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The transport case

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Publication date:
2013

Document Version
Early version, also known as pre-print

Link to publication from Aalborg University

Citation for published version (APA):
Ridjan, I., Mathiesen, B. V., & Connolly, D. (2013). *SOEC pathways for the production of synthetic fuels: The transport case*. Department of Development and Planning, Aalborg University.

SOEC PATHWAYS FOR THE PRODUCTION OF SYNTHETIC FUELS

THE TRANSPORT CASE

AALBORG UNIVERSITY

SOEC pathways for the production of synthetic fuels – The transport case

August, 2013

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Abstract

The focus of this report is analysis of Solid Oxide Electrolyser Cells (SOECs) in the future energy systems. The technical and socio-economic effects of various SOEC application scenarios on the future renewable energy systems are analysed, feasible or ideal locations are identified and recommended, and the competitive strengths and possible weaknesses of the SOEC technology in comparison with other competing technologies are evaluated. This resulted in a detailed overview of technologies involved in the production cycle of synthetic fuels, description of the proposed pathways and the architecture of the system.

Contents

1. Introduction

In future energy systems the renewable energy penetration increases around the world due to the security of supply, climate change and economic benefits. In this respect the pressure on the biomass resources will increase in the future. Currently plans include higher shares of primarily wind power, but solid fuel such as coal is also planned to be replaced by solid biomass [1] and the blend of biofuels should increase significantly in the transport technologies [2]. In this respect fluctuating renewable energy sources such as wind power, photo voltaic and wave power, will serve as a mean to decrease the pressure on the biomass resource.

Electrolysers can convert electrical energy to chemical energy, so for instance water may be split electrochemically into hydrogen and oxygen. Such characteristics give the electrolysers the ability to substitute fossil energy by alternatives in several different ways. The efficiency of electrolysers can be very high in the future. The concrete efficiency depends on temperature, current loading, and the chosen fuel cell technology. Such developments require that the existing electrolysers based on alkaline are replaced by new types of cells. The most promising cells are bases on the Solid Oxide Electrolyser Cells (SOEC). These cells

> *"We need to identify and analyze pathways which enable us to transfer electrons from wind power and PV to synthetic liquid or gaseous fuels for transport"* [4]

are based on ceramics, which potentially enables them to be constructed at low costs avoiding the use of noble metals [3]. They are able to run with rather high temperatures (i.e. > 800 °C). This makes the process more efficient than alkaline electrolysis, as the process of converting water to hydrogen and oxygen is endothermic.

Alkaline electrolysers have been commercially available for decades from a number of suppliers. Megawatt-scale plants are in operation. They are typically used for on-site use in industrial processes where scale or transport costs make hydrogen from conventional fossil fuel processes more expensive. Worldwide however, by far the largest share of global hydrogen production comes from fossil fuels. (Ref. DTU-International energy report - in process)

Polymer exchange membrane (PEM) electrolysis systems have also become available, but until now only very few plants exists. There are no commercial suppliers of SOEC yet, but standard solid oxide fuel cells (SOFCs) can work in electrolysis mode at low current densities [3].

1.1.   Electrolysers in smart energy systems

When the penetration of intermittent renewable resources increases in the electricity grid the demand for *smart energy systems* also increases. Also the penetration of renewable energy sources may increase in the heating and gas sector. In a *smart energy system* the focus is not only on the electricity grid and its balance of supply and demand, but also on sector integration through demand flexibility and various storage options:

- heat storage and district heating with CHP (combined heat and power) plants and large heat pumps;
- new electricity demands from large heat pumps, and electric vehicles for electricity storage;
- electrolysers and synthetic liquid fuels for the transport sector, enabling energy storage in a dense liquid form;
- gas storage and gas grids for biogas and syngas/methane [4].

Such smart energy systems enable flexible and fuel efficient integration of large amounts of fluctuating electricity production from sources such as wind turbines. The idea of erecting wind

turbines or other fluctuating renewable energy sources is to lower the use of fossil fuels or biomass sources.

While CHP and large scale heat pumps in combination with thermal heat storages in district heating systems enable an efficient short term integration of wind, the gas grid´s storage facilities and liquid fuels provide long-term storage and flexibility. If the large-scale renewable energy is accompanied by the integration of sectors, the increased fuel efficiency can potentially decrease the costs of the total energy system. The first and most important step is the integration between the heating and power sectors. In the long run however the transformation to renewable energy is a key challenge regarding biomass when we turn to the transport sector. While there is a large potential for electric vehicles for personal cars, other modes of transport such as trucks and ships require fuels in a liquid or gaseous form. The focus traditionally has been biofuels such as bio-diesel and bio-ethanol, and on whether it is a first or second generation biofuel conversion technology. Recent research in 100% renewable energy systems shows that when including transport it is important to consider fuels in which you can limit the use of biomass [4]. One way in which this is possible is to use hydrogen from electrolysis to create liquid or gaseous fuels for transport.

1.2.   Electrolysers for the transport sector

The most promising application of SOEC electrolysers is in the transport sector for the production of synthetic fuels combined with CO_2 recycling or biomass boosting. Even though significant renewable energy penetrations occurred in some energy sectors, the penetration rate in the transport sector is still rather low. There is no easy solution for meeting transport sector demand due to the wide variety of modes and needs in the sector. To improve the sustainability of the transport sector and to overcome the heavy dependence on fossil fuels there is a need to develop new pathways that can provide liquid fuels that can be used in existing infrastructure. The need for liquid fuels in the transport sector is inevitable due to the fact that many of the transport subsectors are not suitable for electrification and will continue to rely on liquid fuels.

The frequently proposed solution for the transport sector is biofuels, which potentially are not the most sustainable solution in the long term, due to the biomass scarcity and other issues related to their production e.g. land use issues, interference with food supply and other impacts on biosphere and environment. Hence, it is essential to make a detailed analysis of system elements in order to match the demand and to meet the criteria of the renewable energy system.

In this report we identify and analyse different scenarios for the production of fuels for transport, focusing on fuels that enable us to transfer electrons from wind power and PV etc. to liquid or gaseous fuels for transport. This also means that we focus on the electrolysis pathways directed at transport, and not at pathways directed at producing fuels for the heating and power sectors.

1.3.   Report structure

The report contains 6 chapters, starting with Introduction which provides an overview of the report's main findings. Proposed pathways are provided in Chapter 2, and system elements for production of renewable fuels are explained in detailed in Chapter 3. In particular Chapter 3 provides an overview of the individual technologies and possible problems of their use in the production process. Chapter 4 discusses the integration of these pathways in the system, giving the overview of the present infrastructure situation, needed infrastructure for new fuels and the potential solutions of implementing new technologies in the system. Chapter 5 gives a list of existing and demonstration plants for synthetic fuel and biomass gasification. The cost overview for the different production steps is given in the Chapter 6, with proposed plants sizes and locations listed in the Chapter 7. Report ends with an overview of other flexible technologies for the integration of renewable energy sources in the system, the comparison of alkaline and SOEC electrolysers for the production of synthetic fuels and the fuel pathways costs comparison.

2. Proposed pathways

Three main scenarios for using SOEC for producing renewable fuels were identified through literature review:

1. Biomass hydrogenation,
2. CO_2-hydrogenation and
3. Co-electrolysis.

All pathways are adopted from WP 2 Report of CEESA 100% Renewable Energy Transport Scenarios towards 2050, projected as a part of "Coherent Energy and Environmental System Analysis", known as the CEESA project [4].

Synthetic fuel refers to a fuel which does not include the use of fossil fuel in the production process, instead it is produced by combined use of electrolysers with CO_2 source which can be either the recycling of CO_2 from a stationary energy-related or industrial process, in this case from biomass combustion in the heat and power sector, or from biomass gasification. Many different fuels can be can be synthesized from the produced syngas, providing options for both liquid and gas fuel production. Identified fuels analysed in this report are methanol/DME as liquid fuels and methane as a gaseous fuel.

One of the main advantages of synthetic liquid fuels is that requires a limited change in the infrastructure. It requires the alteration of the vehicles to a new type of fuel, alteration of existing fuelling stations. Other parts of the production cycle could include storage and pipeline for syngas and/or CO_2. Wind turbines are used as the electricity source for the electrolysis process. This option is chosen not only because Denmark is a leader in modern wind energy, with 28% of electricity produced from wind in 2011 [5], but also due to the fact that the use of electrolysers in the transport sector enables the integration of wind turbines and the balancing of the energy system.

CO_2 recycling or biomass "boosting" for renewable fuel production would open the door to renewable energy in the transport sector, which was previously not accessible in the form of liquid fuels, with the exception of conventional biofuels production. Moreover this way of fuel production enables flexible fuel choice, since produced syngas can be converted to various liquid or gas fuels. The benefit of converting electricity into a form of liquid/gas fuel via electrolysis provides flexibility in terms of system regulation.

The energy flow charts for pathways are given in the sections 2.1 and 2.2 showing both the methanol/DME and methane production processes.

2.1. Biomass hydrogenation

The principal objective in this pathway is to create a liquid fuel from biomass, which is boosted by hydrogen from steam electrolysis. In this way, the energy potential of the biomass resource is maximized. 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.

Hydrogenation of biomass is a process of upgrading the energy content and density of biomass with hydrogen by gasifying the biomass into a syngas which subsequently reacts with hydrogen [see Fig 7].

The overall efficiency (biomass to methanol) including synthesis losses is 70.9% which is in correspondence to the plant efficiency for the novel concept of methanol production from GreenSynFuels report [6].
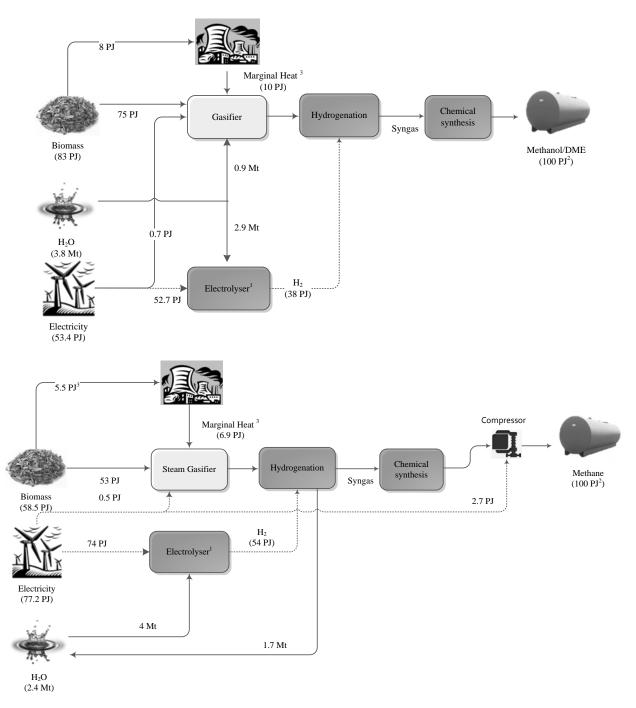
Figure 1. Steam gasification of biomass which is subsequently hydrogenated to methanol/DME or methane. [1]Assumed an electrolyser efficiency of 73% for the steam electrolysis [7]. [2]A loss of 5% was applied to the fuel produced to account for losses in the chemical synthesis and fuel storage. [3]Assuming a marginal efficiency of 125% and a steam share of 13% relative to the biomass input.

2.2. CO_2 recycling pathways

The concept of carbon capturing and recycling is important not just because of global warming issue, but also since there may be a carbon shortage when implementing a 100% renewable system. Moreover these pathways enable a strong connection between the energy sectors, which is important to establish a flexible energy system. Recycling of CO_2 into liquid fuels tackles the energy crisis, enables geographical independence of fossil fuels, provides a cleaner environment, and increases security of supply.

2.1.1. CO₂-hydrogenation

The principal objective in this pathway is to create a fuel which does not require any direct biomass input, by using steam electrolysis and sequestered carbon dioxide. This pathway combines carbon dioxide and hydrogen gases together in the form of syngas, which is thereafter converted by chemical synthesis to fuel [see Figure 2].
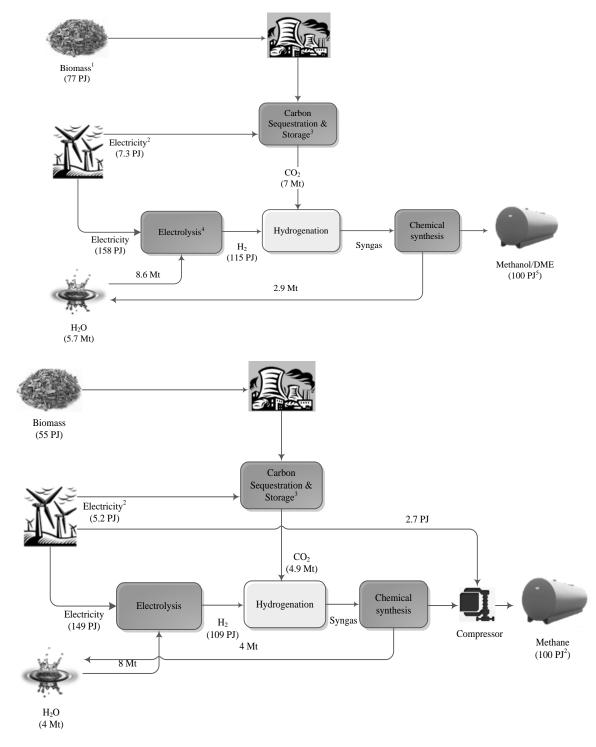
Figure 2. Hydrogenation of carbon dioxide sequestered using CCS to methanol/DME or methane. [1]Based on dry willow biomass. [2]Based on an additional electricity demand of 0.29 MWh/tCO₂ for capturing carbon dioxide from coal power plants [8]. [3]Carbon capture & storage (CCS) was used since it is currently a cheaper alternative to synthetic trees [9,10]. [4]Assuming an electrolyser efficiency of 73% for the steam electrolysis [7]. [5]A loss of 5% was applied to the fuel produced to account for losses in the electrolyser, chemical synthesis, and fuel storage.

2.1.2. Co-electrolysis

This pathway has the same principal objective as *CO2 hydrogenation* but it combines steam and CO_2 electrolysis into a process called co-electrolysis, and the produced synthetic gas can afterwards be catalysed into various types of fuel [see Figure 3]. Co-electrolysis has a higher overall efficiency than steam electrolysis because it also includes the electrolysis of carbon dioxide, which has a higher efficiency than steam electrolysis. The syngas produced from this process contains hydrogen and carbon monoxide in a 2:1 ratio, which is desired for further conversion to methanol. In comparison to the CO_2 hydrogenation pathway, co-electrolysis requires a lower water input but based that the reaction does not provide any excess water, the net water demand is the same for both pathways.
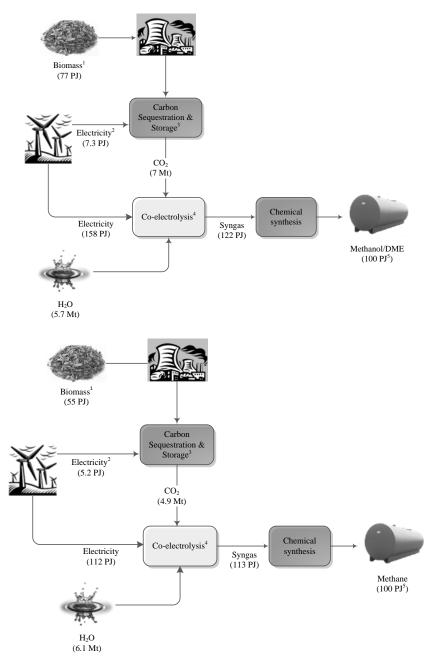
Figure 3. Co-electrolysis of steam and carbon dioxide which is obtained using CCS to methanol/DME and methane. [1]Based on dry willow biomass. [2]Based on an additional electricity demand of 0.29 MWh/tCO2 for capturing carbon dioxide from coal power plants [8]. [3]Carbon capture & storage (CCS) was used since it is currently a cheaper alternative to synthetic trees [9,10]. [4]Assuming a co-electrolyser an efficiency of 78%: 73% for steam and 86% for carbon dioxide [7]. [5]A loss of 5% was applied to the fuel produced to account for losses in the electrolyser, chemical synthesis, and fuel storage.

2.2. Comparison with other possibilities

The proposed scenarios were compared to other alternatives such as electrification and fermentation pathway. They were compared on the basis of the electricity and biomass required for each pathway to produce 100 Gpkm. By knowing specific energy consumption of the different vehicles and the energy losses from production to consumption, it is possible to compare each of the pathways in terms of the resources they require and the transport demand they meet. The comparison is based on the same methodology used in [4].

Direct electrification is by far the most sustainable form of transportation. It requires the lowest amount of electricity and it does not require any direct biomass consumption. In terms of the resources consumed the fermentation pathway is the least efficient and the only not flexible pathway in terms of fuel because the production process is restricted by ethanol. The comparison indicates that if the bioenergy resource is available and it is not restricted, methanol/DME should be produced using the biomass hydrogenation pathway. The production of methane through the same pathway consumes more energy due to the higher demand for hydrogen. The hydrogen is produced via electrolysis by using electricity therefore the electricity demand is higher while biomass demand is lower. Overall, it can be seen that the pathways with methane as the finale fuel consume more energy due to their lower vehicle efficiency, hydrogen to carbon ratio and required electricity for hydrogen production. In the case where no bioenergy resource is available, synthetic methanol/DME should be produced using CO_2 hydrogenation or co-electrolysis.

However, this does not mean that the biomass hydrogenation or CO_2 recycling pathways should be avoided or not implemented. In the future, the ultimate decision will depend on the available biomass resources, technological development, demonstration of these facilities on a large-scale and the infrastructure costs. The chosen pathways are going to depend on the vehicle efficiencies, driving range and specific energy consumption. It is important to point out that the results are very sensitive to vehicle efficiencies, which are currently very uncertain, so the results could vary as more information is obtained.

The aim in the next chapters of this report is to analyse how such infrastructure and technology could be implemented, in which costs, location complexity etc. is taken into account.
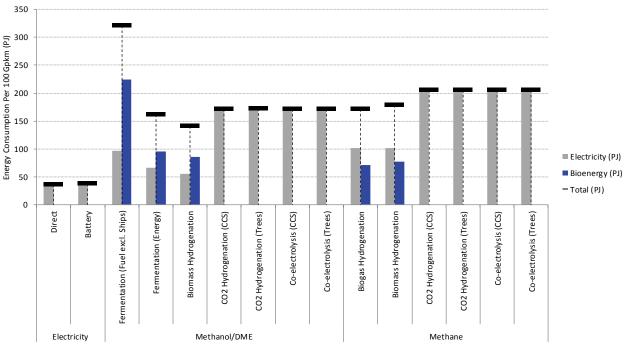
Figure 4. Energy consumption for passenger transport per 100 Gpkm for different pathways

3. System elements for production of renewable fuels

To evaluate the potential of electrolysers for liquid fuel production, it is important to know the individual stages of the synthetic fuel production cycle and technologies implemented. This section will give an overview of each system element needed for the production of the synthetic fuels. Description is based on the literature review and existing data which was validated among the project partners.

The production process is divided in four steps (see Figure 5) and each pathway ends with the chemical synthesis meaning that the choice of fuel is very flexible. Principal difference between Biomass hydrogenation and CO_2 recycling pathways is in the carbon source. Biomass hydrogenation uses direct input of biomass in the gasification process, and the produced gas is later on boosted with hydrogen produced from steam electrolysis. CO_2 recycling pathways do not require any direct biomass input, instead they use emissions from the biomass used in heat and power sector combined with electrolysis. The section on SOECs gives a short description of their advantages, system losses and the future costs projection. Very important part of the system architecture is building the new infrastructure, therefore the syngas and CO_2 transportation was analysed as the possible options for the integration and it was taken in the consideration is it necessary to build it. While CO_2 transportation and storage is established, but still rather expensive at the moment, data for the syngas transportation and storage is difficult to obtain. Fuel synthesis is a well-known process with flexible fuel outputs depending on different catalysis being used in the process. Three different fuels were considered in the analysis: methanol, DME and methane. Existing vehicle technologies and properties of the fuels are described along with the fuel handling and potential safety issues.
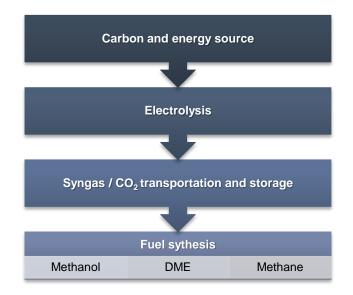
Figure 5. General steps for synthetic fuel production – see pathways to see how steps interact

3.1. Carbon and energy source

The chosen energy source for the electrolysis process is wind energy both for the reason of high share of wind in the Danish energy system but also due to the fact that the integration of electrolysers in the system enables the regulation of intermittent energy sources and subsequent a reduced demand for fossil and biomass fuels.

3.1.1. Carbon-capture and recycling (CCR)

To provide the carbon source, carbon-capture and recycling (CCR), air capturing or biomass gasification is proposed. The difference between CCR and air capturing is that latter is not connected to any specific carbon source. By using carbon-capture and recycling technology to capture and reuse the produced CO_2 expensive storage options are avoided. Air capturing is excluded from the analysis here since CCR is currently a cheaper alternative to synthetic trees [9,10]. From a technical perspective carbon trees would only require approximately 5% more electricity than CCR [9] so the system costs of the carbon capture technology is most likely the only significant variation in the results of the whole system. It should be noted however that carbon trees may require different infrastructure due to the potential dispersed nature of these. With captured CO_2 from the atmosphere, the proposed production process of synthetic fuels could enable a closed-loop carbon-neutral fuel.

An analysis was conducted with the post-combustion CCR process, due to the fact that this method is more established for CO_2 capture than the others. *Post-combustion capture* stands for removing the CO_2 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 the CO_2 for compression and transportation.

3.1.2. Biomass gasification

Biomass gasification is a high-temperature process (500 to 1400°C) for converting complex hydrocarbons of biomass into a combustible gas mixture. The gasification of biomass upgrades the quality and value of biomass into gaseous fuels in the presence of gasification agents. The agent may be oxygen, air, steam or a combination of them [11]. It is similar to coal gasification but it occurs at lower temperatures. Gasification is an endothermic process so it requires heat. Depending on the gasification technology, the final gas mixture product can vary. If the desired product is methane, syngas without nitrogen and with a high level of methane is necessary, which can be obtained using low gasification temperatures <850 to 900°C. If the preferred fuel is another hydrocarbon such as methanol or DME, the desired syngas is without nitrogen and methane which can be produced by oxygen-blown gasification. In case of just heat and power generation without fuel production there is no requirements for the nitrogen content [12].

Gasification can handle a wide range of biomass feedstock, ranging from woody residues and agricultural residues to crops without major changes in the basic process. A variety of biomass gasifier types have been developed and can be divided into three major classifications [13]:

1) *Updraft gasifier* – the feedstock enters the reactor from the top while gasification agents enter at the bottom of the reactor. This kind of gasifier is a mature technology that can be used for small-scale applications, and can handle high moisture content without any carbon in the ash. The main disadvantages of this technology are the feed size limit, high tar yield and slagging potential.
2) *Downdraft gasifier* – both feedstock and gasification agents enter the reactor from the top. This kind of gasifier is used when clean gas is desired. The main disadvantages are low thermal efficiencies and that it cannot handle high moisture or ash contents.
3) *Fluidized-bed gasifier* – both feedstock and gasification agents enter from the bottom of the reactor. These gasifiers are used for large-scale applications and have medium tar yield and high particle content in the output gas.

New technology with multistage gasification represents a way to accommodate the problem of reaching the high efficiency and minimizing the tar in the produced gas. More detailed description of gasification technologies and different types of gasifiers is given in the [12].

Using biomass gasification as the carbon source for synthetic fuels in the transport sector enables that the energy content of biomass is upgraded and reduces the need for biomass resources for transport fuels.

3.2.   Solid Oxide Electrolysis Cell (SOEC)

If SOEC are developed in accordance with the potential of the technology, the high temperature electrolysis produces almost no waste heat, resulting in a very high efficiency, significantly higher than that of low-temperature electrolysis. The high temperature results in faster reaction kinetics, which reduces the need for expensive catalyst materials. Thus, in comparison to low temperature electrolysis, which uses precious materials, high temperature electrolysis enables the use of relatively cheap electrode and electrolyte materials. Further increases in efficiency and improvement of the economy can be accomplished by pressurizing the SOEC. Another potential benefit of the SOEC compared to conventional electrolysis technology is its ability to combine steam and CO_2 electrolysis and thus the possibility to make cheap non-fossil fuel. 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. The high operating temperature and high pressure, which provides further efficiency improvements, enables the integration of synthesis of the synthetic gas to synthetic fuel.

The SOECs are still on the research and development level so the costs available are future cost estimations. According to [14] costs for small scale SOEC are 0.71 M€/MWe and on the large scale 0.28 M e/MW. Based on [15] the calculated costs of SOEC are 0.86 M€/MWe for 2020, 0.28 M€/MWe for 2030 and 0.21 M€/MWe in 2050, with a lifetime of 10-20 years. The prices are based on the stack module costs of 175 US$ in 2007 dollars converted with inflation factor to 2012 dollars.

The implementation of SOECs in the system requires grid connections so these expenses need to be added to the overall costs. The grid costs are estimated to be 66,000 €/MWe with a lifetime of 30 years. The total investment costs of grid connected electrolysers is thus 0.93 M€/MWe in 2020, 0.35 M€/MWe in 2030 and 0.28 M€/MWe in 2050. The fixed operation and maintenance (O&M) costs are approximately 3 % of the initial investment annually which is in 2020 25,800 €/MW/year, in 2030 8,400 €/MW/year and in the case of 2050 they are 6,200 €/MW/year.

Further information on the data, costs and performances of the SOECs is available from [16].

3.2.1.   Electrolyser system losses

For energy system analyses it is recommended to include 10 % of auxiliary losses to account for blowers, dryers, inverters, and surface heat losses [16]. In the future with more optimised module designs the total losses may be lower than the 10 %, first of all because of improved integration and improved components and second because a part of the parasitic heat may be recovered and used e.g. for district heating. The percentage of the lost heat to the surroundings is related to the higher voltage at what the cell must be operated [17]

Insulation of the electrolyser system is important because of the SOEC operating conditions. As it is high temperature electrolysis, insulation needs to provide a good start-up time and minimize heat loss at the operating temperature. Some calculations do not include heat loss to the surroundings because it is expected that the loss can be limited if the system is properly insulated even if cheap materials are used [18]. However, insulation has been used for SOFCs to enable very fast start-up by keeping the operating temperature at the right operation level [19]. Commonly used insulators for SOFC contain silica or conventional high-alumina (low-silica), but new generation of ultra-low silica compositions are now available [20].
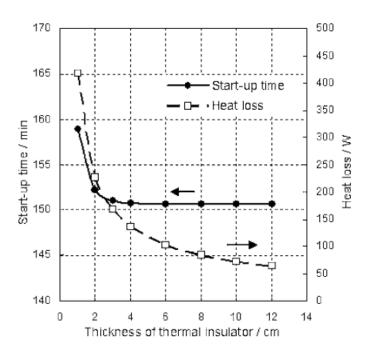
Figure 6. Dependence of thickness of the thermal insulator on start-up time and heat loss at the operating temperature [21]

Figure 6 shows the influence of thickness of the insulator to SOFC performance in relation to start-up time and heat loss. The start-up time stays constant when insulation thickness exceeds 4 cm, however heat losses continue to drop as the thickness is increased and it is approximately inversely proportional to the thickness [21].

3.3.   Syngas storage and transportation

Storing and transporting syngas instead of immediately converting it to liquid fuel could improve system flexibility and possibly provide additional resource and economic benefits.

3.3.1.   Syngas definition and properties

Syngas, as a term usually refers to a 2:1 mixture of H_2 and CO [22]. It is primarily a mixture of hydrogen (H_2) and carbon monoxide (CO) that can also contain significant although lower concentrations of methane (CH_4) and carbon dioxide (CO_2) along with smaller amounts of impurities such as chlorides, sulphur compounds, and heavier hydrocarbons [23]. It is important to point out the difference between syngas and SNG, which is essentially methanated syngas also called synthetic natural gas defined as methane. SNG can be transported through existing natural gas network.

Both of the main components in syngas, H_2 and CO, are flammable gases with the possibility of auto-ignition in air in certain conditions. Two main characteristics of these gasses is that hydrogen is lighter than air and it is difficult to prevent it leaking, while carbon monoxide is highly toxic so transportation and storage of syngas requires a detailed risk assessment. Moreover hydrogen burns with an almost invisible flame which increases the risk of injury in case of fire.

3.3.2.   Syngas storage and transportation via pipeline network

The simplest storage technique is compressed gas storage as it relies only on a compressor and pressure vessel while it is also the most relevant large-scale storage option. Even though leakage is one of the main issues with syngas, industrial experience suggests that excessive diffusion and leakage of syngas through a storage chamber wall is not an issue for daily and relatively short-term storage [24].

The only identified literature about transporting syngas or carbon monoxide via a pipeline system is the report "Carbon monoxide and syngas pipeline systems" [23] and it is based on the technical information and experience currently available to the authors. The purpose of this publication is to further the understanding of those engaged in the safe design, operation, and maintenance of transmission and distribution systems. It has detailed information about design, piping, valves and equipment, cleaning, construction, operation and monitoring.

The main problem with the transportation of syngas lies in its properties. Syngas is a highly toxic mixture and is prone to self-ignition due to the hydrogen content. There are some existing mini syngas networks in the chemical and petrochemical industry. Due to the fact that supply and demand varies, buffer storage is even used to compensate for differences [24].

There can be two types of pipeline networks: underground and above-ground pipelines [23]. Underground piping is vulnerable to damage by lightning strikes or ground fault conditions, which may rupture the pipe material. Above-ground piping systems need to be well planned and maintained due to syngas toxicity, so leakage concerns are much more important than with other gases.

Syngas transportation cannot be done in existing natural gas pipelines because they can only handle up to 15 - 20 % of hydrogen, by volume. However, if the hydrogen rate is lower than 20 % it is possible to store syngas by increasing the operating pressure [25].

One of the possibilities of transporting in the pipes it is to tune syngas with a water-gas shift reaction to 3:1 mixture of hydrogen (H_2) and carbon dioxide (CO_2). The tuned syngas would not be toxic and it would be lighter than air so it would disperse if it leaked. Further, it is expected that carbon dioxide would at least partially offset the heating/self-ignition problem and may solve it entirely [24]. All syngas impurities could be removed prior to syngas transportation via pipelines to minimize corrosion problems.

The "double bus" network was presented in [26]. The system consists of two pipelines: high and low quality one. The "high quality" has low H_2/CO ratio, and if end users need to have syngas with higher hydrogen content, they can use a water-gas shift reaction to increase it. The other "low quality" pipeline collects and transports syngas that is produced in other production processes and it creates flexibility in the system because it can be used for electricity production. The system combines both high and low quality pipelines, which are connected to the methanol plant for the production of liquid fuel. It eliminates the need for a syngas recycle system, which reduces the investment and operating costs.

3.4.   Carbon dioxide transportation and storage

The transportation of carbon dioxide is not new. It was established in the USA for long distance transportation of CO_2 to oil recovery projects. The carbon dioxide needs to be purified of hydrogen sulphide, dried to minimize the corrosion [27], compressed, and cooled to the liquid phase [28]. The transportation of CO_2 in the gaseous phase is inefficient due to its low density.

Transportation can be done through:

- Pipeline system
    - Land pipelines
    - Marine/underwater pipelines
- Marine transportation

Pipelines are identified by a series of studies [27-30] as the most practical method of long distance transportation of large quantities of carbon dioxide. There are seven existing long-distance CO_2 pipelines reported, mainly in the USA and it has been practiced for over 40 years. The oldest pipeline was finished in 1972 and the newest was built in 2000. The overall length of the pipelines is approximately 2,600 km.

The marine transportation includes both temporary land storage and a loading facility. Most of the problems associated with transportation of CO_2 can be related to the problems with liquefied petroleum gas transportation. There are less than ten ships used for CO_2 transportation and they are based on the same technology as existing liquefied gas ships.

Investment costs for the pipeline are highly dependent on the requirement for a compressor station. It is possible to avoid compression by increasing the pipeline diameter or reducing the flow velocity. The pipeline cost model was given in McCoy. et al. [31]. The results show that the estimated levelized costs per ton of CO_2 transported is between US\$1.03 - 2.63 for a 100 km pipeline handling 5 million tonnes of CO_2 per year. The total investment cost for both offshore and onshore pipelines, excluding booster stations, are in the range from 0.1 - 1.5 million US\$/km depending on the diameter [27].

The European technology platform for zero emission fossil-fuel power plants published a report in 2011 detailing an analysis of CO_2 capture, storage and transport costs. Table 1 and 2 show the total annual costs and cost per tonne of CO_2 transported, excluding compression costs at the capture site for pipelines, while the liquefaction cost for ship transportation are separately noted [32]. The results show that pipeline systems are highly dependent on the length of the pipes and the scale, while the shipping costs are stable over different distances. The costs for a short onshore pipeline with a small volume of CO_2 transported (2.5 Mtpa) are 5.4 €/tCO_2, while this price is reduced to 1.5 €/tCO_2 for a large system (20 Mtpa). Offshore pipelines are almost twice as expensive compared to the onshore pipelines.

Table 1. Cost estimates for commercial natural gas-fired power plants with CCS or coal-based CCS demonstration projects with a transported volume of 2.5 Mtpa [32]

Distance	km	180	500	750	1500
Onshore pipeline	€/tCO2	5.4	n.a.	n.a.	n.a.
Offshore pipeline	€/tCO2	9.3	20.4	28.7	51.7
Ship	€/tCO2	8.2	9.5	10.6	14.5
Liquefaction (for ship transport)	€/tCO2	5.3	5.3	5.3	5.3

Table 2. Cost estimates for large-scale networks of 20 Mtpa. In addition to the spine distance, networks also include 10 km-long feeders (2x10 Mtpa) and distribution pipelines (2x10 Mtpa) [32]

Distance	km	180	500	750	1500
Onshore pipeline	€/tCO_2	1.5	3.7	5.3	n.a.
Offshore pipeline	€/tCO_2	3.4	6.0	8.2	16.3
Ship (including liquefaction)	€/tCO_2	11.1	12.2	13.2	16.1

Carbon dioxide can be temporarily stored in compressed tanks or stored long term in geological storage, ocean storage, and mineral carbonation. The compressing of CO_2 is done by the same technology as natural gas compression with certain modifications due to the gas properties. To compress carbon dioxide to the desired pressure of 14 MPa, 119 kWh per ton of CO_2 is needed [33]. The range of compression costs, depending on desired pressure and energy costs is in the range of 6 - 8 US\$/tCO_2 [34].

3.5. Fuel synthesis

Fuel synthesis is a well-known process with a wide variety of possible fuel outputs depending on different catalysis being used in the process. Any of the proposed pathways results in a syngas mixture which can be converted to different transportation fuels, as can be seen from [13]. Fuels include hydrogen, methanol, alkanes, ethanol or larger alcohols.

By using different catalysts, different synthesis reactions will occur. For methanol production Zn/Cr/Cu catalysts are used, and the process favours high pressure (50-300 bar) and low temperature (220 - 380°C). In the case of methane, production takes place over a nickel catalyst at

a temperature between 200-400°C. The pressure under which the methane production occurs is lower than for methanol at approximately 1-10 bar.

There are three types of methanol reformers:

- One-step steam reforming
- Two-step reforming
- Auto thermal reforming

Methanol synthesis is a highly exothermic process; therefore most of the existing plants use this extra energy to produce the electricity required for the process itself. The systems design is defined based on the type of catalyst. Catalysts are crucial for fuel production and there is a large quantity needed in case of adapting transport to synthetic fuels. To produce China's methanol demand (23 billion litres of methanol per year) approximately 3,000 tons of catalysts are required [35]. It is difficult to get data about the efficiency from the producers so the only sources are published data estimations. The conversion efficiency of syngas to methanol is from 71.2% up to 80.1% [36,37].

The production of methane e.g. methanation is well established technology. Methanation was primarily used in industrial applications for removing carbon monoxide and hydrogen from feed gases in ammonia plants. During the oil crisis in the 1970s the development of the technologies for SNG production from coal and lignite was increased. The methanation process converts syngas consisting of hydrogen, carbon monoxide and carbon dioxide to methane and water. The process is strongly exothermic and the reactor needs to be cooled. Production of methane via gasification process is preferable because gasification itself favours methane formation. The overview of technologies for SNG production from coal and dry biomass was given in [38], and short overview of methanation technologies relevant to Denmark was given in [39].

3.5.1. Fuel choices and existing vehicles

Where possible fuel produced from syngas is assumed to be methanol, because it is the simplest and lightest alcohol, it is most suitable as a petrol substitute in Otto engines due to its high octane rating, and methanol cars are a developed technology. Methanol can be blended with petrol by up to 10-20% without the need for engine or infrastructure modifications [40]. Methanol flexible fuel vehicles were available in the United States from the mid-1980s to the late 1990s [35]. More than 20,000 vehicles and 100 fuelling stations were there at the peak of the methanol era in 1997. Methanol has a lower energy density than petrol so vehicles need large flow rates. Methanol vehicles have the same or even better performance than petrol models [41]. The petrol vehicles need to be modified to methanol with some adaptations in the engine due to its corrosive nature. The main reason why methanol did not stay at the transportation fuel market is due to the time when it appeared on it. Declining petrol prices and the introduction of cleaner petrol excluded it from the market. China is the leader in using methanol for transportation with five different methanol gasoline mixtures available on the market mainly by private fuel stations - M5, M10, M15, M85 and M100 [35]. In China methanol has low production costs and it is locally produced. Moreover methanol reduces greenhouse gas emissions with better vehicle performances. The reason for improved vehicle performances is due to the higher octane rating, heat of vaporization, flame speed, heat capacity of combustion products etc. It is proven that no technical barriers exist for manufacturing methanol vehicles or converting the existing petrol cars. Conversion of existing petrol vehicles to methanol flexi fuel vehicle (FFV) has a cost range of US$100-300 [41]. However M100 vehicles have 50% less driving range than petrol vehicles due to the lower energy density of the fuel. Methanol is also a platform chemical used to produce a range of other chemicals and fuels so it is a flexible solution [13].

Dimethyl ether (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 alternative to conventional diesel. DME can be produced directly from syngas by chemical synthesis or it can be

converted from methanol by the dehydration process. The advantage is that both methanol and DME can be produced in the same plant. The energy consumption for dehydration of methanol is marginal. DME is a liquefied gas with similar characteristics to those of liquefied petroleum gas. DME has a higher cetane number than diesel and it has a low boiling point (-25°C) which eliminates cold start problems [42]. The first DME fuelled heavy vehicle was developed by Volvo as part of a development project from 1996-1998 [43]. In 2005 Volvo launched the second generation of DME trucks. These engines are characterized by a low-pressure, common rail system, with an injection pressure less than 20% that of an equivalent diesel engine [43]. DME cars have ultra-low exhaust emissions with nearly no NOx emissions and low CO_2 emission as a result of using lubrication oil. Because of this DME vehicles do not need any exhaust treatment devices. 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 [42]. The Danish Road Safety and Transport Agency together with The Danish Environmental Protection Agency have carried out a project on DME as a transportation fuel to demonstrate and evaluate the feasibility of DME as a clean diesel substitute fuel for busses (by testing Volvo buses) [44]. Heavy duty DME-fueled vehicles have completed 100,000 km of driving trials in Japan, Shanghai and in Europe. It is expected that the results will demonstrate the effectiveness of DME vehicles and initiate their wider use. Similar to methanol, DME cars have a 50% lower driving range compared to diesel cars, so to overcome the lower energy density of DME the fuel tank needs to be twice as big to enable the same driving range [45].

The conversion losses during dehydration of methanol to DME are regained due to the higher efficiencies of diesel compared to petrol engines. Therefore, the results for methanol and DME are rather similar and no distinction is made here. It is assumed that methanol/DME could be used directly in all modes of transport except aviation.

Table 3. Comparison of fuel properties. Adapted from [45]

		Methane	Methanol	Dimethyl ether
Formula		CH_4	CH_3OH	CH_3OCH_3
Molecular weight	g/mol	16.04	32.04	46.07
Density	g/cm^3	0.00072	0.792	0.661
Boiling point	ºC	-162	64	-24.9
LHV	kJ/g	47.79	19.99	28.62
Carbon content	wt. %	74	37.5	52.2

Methane can also be used in existing internal combustion engines, with performances similar to petrol or diesel vehicles. The efficiency of methane vehicles could be improved with turbo supercharging due to low engine knocking [46]. It has a higher octane rating than petrol (120-130) so it can be used in spark ignition engines with a high output [47]. Methane can be used in light duty CNG vehicles, heavy duty CNG vehicles and as a liquid fuel in the form of LNG for long distance and freight transport vehicles such as boats and trucks. Compared to petrol and diesel, methane produced from coal has lower greenhouse gas emissions with theoretical reductions of almost 30% CO_2 emissions with particulate emissions close to zero. CNG vehicles are a well-established commercially available technology; however the operating range of methane vehicles is almost half of the DME vehicles due to the energy density, therefore the engine efficiencies needs to be high to overcome the density issues of gaseous methane over liquid DME. The driving range can be increased with additional storage tanks but this can displace payload capacity [48]. In 2010, 1.4 million natural gas vehicles were reported in Europe, of which 145,000 buses and 108,000 trucks with 3,700 public and private fuelling stations [49]. There are roughly 14.8 million natural gas vehicles worldwide [50]. These types of vehicles are a good choice for journeys within a limited area due to their low driving range. There are a limited number of vehicles that can be purchased as methane/natural gas vehicles, but vehicles can be retrofitted to enable the operation on gaseous fuel and the costs vary depending on the car model.

Due to the fact that the methanol, DME and methane are not natural resources their price is strictly connected to a feedstock used for their production. Table 4 shows the comparison of DME and methanol prices produced from fossil fuels to other common fuels for different price ranges from 1990s to 2005.

Table 4. Price comparison for fuels with the US price range. Adapted from [45]

	Natural gas	Gasoline	Diesel	Methanol	DME
US$/GJ	4-7	6-12	6-12	5-17	5-14

3.5.2. Fuel handing, storage and safety issues

Methanol is one of the most widely used chemicals and it is metabolized in human bodies in small amounts as well. Methanol is tasteless and odourless so it could be accidently ingested. The poisoning from direct ingestion of methanol takes 10-48 h to lead to acute symptoms and the cure is well known. Methanol fumes are not as dangerous as petrol ones. The only toxic component of 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. Methanol burns 75% slower than gasoline, and methanol fires release heat at only one-eighth the rate of gasoline, so methanol is safer than gasoline in terms of fire security. Methanol vapours must be four times more concentrated in air than the gasoline ones to ignite, however methanol flames are almost invisible so it can be a potential issue for fire fighters [51]. 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.

In contrast to methanol, *DME* is not corrosive to metals and it is not poisonous, but it is not compatible with most elastomers. DME has a low viscosity and therefore, it needs a lubricant improver to ensure normal service to the injection system. DME is a gas at ambient pressure and it has a sweet ether-like odour [45]. It is thermally stable with similar fire safety measures as LPG. Due to its similarity with LPG, storage facilities are developed based on LPG samples. However, new materials need to be used due to the dissolving capability of DME towards the materials normally used for oil and gas storage. DME is not toxic or carcinogenic within exposure limits and it has minimal impact on land/water due to its volatility [52].

Methane is non-toxic and has no impact on land/water contamination in case of a fuel leakage. It is lighter than air and has no odour so an odorant needs to be added. Due to its limited range of flammability, which is the case for concentrations between 5-15% when it is mixed with air, methane is much safer than petrol and gasoline. Even though it is easy to ignite a mixture of methane and air, the temperature of burning is lower than conventional liquid fuels [53]. If the methane is compressed it is very difficult to ignite, so methane is used in the spark-ignited engines as a direct substitute to petrol [54].

Table 5. Comparison of methanol, DME and methane properties

	Odour	Toxic	Corrosive	Reactivity
Methanol	No	Yes	Yes	Medium
DME	Yes	No	No	Medium
Methane	No	No	No	Low

4. Integration of synthetic liquid or gaseous fuel production in renewable energy systems

It could be argued that the system integration of different renewable energy based synthetic fuel pathways depends on existing infrastructure and the possibility of continuing its exploitation. The production process includes different steps and plants, so it is important to implement it in the best manner possible to ensure efficiency and flexibility. Although the outset of implementation in the short term may be the existing infrastructure one should remember the costs in the very long term, which is independent on the existing structures and infrastructure design.

In this chapter we use Denmark as a case study of how such infrastructure for producing synthetic liquid or gaseous fuels in renewable energy systems could be configured.

4.1. Existing infrastructure in Denmark

The road transport causes the largest air pollution and CO_2 emissions in the transport sector. Transportation means are used on the daily basis, and the reliability of the transport system is required to facilitate an efficient transport of both goods and passengers. Oil represents 36% of the Denmark's total primary energy supply of which two-thirds accounts for the transport sector [55]. Cars consumed approximately 70% of the energy for passenger transport in Denmark in 2010 [4]. In 2009 road density in Denmark was 170 km of road per sq. km of land area [56], and it is expected that the traffic will grow by approximately 70 % over the period from 2005 to 2030 [57].

The 77% of the annual passenger transport in Denmark is done by car, 12% by bus and coach, 7% by train and 3% by bicycle. 85 % of international freight transport is covered by lorry and 15% is done by rail [58]. The main Danish traffic routes are shown in the Figure 7. which are part of 73,574 km of the total Danish road networks including 1,130 km of motorways [59].
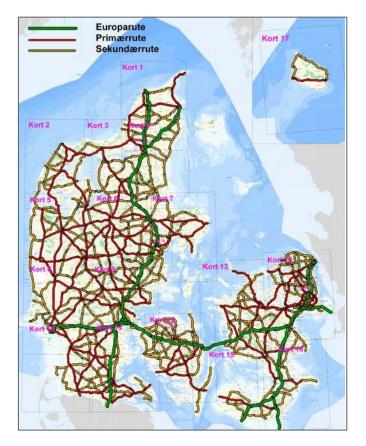

Figure 7. Main Danish traffic routes [60]

Denmark started oil production in 1972 and the production rose steadily reaching the peak in 2004. It is expected that in the years after 2035 oil import dependency will rise and Denmark will become the fuel importer, while now it is still a net exporter. There are two refineries producing fuel products, one in Kalundborg and the other in Fredericia. The Fredericia refinery, owned by Shell, processes 35% of all Danish fuel products. The oil products are transported via a pipeline system that extends from Heide to North Jutland, and one from Kalundborg refinery to the Hedehusene terminal supplying products to the Copenhagen area (see Figure 8).

Figure 8. Oil products pipeline system [55]

There are 8 major gas station chains in Denmark with over 2,000 gasoline/diesel tank stations and only one CNG fuelling station in Odense (see Figure 10). The transportation of liquid fuels is well established, and it is being done either by pipelines, trucks or railways. The pipeline network covers the transportation of crude or refined liquid petroleum products or liquid natural gas. In total there is 1,771 km of pipelines installed in the pipeline network (see Table 6). The gas grid is designed to follow the customers demand, it consist of the main distribution grid, secondary grid and storage facilities. The natural gas system covers most of the country except few islands (see Figure 9). The natural gas is transported through pressurized submarine transmission pipelines from the North Sea fields [61].

Table 6. Pipeline network by type of pipelines [62]

km	Gas trunk pipelines	Gas trunk pipelines, North Sea	Gas trunk pipelines, in the Belts	Gas trunk pipelines, at land	Oil pipelines, North Sea	Oil pipelines, at land	Total
2011	1 441	611	63	767	220	110	1771
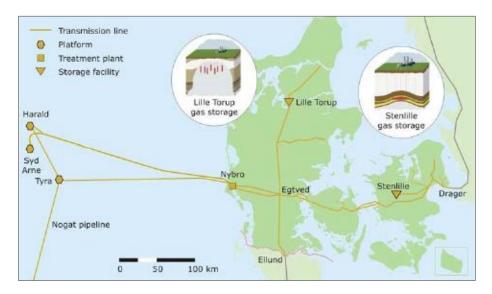
Figure 9. Natural gas transmission system [55]

Figure 10. Fuel stations in Denmark

4.2.   Infrastructure for new fuels

The existing infrastructure can be modified or used as it is to implement new fuels. Today's transport infrastructure is fully adapted for liquid fuels. Oil is the main source used in the transport sector covering almost 100% of total transport demand while using nearly 60% of total world oil demand. The transition from existing fossil fuels to the new renewable fuels could lead to large

capital costs and a long time frame for establishing new infrastructure unless a suitable infrastructure is present. The system integration of synthetic fuels will therefore depend on the existing infrastructure and the possibility of continuing its exploitation to minimize the cost and maximize the use of the current infrastructure in place. The transition to new fuels will only be possible if the infrastructure is fully developed. The decision to new fuels will not only depend on the implementation costs but the environmental factors as well. Building parallel infrastructure system is not impossible, it was done before and parallel fuel infrastructure exist. It is therefore possible to undertake that kind of approach in order to preserve future security of energy supply.

4.2.1. *Infrastructure overview for methanol, DME and methane*

The transition to new fuels requires new fuelling infrastructure. Since the chemical properties of methanol or DME are not the same as petroleum products some materials that are nowadays commonly used for gasoline and/or diesel storage and transportation may not be suitable. Compare to hydrogen that requires completely new infrastructure with high investment costs in case of DME and methanol the costs are lower. The estimated costs for new infrastructures in the USA are US$18 billion for hydrogen and US$4 billion for methanol and DME [45].

The two most likely scenarios for developing a methanol distribution are:

1) utilising existing gasoline stations by adding methanol fuelling capacity or
2) converting stations to methanol.

The equipment in existing diesel and petrol stations is essentially the same as the one for methanol, so there is no reason why the existing infrastructure should not be used. Even though there were some concerns at the beginning that existing tanks should not be reused for storing methanol, it was concluded that there is a wide range of equipment available that is fully methanol compatible.

The costs of methanol refuelling stations are given in [63]. In case of the expansion of the existing petrol station storage capacity with methanol capacity the price of adding above-ground storage is US$54,600 and for an underground tank the price is US$62,407. To convert existing petrol stations to methanol, the costs are US$19,200 for cleaning the existing tank, US$31,000 to install the fiberglass liner in the tank for extra protection or US$70,000 to replace the underground tank.

Applying these costs to Danish infrastructure would mean that if all the existing stations are converted to methanol with equal portions of possible refurbishment, the average cost per station would be US$40,066. As it was mentioned before, today there are approximately 2,000 petrol stations meaning that the cost would be MDKK 460. It is assumed that the DME stations have approximately the same expenses as the methanol ones.

Methane infrastructure partly exists in Europe, including natural gas for different applications. Even though methane can be transported in the existing natural gas network, it cannot be distributed in the existing fuelling infrastructure. The CNG fuelling infrastructure exists in a few countries such as Germany, Sweden and Austria, however in other countries infrastructure is very poor or is still not developed. To enable the usage of methane in the cars around Europe it is necessary to build more homogeneous infrastructure due to the low driving range of the existing vehicles. The infrastructure for LNG is different than CNG infrastructure, due to its different properties and fuel handling. The cost for smaller CNG stations is lower than for LNG, but in both cases they are more expensive than petrol/diesel stations [54].

The cost of installing natural gas infrastructure varies based on size, capacity, and the type of natural gas (LNG, CNG, or both). It also varies in the way the natural gas is dispensed (fast-fill, time-fill). According to a 2010 report published by Pacific Northwest National Laboratory for the U.S. Department of Energy, costs for installing a CNG fuelling station can range from US$400,000 to US$2 million depending on the size and application. According to [64], an LNG fuelling site can

range from US$1 to 4 million. In the German national report for CNG and biomethane filling stations [65] the investment cost for a CNG filling station is between € 190,000 and € 350,000 excluding building costs. Comparable to this conventional filling stations costs from US$50,000 to US$150,000. Therefore, converting existing transport infrastructure to DME/methanol is probably less costly than converting it to methane [54].

4.3.   Potential solutions for utilizing renewable fuels

In this study there are two proposed ways to utilize renewable fuels: the decentralized and centralized solution. Solutions differ in the design of supply chain for liquid or/and gas fuels.

The decentralized option enables local optimisation and smaller production plants to be used. Decentralization can be done on two levels. The gas sources can be dispersed in the country e.g. smaller biomass gasification plants with smaller electrolyser capacities and the chemical synthesis plants can also be regionally spread.

Decentralized solutions are characterized by local micro grids connected with production plants and therefore transport either syngas or final product - liquid fuels like methanol/DME or methane as a gas fuel. The advantage of the micro grids is that they can function autonomously if they are disconnected from the macro grid (in this case natural gas grid). If connected, the natural gas grid can be used as a buffer for the micro syngas grid.

The centralized solution involves large scale production plants and high electrolyser capacities. Centralization can be done on two levels. The syngas source can be centralized e.g. large biomass gasification plants or carbon capture and recycling (CCR) plants. The second centralization level refers to chemical synthesis which can be performed on a larger scale located closely to a syngas source or connected via a pipeline.

Chemical synthesis plants can produce either liquid fuels which can then be transported through the country or it can transport methane, via the existing natural gas grid, which can then be converted into liquid fuels at the costumers end. The latter is not the most preferable option even though the transportation of methane would not require change in the grid infrastructure. The reason is that conversion of methane to methanol/DME is a two-step process. Firstly methane needs to be partially oxidised back to syngas in a process called cracking and then synthesized to methanol/DME at high pressure. This process is not suitable for highly efficient energy utilization [66] which is important for renewable systems.

The proposed solutions here are based on several starting points:

- One grid (or very few) solution(s) is preferred – instead of having a combination of CO_2, syngas and methane/existing natural gas grid
- Transportation of electricity is a well-known established process so it is in some cases preferred instead of the transportation of CO_2 and syngas
- The capture of carbon from air using synthetic trees is excluded from the analysis because it is more expensive solution than CCR [9,10], and due to the small difference in the electricity needed for CO_2 extraction compared to the carbon capture from stationary source.
- The exothermic nature of the synthesis process could define the system structure because it can be used to provide steam for electrolysis and gasification.
- The modularity of the electrolysers does not put the restrains on the plant sizes.

It is important to distinguish between biomass hydrogenation and CO_2 recycling pathways are chosen as two different methods to produce synthetic fuels, one boosts a biomass resource and one uses captured CO_2. In the future, the ultimate decision will depend on the technological development and demonstration of these facilities on a large-scale and depending on the biomass resource available.

4.3.1. CO₂ sources in 100% renewable energy system

Presently, all energy sectors are mainly based on the burning of fossil fuels to produce energy and enable transportation, and fossil fuels produce large CO_2 emissions. Therefore there are plenty of CO_2 emissions that can be recycled and be used to produce renewable fuels. These emissions can be captured from concentrated sources as power plants and industrial plants. However, at some point in the future when the dependence on fossil fuels diminishes the carbon sources are not going to be that accessible anymore. The only reliable carbon source that could be used for the fuel production will be biomass based CHP plants and biomass used in the industry sector. These sources are going to be spread out in the system and their smaller scale will require new smaller CO_2 recycling systems or a different solution. The capture of CO_2 from the atmosphere presents a good flexible solution because it is not directly connected to any specific kind of source. The air capturing technology could capture not only emissions from the fuel gases from the concentrated sources but also the emissions from mobile sources such as cars and planes. The results are applicable for the cases of air-capturing the only difference would be the investment costs of the capturing technology.

The calculations for Denmark show that the CO_2 emissions from biomass plants and industry meet the demand for CO_2 needed for fuel production [4]. However, this cannot be guaranteed in other energy systems, therefore air-capturing could play big role in the future 100% renewable systems

4.3.2. Infrastructure solutions for the Biomass gasification pathway

Biomass gasification can be either centralized or decentralized (see Figure 11), and this to some extent depends on the biomass transportation costs [67]. The overview of possible solutions is provided in the Table 7.

The chosen pathway will depend on the amount of excess heat from the synthesis process, particularly on if it will be enough to meet the needs for both the gasification and electrolysis process and the costs of the establishing a syngas network.

Table 7. Potential biomass gasification pathway solutions

Pathway	Decen. biomass gasification	Cen. biomass gasification	Local syngas grid	Cen. syngas grid	Cen. chemical synthesis	Decen. chemical synthesis	Transport of liquid/gas fuel from cen. unit	Transport of liquid/gas fuel from decen. unit
Decen. MeOH 1	✔		✔			✔		✔
Decen. MeOH 2	✔			✔		✔		✔
Cen. MeOH 1		✔			✔		✔	
Cen. MeOH 2		✔		✔	✔		✔	
Cen. MeOH 3		✔		✔		✔		✔
Decen. CH₄	✔		✔		✔			
Cen. CH₄ 1		✔		✔	✔		✔ (natural gas grid	
Cen. CH₄ 2		✔		✔		✔		✔ (natural gas grid)
Cen. CH₄ 3		✔			✔		✔ (natural gas grid)	

Figure 11. Decentralized and centralized solution for utilizing renewable fuels with the biomass gasification pathway

It is important to establish good synergy in the production cycle so that the process can be more efficient. Water electrolysis produces surplus oxygen while producing hydrogen needed for boosting the gasified biomass. However by using the oxygen blown gasification process surplus oxygen from electrolysis process can be utilized for the gasification. The gasification process is performed on high temperatures (>500°C) meaning that it requires steam input as well. By combining gasification process together with water electrolysis and chemical synthesis, chemical

synthesis could enable full synergy by providing surplus heat needed for high temperature electrolysis and gasification. Moreover, to avoid syngas transportation because of its uncertainties, combined production of synthetic fuels at the same location could be one of the preferable solutions for this pathway.

4.3.3.   Solutions for CO_2 hydrogenation and co-electrolysis pathway

Four scenarios are proposed and analysed here of which two are chosen as the potential solutions (see Table 8). One solution would include decentralized CCR with a CO_2 network, combined with electrolysis and synthesis plant either as centralized units or decentralized smaller units. Another solution combines CO_2 source with electrolysis and synthesis at the same location to avoid CO_2 transport and concentrate on the end-fuel transportation. The combinations for decentralized and centralized are presented in the Table 9.

There are strong synergies for combining chemical synthesis with electrolysis process. The excess heat produced in the chemical synthesis plant could be used for providing steam for steam electrolysis. High temperature electrolysis needs the heat or steam source to generate the hydrogen. Even though CO_2 transportation and storage is known technology, there are some indications due to the costs that long distance transportation is not feasible meaning that it should be restricted to lower distances. If this is taken into account transportation could be avoided by building centralized combined units that have all production steps at the same place, location electrolysis and chemical synthesis by carbon source. This could also be argued by possible carbon bottleneck in the future renewable energy system where accent will be on distributed smaller power plants with few larger centralized plants, therefore combining the process with carbon source and transportation of end fuel could be preferred solution. Depending on preferred fuel different CO/H_2 or CO_2/H_2 ratios are desired, meaning that optimisation of the process can be challenging.

Table 8. Four scenarios for CO_2 hydrogenation and co-electrolysis

	Plant	Grid	Plant	Transport of end product
A	CCR + electrolysis	Syngas	Synthesis	MeOH/DME or CH_4 grid
B	Electrolysis	H_2	CCR + Synthesis	MeOH/DME or CH_4 grid
C	CCR	-	Electrolysis and chemical synthesis	MeOH/DME or CH_4 grid
D	CCR	CO_2	Electrolysis and chemical synthesis	MeOH/DME or CH_4 grid

Table 9. Variations of pathways C and D for CO_2 hydrogenation and co-electrolysis pathway

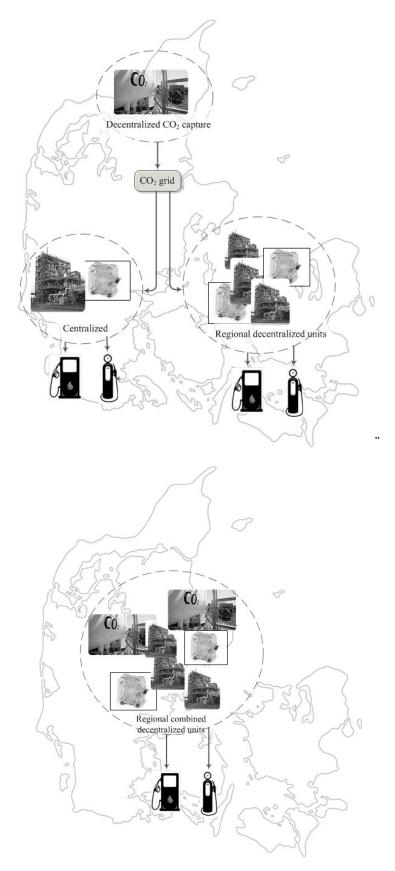| Pathway	Decentralized CCR	CO_2 grid	Cen. electrolysis and chemical synthesis	Decen. Electrolysis and chemical synthesis	Transport of liquid fuel from cen. unit	Transport of liquid fuel from decen. unit	Transport of methane from cen. unit	Transport of methane from decen. unit
1) MeOH	✔	✔	✔		✔			
2) MeOH	✔	✔		✔		✔		
3) MeOH	✔		✔		✔			
1) CH_4	✔	✔	✔				✔	
2) CH_4	✔		✔				✔	
3) CH_4	✔	✔		✔				✔

Figure 12. CO₂ hydrogenation and co-electrolysis decentralize and centralized solution for utilizing renewable fuels

5. Synthetic fuel technology plants and demonstration plants

The production of methanol is increasing worldwide, exceeding 40 million tons of fuel per year. Most of the methanol nowadays is produced from natural gas, but in the locations where natural gas is not available coal can be used. The capacity of methanol plants has been increased significantly in the last decade. Today there are several plants in operation with a capacity of 5000 MTPD [68].

However, in the 100% renewable energy system biomass gasification will most likely be one of the key technologies. Therefore, the following examples are biomass gasification demonstration and commercial plants for electricity and heat generation as well as fuel production (see Table 10). Even though commercial gasification plants for heat and power generation already exist, the first plant for transport fuel production is still not established.

There are already many demonstration and commercial plants for biomass gasification in countries such as Denmark [69], Japan [70], Sweden [71,72] , and China [73]. With total of 373 MWth syngas capacity there were 9 commercial biomass gasification plants (>100MWe) operating in 2010 [74]. A variety of biomass feedstocks can be used in this process: wood gasification is already being commercialised on a large scale [71] while the gasification of biomass from energy crops and straw is currently at the demonstration phase [75,76]. The latest success achieved in Denmark is developed under the project Pioneer: it is a 6MW$_{th}$ demonstration gasifier plant fired with straw, manure fibres or local residue. The capacity is 1.5 tons/hour with a 95% thermal efficiency (based on fuel input and losses) and it operates at lower temperatures than normal gasifiers [77]. 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 [71]. The company Chemrec inaugurated in 2010 a DME pilot production plant under the BioDME project in Piteå, Sweden. The first bio-DME and bio-methanol were produced in July 2011 [72]. Another planned bioDME plant base on black liquor gasification in Domsjö, was withdrawn in May 2012.

The world's first plant that produces methanol from the CO_2 emissions of a geothermal power plant the Svartsengi Power Station on Iceland was started in April 2012. The power plant will produce about 5 million litres per year, fuelling about 2.5% of the Icelandic gasoline market. It will use around 40,000 MWh per year of electricity and recycle approximately 5,000 tonnes of CO_2 per year [78]. The company Blue Fuel Energy is planning to build a CO_2 recycling to methanol power plant built in Canada. It will produce about 10,000 barrels of methanol, or 4000 barrels of gasoline, per day. This level of production requires 280 tonnes of hydrogen and 2100 tonnes of CO_2 per day. Producing 280 tonnes of hydrogen per day requires 500 MW of renewable electricity to power a huge array of 265 x 2 MW electrolysers. Getting the 2,100 tonnes of CO_2 poses much less of a challenge [79].

The Swedish gas centre study from 2008 gives the range of production costs for bio-SNG from 43-46 €/MWh The cost of Bio-SNG is based on the production cost from 100 MW SNG plant with an annual operating time of 7500 h for 3 different scenarios for 2007, 2012 and 2020 [80].

Table 10. Overview of existing and planned biomass gasification plants larger that 1MWth in Europe

Plant name /Location	Production start	Thermal fuel power	Type of gasifier	Feedstock	Product / purpose	Source
Bio-SNG plant / Güssing	2009	1MW$_{th}$	Dual fluidized bed steam gasifier	Wood chips	Bio-SNG / transport	[81]
Biomass CHP plant / Güssing	2002	8 MW$_{th}$	Dual fluidized bed steam gasifier	Wood chips	Bio-SNG / heat and power generation	[82]
GoBiGas / Gothenburg	2016	32 MW$_{th}$	Indirect gasification at atmospheric pressure	Branches, stumps and forest residue	Bio-SNG for regional gas network	[83]
Biomass CHP Plant / Senden	2012	14.3 MW$_{th}$	Dual fluidized bed steam gasifier	Wood chips	Bio-SNG / heat and power generation	[84]
Choren /Freiberg	2005	45 MW$_{th}$	Entrained flow (Choren Carbo V)	Wood chips	Fischer-Tropsch Diesel	[85]
VärmlandsMetanol AB[1] / Hagfors	2014/2015	111 MW$_{th}$	HTW-gasifier	Forest biomass residues	Methanol	[71]
BioDME project / Piteå	2011	3 MW$_{th}$	Pressurized black liquor gasifier	Black liquor	DME	[72]
Oberwart	2008/2009	15 MW$_{th}$	Indirect gasification	Wood chips	Bio-SNG / power generation	[86]
Skive	2008	11.5 MW$_{th}$	Air-blown pressurized bubbling fluidized gasification	Wood pellets	Bio-SNG / heat and power generation	[87]
Götaverken	1987	28 MW$_{th}$ (35MW)	Air-blown atmospheric circulating fluidized bed gasification	Dried bark	Bio-SNG / lime kiln	[88]
Harboøre	2007	3.5 MW$_{th}$	Air-blown updraft gasification	Wood chips	Bio-SNG / heat and power generation	[89]
Pyroneer Gasifier / Asnaes Power Plant	2013	6 MW$_{th}$	Low temperature circulating fluidized bed	Straw, manure fibres, local residue	Bio-SNG / heat and power generation	[77]
Grevè di Chianti, Italy	1991	15 MWth	TPS CFB gasifier	RDF pellets	Power generation	[90]
Lahti, Finland	1998	40-70 MWth	Circulating Fluidized Bed gasifier	RDF pellets	Power generation	[91]
Varnamo, Sweden	2000	9 MWth	Pressurized Circulating Fluidized Bed gasifier	Wood chips, pellets, RDF	Power generation	[92]
Kokemaki, Finland	2005	3.3 MWth	Updraft fixed bed	Wood fuel	Heat and power generation	[93]
Vaasa, Finland	2013	140 MW	Circulating Fluidized Bed gasifier	Forrest residues	Heat and power generation	[94]

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[1] World's first known commercial biomass to methanol plant

6. Pathway cost overview

The costs for alternative fuels are higher than for conventional fossil fuels. However the economics of these fuels are not yet comparable to existing ones. The given costs for oil products do not reflect security of supply, or the costs for pollution, while it partly includes costs for CO_2 and product disposal [46].

The overview of costs for technologies involved in described production steps is given in the Table 11. The table gives three types of costs where it is possible, low, high and average costs are given based on different sources. The costs for syngas transportation and methane synthesis from syngas could not be obtained so they are excluded from the table.

The total investment cost for biomass gasification to methanol/DME pathway including all the needed equipment is approximately M€ 200 [95]. The total investment cost for biomass gasification to methane is M€ 500 [96].

Table 11. Costs for different steps in the production chain of synthetic fuels

	Type of costs		Low	High	Average	Source
CO_2 capture and recycling	Specific investment costs	M€/MW	1.835	3.241	2.7	[8]
CO_2 transportation[2]	Transport costs for onshore pipeline	€/tCO_2	1.5	5.4	3.5	[32]
Natural gas transportation		€/MW per 100km			0.2	[97]
		US$/Mbtu (distance 1000km)	0.2	0.6	0.4	
		US$/ Mbtu (distance 1000km)	0.3	0.7	0.5	[98]
Biomass gasification	Investment cost	M€/MW$_e$	3.4	4.1	3.75	[99,100]
SOEC electrolysers	Investment cost	M€/MW$_e$	-	-	0.25	[16]
Methanol synthesis		M€[3]			43,6	[6]
Methanol / DME fuelling stations	Investment cost of converting gasoline station	DKK/station	110,000	400,500	250,000	[63]
Methane fuelling stations (CNG fuelling station)		M€/station	0.3	1.5	1	[65]
Biomass gasification to methanol	Production cost	M€/PJMeOH	5.23	12.88	8.5	[35]

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[2] Detailed costs are given in the Chapter CO_2 transportation
[3] Costs for the plant that has maximal capacity of 200t/day dry wood

7. Plant sizes and locations

Typical plant size is defined by many factors a variety of which have already been discussed, technology cost (Section 5), system architecture (Section 4), available resources, etc. In the future energy system, the system structure will be more decentralized oriented therefore big fuel production plants would probably be replaced by smaller ones. Therefore, it is important to find the good size plant due to the economy of scale.

The biomass as a resource of CO_2 in the *CO_2 pathways* or used for gasification in *Biomass hydrogenation pathway* is highly distributed around the country and usually not located close to the demand. Therefore is important to minimize biomass transportation cost and locate production plants closer to the available resources. Today is a case that for some power plants biomass is transported from far away which is not the best solution and it is costly approach. Geographical cost-supply analysis for distributed bio-energy plants was conducted in [101]. The study has modelled 35 energy plants using wood chips as their main or co-firing fuel and calculated the biomass supply cost.

The overall demand for fuels in 2050 based on CEESA scenarios is 116 PJ of synthetic fuels. To meet this demand, the proposed size of the plants for CO_2 hydrogenation pathway is based on the planned CO_2 to methanol power plant on Iceland [103]. The plant will produce 40,000 t of methanol per year e.g. 796,000 GJ of methanol. If all the demand is met with this pathway there is a need for 145 plants in Denmark. The biomass hydrogenation pathway would require less production plants based on the existing technology. The recommended size of the plant is 5.97 PJ of methanol per year [95], meanings that 20 plants are needed to meet the total fuel demand. This is in correspondence with available biomass resources.

8. Overview of different technologies for the integration of renewable energy

There are different flexible technologies that can be used for the integration of fluctuating renewable energy sources, such as wind power. One of the primarily options for dealing with intermittency of wind generation is to increase grid connections. Danish experience indicates that interconnections are not an ideal solution due to the import/export pricing problem of wind energy. Moreover, Danish studies have shown that from the financial perspective the large interconnection is not preferred compared to the implementation of other technologies for creating the flexible system [7,104]. Energy storage is a well establish solution proposed to aid the integration of intermittent renewable energy in the system. It can reduce the mismatch between energy supply and energy demand, and it is important for energy conservation. Energy storage can also improve the overall power quality and reliability. Energy storage can be classified in different ways, the following is overall division disregarding the storage capacities and power:

- Electricity storage
- Thermal storage
- Fuel/chemical storage

The principal of electricity storage is to charge an energy storage facility when excess electricity production occurs and discharge the facility when a shortfall in supply occurs, which ensures a match between supply and demand. At present however, there are only two large-scale (i.e. >100 MW) electricity storage technologies that have been implemented: pumped hydroelectric energy storage (PHES) and compressed air energy storage (CAES). With both of these there is an inherent energy loss, with each having a round-trip efficiency of approximately 85% and 65% respectively. Therefore, when assessing electricity storage, there is a balancing act between integrating more intermittent renewables and reducing the overall efficiency of the system Connolly et.al. has shown that for the Irish case, the investment in PHES would increase the operating costs of the energy system while not providing high savings [105]. Both PHES and CAES are heavily dependent on the availability of suitable locations, while CAES also relies on the price and availability of gas. The role of CAES is assessed in a series of papers [106-108] analysing its optimal operational strategies, energy balances in the system with CAES and value of integrating CAES in the future energy systems. CAES can be used for load levelling in the electricity supply in the system. Analysis shows that CAES can integrate around 55% of wind power for its maximum operation, however excess electricity production cannot be eliminated in the systems with high percentage of combined heat-and-power plants. Even in systems with high shares of wind power, CAES alone is not able to eliminate excess electricity production [106], nor there is any justification to invest in this kind of system [107].

The thermal storage refers to different technologies to store thermal energy at high or low temperatures for later use. There are large number of possible technical solutions and the variety of storage systems that can be divided into three groups:

- Sensible heat storage
- Latent heat storage
- Bond energy storage

Both sensible and latent heat storage systems are in use, while bond energy storage systems are being proposed for use in the future for medium and high temperature applications [109]. Many previous studies have focused on thermal storage in energy systems [7,110] and its effectiveness to increase the flexibility of the system.

An excellent option to improve the flexibility of the system is to integrate the three primary energy sectors: electricity, heat and transport. The comprehensive review of different energy storage technologies given in [111] shows that energy storage systems could be more promising solution

than individual technologies in terms of integrating intermittent renewable sources because they often disregard the heat and transport sector.

Fuel/chemical storage is the dominant form of energy storage in the electricity and transport sectors. However, synthetic fuels offer a bridge between all three sectors of an energy system. Interactions between sectors is done by increased wind integration, possible excess heat that can be used in the heat sector and combustible fuel output that can be used not only for transport purposes, but in the other two sectors also.

If the storage options are compared just on the size of the plant and amount of energy being stored, the difference on storage capacity is rather big. The electricity storage (PHES) has the lowest storage capacity compared to the area needed for building the facilities. If we look at only pump hydro facility in Ireland (Turlough Hill) it has a storage capacity of 1.7 GWh [112], while it has area of approximately 1,125,000 m^2. If we look at the thermal storage case in Marstal, pit heat storage will be able to store 6 GWh with a water capacity of 85,340 m^3 when the project finishes. The total oil storage in Denmark is 50 TWh, while one facility with 7.92 TWh has 7 times lower area than electricity storage in Ireland, therefore it requires significantly lower area and can store bigger amounts of energy. It is clear that the fuel storage is the most effective type of storage and converting the electricity to fuel can enable long term storing option.

Seven integration technologies for facilitating large share of intermittent renewable sources were analysed in terms of their ability to improve the balance between demand and supply in the system in [113]: electric boilers, heat pumps, electrolysers with local CHP, electrolysers with micro CHP, hydrogen fuel cell vehicles, battery electric vehicles and flexible electricity demand. In terms of costs heat pumps are the most promising technology, electric boilers are not feasible with low amounts of wind power production and can increase fuel consumption if it is not implemented correctly. Flexible electricity demand results in a low fuel saving costs. Battery electric vehicles compared to hydrogen fuel cell vehicles represent better fuel and cost-effective solution. The results of using electrolysers are very sensitive to their efficiencies and to the possibility of using waste heat. Despite this, the electrolysers may prove to be important in 100% renewable energy systems where biomass resources are limited.

9. Comparison of alkaline and SOEC as integrating technologies

Electrolysers enable the conversion of intermittent electricity from renewables into different fuel types whilst balancing the grid and providing flexibility. The produced synthetic fuels can be perceived as a storage media for intermittent renewable energy sources. The main differences between alkaline and SOEC electrolysers are regulation abilities, efficiencies and costs. The most readily available electrolysers, mainly alkaline electrolysers with bipolar electrodes [114], are designed for stationary grid-connected operation [115]. However, new electrolysers available on the market have exceptional dynamic range and operating flexibility, with the response time in the range of milliseconds, allowing production down to 10% of the capacity [116,117]. SOEC cells may have fast regulation abilities if the cell temperature is kept at the operating temperature (from 0% to 100% power in less than a few seconds) so they have the needed flexibility for integration of intermittent sources. The efficiency of SOECs is higher compare to alkaline electrolysers mainly due to the high operation temperature. Moreover, SOECs conducts oxide ions, so it is possible to perform CO_2 electrolysis and combined steam and CO_2 electrolysis (co-electrolysis). The costs and efficiencies of alkaline and SOECs are defined in the [16].

The comparison of alkaline and SOECs in this study was done by using EnergyPLAN model. EnergyPLAN is a deterministic mathematical tool for national or regional energy system analysis according to inputs defined by the user. It simulates the energy system operation on hourly basis over a period of one year, providing technical and economic analysis of different technologies implemented in the system. The difference between alkaline and SOEC in the energy system modelling is in their costs and efficiency. At the moment it is not possible to model the better flexibility of SOECs. Based on the input data from [16], the analysis was carried out for the total system costs and the estimation of synthetic fuel production costs. The analysed system is 100% renewable Denmark developed in the CEESA report [4], which has approximately half of the fuels produced from biomass gasification pathway and the rest covered with hydrogenation of CO_2.

The total system costs sensitivity analysis is based on three different biomass prices (Table 12) because the biomass gasification pathway is directly depended on the consumed biomass, while CO_2 recycling pathways are not directly dependent but are connected as the carbon source is biomass used in electricity and heat sector. Three fuel price assumptions are used due to uncertainty of fuel prices in a long-term planning.

Table 12. Different biomass prices depending on the fuel cost scenario for 2050

DKK/GJ	Medium	Low	High
Straw/wood chips	42,2	32,2	62,1
Energy crops	56,1	40,2	87,9

It can be seen from the Figure 13 that the costs of the system with implemented alkaline electrolysers are more expensive than SOECs due to their higher investment costs. The graph shows the system dependency on the fuel costs in connection with the amount of integrated wind. As the wind production is increasing, the scenarios with lower biomass costs are levelling with basic cost scenarios. This is caused because the amount of biomass used in the scenarios when the large amounts of wind is being exported, is so low that the costs are very similar. The difference between high and basic biomass cost is higher so the convergence is not occurring. These results are solely dependent on whether SOEC is developed as expected or not.
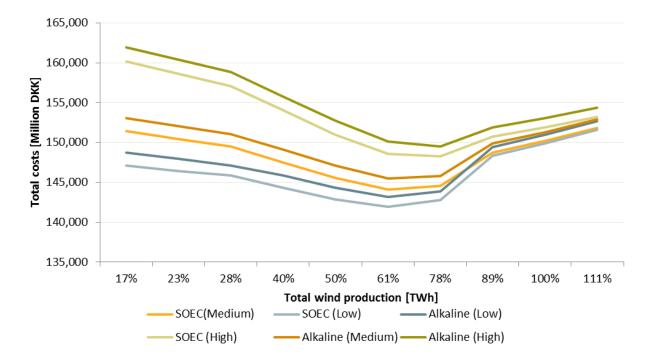
Figure 13. Sensitivity analysis of different fuel price and off shore wind integration effect on the total system costs for both SOEC and alkaline from 17% to 111% of total electricity demand

Due to the lower efficiency scenario with alkaline electrolysers, the more biomass and wind is used to compensate for the efficiency difference with SOECs (see Figure 14).
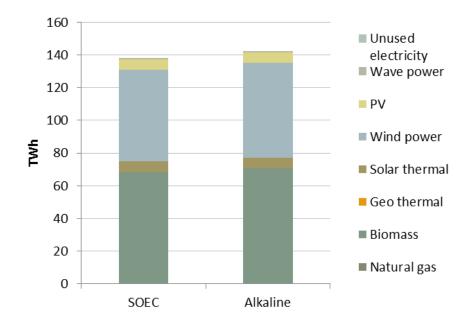

Figure 14. Primary energy supply in SOEC and alkaline scenarios

The rough estimation of synthetic fuel prices was done based on annualized investment and O&M costs for production plants and the amount of resources required (see Figure 15). Included plants are off-shore wind turbines, electrolysers, gasification plant and chemical synthesis plant. The estimation did not include infrastructure expenses. It can be seen that the costs of fuel produced with SOEC electrolysers are cheaper which directly reflects the difference in the price between alkaline and SOEC.
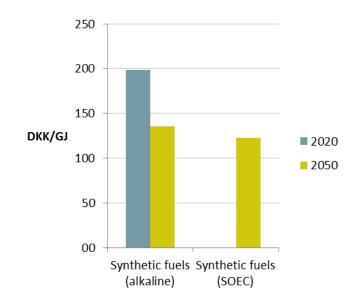

Figure 15. Synthetic fuel price estimation

10. Comparison of fuel pathways

The scenarios were compared from the aspect of the total system costs for the case that all investigated fuel demand is replaced by synthetic fuels produced in each pathway. The differences in the total system costs are rather low (see Figure 16), however they exclude grid infrastructure costs (syngas and CO_2 grid costs) due to the inability of good estimation of required infrastructure or no costs available in case of syngas grid. Therefore it was assumed that all the pathways are centralized with production process at the same location.
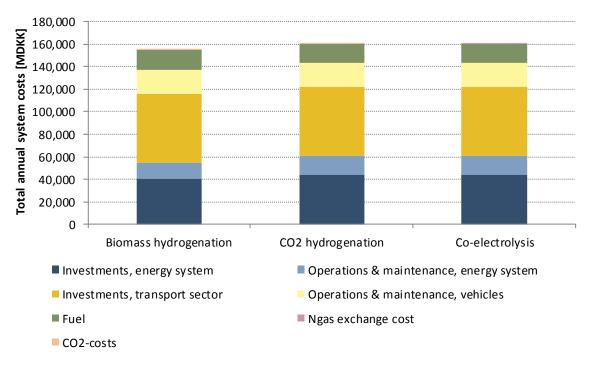

Figure 16. System costs for three pathways with centralized production

The biomass consumption is highest in Biomass hydrogenation pathway, while CO_2 hydrogenation and co-electrolysis have lower consumption, which is used in the heat and power sector to provide carbon for the fuel. The CO_2 recycling pathways show the flexibility that provides implementation of electrolyser in the system that enables high wind integration (see from Figure 17.) However, this reflects on the investment costs, but in this case does not change the overall picture because investment in biomass gasification is also very significant.

These results represent extreme cases where all the need for liquid fuel is supplied by one pathway, the future development of the technologies will define the choice and probable combination of different fuel pathways.
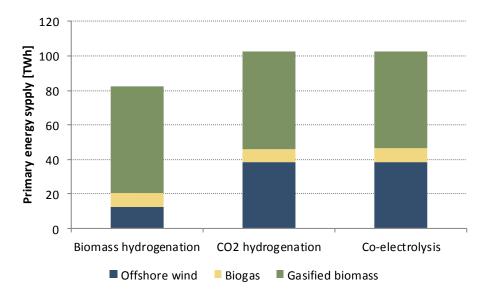
Figure 17. Difference in primary energy supply for offshore wind, biogas and biomass for biomass gasification

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