrolyser Cells, synthetic fuels could be competitive and have market advantage over biomass derived fuels based on their supply related issues, land use shortage, limited biomass resources, etc.

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