GreenSynFuels

Economical and Technological Statement regarding Integration and Storage of Renewable Energy in the Energy Sector by Production of Green Synthetic Fuels for Utilization in Fuel Cells



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Preface

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2 Terms, Abbreviations and Definitions

| Abbreviation: | Explanation: |
|---------------|--------------------------------|
| | |
| DME | Dimethylether, CH_3OCH_3 |
| RE | Renewable energy |
| SNG | Synthetic Natural Gas |
| MeOH | Methanol, CH₃OH |
| CHP | Combined heat and power |
| RMFC | Reformed Methanol Fuel Cell |
| FC | Fuel Cell |
| TSO | Transmission System Operator |
| OPEX | Operating Expenses |
| CAPEX | Capital Expenditures |
| LHV | Lower Heating Value |
| HT-PEMFC | High Temperature PEM Fuel Cell |
| PEM | Proton Exchange Membrane |
| SOEC | Solid Oxide Electrolyzer Cell |
| SOFC | Solid Oxide Fuel Cell |
| DMFC | Direct Methanol Fuel Cell |

3 Executive Summary

This report constitutes the dissemination of the EUDP project Green Synthetic Fuels (GreenSynFuels). The purpose of the project is to select and validate technology concepts for the establishment of a Danish production of green synthetic fuels primarily for fuel cells. The feasibility of the selected concepts is assessed trough a techno-economical calculation, which includes mass and energy balances and economics including CAPEX and OPEX assessments.

It is envisioned by the project partners that a production of green synthetic fuels, such as methanol, can 1) bring stability to a future electricity grid with a high share of renewable energy, 2) replace fossil fuels in the transport sector, and 3) boost Danish green technology export.

In the project, two technology concepts were derived through carefully considerations and plenum discussions by the project group members:



Concept 1): Methanol/DME Synthesis based on Electrolysis assisted Gasification of Wood



Concept 2): Methanol/DME synthesis based on biogas temporarily stored in the natural gas network

Concept 1) is clearly the most favored by the project group and is therefore analyzed for its technoeconomic feasibility. Using mass and energy balances the technical perspectives of the concept were investigated, along with an economic breakdown of the CAPEX and OPEX cost of the methanol production plant. The plant was technically compared to a traditional methanol production plant using gasified biomass. The project group has decided to focus on large scale plants, as the scale economics favor large scale plants. Therefore, the dimensioning input of the concept 1) plant is 1000 tons wood per day. This is truly a large scale gasification plant; however, in a methanol synthesis context the plant is not particularly large. The SOEC electrolyzer unit is dimensioned by the need of hydrogen to balance the stoichiometric ratio of the methanol synthesis reaction, which will result in 141 MW installed SOEC. The resulting methanol output is 1,050 tons methanol per day. In comparison to a traditional methanol synthesis plant operating on biomass gasification without electrolysis, the plant methanol output is doubled and the methanol production efficiency is boosted from 59 % to 71 %. The total plant efficiency was 81.6 %.

The economic analysis revealed that green methanol can indeed be produced at prices very close to the current oil price. In the scenario using the present energy prices and assuming that the critical plant components were readily available, the methanol production was found to be 120 USD/barrel equivalents, which is very close to the current oil price. Interestingly, it was found from the studies that the methanol production prices are not favored by the expected increasing market of cheap electricity, as the general energy prices are expected to increase, see figure below. However, it will be possible to use the plant as an intermediate storage of renewable energy, and thereby increase the share of renewable energy in the energy system. The figure below also shows that the use of SOEC as the electrolyzer significantly improves the production price and plant economy.



Based on the work presented in the present report, the project group can recommend that further work should include:

- 1. Engineering of the suggested plant concepts in order to provide precise cost estimations
- 2. The concepts presented illustrates the large potential of SOEC technology, therefore priority should be given to improving and demonstrating durability and reliability of SOEC stacks and systems
- 3. To further improve SOEC, more fundamental work of finding better electrode materials and defining optimal structures plus research in cheap fabrication procedures for making these electrode structures of the new materials is needed
- 4. Further work should be conducted on gasification concepts, in which special attention must be directed towards handling of the syngas tar
- 5. The project group recommends that both the biogas and the gasification plant concepts are scale demonstrated, once the technological challenges mentioned in the above points are solved
- 6. It is pivotal for a future sustainable energy system that the scarce global biomass supplies are used efficiently. It is therefore recommended that future energy conversion plants are assessed with regards to their carbon efficiencies
- 7. Partial well-to-wheel data for a bio-methanol to fuel cell case has been given. It is recommended that the present publication "Alternative Drivmidler for Transportsektoren" is updated using the data supplied in section 3.5.1, in order to obtain a full well-to-wheel data for the bio-methanol to fuel cell case.
- 8. A techno-economic analysis for a 2050 scenario was not conducted in this project. It was chosen to omit this scenario as the data foundation for such a scenario is too weak. It is therefore recommended that the publication "Forudsætninger for samfundsøkonomiske analyser for energiområdet" is update and extended from 2030 to 2050, so that more accurate 2050 scenarios can be conducted.

Lastly, it can be concluded that the present report has shown that green methanol can indeed be produced at competitive prices and be used as step towards expanding the share of renewable in the energy system and especially in the transportation segment. Therefore, producing methanol from using electrolysis assisted gasification it is possible to produce green methanol from biomass with this ratio:

1,000 t wood = 1,053 t methanol @ 120-170 USD/barrel equivalent (1.5 - 2 times the existing oil price - February 2010)

4 Introduction

This report contains the economic and technical dissemination of the EUDP project "Production of Green Synthetic Fuels for Utilization in Fuel Cell Applications" also named GreenSynFuels. GreenSynFuels is originated in the framework of Danish partnership for Hydrogen and Fuel cells and is funded by the Danish Energy Agency (Energistyrelsen) within the EUDP programme.

The different chapters/sections in this report are written by the different stakeholders and participants. The writer and institution is highlighted in the beginning of the chapter or section unless it is written by the editor. The final report is assembled and edited by Danish Technological Institute.

4.1 Purpose and Background

The overall purpose of this study is to find and define future areas of research within the development of green synthetic fuels for the transportation sector, in which fuel cells are expected to play an important role in the future. It is the objective that this study will map the Danish stakeholders and their key competences. From that, recommendations will be given for future business opportunities and research areas needed to establish a Danish production of green synthetic fuels. It is therefore envisioned that:

Production of Green Synthetic Fuels in Denmark can become a feasible Danish business case and assist in meeting the requirements of a fully renewable energy system

Danish fuel cell manufacturer seeks a green and logistically better alternative to pure hydrogen and natural gas as fuel option for their fuel cell products in the transportation market segment. Both a national¹ and a Nordic platform² are established that seek to develop a hydrogen infrastructure in the Nordic countries. There is however a lack of knowledge how feasible other fuels, such as methanol, DME and ammonia, are in a Danish context.

Most Danish fuel cell companies have products than can operate on various fuels, such as natural gas, methanol, ammonia and DME. These fuels benefits, in comparison to pure hydrogen, from being easier to handle logistically and the infrastructure may already be present or easy to erect. Therefore, better access to these strategic fuels could speed up the market access for Danish fuel cells as the infrastructure problems are readily solved.

Below, the background for the fuels (methanol, ammonia and DME) considered in this study are reviewed. Synthetic or Green Natural Gas (SNG) is excluded from the project, as it is assessed that this is a matured and well-established technology.

4.1.1 Political Background

Aksel Mortensgaard, Danish Partnership for Hydrogen and Fuel Cells

The Danish Commission on Climate Change Policy has prepared a report concerning the vision of how

¹ http://www.hydrogenlink.net/

² http://www.vatgas.se/shhp/

Denmark can become independent of fossil fuels and reduce greenhouse gas emissions markedly by 2050. As part of the effort to reach the aims in 2050, there is a need to take all possible solutions into consideration. The aim is to create a flexible energy market based on sustainable energy technologies.

One of the main sources for sustainable energy, identified by the Climate Commission, is wind power (Klimakommisionen, 2010). Wind power has a very large potential in terms of supply and could according to the Commission report more than fully cover the total Danish energy need in 2050. However, the wind does not blow constantly, and the need for storage of the surplus electricity calls for a solution in order to optimize the use of the wind energy.

Biomass is an obvious alternative to fossil fuels. Unlike fossil fuels, biomass is a renewable resource. However, there are limits to how much biomass can be produced, both in Denmark and in the world. The Climate Commission has therefore made analyses based on two different scenarios: A scenario where the consumption of biomass is limited to a level corresponding to Denmark's own production with unchanged food production, and a scenario with import of biomass dependent on trends in the price of biomass. In the transport area, the need for sustainable solutions is relevant, as the transport sector accounted for 26 % of the total energy consumption in 2008. This also makes the sector a challenge regarding the goal of being independent on fossil fuels by 2050.

Battery electric vehicles, plug-in hybrid electric vehicle and fuel cell electric vehicles not only have zero tailpipe emissions while driving – significantly improving local air quality – they can be made close to CO_2 -free over time and on a well-to-wheel basis, depending on the primary energy source used. Zero emission power-trains therefore go hand in hand with the decarbonisation of the energy supply.

One of the main routes for converting the transport sector into a sustainable sector would be by converting renewable produced electricity to hydrogen as a storage mechanism. Another main route could be by upgrading of biomass to liquid biofuels by use of hydrogen from electrolysis. Biofuels have the great advantage that it can replace petrol and gas with minor technical challenges. Furthermore, the requirements for changes in the infrastructure in society are less comprehensive than other possible solutions.

The aim of the project GreenSynFuels is to define the future perspectives on time, efforts and economy in order to obtain coherence in the chain of supply and use of green synthetic fuels in fuel cells. The project will be a critical review on how to develop new and improved production methods for green synthetic fuels as methanol, DME, SNG and ammonium. The aim is to elaborate a full and unbroken value chain from green biofuels as fuels for fuel cells.

As the project is based on the use of biomass to produce biofuels, the strategy will work as a supplement to the national strategy on biofuels from 2005, as well as the gasification strategy which is in progress. This report serves as a tool in the process of producing a green liquid biofuel, which is very applicable as fuels for fuel cells in the future.

However, the production of a green synthetic biofuel, such as methanol, does not only serve as a product for the transport industry, it also offers a solution to the future challenges of integrating more and more renewable energy. Synthetic fuels are a source for long-term storage, and can be a mean in regulating the future power supply by Smart Grids.

A Smart Grid is an electric network that can intelligently integrate the actions of all users connected to it – generators, consumers and those that do both – in order to deliver sustainable, economic and secure electricity supplies.

A Smart Grid employs innovative products and services together with intelligent monitoring, control, communication, and self-healing technologies to better facilitate the connection and operation of generators of all sizes and technologies. Also it allows consumers to play a part in optimizing the operation of the systems – it provides consumers with greater information and choice of supply. Finally, it reduces the environmental impact and it delivers enhanced levels of reliability and security of supply.

With a Smart Grid system, the energy supply can be regulated according to the supply level in the network. Electricity can be generated by a decentralized CHP fuel cell plant and sent into the net, when the supply from other energy sources is low. In a scenario with an oversupply of electricity in the network, the surplus can be absorbed and stored as methanol as a result of an electrolysis process.

4.2 Danish Stakeholders

The following section lists the Danish stakeholders who are the primary companies that hold a future market potential for the technologies described in this report. Universities and knowledge institutions are neglected from the list. The list contains the main stakeholders and may not be complete.

4.2.1 Technology Providers

These are the Danish companies that hold a technology or process that can be utilized in the production of green synthetic fuels.

Haldor Topsøe:

Being one of the world leading manufacturer of catalyst and process plants, Haldor Topsøe is probably the Danish company which holds the largest business potential in relation to the production of green synthetic fuels, such as methanol, DME and ammonia. These chemicals already constitute a very significant share of the present business portfolio.

Topsøe Fuel Cells:

Topsøe Fuel Cells manufactures SOFC stacks and cells; this is however not particular relevant for the present project. However, one of the future's very promising markets are the SOEC technologies, with which Topsøe Fuel Cells through their strategic research partnership with DTU Risø have created world leading results and holds the world record in the highest output in electrolysis mode.

GreenHydrogen.dk:

Greenhydrogen.dk manufactures and develops electrolyzers based on alkaline technology. Recently,

Greenhydrogen.dk announced a breakthrough in the efficiency of their alkaline electrolyzer reducing the cost by 40 $\%^3$.

TK Energi A/S:

Development and production of gasifiers and auxiliary equipment for gasifiers are the main business of TK Energi. The company has over the past two-three decades been involved in several R&D projects concerning gasification.

Babcock & Wilcox Vølund:

Vølund has worked on gasification projects for the last 10 years and gained significant experience, primarily through the Harboøre gasifier plants. Vølund's gasifier concept is based on the updraft gasification principle.

Weiss A/S:

Based on experience from DTU on the Viking Gasifier, Weiss offers gasifier systems with capacities of 200, 500 and 1000 kWe. The Viking gasifier features tar free gas, which can be utilized directly in an internal combustion engine.

Solum Gruppen:

Solum Gruppen treats household biodegradable waste through their Aikan[©] process concept, in which the waste is separated and converted into biogas and fertilizer.

IRD Fuel Cells:

IRD A/S is developing and producing PEM-based fuel cells, stacks and systems, running on methanol or hydrogen. Currently a PEM-based electrolyzer system is under development.

4.2.2 System Integrators and Utility Companies

The main Danish system integrators and utility companies constitute:

Dong Energy:

Being both a natural gas provider and electricity provider, Dong Energy has an natural interest in searching for alternative solutions for storage of renewable electricity, in particular the current plans for installing huge amounts of wind energy in great concerns regarding the stability of the electrical grid.

Energinet.dk

Being the Danish TSO, Energinet.dk is responsible for the operation of the main Danish electricity grid. The amount of fluctuating renewable energy that is to be installed in the Danish electricity grid is a very big challenge in terms of ensuring a stable supply. Therefore Energinet.dk is very interested in solutions that can convert/store large amount of electricity. Energinet.dk is also responsible for the main natural gas pipeline network.

³ http://ing.dk/artikel/114699-ny-dansk-brintgenerator-baner-vejen-for-det-fossilfri-samfund

4.3 Previous Studies – Review of Recent Literature

The purpose of this section is to provide a condensed overview of the most important recent studies. This review does not cover all the published studies, but contains the work that, in the view of the GreenSynFuels project group, is worth mentioning in relation to this project.

Methanol Production – Feasibility Studies:

4.3.1 (Weel & Sandvig, 2007)

This Danish feasibility report investigates the possibility of converting biomass into fuels that can be used in future transportation sector with fuel cells as the vehicle power source. Ammonia and methanol are the fuels in focus of the report, and the report suggests possible routes to produce these fuels from biomass. The study finds that methanol can be produced from biomass (wood chips) with an efficiency of 41%, if the plant is connected to the district heating network; assuming that the produced heat can be used, the total plant efficiency becomes 88%. The production price of methanol is 1.21 DKK/L (64 DKK/GJ) if the heat can be sold to district heating and 2.09 DKK/L (110 DKK/GJ) if no district heating is available. For ammonia production the numbers found were slightly different, 1.27 DKK/L (67 DKK/GJ) if district heating is available and 2.07 DKK/L (109 DKK/GJ) if no district heating is available.

4.3.2 (Lasse R. Clausen, 2010)

This article published in Energy conducts a techno-economic analysis of gasification of biomass (wood) combined with electrolysis of water for methanol production. The study investigates six different plant configurations, from which the calculated production prices range from 1.49 DKK/L to 3.28 DKK/L, assuming that low temperature waste heat is used for district heating. The total plant energy efficiency was 90 % for the best configuration.

4.3.3 (Kazuhiro Kumabe, 2008)

This scientific article from a Japanese research center has investigated the production of methanol based solely on gasification of biomass. Based on an estimated wood price of approximately 650 DKK/ton as used in (Lasse R. Clausen, 2010) and (Weel & Sandvig, 2007), the calculated methanol production price ranges from 3.9 DKK/L to 7.2 DKK/L. The methanol yield from the calculations ranges from 47.7 (wt%) to 30.9 (wt%).

4.3.4 (Sylvain Leduc, 2009)

The study of this paper focuses on the geographical sensitivity of methanol production based on gasification. The results emphasize the importance of placing a methanol production plant based on biomass gasification. The model output ranges from 2.12 DKK/L to 8.78 DKK/L for the total methanol cost, when varying the cost of wood, the plant position, the plant efficiency and plant operating hours.

4.3.5 (Dimitri Mignard, 2008)

This very interesting paper investigates the possibility of combining electrolysis with biomass gasification (wood), in which the oxygen is used in the gasifier and the hydrogen is used for supplementing the syngas. The study compares itself with a "traditional plant" without electrolysis. The produced methanol price is not surprisingly very dependent on the electricity price. If an electricity price of 0.3 DKK/kWh, such as used in (Lasse R. Clausen, 2010), then the produced methanol price becomes 3.16 DKK/L assuming that 75 % of

the plant capacity is used and the price of wood is 300 DKK/ton (dry wood). Interestingly, the study shows that the methanol outcome per weight is increased by 2.3 if electrolysis is used combined with gasification of wood. However, a low electricity price is a prerequisite for a feasible methanol production.

Future Wind Energy Predictions

4.3.6 (Claus Jørgensen, 2008)

The future wind energy market is naturally very hard to predict. In the present paper a simple extrapolation is made concerning the effect of wind power penetration (20 %, 50 %, 75 % and 100 %) in the Danish energy system, based on previous year's data (2000-2007). Below a figure from the paper shows the estimated power spot prices for different levels of wind penetration, this data could be used as reference for future power spot prices.



Figure 1: Current (20 % wind power) and extrapolated power spot prices as a function of available operating hours per year (Claus Jørgensen, 2008)

4.3.7 Literature Survey Summary

The literature on production of green synthetic fuels is vast and very comprehensive. Therefore, only recent and by the project group selected publications are covered in the review. From Table 1 the variations in calculated methanol production price from different studies, that deals with gasification in conjunction with electrolysis, are displayed. There is a significant variation in the prices listed; this is mainly due to the variation in the OPEX assumptions in the different studies. Naturally, the electricity prices are very important for the resulting methanol price. Jørgensen and Ropenus (Claus Jørgensen, 2008) published a study on the calculation of future wind power prices, based on extrapolation of previous recorded data from the West Danish power market. The data provides spot market power prices for 100 % wind penetration scenario, which is coherent with the current plans concerning a fully renewable-based electricity grid by 2050. The project group has decided to use the data provided by Jørgensen and Ropenus, adjusted with the recent energy price forecast supplied by the Danish Energy Agency (Energistyrelsen, 2010) as the OPEX input in the subsequent techno-economical calculations, see section 3.2.1 of Phase II.

| Sources: | Calculated Methanol price [EUR/T] | Calculated Methanol price [USD/MWh] | Calculated Methanol price [DKK/L] |
|--------------------------|--------------------------------------|--|--------------------------------------|
| (Weel & Sandvig, 2007) | 129 – 222 | 43 – 75 | 1.21 – 2.09 |
| (Lasse R. Clausen, 2010) | 158 – 349 | 53 – 117 | 1.49 – 3.28 |
| (Kazuhiro Kumabe, 2008) | 414 –765 | 139 – 258 | 3.9 – 7.2 |
| (Sylvain Leduc, 2009) | 225 – 933 | 76 – 314 | 2.12 - 8.78 |
| (Dimitri Mignard, 2008) | 336 | 113 | 3.16 |

Table 1: Overview of different feasibility studies concerning methanol production from biomass.

The electricity is however not the only OPEX parameter that has a significant influence on the resulting methanol price. The biomass price is naturally also important, but more importantly some studies also incorporates revenue of supplying excess heat from the process plant to a nearby district heating network. The latter can have a very significant effect, in the study by (Weel & Sandvig, 2007) the resulting methanol price is reduced by more than 40 % when excess heat is being sold for district heating. Prices for biomass and district heating are found in (Energistyrelsen, 2010).

4.4 Synthetic Green Fuels

A synthetic green fuel is an industrial produced fuel based on energy from renewable sources, such as wind, solar, wave or biomass. An example of a synthetic fuel that in recent years has been discussed very widely is hydrogen. In many ways hydrogen is an ideal fuel for a fuel cell; however, in system and logistical context, hydrogen is very difficult to handle. Below the synthetic fuels considered in the present project are briefly described.

4.4.1 Methanol

Methanol is the lightest of alcohols and is often referred to as wood alcohol. It is a colorless, tasteless and poisonous fluid that is liquid at ambient conditions. The chemical formula is CH₃OH. Methanol is primarily produced from a synthesis gas based on steam reforming of natural gas. Therefore, the price of methanol is strongly dependent on the natural gas price. Methanol is widely used in chemical processing.

4.4.2 Ammonia

Ammonia must be stored under pressure or at low temperatures (below -33 °C) in order to be on liquid form. Ammonia is widely used in chemical processes, for cleaning agencies and for fertilizing fields. It has a very distinct smell, and is toxic. The chemical form of ammonia is NH₃. Ammonia is typically produced from natural gas through conversion into hydrogen, which is subsequently reacted with nitrogen into NH₃.

4.4.3 DME

DME or DiMethylEther has the chemical formula CH₃OCH₃. It is gasous at ambient conditions and is typically stored under a relatively low pressure in order to be on liquid form. DME is primarily used for household heating and cooking but is also used as a propellant in aerosol canisters, and can be used as an alternative to diesel fuel and for fuel cells. DME is primarily produced from natural gas and coal through gasification. Methanol is typically produced and further processed into DME in a two or one step process.

4.4.4 Green Synthetic Natural Gas (SNG)

Green synthetic natural gas has the same properties as fossil natural gas, except that it is based on biomass resources. The Danish natural gas composition has a relatively high content of methane $(n_{CH4,mol,\%} = 90 \%^4)$, the produced green synthetic natural therefore has similar properties, as lower or higher methane content will create problems at the user sites, as seen with recent import of lean German natural gas. The present known Danish fossil natural gas resources can supply the present Danish consumption for another 13 years.

4.5 Methanol Background Information

Per Koustrup, Serenergy

The following section provides background information regarding the current methanol prices and strategic delivery options. There is a strong interest in methanol from the project group members as methanol is considered the optimal fuel for fuel cells in transport applications for logistical reasons.

4.5.1 Methanol Prices

Methanol prices have a strong bearing on petrochemical prices due to their dependence on natural gas for feedstock supply, and since natural gas prices are closely linked to crude oil prices, it is expected that the price of methanol is also closely linked to the price of crude oil. In the figure below one can see the correlation between WTI crude oil price on the US market and the price of methanol from May 2001 to November 2010. The data used in the graph origins from historic methanol prices listed on Methanex's homepage and from historic prices on crude oil as listed on <u>www.eia.org</u>. From the figure below one can see methanol price at N.Y. harbor (FOB) as a function of crude oil price measure in USD/bbl of crude oil WTI.



Figure 2: Price of crude oil and methanol 2001 - 2010

⁴ www.naturgasfakta.dk

The adjusted coefficient of determination (\mathbb{R}^2) is 0.54, meaning that 54 % of the variance can be explained be the linear formula 4.08x + 97.21, where x is the price of one bbl of WTI crude oil. The same analysis has been made on \notin /MT methanol in Rotterdam harbor linked to both \notin /bbl of crude oil Brent and USD/bbl Crude oil Brent. In both cases the adjusted coefficient of determination was below 0.3. This is a very strong indication of the price of methanol being determined in USD (and not in \notin) and that it is the price of crude oil WTI that determines the world market price of methanol and not Brent or any other kind of crude oil.



Figure 3: Correlation between oil and methanol price in North America

In the figure above one can furthermore see two periods with price-shocks. Marked with yellow is the period from September 2006 to March 2007 and marked with red is the period from October 2007 to March 2008. If price-shocks are stripped from the above linear regression, then the adjusted coefficient of determination (R^2) increases to 0.76. The formula also changes to 3.22x + 116.59.



Figure 4: Correlation between oil and methanol price in North America

4.5.2 Market Structure and the Influence on Methanol Price

The methanol industry is a typically oligopolistic market, meaning that there are a number of mid-size players but that none can dominate the market. The four and eight-firm concentration ratios (CR_4 and CR_8) in 2010 where 39 % and 52 % respectively, meaning that the industry has a low to medium concentration.⁵ The top eight companies from a market share point of view as of 2010 are: Methanex (15.5%), SCC/Helm (Methanol Holdings Trinidad Ltd/MHTL) (9.5%), Saudi Basic Industries (SABIC) (9%), MCG (5.0%), Mitsubishi (MSK) (4.5%), Iran Petrochemical Commercial Company (IPCC) (3.5%), Mitsui Chemical Inc. (3.0%) and Petronas (2%).



Figure 5: The top 8 global players held more than 50% of the total market share in 2010

Because there are relatively few producers of methanol, each oligopolist is likely to be aware of the actions of the others. The decisions of one firm influence, and are influenced by, the decisions of other firms. Strategic planning by companies producing methanol needs to take into account the likely responses of the other market participants. Methanol is one of only a very few completely uniform products. This should in theory result in a cost of methanol equal to marginal costs of the methanol plant with the highest production price. The price of 1 ton of methanol at a specific grade is in summary believed to be equal to the marginal cost of the plant/producer with the highest marginal costs.

⁵ <u>http://www.methanex.com/investor/documents/2010/Methanex_Investor_Presentation_Dec-2010.pdf</u>



Figure 6: China methanol production and net imports

Recent history has demonstrated that it is exactly what happens. High cost capacity, which is mainly concentrated in China and based on coal-to-methanol technologies, has acted rationally and has shut down the production in the lower methanol price environment. From October 2008 to December 2008 the price of methanol on the Chinese market plummeted from more than 400 USD/ton to less than 200 USD/ton. In the same period Chinese production fell significantly and import increased manyfold. Based on the above argumentation it is concluded that at least some of the Chinese producers acts as swing-capacity. This can be seen in the figure below.⁶

Methanol plants elsewhere in the world have the same function. A two times 500,000 t/year methanol plant in the northern part of the Netherlands was closed down due to too high prices on natural gas. If however methanol prices are to increase and stay at a high level and natural gas prices in the Netherlands are low, this plant might be re-opened. A large multi mill \in investment is needed to put the plant into operation again.⁷

4.5.3 Methanol Distribution to Denmark

At least one of the Danish importers buy methanol from the Tjelbergodden's methanol plant near Tronheim in Norway.⁸

Tjeldbergodden's methanol plant

Tjerldbergodden's methanol plant was officially inaugurated on 5 June 1997 and is Europe's biggest methanol plant. Deriving its natural gas feedstock from the Heidrun field in the Halten Bank area of the Norweigan Sea, the facility has an annual capacity of about 900,000 tons of methanol. That volume corresponds to 25% of Europe's total production capacity for this methanol, and 13% of the continent's

⁶ http://www.methanex.com/investor/documents/2010/Methanex Investor Presentation Dec-2010.pdf

⁷ Based on personal communication with representtives from BioMCN.

⁸ <u>http://www.statoil.com/en/OurOperations/TerminalsRefining/Tjeldbergodden/Pages/default.aspx</u>

consumption. Statoil has an 81.7% interest in the plant, with ConocoPhilips owning the remaining 18.3%. Total development costs for this facility were about NOK 3.6 billion. Statoil claims the Tjeldbergodden plant is one of the world's most energy-efficient methanol producers, which means that the carbon dioxide emissions per ton produced methanol are low. As one can see on the map below, the Tjerdbergodden methanol plant is located far away from main-land Europe and is also located several hundred kilometers away from the natural gas-grid of the North Sea. Methanolplants are typically located in remote areas, where no gas distribution exists and/or where gas distribution is very costly to build, and the Tjeldbergodden is therefore what one can term as a typical new methanol plant.



The methanol is then shipped to Esbjerg and Aarhus in large vessels.

4.5.4 Methanol Storage

Typically 1,000 to 1,500 tons of methanol is shipped to Esbjerg per shipment. The harbor of Esbjerg typically receives one shipment of methanol per month except for July and December. In total the harbors of Esbjerg receives approx. 10,000 tons of methanol per year. The distance by sea from Tjeldbergodden to Esbjerg is approx. 1,100 km. IAT has a 15,000 Nm³ storage facility in Esbjerg.⁹ It is unknown how much methanol can be stored at the facility.

Typically 1,000 to 3,500 tons $(1,266 - 4,430 \text{ Nm}^3)$ of methanol is shipped at a time to Aarhus.¹⁰ On Samoavej 1 in Aarhus there are two methanol tanks. Both tanks have a capacity of 2,500 Nm³ (2,000 tons). They were made of plain steel in 1974. The company is allowed to consume up to 55,000 tons of methanol per year including methanol for reselling. It can receive methanol at a flow rate from vessel to on-land storage capacity of up to 350 Nm³/hr. The company is allowed to use the harbor facility up to 35 hrs/month but it normally only uses the harbor facility 15 – 20 hrs/month. The company uses methanol for the production of formaldehyde, which is produced via catalytic oxidation of methanol.

There are also methanol storage facilities at the harbor of Aabenraa. The company IAT has a 20,000 Nm³ storage facility in Aabenraa. It is unknown how much methanol that can be stored at the facility. The pictures below are from the facility in Aabenraa.

⁹ <u>http://www.iat.dk/chemicalhandling/index.asp?q=page{:}37{|}vpath{:}37{{}}lang{:}UK</u>

¹⁰ http://www2.blst.dk/download/aar/aaa/www/pdf/nordalim.pdf



Figure 7: Tank capacity in Aabenraa

Methanol might also be stored at facilities on other harbors.

4.5.5 Strategic Oil Stocks

If in the long run methanol is to be widely used in HTPEM fuel cells for automotive applications then one has to have a close look at the strategic energy stocks requirements. According to Council Directive 2006/67/EC of 24 July 2006 the EU Member States are obligated to maintain certain minimum stocks of crude oil and/ or petroleum products. In the text box below is seen a short version of the Council Directive which is taken from the European Union legislation homepage:

Strategic oil stocks

The obligation of the Member States to build up and maintain a minimum petroleum reserve gives security of supply of petroleum resources to the European Union (EU).¹¹ Due to the importance of oil in the EU's energy mix, the EU's strong external dependence for supply of petroleum products and the geopolitical uncertainty in many producer regions, it is vital to guarantee consumers' continuous access to petroleum products. Council Directive 2006/67/EC of 24 July 2006 imposing an obligation on Member States to maintain minimum stocks of crude oil and/or petroleum products. Member States are required to build up and constantly maintain minimum stocks of petroleum products equal to at least 90 days of the average daily internal consumption during the previous calendar year. The calculation of the daily internal consumption is based on motor spirit and aviation fuel, gas oil, diesel oil, kerosene and jet-fuel of the kerosene type, as well as fuel oils. Amongst the petroleum resources accepted in the statistical summary of strategic stocks are supplies held in ports of discharge, or those on board oil tankers in port for the purpose of discharging, once the port formalities have been completed, supplies held in tanks at the entry to oil pipelines and also those held in refinery tanks. On the other hand, certain resources may not be included in the statistical summary, such as crude oil not yet extracted, supplies intended for the bunkers of sea-going vessels, supplies in pipelines, in road tankers or rail tank-wagons, in the storage tanks of retail outlets and those held by small consumers, as well as quantities held by or for the armed forces. Member States may include in their statistical summary of strategic stocks only quantities that are at their full disposal in the event of an oil supply crisis.

¹¹ <u>http://europa.eu/legislation_summaries/energy/external_dimension_enlargement/l27071_en.htm</u>

Since the end of the 1960s, the European Union has been aware of the need to prevent potential oil supply shortages. The minimum requirements have been raised from at least 65 days of the daily internal consumption to an obligation for stocks equivalent to at least 90 days. Council Directive 98/93/EC developed and strengthened the provisions of Directive 68/414/EEC. In the interests of clarity and effectiveness, these Directives were consolidated in, and thus repealed by, Council Directive 2006/67/EC. This Directive will be repealed by Directive 2009/119/EC from 31 December 2012.

As seen from the above text box there is a minimum requirement to store the equivalent of 90 days use of oil product. The daily consumption of the different categories is seen in the table below.

| Country ¹² | Cat. I | Cat. II | | Cat. III | Total |
|-----------------------|--------|----------|-------|----------|--------|
| | | Jet fuel | Other | | |
| | | 1,660 | 7,510 | | |
| Denmark | 3,380 | 9,170 | | 800 | 13,350 |

Table 2: Daily consumption 2009 in tons

Category I is "Motor spirit and aviation fuel of gasoline type", category II is "Gasoil, diesel oil, kerosene and jet-fuel" whereas category III is "Fuel oils".

In the table below is seen the minimum requirement measured in tons and the actual stocks.

| Country | Cat | t. I | Cat | t. II | Cat | t. III | То | tal |
|---------|---------------|--------|---------------|--------|---------------|--------|---------------|--------|
| Denmark | Days of cons. | 1000 t |
| Minimum | 90 | 304 | 90 | 825 | 90 | 72 | 90 | 1,201 |
| Actual | 181 | 613 | 181 | 1,661 | 1,273 | 1,018 | 247 | 3,292 |

Table 3: Minimum and actual stocks of category I, II and III in Denmark

Large parts of the Danish strategic stock holdings are located at the Fredericia and Kalundborg oilrefineries. The combined storage tank capacity is 660,000 m³ for Fredericia and 790,000 m³ for Kalundborg.¹³ At a density of approximately 0.8 kg/l these two facilities have a capacity measured in 1,000 t of 1,160¹⁴, which is equivalent to 96% of the minimum stock requirements and 35% of the actual stock.

¹² <u>http://ec.europa.eu/energy/observatory/oil/stocks_en.htm</u>, <u>Oil stock position: Member States with a 90-day</u> <u>obligation (June 2010)</u>

¹³ Udvidelse af Statoil Raffinaderiets tanklager samt etablering af en bioethanolfabrik, Vestsjællands Amt, Regionsplan 2005 - 2016, Tillæg 15,

http://www.shell.dk/home/content/dnk/aboutshell/our_business/refinery/about_the_refinery/

¹⁴ (660.000 m3 + 790.000 m3)/1000 l/m3 * 0.8 kg/l =1.160.

4.5.6 Methanol Import to Denmark

There are at least six importers of methanol in Denmark. One of the importers has specialized in selling to laboratories and for R&D purposes, one of them only imports green methanol and four of them are bulk importers. Of the four bulk importers it is believed that most of the Danish market both in terms of quantity and in terms of turnover is covered by two to three of the four bulk companies. Four of the companies have their (Danish) head-office in The Capital Region of Denmark, one in the Central Denmark Region and one in the Region of Southern Denmark. Two of the companies are under Danish ownership. The ownership of the remaining companies is either foreign owned or has unknown owners.

4.5.7 Methanol Distribution in Denmark

All transport of methanol in Denmark is done by IAT which is the only certified chemical carrier in the country. IAT is member of Tankceu – Tank Combination Europe, which is a European cooperation organization between carriers, who specializes in transport and handling of dangerous goods.

An estimated 95 % of the methanol, which is not used directly on the harbors, is trucked to the customers. The trucks have a capacity of 28 t. However, they normally only transport 23 t at a time. They weigh the empty truck, fill it up with methanol and weigh it again. Thereby they know exactly how much methanol they have filled onto the truck. They then drive to the customer and unloads the amount of methanol that the customer has bought. When they return they weigh the truck again. Thereby they know exactly how much methanol the customer has bought. Some customers have their own weighbridge. In the picture below one can see such a 28 t capacity truck from IAT at the facility in Aabenraa and a weighbridge.



Figure 8: 28 t truck at IAT Aabenraa (left) and weighbridge (right)

For smaller quantities either 1000 L pallet tanks, 250 L steel drums, 50 L steel drums, 20 L plastic cans and glass bottles are used. Some 1000 L pallet tanks and some 250 L drums are seen on the picture below. IAT taps methanol into pallet tanks, drums or cans using the tapping and mixing equipment shown on the picture below to the right. Mixing, tapping and distribution take place from both Aabenraa and Esbjerg.



Figure 9: 1000 L tanks & 250 L drums (left), mixing and tapping equipment (right)

For laboratory use plastic cans and glass bottles are used. In the table below the estimated market shares for different kind of distribution forms for methanol is seen.

| Distribution form | Capacity | Estimated market share |
|------------------------------|----------------------------------|------------------------|
| | (kg / L) | (quantity, %) |
| Truck | 28.000 / 35.440 | 95 |
| Pallet tanks | 790 / 1000 | 2.5 |
| Steel drums | 198 / 250 , 40/ 50 | 2.0 |
| Plastic cans | 16 / 20 | 0.5 |
| Plastic cans / glass bottles | Up to 20 L | 0.2 |

Table 4: Market share for different kinds of distribution

1 Introduction

In this phase of the project the base foundation for phase II of the project is made. Green Synthetic Fuels can be produced from various sources and through various production methods. The purpose of phase I is to find 1-3 production routes that indicates a feasible business cases for Danish companies. The Baseline description given in this section serves as basis for making the decision of how to proceed in Phase II. The purpose is to give a general overview of the state-of-art within the given areas of technology.

2 Resources

In this section an overview is given of the biomass resources in Denmark, which can form a basis for a production of Green Synthetic Fuels. The resources are divided into the following segments: Wood-based biomass, Straw-based biomass and Biogas potential. Algae is not taken into consideration, since it is still on research basis; the wind potential is briefly described in section 4.3.6.

2.1 Wood Potential in Denmark

(Allan Schrøder, Risø, Aksel Hauge, Dong Energy)

Denmark was formerly covered by extensive forests of leaf-bearing trees. However, because of uncontrolled cutting down, the Danish forest areas decreased drastically until it finally by the start of the 19th century reached a low of 5% coverage. In 1805 the "Fredsskovsforordningen" was introduced and since then the forest area in Denmark has been increasing so that today Denmark is covered by 570,000 ha forest (Thomas Nord-Larsen, 2009) corresponding to 13.2% of the area of Denmark. In 1989 the Danish parliament decided that the Danish forest area should be doubled in one tree generation. This means that by 2089 the forest area should reach 20-25% and thus the future will probably bring even more forest to Denmark because of political intentions.

| Year: | 1990 | 2000 | 2008 |
|------------------|---------|---------|---------|
| Forest area [ha] | 445,390 | 486,235 | 570,800 |

 Table 5: Development of forest area in Denmark¹⁵ (Thomas Nord-Larsen, 2009)

Historically, firewood was a dominating source of energy (heat) in Denmark until fossil sources took over approx. 150 years ago. Even today firewood still contributes visibly to the Danish energy economy (3.7%, (Energistyrelsen, 2009)).

The harvesting of wood in Denmark varies over years depending on demand/economy and to some extent also on meteorological circumstances (heavy storms may imply undesired wood harvest – see for instance 2000 in Figure 10). The specific numbers for the Danish cutting down of trees in the period 1990 to 2008 is shown in Figure 10. Approx. 20% is hardwood and 80% is softwood.

¹⁵ <u>http://www.statistikbanken.dk/statbank5a/default.asp?w=1440</u>



Figure 10: Total annual wood harvest in Denmark including both energy and non-energy purposes

Figure 11 shows the use of Danish wood for energy purpose. The difference between the numbers of Figure 10 and Figure 11 can be ascribed to the production of timber for use as a material (e.g. for construction and furniture).

The use of different types of Danish wood for energy purposes is shown in Figure 11. In the report (Evald, 2006) it is estimated, that approx. 50% of the total demand for firewood in private woodburning stoves and boilers (which in the report is estimated to be approx. 20,000 TJ/year) are provided from private gardens, hedges and similar). Those sources are difficult to make up and therefore give uncertainty to the data in Figure 11.



Figure 11: Use of Danish wood (m3) for energy purposes¹⁶

The total contribution from wood (excluding waste wood, though) to the total Danish energy supply constitutes approx. 35,000 TJ or 2.7 %. This number, however, includes imported material.

¹⁶ <u>http://www.statistikbanken.dk/statbank5a/default.asp?w=1440</u>





| Wood chips | Hardwood | Softwood | Wood pellets | | |
|-----------------------|------------------------|-----------------------|--------------|--|--|
| 2.8 GJ/m ³ | 10.4 GJ/m ³ | 7.6 GJ/m ³ | 17.5 GJ/ton | | |
| | | | | | |

Table 6: Energy content (combustion) for different types of wood (Energistyrelsen, 2009)

As can be seen in Figure 10, the total wood harvested in Denmark has been more or less stable since 1990, perhaps increasing slightly in the years 2005-2008. This behavior is found in spite of the fact that the total forest area has increased by 25%. Similarly (Figure 11) the use of Danish wood for energy purposes has also been more or less constant and the increase in energy production from wood illustrated in Figure 12 must consequently be ascribed to imported wood. When considering the future Danish wood energy resources, the following should be taken into account:

- 1. The distribution of the future use of wood between energy and non-energy applications will be determined by market mechanisms unless overruling political decisions are made for wood as a resource
- 2. The political aim of increasing the Danish forest area sooner reflects a demand for recreational resorts than a need energy supply. This prioritization may change and furthermore the two objectives are not necessarily in mutual contradiction.

2.2 Straw Potential in Denmark

(Allan Schrøder, Risø, Aksel Hauge, Dong Energy)

In Denmark, straw is used for cattle feed and an increasing amount for energy purposes in the energy industry. The energy industry is mainly using the straw for combustion in heating plants and CHP plants, but in the future straw is also expected to be used for other energy purposes like production of bioethanol and gasification. That is why straw will be one major resource to manage the Danish goals for sustainability for the energy sector.

2.2.1 Straw Used for Energy Purposes

Approx. 150 biomass district heating plants in DK:

- 60 straw fired
- 90 wood chips and/or wood pellets
- Typical 1-10 MW
- Several large co-fired CHP plants.

For the period from 2004 to 2008 the total straw production in Denmark was 5.5 mill tons/year (82,5 PJ at 15% water). 1.4 mill tons was used for combustion, 1.1 mill tons for cattle feed, and 0.7 mill tons for bedding material for cattle. This gives a surplus of 2.2 mill tons straw per year or 40% of the total production.



Figure 13: Yearly production of straw in Denmark – for different purposes¹⁷

The total agricultural area in Denmark is 2,7 mill. acres, of which straw producing crops is covering 1,7 mill. acres. This area seems to be rather constant in the future, so the future amount of the straw surplus in Denmark for energy purposes will be dependent of how much straw that will be used in other areas. The amount of straw for bedding seems to go down, still the amount for cattle feed seems constant. In total the amount of straw for energy purposes seems to grow slightly in the future. Still the yearly variation in production due to climate conditions seems to be the most important factor upon the possible surplus of straw for energy purposes.

¹⁷ Data from http://www.statistikbanken.dk/, tables HALM og HALM1).

2.3 European Biogas Potential

Martin Wittrup Hansen, Solum Gruppen

The biogas potential in Europe is large, but only a small fraction of the potential is used.

166 Mtoe is the theoretic potential of primary energy production from biogas in 2020, according to a German study ¹⁸. Compared to the present use of 5.9 Mtoe this is a theoretical figure that will not be reached in the next decades.

1 TWh primary energy from biogas per 1 million people in Europe.

This potential of 500 TWh (43 Mtoe) for the 500 million people living in the EU27 is derived from agricultural byproducts and waste alone (organic waste from households and industries, sewage sludge, manure, catch crops, landscape cleaning). These waste streams strongly correlate with the size of the population and studies from Austria, Sweden, Germany and the United Kingdom all arrive at a magnitude of approximately 1 TWh per 1 million people, which if used for example as a vehicle fuel could more than cover the 10% target to the share of renewables in the transportation sector for 2020.

20% yearly growth

In 2007 the production in Europe reached 5.9 Mtoe, an increase of over 20% compared to 2006.

Based on different studies and the experience of member countries, the realistic potential for biogas until 2020 can be calculated for the EU27 as follows:

AEBIOM assumes that 25 mill ha agricultural land (arable land and green land) can be used for energy in 2020 without harming the food production and the national environment. This land will be needed to produce raw materials for the first generation fuels, for heat, power and second generation fuels and for biogas crops. In the AWB IOM scenario:

- 15 mill ha land is used for first generation biofuels (wheat, rape, sugar beet, etc.)
- 5 mill ha for short rotation forests, miscanthus and other solid biomass production and
- 5 mill ha for biogas crops.

On this basis the potential for biogas in 2020 is estimated as follows:

¹⁸ IE Liepzig, 2007

Biogas potential in 2020

| | 2020 | | | |
|---|---------------------------------------|---|---|---------------------------|
| Origin (according to template for National Renewable Energy Action Plans) | Potential Billion m³ Biomethane | Assumed percentage of use until 2020 | Primary energy Billion m ³ Biomethane | Primary energy Mtoe |
| Agriculture | 58,9 | 62% | 36,4 | 31,3 |
| Agricultural crops directly provided for energy generation (5 % of arable land; calculation in annex) | 27,2 | 100% | 27,2 | 23,4 |
| Agricultural by-products / processed residues | 31,7 | 28% | 9,2 | 7,9 |
| • straw | 10,0 | 5% | 0,5 | 0,4 |
| • manure | 20,5 | 35 % | 7,2 | 6,0 |
| • rest (landscape management) | 1,2 | 40 % | 0,5 | 0,4 |
| Waste | 19,0 | 50% | 9,5 | 8,2 |
| Biodegradable fraction of municipal solid waste including biowaste (biodegradable garden and park waste, food and kitchen waste from households, restaurants, caterers and retail premises, and comparable waste from food processing plants) and landfill gas | 10,0 | 40% | 4,0 | 3,4 |
| Biodegradable fraction of industrial waste (including paper, cardboard, pallets) | 3,0 | 50% | 1,5 | 1,3 |
| Sewage sludge | 6,0 | 66% | 4,0 | 3,4 |
| Total | 77,9 | 59% | 45,9 | 39,5 |
| Source: AEBIOM | | | | |

[#] IE Liepzig, 2007

Figure 14: Biomass potential in 2020

The realistic potential of methane derived from animal manure and energy crops and waste lies in the range of 40 Mtoe in 2020 as compared to a production of 5.9 Mtoe in 2007. The use of catch crops for biogas production was not considered in the calculation and offers an additional potential.

In 2020 biogas could deliver more than a third of Europe's natural gas production or around 10% of the European consumption (433,7 Mtoe in 2007).

Within the overall potential of biomass for energy in Europe, biogas could reach 15 to 25% of total bioenergy, as compared to 7% in 2007. The biomass potential for energy as a whole is much bigger than its present use, but this potential has to be developed by activities on local, regional, national and international level.

Looking at the overall contribution to bioenergy, forest-based biomass is currently the main contributor, but the agricultural sector has a greatest potential and could be the most important energy supplier already by 2020. Biogas will especially profit from this development as it offers effective alternatives for the fast growing sectors of bioelectricity and vehicle fuels.

| Outlook | for | bioenergy | sources | in Mtoe |
|---------|-----|-----------|---------|---------|
| | | | | |

| Source | 2004 | | 2020* | |
|------------------------------|------|--------|-------|--------|
| Forest based biomass | 61,5 | (85%) | 75 | (34%) |
| Agriculture based biomass | 3,5 | (5%) | 97 | (44%) |
| Waste | 7,3 | (10 %) | 23 | (11 %) |
| Imports | - | | 25 | (1196) |
| Total | 72,3 | | 220 | |

* AEBIOM estimates

Figure 15: Outlook for bioenergy sources in Mtoe

Maize is already established as an energy crop for biogas production and in the future other energy crops will be used in order to optimize the yield per hectare agricultural land. Together with manure from animal production (mainly cattle and pig farms) decentralized co-digestion plants have the greatest potential for biogas production but also the use of sludge and food industry waste and household waste offers big opportunities.

At the moment, about 109 million hectares arable land exists in Europe. If 5 % of this land is used for energy crops a yield of 15 tons of solid dry matter per hectare could provide 23.4 Mtoe of energy if converted into biogas (see Figure 16).

In the coming 10-20 years an increasing utilization of crops for energy and industrial purposes is expected to be seen. Scenarios of 10-20% or even 30% of the arable land shifting from food and feed towards energy farming will gradually occur. Large European countries with significant fertile agricultural area of cropland, might play a major role in bioenergy production; examples can be Ukraine and France. An average total crop yield of around 20 t/ha is considered feasible in the near future. Maize, sugar beet and various other crops will increase in importance European wide. Crop paradigm changes are in progress.

| Country | Arable land | Biogas potential | Total manure from crops* | Biogas potential from manure** | Total biogas potential |
|----------------|-------------|--------------------------|-----------------------------|-----------------------------------|---------------------------|
| | | 5% land; yield 15t/ha | Cattle and pigs | 35% manure used | 5 % land & 35 % manure |
| UNIT | 1000 ha | Mtoe | Mt | Mtoe | Mtoe |
| Austria | 1382 | 0,30 | 34,0 | 0,13 | 0,43 |
| Belgium | 840 | 0,18 | 48,6 | 0,19 | 0, 37 |
| Bulgaria | 3086 | 0,66 | 10,7 | 0,04 | 0,71 |
| Cyprus | 115 | 0,02 | 1,7 | 0,01 | 0,03 |
| Czech Republic | 3032 | 0,65 | 24,6 | 0,10 | 0,75 |
| Denmark | 2306 | 0,50 | 47,2 | 0,18 | 0,68 |
| Estonia | 598 | O,13 | 4,1 | 0,02 | 0,14 |
| Finland | 2253 | 0,49 | 15,7 | 0,06 | 0,55 |
| France | 18433 | 3,97 | 299,1 | 1,16 | 5,13 |
| Germany | 11877 | 2,56 | 225,8 | 0,88 | 3,43 |
| Greece | 2548 | 0,55 | 10,5 | 0,04 | 0,59 |
| Hungary | 4592 | 0,99 | 17,2 | 0,07 | 1,06 |
| Ireland | 1060 | 0,23 | 97,2 | 0,38 | 0,61 |
| Italy | 7171 | 1,55 | 102,9 | 0,40 | 1,94 |
| Latvia | 1188 | 0,26 | 6,1 | 0,02 | 0,28 |
| Lithuania | 1835 | 0,40 | 13,9 | 0,05 | 0,45 |
| Luxembourg | 61 | 0,01 | 2,9 | 0,01 | 0,02 |
| Malta | 8 | 0,00 | 0,4 | 0,00 | 0,00 |
| Netherlands | 1059 | 0,23 | 73,7 | 0,29 | 0,51 |
| Poland | 12502 | 2,69 | 113,4 | 0,44 | 3,13 |
| Portugal | 1083 | 0,23 | 24,0 | 0,09 | 0,33 |
| Romania | 8553 | 1,84 | 53,8 | 0,21 | 2,05 |
| Slovakia | 1377 | 0,30 | 9,2 | 0,04 | 0,33 |
| Slovenia | 177 | 0,04 | 7,4 | 0,03 | 0,07 |
| Spain | 12700 | 2,74 | 138,6 | 0,54 | 3,27 |
| Sweden | 2643 | 0,57 | 25,0 | 0,10 | 0,67 |
| United Kingdom | 6085 | 1,31 | 149,3 | 0,58 | 1,89 |
| EU 27 | 108564 | 23,39 | 1556,9 | 6,04 | 29,43 |

A case example: Calculation of biogas potential from energy crops and manure for 2020 (FAOSTAT 2009, AEBIOM calculations)

* see calculation example in the annex Approximately 5 Mio ha land in Europe ** Assumed methane content in biogas 65%; assumed yield of 20 m³ biogas per ton of manure

Figure 16: Case example for biogas potential from energy crops

The fermentation of manure alone does not result in high biogas yield, but its high buffer capacity and content of diverse elements have a positive impact on the anaerobic digestion process stability. Higher methane yield can be achieved through co-digestion of manure with other substrates, such as energy crops and agricultural by-products. The theoretical potential of methane achieved from 35% of all European animal manure and energy crops (5% of the arable land in EU-27) produced through anaerobic digestion

process could supply 29.4 Mtoe which equals almost a fifth of Europe's natural gas production or 6.7% of the consumption in 2007 (BP, 2008).

As a rule of thumb it can be said, that 1/5 of the biogas could come from manure, 1/5 from different byproducts and waste streams and 3/5 from energy crops. Until 2020 biogas could deliver 2-3% of the total primary energy, predominantly as electricity, vehicle fuel and as heat.

2.4 Resources for Biogas Production in Denmark

Jørgen Hinge, Danish Technological Institute

2.4.1 Biomass Used in Danish Biogas Plants

The energy production from biogas in Denmark is at present approx. 4 PJ. About 75% of the biomass used in the biogas production is animal manure, mainly in the form of slurry. The other 25 % is mainly different types of organic waste, see list below.

Types of biomass used in Danish biogas plants:

- Animal manure
- Slaughterhouse waste
- Dairy waste
- Waste from plant oil production
- Waste from fish industries
- Sewage sludge
- Separated household waste
- Waste from breweries
- Energy crops.

A small amount of biogas is produced at municipal sewage plants, and some 122 mill m³ methane is collected from landfills.

In other countries – especially Germany – energy crops such as corn and grass are widely used in biogas production; in Denmark however, the use of energy crops in biogas plants is very limited at present, although there is a lot of interest from existing and planned biogas plants to utilize this biomass resource.

2.4.2 Potential for Biogas Production in Denmark

There have been made several different assessments of the potentials concerning utilization of domestic animal manure for energy purposes in Denmark. The most important reason for the often very big differences in those assessments is of course due to the different preconditions, for example: different assessments of the biogas potential in one ton "average organic fertilizer" and how much of this is actually utilized in the biogas plant, dry matter content in the dry matter fraction that is incinerated (or gasified).

A very essential aspect in the assessment of the potential concerning utilization of domestic animal manure for energy purposes is the dry matter content in the different products. Thus, the Danish Institute of Food

and Resource Economics (Fødevareøkonomisk Institut), FOI, states that the net energy gain by degasification (biogas) is increased from 120 kWh/ton manure at an organic dry matter content of 4% to 600 kWh/ton manure at a dry matter content of 20%. Incineration provides a positive net energy gain in domestic animal manures with a dry matter content of 15% or more. At 30% dry matter, incineration provides a net energy output of app. 600/kWh manure (FOI, 2005).

It is commonly agreed that the total amount of domestic animal manure corresponds to approx. 30 million tons of slurry annually (i.e. not included the manure produced by animals in the field). The average content of organic matter is assessed to constitute approx. 5% – or 50 kg/ton slurry.

On the basis of the content of protein, carbohydrate and fat coming from domestic animal manure, Faculty of Agricultural Sciences – Aarhus University, DJF-AU, assesses that the average energy content in 1 kg of organic matter from domestic animal manure is 20 MJ. The total theoretical energy content in the organic fertilizer is considered to constitute: 30 x 106 tons x 50 kg/ton x 20 MJ/kg = 30 x 109 MJ = 30 PJ.

Furthermore, DJF-AU assesses that in biogas plants an average of 55% of the organic matter is converted (a little more for pig manure – a little less for cattle manure).

With these preconditions, the theoretical biogas potential by degasification of all domestic animal manure can be calculated to $30 \text{ PJ} \times 0.55 = 16.5 \text{ PJ}$. Note that this does not including the biogas production from the organic industrial waste which is supplied to the plants.

3 Thermal Gasification

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3.1 Global Gasification Activities

The U.S. Department of Energy's (DOE) 2010 Worldwide Gasification Database shows that the current gasification capacity has grown to 70,817 megawatts thermal (MW_{th}) of syngas output at 144 operating plants with a total of 412 gasifiers (NETL, National Energy Technology Laboratory 2010). In order to be consistent with prior databases, only commercial operating plants with a capacity exceeding 100 MW electric equivalent (MW_{e}) are included in the database.
| Feedstock | | Operating 2010 | Under Construction 2010 | Planned 2011-2016 | Totals |
|---------------|--|-------------------|-------------------------------|----------------------|---------|
| | Syngas Capacity (MW _{th)} | 36,315 | 10,857 | 28,376 | 75,548 |
| Coal | Gasifiers | 201 | 17 | 58 | 276 |
| | Plants | 53 | 11 | 29 | 93 |
| | Syngas Capacity (MW _{th}) | 17,938 | | | 17,938 |
| Petroleum | Gasifiers | 138 | | | 138 |
| | Plants | 56 | | | 56 |
| | Syngas Capacity (MW _{th)} | 15,281 | | | 15,281 |
| Gas | Gasifiers | 59 | | | 59 |
| | Plants | 23 | | | 23 |
| | Syngas Capacity (MW _{th)} | 911 | | 12,027 | 12,938 |
| Petcoke | Gasifiers | 5 | | 16 | 21 |
| | Plants | 3 | | 6 | 9 |
| | Syngas Capacity (MW _{th)} | 373 | | 29 | 402 |
| Biomass/Waste | Gasifiers | 9 | | 2 | 11 |
| | Plants | 9 | | 2 | 11 |
| Tota | al Syngas Capacity (MW _{th}) | 70,817 | 10,857 | 40,432 | 122,106 |
| | Total Gasifiers | 412 | 17 | 76 | 505 |
| | Total Plants | 144 | 11 | 37 | 192 |

Figure 17: Summary of the gasification industry. Source: (NETL, National Energy Technology Laboratory 2010)

Coal retains its leading position as the predominant gasifier feedstock (51%). Petroleum provides 25% of feedstocks, with natural gas increasing to 22% due to the Pearl GTL in Qatar. All 11 plants currently under construction will be coal-fired. Of the 40,432 MW_{th} syngas capacity that is in the planning stages for the 2011-2016 period, more than 70% is expected to be coal fed, with petcoke to account for almost all of the remaining 30% capacity growth.



Figure 18: World Gasification Capacity and Planned Growth – By Feedstock. Source: (NETL, National Energy Technology Laboratory 2010)

Gasification plants are now operating in 29 countries. The Asian/Australian region has 37% of the total operating capacity. The African/Middle East region has strengthened its second position, due to the rapid growth in Qatar. Of the 10,857 MWth syngas capacity that is presently under construction, 65% is being built in the Asian/Australian region, 18% in Europe, and 17% in North America. With 63% of total planned capacity growth, North America has the potential to lead the world's regional growth through 2016. Another 34% will originate from the Asian/Australian region, with China leading this increase.

Marketable products generated from "syngas" include chemicals in the leading position (45%), followed by liquid transportation fuels (38%), power (11%), and gaseous fuels (6%). Seven of the plants under construction will produce chemicals and four will generate power.

Besides the facilities mentioned in the Gasification World Database 2010, there exists a huge undergrowth of smaller plants (<100 MW_e). From appendix 8 in "Economic Evaluation of CO2 Sequestration Technologies, Task 4 – Biomass Gasification-Based Processing" (Martha L. Rollins L. R., 2002) appear 25 different biomass gasification systems and this list is by far complete. In e.g. China, India and Brazil exists an unknown number of simple gasification plants. To give an impression of the volume it should be mentioned that just one single company in India, Ankur Scientific Energy Technologies PVT, LTD has built more than 100 installations (Ankur Scientific Energy Technologies Pvt. Ltd. 2010) in the size from 100 to 400 kW_{el} where electricity is produced by gasification of wood chips, nut shells, cotton stalks, rice husks etc.

3.1.1 Status in Europe

IEA Bioenergy, Thermal Gasification of Biomass, Task 33 has published a status report in 2004 (Kees W. Kwant, 2004). In the following the evident projects are mentioned. Some IEA members have updated their country reports in 2008. These results are included here.

Large plants

Main feedstock (Municipal Solid Waste (MSW), Refuse-derived fuel (RDF), Biomass)

- Thermoselect (Switzerland) which is suitable for the gasification of waste (7 plants in Japan, 3 in Germany and 1 in Italy with a daily capacity between 100 and 800 ton/day).
- Foster Wheeler (Finland, Sweden, UK) Värnamoverket 18 MW_{th} Integrated Gasification Combined Cycle (IGCC) based on CFB-gasifier (the plant is shut down now). 50 MW_{th} CFB-gasifier, cocombustion in steam boiler in Lahti, Finland. 40 MW_{th} BFB-gasifier for aluminium recycling in Varkaus, Finland.
- TPS Termiska Processer AB (Sweden) 15 MW_{th} CFB-gasifier in Grève-in-Chianti, Italy (unstable operation). ARBRE-project 8 MW_{el} IGCC plant based on CFB-gasifier in Eggborough, UK.

Smaller gasification plants for power production

- Pyroforce(Switzerland) 2 MW_{el} Fast Internal Circulating Fluid Bed (FICFB) gasifier in Güssing, Austria in operation.
- Pyroforce(Switzerland) 2.7 MW_{el} FICFB-gasifier in Oberwart in commissioning.
- Condenc and VTT(Finland) 1.8 MW_{el} updraft NOVELgasifier in Kokemäki, Finland.

Entrained flow gasification of biomass

Normally the entrained flow system (also talked about as the rising star) is used in connection with the above-mentioned coal gasification activities but particularly in Freiberg, Germany three EF-gasifiers are in operation for syngas, methanol, hydrogen and Fischer-Tropsch diesel production on biomass. The status in Freiberg is:

- Carbo-V (CHORen) is operating a $1MW_{th}$ EF-gasifier at atmospheric conditions (biomass 15 20 % H₂O).
- A 45 MW_{th} Beta-plant is started-up in these days (2010) and CNIM, France has placed an order on a comparable 45 MW_{th} plant at CHORen. Development of a containerized gasifier trade-named Carbo-Compact by TAF, UET and CHORen.
- Future Energy GmbH, a new company after Babcock Borsig Power (BBP) (ex. Noell-KRC, ex. Deutsches Brennstoff-Institut) operate a 5 MW_{th} pressurized EF-gasifier. Future Energy is conducting the engineering for a 140 MW_{th} syngas production in Czech Republic. The IGCC-plant is build By Siemens, commissioning 2007.
- A third EF-gasifier is in operation at the Freiberg Technical University.
- Other commercially operated EF-gasifiers are installed at SVZ Schwarze Pumpe, Germany and BASF, Seal Sand, UK, CHEMREC black liquor gasifier in Piteå, Sweden.

Process heating and cofiring (BtG)

- Batelle (Vermont, USA) Gasification with heated sand 60 MW_{th} (likely unstable operation).
- Bioneer now Condens (Finland) Fixed-bed, several updraft gasifiers.
- Foster Wheeler (Finland, Sweden, UK) Different CFB gasifiers up to 50 MW_{th}
- Götaverken/KTH (Sweden) 30 MW_{th} CFB-gasifier for firing in lime kiln in Värö, Sweden.
- Lurgi Umwelt (Germany) Different CFB-gasifiers up to 100 MW_{th} for cofiring.
- PRM Energy(USA) Fixed-bed, updraft.

Fixed-bed gasification of biomass for power production

- Xylowatt (Belgium) 3 downdraft CHP plants, 0.2 -0.6 MW_{el} in Belgium and Switzerland.
- Exus Energy (UK) 2 downdraft CHP plants, 0.13 -0.2 MW_{el} in UK.
- PRM Energy (USA) 1 updraft CHP plant 4,5 MW in Italy, gasification of olive pits.
- Pyroforce (Switzerland) Fixed-bed with two oxidation zones. 3 plants in Switzerland and Austria Entimos (Finland) 2 MW_{th} updraft gasifier CHP plant in Tervola.

In 2010 a new project in Gothenburg in Sweden GoBiGas Phase 1 with an input of 32 MW_{th} of wood for production of Bio-SNG was started.

3.1.2 Status in Denmark

In Denmark different companies and institutes have worked on biomass gasification since the mid 1980'ies. Some of the first plants (Kyndbyværket, Høgild, Blære) are shut down primarily due to technical failings or too high expenses. But some of the Danish plants are performing very well.

- Babcock & Wilcox, Vølund (USA, Danmark) 1.5 MW_e updraft gasifier CHP with 2 gas engines. Commercial, more than 100,000 hour's operation.
- DTU Viking gasifier (Technical University of Denmark) 0.017 MW_e 2-stage gasifier. In periodic operation since 2002.

- BioSynergi (Denmark) 0,075 MW_e open core gasifier on wood chips. Dec. 2003 start-up, 3000 hours operation on gas engine until 2009.
- TK Energy (Denmark) 2.3 MW_{th} GCHP. Project interrupted and perhaps terminated in 2008 because of budget exceeding.
- Danish Fluid Bed Technology (Denmark) Low temperature CFB pilot plant for co-firing on steam boiler.
- Dong (Denmark) constructing a 6 MW LT-CFB demonstration plant in connection with Asnæs Power Plant in Kalundborg. Scheduled to be operational in the spring 2011
- Weiss (Denmark) Scaling up the DTU Viking gasifier to 0.6 MW_{th}.
- ANDRITZ Carbona (Austria, Finland) Skive 19.5 MW_{th} wood pellets input, Bubbling Fluid Bed (BFB) gasifier, 3 x 2 MW gas engines.

3.2 Oxygen Blown Gasification

In order to achieve the most optimal downstream fuel synthesis, the gasification process is optimized in relation to the production of CO and H_2 i.e. avoidance of inert N_2 in the syngas. In order to achieve this, the gasification process is run on pure oxygen instead of atmospheric air and thereby the handling of bulk nitrogen gas is avoided in the syngas downstream of the gasifier. Oxygen blown gasification also has another advantage, i.e. generation of high temperatures, which is favorable to the formation of H_2 and CO. The high temperatures also ensure that the formation of troublesome by-products such as light hydrocarbons and tars should be minimized and thereby reduce the required gas cleaning.



Figure 19: General concept for oxygen blown biomass gasification

In this case study, the input fuel to the gasification process has been selected to be:

- Wood pellets
- Water content: 5% ý Corresponding to 200 MW or 11.57 kg wood pellets per second
- 1000 tons/day.

For gasification plants in this size, there are two oxygen blown gasification process options:

- Entrained Flow Gasifier.
- Fluidized Bed Gasifier.

To understand the two mentioned options, a description of the gasification process, and of the operating modes of the different gasifier technologies, follows.

3.2.1 Entrained Flow Gasifier

An Entrained Flow Gasifiers is a co-current device, advantageous in that it consumes oils and tars in the early stages along the flow path, and consequently limits the production of methane and ethylene as by-products.

Below is shown principals for different types of Entrained Flow Gasifiers.





Figure 20: Texaco Entrained Flow Gasifier using coal slurry as feed stock.

Figure 21: ConocoPhillips E-Gas Gasifier using coal slurry as feed stock



Figure 22: Siemens Entrained Flow Gasifier using dry-feed as feed stock

An Entrained Flow Gasifier requires (sub-)millimeter size feedstock particles. It is difficult and expensive to reduce biomass directly to this size due to the fibrous structure and the tenacity of many woody biomasses

(Patrick C.A. Bergman 2004). A solution to this problem is to introduce another type of pretreatment processes for preparation of the biomass for use in an Entrained Flow Gasifier:

- 1. Pyrolysis (resulting in pyrolysis gas, pyrolysis oil and char)
- 2. Torrefaction.

The char from the pyrolysis pretreatment and the torrified biomass can easily be reduced in size compared to untreated biomass.

The feed stock to the Entrained Flow Gasifier can either be wet-feed (pyrolysis oil or a sludge consisting of pyrolysis oil/water/ steam and char/torrified biomass) or dry-feed (char/torrified biomass). The dry-feed systems however need a fluidizing media, for the transport of the fine particles. If the oxygen flow is insufficient for this purpose, an inert gas (e.g. CO₂) has to be used as a supplement in order to ensure the right fluidization of the dry-feed.

3.2.2 Fluidized Bed Gasifier

The main advantage of fluidized bed operation is its ease of scale-up and its ease of control. The heat is stored in fluidized sand, and thorough circulation and mixing of the sand results in a uniform temperature throughout the bed. This helps prevent undesirable occurrences such as bridging or deposition.



Bottom Ash

Figure 24: Foster Wheeler CFB gasifier. Source: Foster Wheeler

Close contact between char, fresh biomass, pyrolysis oils, oxygen and reducing gas, means that pyrolysis and combustion are occurring at the same time and place as the gasification itself. This would result in the persistence of tars and light hydrocarbons, a situation also enhanced by a temperature that is lower than the maximum temperature achieved in the Entrained Flow Gasifier previously considered, see section 3.2.1.

Possible solutions would include operation at higher temperature, and longer residence times. The risk, particularly with higher temperature, is that the ashes can melt and coalesce (ashes from biomass may melt at temperatures as low as 800 °C in the case of straw, and are corrosive to refractory materials) (Dimitri Mignard, 2008).

3.2.3 Ability of the Different Gasifiers to Handle Variable Oxygen Feed and Biomass Throughput

For oxygen-blown fluidized bed gasifiers, low-oxygen flow rate at times of low-power input to the electrolysis plant might cause a drop of the superficial velocity to a value below the minimum fluidization velocity. Even at nominal flow rate, while air-blown gasifiers may have high-turn-down ratios of up to 10:1, the operation with oxygen would entail volume flow rates that are typically 5 times lower, and hence lower superficial velocities at nominal load. The operability of the fluidized bed at low oxygen flow rate could be a concern, since the occurrence of defluidized regions may favor agglomeration. However, the addition of inert gas might alleviate this problem. Circulating fluidized bed (CFB) gasifiers such as those developed for the Lurgi process, the Foster-Wheeler process or the Carbona process may be the answer to this problem, as they would present a wider range of operating loads: E.g. at 20% of the nominal load, the Lurgi CFB gasifiers simply behave like a bubbling fluidized bed. Because of the high-slip velocity between particles, circulating fluid beds should also prevent slagging of ashes and therefore allow operation at higher temperature, which would help manage the tar and methane levels. Finally, CFB gasification processes for biomass have the advantage that they are well developed to scales of the order of hundreds of tons of biomass per day. Entrained Flow Gasifiers require substantial biomass preparation. On the other hand, fluidized beds may not permit a very high-turn-down ratio when operated with pure oxygen. This problem might be alleviated by recycling some of the synthesis gas to assist fluidization, or by using carbon dioxide as a fluidizing agent, in which case the carbon dioxide could be used downstream in the synthesis loop as carbon source for methanol synthesis (Dimitri Mignard, 2008).

Today methanol is produced by gasification of coal followed by syn-gas cleaning and synthesis. The gasification technology primarily used is Entrained Flow Gasification. This is mainly because the synthesis plant needs a substantial size (5,000 - 6,000 tons/day in a single train) to be profitable and therefore the gasification technology selected to supply the syngas also needs to be in the same size category.

4 Anaerobic Digestion (Biogas)

4.1 Biogas Production Technologies

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4.1.1 The Biogas Process

Biogas is produced from organic materials when it is broken down in the absence of oxygen. The gas consists of a large part methane (50-75%) and CO_2 (25-50%), and some nitrogen (0-10%), hydrogen (0-1%), hydrogen sulfide (0-3%) and oxygen (0-2%). Overall the biogas production sites can be divided into the rather small farm scale biogas plants and the larger central biogas plants.

4.1.2 Farm Scale Biogas Plants

Facts about farm scale biogas plants:

- they typically treat animal slurry from only one farm, but sometimes the farm scale biogas plant gets the slurry from two farms that cooperate
- the treated amount of organic slurry makes up approx. 1,500 20,000 tons per year
- almost all farm scale biogas plants use supplementary easily digestible organic material with the purpose of increasing the gas production
- a few plants use energy crops as a supplement to the organic fertilizer, but no plants are completely (or mainly) based on energy crops, as it is seen in Germany
- the produced biogas is typically used in own combined heat and power units (CHP units), where the produced electricity is allocated to the electricity net; the heat is used for heating of the biogas plant (25-40% of the produced heat) and heating of residence(s) and production buildings at the property
- typically there is a considerable excess heat production in the warmest months of the year; this excess heat is blown away in cooling systems to maintain the production of electricity.

Spreading and potentials

Today, approximately 60 farm scale biogas plants are operating in Denmark. Almost all of them were established until year 2001, which is due to the fact that considerable contributions were given to the plants by the Danish Energy Agency until 2001, and the years hereafter were subject to some uncertainty on the settlement price for the produced electricity. After the most recent agreement on energy policy in the Danish Parliament which ensures DKK 0.745/kWh for electricity produced on biogas, there is however restored a certain interest among larger pig breeders of establishing own farm scale biogas plants.

Farmers' incentive for establishing a farm scale biogas plant has until now been closely associated with the achievement of a positive business in the actual biogas plant (contrary to the centralized biogas plant where the aspect of slurry distribution is more important). And there is no reason to believe that this will change. The potential for the spreading of farm scale biogas plants should therefore be seen in the light of the opportunities of obtaining a profitable operation on each farm.

Since no considerable amount of heat is used in the production buildings on cattle farming, it is not likely that farm scale biogas plants in large numbers will be established at cattle farms. Poultry producers can have huge heat requirements (especially broiler producers), and the poultry manure has furthermore a high energy content; however, huge process challenges in operating a biogas plant on pure (or mainly)

poultry manure due to the high nitrogen content, and therefore it must be assumed that poultry manure largely will be supplied to centralized biogas plants – or possibly incinerated directly.

So it is the pig farms that seriously have the potential for farm scale biogas plants. There is quite a considerable economy of scale in farm scale biogas plants – most modern plants are mainly established on farms with more than 10,000 tons of manure annually. The structural development of the Danish Agriculture still points seriously towards even bigger farms, meaning that the possibilities for establishment of farm scale biogas plants are improved. Another important factor promoting the establishment of farm scale biogas plants is the improvement of possibilities for upgrade and delivery of biogas to the natural gas distribution network.

Whereas no considerable number of farm scale biogas plants has been established in Denmark during recent years, the development has been quite different and tremendous in other countries, especially in Germany. Here, the number of farm scale biogas plants has increased from some few hundred in year 2000 to more than 3,700 today. The reason for this development is a significant political aiming where the farm scale biogas plants have been guaranteed a price up to approx. DKK 1.40/kWh for produced electricity, dependent on which biomasses that are used in the plant and to which extent the heat can be used from the CHP production.

4.1.3 Centralized Biogas Plants

Facts about centralized biogas plants:

- they treat slurry and other kinds of domestic animal manure from a number of farms, from a few to more than 100
- the slurry is transported to and from the plant by road tankers the transport makes up a very large part of the costs at centralized biogas plants
- the treated amount of slurry amounts to approx. 1,500 20,000 tons per year
- all centralized biogas plants use supplementary easily digestible organic material to increase the gas production
- centralized biogas plants should be provided with equipment to pasteurize the biomass
- a few plants use small amounts of energy crops as a supplement to the organic fertilizer
- the produced biogas is most often used in CHP units where the produced electricity is allocated to the electricity net
- besides heating of the centralized biogas plant (10-25% of the produced heat), the produced heat is
 distributed from the CHP plants via the district heating network to private residences where it
 (contrary to the heat from farm scale biogas plants) substitutes out taxed heat.

Spreading and potentials

Today, 22 centralized biogas plants exist in Denmark. Apart from the plant on Bornholm, all plants were established before year 2000. In the period from 2000 there have been more than 10 preliminary projects for centralized biogas plants distributed throughout the country, but until now, only one of those projects has come to establishment. The reasons for the poor increase in the numbers of centralized biogas plants should be found in the following facts:

- it is often difficult to find a suitable placement of a centralized biogas plant which, at the same time, can be accepted by neighbors and authorities. For optimizing the transport costs the plant should be placed centrally in an intensive animal husbandry area; at the same time it is decisive that the heat of the CHP production can be delivered to the district heating network. Moreover,

some local opposition against ideas of placement has been seen, as neighbors fear obnoxious smell and inconveniences due to the increased transport. Several projects have been abandoned due to the simple fact that a suitable placement was impossible to find

- as for farm scale biogas plants there has been some uncertainty regarding the economy in the projects, since the settlement price for produced electricity has been negotiated for a long time
- the economy of the centralized biogas plants has until now been dependent on the supply of easily digestible organic waste from the agro and food industry, since between ¼ and 1/3 of the biogas production at slurry-based plants comes from the organic waste which is supplied to the plants. However, the amount of accessible organic waste which favorably can be supplied to biogas plants is limited; therefore and rightly so there has been some retention in establishing new projects on massive supply of other organic material.

The Danish Energy Agency indicates a potential for the annual biogas production in Denmark of approx. 39 PJ, of which approx. 26 PJ are farm plants based on domestic animal manure. It is assessed that only approx. 3.5% of this potential are used (Birkemose, 2006). It should also be noted that DONG Energy informs that 39 PJ cannot be used at decentralized plants (Møller, 2009). This means that if the potential should be realized, a considerable part of it should be applied at central plants or be upgraded and sent to the natural gas distribution network.

During the recent years, the farmers' interest has increasingly been directed towards a combination of biogas plants and slurry separation, since this can result in improved possibilities for distribution and allocation of excess nutrients locally and regionally. Within organic fertilizer technology – including biogas and organic fertilizer separation – there are often considerable size-economical advantages, and therefore the centralized biogas plants have an opportunity of rational handling and utilization of the nutrients coming from domestic animal manure and energy potential. Since the biogas at the same time is a very cheap way to reduce CO_2 compared to other renewable energy sources, there is also a considerable political focus on establishing framework conditions which ensure a large increase in the numbers of biogas plants.

Besides political initiatives there are a lot of other conditions that seem to contribute to promoting the spreading of biogas plants. The improved possibilities for allocation of additional nutrients through a combination of centralized biogas plants and organic fertilizer separation mean that the farmers are still more willing to pay a treatment fee per ton of slurry treated on the centralized biogas plants. Slurry separation on farm level and its addition of dry matter fraction to the centralized biogas plants (contrary to transporting the total amount of slurry to and from the plant) can contribute in optimizing the output and costs and thus reducing the plant's dependence on organic waste from the agro and food industry.

Denmark has absolutely been a leading country regarding development and establishment of centralized biogas plants. The concept of transporting domestic animal manure from several farms to an overall treatment at a centralized biogas plant has only been implemented a couple of places outside Denmark. In Denmark, the use of energy crops as a supplement to the domestic animal manure has not been an attractive issue compared to e.g. Germany, where hundreds of farm scale biogas plants solely operate with energy crops. The reason for this is the difference in the settlement price of electricity. In 2006, Danish Agricultural Advisory Service calculated that a settlement price of electricity of approx. DKK 0.72/kWh will

result in a positive economy when adding maize silage to the biogas plant – provided that the produced heat can be utilized as well.

Recently, there has been focus on the possibilities of utilizing plant residues form environmentally-sensitive areas etc. This itself is not economically attractive, but if biomass anyhow should be removed from these areas with the purpose of removing nutrients, it will be common sense to utilize the biomass in the biogas plant. In 2008, the Danish Ministry of Food, Agriculture and Fisheries assessed that using this resource has a potential of approx. 5.1 PJ.

4.1.4 Centralized Biogas Plants, State-of-the-art

In the report from 2002 (Lars Henrik Nielsen, 2002), the economy of different sizes was calculated – from 300 to 800 m³ biomass/day (app. 110,000-292,000 m³ annually) – based on "today's technology". By way of comparison, the supply to the projected plant at Maabjergværket is expected to reach app. 450,000 tons per year, whereas the two projected plants on Djursland each are expected to be supplied with about 175,000 tons per year.

The report concludes that it is possible to establish centralized biogas plants that are economically profitable. However, in all cases it is provided that other organic material than organic fertilizer is supplied to the plant, and that an amount of DKK 0.27 kWh is contributed to the electricity production. The economic advantages due to the size of centralized biogas plants mean that the need for supply of other organic waste than organic fertilizer is less (10% of the supplied biomass amount) for the plant of 800 m³ compared to the plant of 300 m³ (20% of the supplied biomass amount).

The report includes a number of assessments of scale effects. For what concerns the budget items, these are considerable, and they dictate that the plants should be built as big as possible. However, in each case a specific counting of the biomass potential should be carried out in a given area. Since the transport of slurry to and from the plant represents a very essential budget item, the slurry concentration in a given area will have a heavy influence on how big the plant should be built (in which physical distance is it still profitable to collect the fertilizer?).

Furthermore, it has until now been an essential factor, that it is possible to sell the heat from the centralized biogas plant to a district heating network. This precondition will no longer apply if it becomes possible to pump the biogas into the natural gas network.

Since the FOI report was elaborated in 2002 (Lars Henrik Nielsen, 2002), the possibility of optimizing the concept of the biogas plant has been discussed, e.g. pretreatment of the biomass to increase the gas production and addition of dry matter fraction to the plants (which is more concentrated compared to slurry). But compared to the experiences that have been made in connection with projecting of the latest plants, there is no basis for altering the following conclusion:

- From an economical point of view it will be optimal to establish the centralized biogas plant as big as possible based on a series of preconditions of which the most important are the slurry

concentration in the area and the allocation of biogas. The preconditions should be assessed thoroughly in each project.

4.1.5 Upgrading of Biogas

Generally speaking, in Denmark all produced biogas is used for CHP production. Except from cleaning of sulphur, the biogas is applied as a finished product, i.e. no further cleaning (CO₂, etc.) is carried out, nor actual compression.

If biogas should be used for transport purposes, the upgrading to natural gas quality is necessary. Further, this will permit the natural gas network to be used for distribution of the biogas. Upgrading of biogas for natural gas quality is therefore assessed to be an important parameter when speaking of the desired spreading of biogas in Denmark.

The price for upgrading of biogas for natural gas quality is by Danish Gas Technology Centre calculated to DKK 1.09/m³ upgraded biogas with a biogas plant size of 300-500 m³/hour. In the same way, the Danish Energy Agency informs that the costs amount to DKK 1-2/m³ methane when upgrading the biogas, whereas the price for sending biogas from a biogas plant to a CHP plant amounts to approx. DKK 0.1/m³ methane.

Abroad, e.g. in Sweden and in Germany, the use of biogas in the transport sector is more widespread, and thus more experiences have been earned with the upgrading of biogas.

| Stakeholder (examples) | Specific interest in biogas production |
|--|--|
| Danish farmers | Production of biogas from animal manure is a potential way of increasing the business area for farmers, mainly if the farmer establishes his own farm scale biogas plant. The quality of the manure in terms of nutritional quality is improved after treatment in a biogas plant. This is especially the situation with treated manure from centralized biogas plants, where cattle and pig manure is mixed. By joining centralized biogas plants, farmers optimize the distribution of manure in the area, and it is easier for them to "get rid of" excess manure; because of the improved quality of the treated manure, many plant producers are interested in taking the product, and the logistic organization of the centralized biogas plants makes it easier to distribute it. |
| Agro and food industry (slaughterhouses, dairies etc.) | Biogas production is an environmentally friendly way of treating organic waste products. Through biogas treatment, the waste is heated and pathogens are killed. Furthermore, by treating organic waste together with manure, nutrients from the waste are re-circulated back to the agriculture, when the treated manure/waste mixture is applied in the field. |
| Environmental organizations | Environmental organizations, which are questioning the sustainability of modern farming (especially large scale pig production), will find biogas treatment of manure an environmental friendly way of dealing with the waste. The treated manure will, if handled properly, result in less loss of nutrients to the environment, as the production and renewable energy will help reducing the use of fossil fuels. |

4.1.6 Discussion of Technologies

| Biogas industry | Obviously, the industry producing biogas plants (and other manure-handling equipment) will profit from growth in the sector. In Denmark, the establishing of new plants has been rather limited since 2001, so biogas activities have mainly been focused on the international market, and several companies have been closed or have stopped their biogas activities. |
|--------------------|---|
| Society in general | From a society point of view, biogas plants as multifunctional systems present solutions for a number of environmental challenges: Production of renewable energy and substitution of fossil fuels Reducing odor nuisances when applying animal manure and slurry in the field Reducing loss of nutrients to the environment Re-circulation to the farmland of nutrients from the agro-industrial production. |

Table 7: Biogas stakeholders in Denmark

5 Gas-conditioning/Upgrading/Cleaning

John Bøgild Hansen, Haldor Topsøe A/S

The different gases stemming from wood gasification, biogas from anaerobic digestion and gas from the natural gas grid represent widely different challenges with respect to conditioning of the gas to the required quality needed for methanol and DME synthesis.

For the manufacture of *methanol*, desirable properties of the synthesis gas are:

• Close to stoichiometric composition with respect to formation of the end-product, i.e. a "module"

$$M = \frac{H_2 - CO_2}{CO + CO_2}$$

equal to or slightly above 2. Under stoichiometric gas, i.e. module below 2, should be avoided since it leads to a high formation of by-products and to loss of synthesis gas as increased purge.

- Relatively low ratio between carbon dioxide and carbon monoxide. High concentration of carbon dioxide leads to unfavorable equilibrium, high water concentration in the raw product, low reaction rate and increased rate of catalyst deactivation.
- Low concentration of inerts, i.e. methane and nitrogen, and argon.

DME is produced from methanol, or the DME synthesis may be completely integrated with the methanol synthesis i.e. below reactions occur simultaneously on a special dual function catalyst system:

$$CO + 2H_2 = CH_3OH$$
$$2CH_3OH = DME + H_2O$$
$$CO + H_2O = CO_2 + H_2 \text{ or overall}$$

 $3CO + 3H_2 = DME + CO_2$

In that case the optimum H_2 /CO ratio is around 1 as seen on Figure 25.





Furthermore, the gas should be free of catalyst poisons like sulphur or chlorine.

5.1 Biomass Gasification

5.1.1 Tars and Ammonia

At the temperatures prevailing in the biomass gasifiers, significant amounts of tar remain in the gas produced. The tars represent a significant portion of the heating value of the synthesis gas and are likely to create problems in downstream processing equipment. The main problems facing large scale industrialisation of biomass gasifiers have indeed been related to fuel feeding and tar handling.

Various non-catalytic tar removal methods have been tested with various degrees of success. They include scrubbers, filters and electrostatic precipitators. The water-based scrubbers can achieve satisfactory tar and particles removal, but they are fairly expensive, the energy in the tar is lost and a lot of heavily contaminated water is generated. Others have employed oil-based washing systems, like e.g. tepotec in Austria, where RME is used as absorbent in the Güssing plant. ECN in the Netherlands has developed a special oil-based system called OLGA. The tars are in both cases returned and used in the combustion leg in the FICFB allothermal gasifiers developed and used by Repotec or ECN. The oil washes leave



the methane and lighter hydrocarbons in the gas unaffected, so they would be most useful for SNG production. For methanol or DME synthesis the methane and other lighter hydrocarbons would have to be steam reformed in order to generate a suitable synthesis gas.

An efficient tar reforming step used right after the gasifier would thus represent a truly enabling technology. Topsøe has initiated work to develop such technology. A number of Topsøe catalysts have been tested with good results at different institutes, demonstration plants and also one commercial plant.

The catalysts tested have been conventional nickel-based reforming catalyst, dedicated special nickel catalysts as well as noble metal catalysts. Both ring types and monolith types have been tested.

Ammonia decomposition is also very important in order to avoid downstream problems with for instance waste water treatment. The catalysts should also be optimized for this service. DOE-sponsored tests in the 1990'ies showed superior ammonia decomposition activity as well as thermal stability for one specially designed Topsøe catalyst.

Finally it should be mentioned that it is not only catalyst formulation but also the reformer design which is important. A special challenge is of course the dust laden gas coming from the gasifier, which requires special attention.

The state-of-the-art designs employ a series of adiabatic beds with monolithic catalysts and provisions for intermittent removal of dust by nitrogen or carbon dioxide blasts. Due to the sulphur content of the gas relatively high temperatures are required in order to obtain a reasonable tar reforming rate. Air or oxygen is mixed with the gas after the cyclone in order to raise the temperature above the gasifier temperature by partially burning of the synthesis gas. This can be repeated one or more times in order to achieve the required tar and ammonia conversion because at the same time the methane in the synthesis gas is steam reformed partially causing the temperature to drop.

Recent progress in high temperature filtration has, however, opened up the possibility of operating a "clean" reformer with conventional catalysts shapes like rings or pellets in a fired reformer. This would provide more active reforming catalyst inventory leading to higher activity per reformer volume and greater resistance against poisons in the syngas. Furthermore, independent control of the reformer temperature profile can be obtained. This development will also be pursued by DTI and Topsøe in a recently started EUDP project.

5.1.2 Water Gas Shift Conversion

Adjustment of the H2/CO ratio is carried out using the water gas shift conversion, see Figure 26.

$$\mathrm{CO} + \mathrm{H}_2\mathrm{O} = \mathrm{CO}_2 + \mathrm{H}_2$$

Figure 26 illustrates the sour gas shift conversion. If needed, or convenient, one may remove the sulphur and proceed to a sweet shift system. Biomass-based synthesis gases often contain too low sulphur contents to allow the use of sour shift catalysts.

Topsøe has developed new generations of WGS catalysts for use in the sour shift or sweet shift mode. In the sweet shift mode, limitations were previously imposed by the old Fe/Cr catalysts with respect to temperature and steam/dry gas ratios. Low steam contents transformed the magnetite content of the

catalyst into Hägg carbide, which then acts as Fischer Tropsch catalyst. These limitations have been drastically reduced by new catalyst formulations resulting in very low steam consumption. The new sour shift catalyst has also been formulated in a way there allows a larger operational space.

Before sulphur removal it may be convenient to convert as much COS as possible. At the gasification temperature, equilibrium of the two below reactions may be assumed resulting in a relatively large COS content:

$$COS + H_2O = CO_2 + H_2S$$
 and/or $COS + H_2 = CO + H_2S$.

If the WGS reaction is in equilibrium then it does not matter which of the above reactions proceed. The sour gas shift catalyst would equilibrate the COS hydrolysis. The stream bypassing the WGS reaction should, however, then pass through a catalytic bed for COS hydrolysis.



Figure 26: Gas conditioning with water gas shift

5.1.3 Acid Gas Removal and Final Gas Clean Up

There exist a number of processes for acid gas removal. The choice of process may be determined by the requirements to the synthesis gas. In the existing IGCC plants MDEA has been favored as the gas is combusted in a gas turbine and not used for any chemical synthesis. At Eastman Chemicals, rectisol is used for purification of a module adjusted coal gas to be used for methanol synthesis whereas at Coffeyville, selexol is used for purification of a synthesis gas used for ammonia production.

The CO_2 formed may be removed for venting, for sequestration or as feedstock for a SOEC unit, in which case special care must be taken to remove the last traces of sulphur, etc.

No matter which acid gas removal system is used, Topsøe has found it necessary to include additional purification for e.g. downstream methanol synthesis. The complexity of the purification system depends on the acid wash. This can be illustrated in Figure 26, which shows a pilot purification train downstream a MDEA wash.

Typically the ammonia removal may be optional. Today amines are removed in the methanol distillation and in ammonia plants it is obviously not necessary to remove ammonia. Sulphur removal will in all cases be of importance except in plants for power production using gas engines or turbines. Larger amounts of sulphur may make the use of regenerable sulphur removal systems attractive.

Each of the trace elements may lead to a final clean up lay out. Iron and nickel carbonyls are not formed in the hot part of the gasifier but may rather be a function of the choice of construction materials. Iron and nickel poisoning of methanol catalysts are known even in natural gas-based plants.

5.2 Biogas from Anaerobic Digestion

The gas conditioning required will depend on the feedstock. Manure plus agricultural waste will be relatively easy to handle as the main pollutant will be hydrogen sulphide, but in relatively large amounts. Landfill gas of gases from Municipal Solid Waste treaters as well as waste water treatment plants can be more difficult because they can contain troublesome siloxanes and halides as well as higher hydrocarbons.

5.2.1 Gas Cleaning

The main impurity in biogas will be hydrogen sulphide in concentrations up to 0.1 vol%. Its concentration can be reduced by biological means. This technology employs oxidation and will leave traces of oxygen in the gas, which will represent an efficiency loss to its combustion of syngas in downstream catalytic conversion steps. Other techniques employ activated carbon beds, iron oxide absorbers and for final clean activated zinc oxide can be used.

Siloxanes and halides can be found in gases from landfills and waste water treatment plants stemming from e.g. scrapped electronic equipment, hair conditioning formulations, etc. Some results from a landfill site in Finland are shown in Figure 27.



Figure 27: Landfill gas impurities

Wärtsilä has – in collaboration with Topsøe Fuel Cell A/S and Haldor Topsøe A/S – designed, constructed and operated a 20 kW_e SOFC unit including gas clean up and prereforming at Vasaa in Finland. The units operated very successfully for more than 2,000 hours proving the adequacy of the gas clean up steps. A major challenge was, however, also the large fluctuation of methane and carbon dioxide concentration in the landfill gas.

5.2.2 Biogas Reforming

The methane in the biogas can be reformed directly with the CO_2 , already present in the gas as well.

$$CH_4 + CO_2 = 2 CO + 2 H_2$$

CO₂ reforming cannot be employed without carbon formation unless a considerable amount of steam is added. Haldor Topsøe has, however, developed a special reforming process, SPARG (Sulphur Passivated Reforming), where small amounts of, H_sS, are used to prevent the carbon formation. The SPARG process has been used in full scale commercial plants for reduction of iron or for steel production and for syngas generation for acetic acid synthesis. Equal amounts of CO and hydrogen are generated, which makes the gas especially suited for DME synthesis or it can be used after water gas shifting for methanol synthesis. The concept has, however, not been tested with biogas and more research and development including engineering studies are needed to prove the economic feasibility.

5.2.3 Electrochemical Upgrading of Biogas to Pipeline Quality

Instead of paying for removing the CO_2 by physical water washing, PSA or like as described in section 4.1.5 it is possible to upgrade the biogas by means of SOEC technology.

State-of-the-art technology for biogas upgrading is based on removing the CO_2 in the biogas by washing or pressure swing adsorption as described in section 4.1.5. The technologies are relatively expensive and add a cost in the order of 0.8 - 0.9 DKK/Nm³ biogas. The separated CO_2 will also contain small amounts of methane, which eventually will act as greenhouse gas.



Figure 28: SOEC biogas clean-up concept I

If instead the CO₂ in the biogas is co-electrolysed with steam to produce CO and H₂, see Figure 28, the synthesis gas can be converted to methane at pipeline quality at relatively low pressure. The present SOEC electrodes based on nickel are, however, active for the reverse reaction of methanation: steam reforming. This will result in an inefficient plant. There is the possibility of leaving a small amount of sulphur in the biogas feed to the SOEC, which will reduce the steam reforming activity to almost zero without sacrificing too much of the electrochemical electrolysis activity. This remains to be proven by experiments.



Figure 29: SOEC biogas clean-up concept II

Should this strategy prove uneconomical, another plant layout as shown in Figure 29 could be feasible. Steam is electrolysed to hydrogen separately and mixed with the cleaned biogas and then the CO₂ is converted to methane. In both lay outs the steam can be raised by means of high temperature waste heat generated by the methanation reaction. The steam electrolysis route has to be carried out at higher pressures in a more complex plant in order to meet the pipeline quality requirements. Preliminary calculations show that both routes will have low electricity consumption for the SOEC stacks of around 13 to 14 kWh per Nm³ additional methane generated in the plant. The lower heat value of methane is 9.94 kWh/Nm³. The overall efficiency of the stacks are close to 100 % calculated on the lower heat value of the CO and the hydrogen generated, but the transformation into methane will be accompanied by heat generation. This heat can, however, be used to raise steam and the surplus used in the biogas plant.

Electrolysis of steam can also be carried out using commercial alkaline or polymer based electrolysis cells but the electricity consumption will be approximately 60 and 40 % higher, respectively. SOEC technology thus holds the potential for significantly lower cost of upgraded biogas production. Funding for further studies, both engineering, economic and experimental has been applied for.

SOEC technology is still in an early R&D stage; however, years of extensive R&D within SOFC technology has been undertaken. A world leading R&D effort on SOEC is already taking place in Denmark. In connection with the now commercial high temperature methanation technology developed by Haldor Topsøe A/S this provides a strong platform for an accelerated commercialization.

5.3 Pipeline Gas

If the feedstock for methanol or SME production, is gas from the natural gas grid, the only gas clean up needed is removal of sulphur compounds. The THT (tetra hydro thiophene) is unfortunately not especially easy to remove but it can be done in a conventional desulphurization unit based on hydrotreatment of the THT to hydrogen sulfide followed by a ZnO absorber preceding the reforming section, which will be described in the next section.

6 Synthesis

John Bøgild Hansen, Haldor Topsøe A/S

There are only a handful of companies worldwide, which are able to supply complete methanol or DME plants including catalysts, since this requires extensive activities both in catalyst research and in all aspects of process engineering and the design of critical equipment like synthesis gas generators, gas clean up, catalytic synthesis reactors and distillation columns. Haldor Topsøe A/S is one of them. More than 240 steam reformers, 26 autothermal reformers, 23 complete methanol synthesis units and 30 charges of methanol synthesis are currently in operation. Plants with capacities ranging from 50 MTPD to the world largest of 7,500 MTPD have been designed and constructed. The world largest DME plant as well as a range of smaller plants based on dehydration of methanol has also been sold.

So far no commercial methanol or DME plants based on biomass have been constructed but there are advanced plans especially in Sweden and Haldor Topsøe has carried out a number of feasibility studies and

has also designed a complete methanol/DME plant based on black liquor gasification located in Piteå, Sweden.

6.1 Methanol Synthesis

Methanol synthesis has been a commercial process for about 80 years. In the beginning coal was the feed stock; with the advent of steam reforming and the resulting very clean synthesis the much more active Cu based synthesis catalyst discovered in the 1920's was reintroduced. In China there is still being build a large number of coal-based methanol plants. Eastman Chemicals has been operating one in the US for more than 20 years. Both the Eastman plant and the Chinese plants use the Cu catalyst for methanol synthesis.

6.1.1 Natural Gas or Pipeline-Based Plants

Most methanol plants today are based on natural gas as feedstock as this provides the most efficient and cheapest plants.

A modern methanol plant consists of 3 major sections:

- Synthesis gas preparation section
- Synthesis
- Distillation.

A typical investment breakdown is shown in Figure 30.



Figure 30: Investment breakdown by plant section

There are three types of reforming technologies used:

- One-step steam reforming
- Two-step reforming
- Autothermal reforming.

In the synthesis loop a boiling water reactor, BWR, or a series of adiabatic reactors can be used. Topsøe has also developed a revamp option: CMD for collect, mix and distribute the gas for quench type reactors. For smaller capacities the most efficient type, BWR, is normally used but for larger capacities the adiabatic reactor options are more cost-efficient.





The choice of technology depends on plant capacity and requirement to the product quality as seen in Figure 31.

6.1.1.1 Advanced Tubular Reforming

This lay-out shown in Figure 31 was traditionally the dominating. It is based on tubular steam reforming without the use of oxygen. Today it is mainly considered for capacities up to 2,500 MTPD of in case the natural gas contains significant amounts of CO_2 or it is available from other sources.

The conditions for the steam are chosen to give a reasonably low methane slippage (high temperature and relatively low pressure). The syngas composition is determined by the C/H ratio of the natural gas and is only adjustable within a narrow range. Typically a hydrogen surplus of around 40 % will be the result. Although the hydrogen surplus will enhance the methanol synthesis rate it will increase the volumetric flows and will result in a large purge from the synthesis loop, which is used as fuel in the reformer. If CO_2 is available a module M closer to the desired value of 2 can be obtained (without CO_2 it is 3).

With one-step reforming, all the heat consuming reactions take place in the fired tubes. This requires a large radiant section with a large flow of flue gas resulting in a substantial heat surplus in the convection section. As a result a steam surplus will be produced. This surplus can be reduced by combustion air preheat or adiabatic prereforming or a combination thereof. The energy consumption for a modern well-optimised design is from 30-32 GJ/MT depending on natural gas composition and local conditions. If CO_2 is available, the energy consumption can be reduced to 29 GJ/MT. A 1 million MT per year was built by Topsøe in the Middle East and has been in operation with CO_2 addition to the natural gas since 2004. If the CO_2 is not available the plant can still operate but at 5/6 capacity.



Figure 32: Lay out of methanol plant based on one-step reforming

6.1.1.2 Two-Step Reforming

Two-step reforming combines tubular reforming with oxygen fired secondary reforming. Oxygen-fired reforming alone inherently produces a synthesis gas with a 145 -20 % deficiency in hydrogen, but combining the two reforming technologies allows adjustment to the optimum modulus M around 2.05.

Typically 35 to 45 % of the reforming reactions occur in the fired reformer, the rest in the oxygen fired reformer. The tubular can operate at much less severe conditions, e.g. lower temperature, lower steam to carbon ratios and at the same time at higher pressures. The 60 to 65 % reduced fired duty combined with the less demanding operating conditions for the expensive reformer tubes leads to a reduction in the tube weight of 75 to 80 %.

The two-step lay-out shown on Figure 33 was chosen for the Statoil plant at Tjelbergodden, Norway, from where a major part of the methanol used in Denmark is imported.



Figure 33: Lay-out of two-step reforming methanol plant

This plant started in 1997 and features a number of innovative technologies never demonstrated before in a world scale grass root methanol plant, viz.: falling film saturator, adiabatic prereformer, two step low S/C reforming and a three column distillation section. The energy consumption has been as low as 28.8 GJ/MT, which corresponds to an overall conversion efficiency on a lower heating value basis of 69 %. This can be compared with the theoretical efficiency of the conversion:

$$CH_4 + 0.5 O_2 = CH_3OH$$

which is 79.5 %. The actual conversion efficiency is thus in other words 87 % of what theoretically could be achieved under ideal conditions. This illustrates how highly optimised modern methanol plants are as energy converters.

6.1.1.3 Autothermal Reforming and Hydrogen Recycle

For very large plants producing fuel grade methanol a new layout shown on Figure 34 based on autothermal reforming alone has been developed.

The ATR operates at very low S/C ratio and CO_2 is not removed. Hydrogen is recovered from the purge gas to adjust the gas composition. The first plant based on this technology is the world largest methanol plant with a capacity of 7,500 MTPD. The methanol will be used in a methanol-to-olefins (MTO) plant.



Figure 34: Methanol plant based on ATR and hydrogen recycle

To sum up the choice of reforming depends on the economy of scale. Tubular reformers have a scaling exponent close to 1, whereas oxygen plants scale closer to the square root of capacity. This is illustrated in Figure 35. The availability of "free" oxygen from an SOEC may change the breakpoints for the technology choices.



6.1.2 Gasification or Electrolysis Based Plants

When using gas from biomass gasifiers or SOEC units more freedom with respect to the gas composition is possible. As mentioned above there are no biomass-based methanol plants in operation. Preliminary studies and calculations indicate that a conversion efficiency of around 50 % on a LHV basis can be achieved. Topsøe invented a new methanol synthesis process in the 1990's. In this process the catalyst is operated with a stoichiometric synthesis gas:

$$M = \frac{H_2 - CO_2}{CO + CO_2} = 2$$

at relatively low temperature and high pressure. The formed methanol actually condenses out on the



Figure 36: Conversion of a synthesis gas (30 % CO, 2 % CO₂ and balance H₂ at 9.6 MPa in isothermal reactor

catalysts which remove the limitations imposed by gas phase equilibrium as illustrated on Figure 36. The optimum CO₂ with respect to reaction rate is around 2- 4 mole %. The relatively "dry gas" also leads to very low deactivation rates for the catalyst system. Recently, an improved version of the condensing methanol reactor design has been introduced. This technology will be demonstrated in the Piteå DME plant. Table 8 below shows a comparison between a conventional layout and the new concept.

| | Industrial layout | New technology |
|-------------------------------|-------------------|----------------|
| Methanol capacity, index | 100 | 100 |
| M.Ugas flow, (H2 + CO), index | 100 | 99 |
| Reactor inlet flow, index | 255 | 99 |
| H2/CO inlet reactor | ~ 5.5 | 2.3 |
| CO/CO2 inlet reactor | ~ 3.8 | 6 |
| Recycle ratio | 1.6 | 0 (!) |
| Catalyst volume, index | 100 | 40-80 |

 Table 8: Comparison between conventional and new technology

6.2 DME Synthesis

DME can be produced directly from synthesis gas as mentioned above, but it can also be produced by dehydration of methanol, either crude or distilled methanol as shown on Figure 37. By this technology both the market for methanol and DME can be serviced by the same plant. DME is an excellent diesel fuel which could be used for the transportation sector in heavy duty vehicles, where fuel cells have difficulties competing with large, very efficient diesel engines.



Figure 37: DME plant based on methanol dehydration

The main features of a methanol dehydration plant to DME are a simple adiabatic reactor and a product purification section. Normally a two column system is applied where the first column serves to up-concentrate the DME and the second column separates water and methanol. The energy consumption for the plant is marginal.

7 Electrolysis

Mogens Mogensen, RISØ-DTU

A Danish strategy for electrolysis was issued in 2009 (Partnerskabet Brint og Brændselsceller i Danmark, 2009). This strategy is treating the three main electrolysis technologies that are being developed in Denmark as well as internationally, namely: alkaline electrolysis cell (AEC), PEM electrolysis cell (PEMEC) and solid oxide electrolysis cell (SOEC). The following paragraph (Electrolysis technologies) is extracted directly from (Partnerskabet Brint og Brændselsceller i Danmark, 2009). A more detailed Danish review of the electrolysis technologies was carried out and published in 2008 (Jens Oluf Jensen, 2008)

7.1 Electrolysis Technologies

Electrolysis can in several ways contribute to increase the share of renewable energy in the total energy system. Through the actual electrolysis process, the electrolysis can contribute as regulating power/peak shaving in the electricity network, while the electrolysis end products, hydrogen and synthetic fuels, can be stored so that it can be used for either energy production such as electricity and heat, or for transportation purposes. Price and indirectly efficiency are the two most important parameters when the future potentials for electrolysis technology are to be valued. It is a goal for the Danish effort that we from 2020 will be able to produce fuels through electrolysis from electricity produced from renewable energy sources at a production price which does not exceed the price of corresponding fossil fuels such as hydrogen production by reforming of natural gas. On the basis of the Danish fuel cells development and on the background of the Danish systems competences Denmark is well qualified to develop and commercialize technologies for electrolysis.

Electrolysis of water is a well-known technology but the method has so far not gained large ground since the production of hydrogen by reforming of fossil fuels, typically natural gas, so far has been cheaper. The political goals of reducing the release of greenhouse gasses, promote the independence of fossil fuels, and increase the share of renewable energy, can however lead to the result that the market environment will change in favour of electrolysis. There are indications that electrolysis in the long run will play an important role in the energy conversion in connection with increased use of renewable energy. The two main factors are 1) the increasing need of the electricity system for regulating power/peak shaving, for which the need is urgent already now, and 2) the need to be able to produce fuels, especially for the transportation sector (synthetic fuels/hydrogen) that by conversion of surplus of renewable electricity does not imply release of CO₂. An increased share of fluctuating renewable energy in the form of wind, sun and wave energy will increase the need for energy conversion from electricity to other forms of energy. On one hand because there will be a need for storage of energy from periods with large production rate of renewable energy that can be used in periods with low energy production rate, and on the other hand because large resources have already been invested in the established energy infrastructure, which therefore should be utilized as effectively as possible, e.g. by production of synthetic hydrocarbons through electrolysis. Furthermore, there is a big need in the transportation sector for fuels with high energy density such as synthetic hydrocarbon fuels.

The main technical characteristics of the three types of electrolysers are summarised in Table 9.

7.2 Estimates of Cost of Electrolysis

A main cost of the electrolysis products is naturally electricity, and thus the actual electrical efficiency of the electrolysis becomes important, yet it is not the only important parameter. The actual price of the hydrogen or syngas will naturally also be very dependent on the investment and operational costs per Nm³ of hydrogen and CO produced. Projections of cost of electrolysis products were attempted in (Jens Oluf Jensen, 2008) for AEC and SOEC. Examples are given below in Figure 38 and Figure 39 and the assumptions behind the data in the figures are given in Table 10, Table 11 and Table 12. Please note, that the assumptions and numbers used in this section are not coherent with the subsequent techno-economical calculations conducted in phase II of the project.

| | AEC | PEMEC | SOEC |
|---------------------|-------------------------------------|--------------------------------------|----------------------------------|
| Temperature | 60-80 °C standards. | 60-80 °C standards. | 750-950 °C |
| | Potential for 100-200 °C | 100-200 °C under | |
| | | development | |
| Pressure | 32 bar in large scale | Potential for high | Potential for high |
| | industrial plants | pressure (100 bar) due | pressure (100 bar) due |
| | | to solid electrolyte | to solid electrolyte |
| Electric efficiency | 75 -85 % at 0.2 A/cm ² , | 80 – 85 % at 1,0 A/cm ² , | 90 % at 1 – 3 A/cm ² |
| (HHV) | Potential for 85 - 95% | 100 % at 0.2 A/cm ² | (thermo-neutral). If |
| | | | heat is added it may |
| | | | exceed 100 % of the |
| | | | supplied electricity |
| Stage of | Commercial for industrial | Commercial for | Under development |
| development | hydrogen production. | industrial production. | |
| | Potential for development | Potential for | |
| | into energy plant | development into | |
| | | energy plant | |
| Price for a plant | Relatively low due to | Comparable with AEC | Long-term potential |
| | cheap materials | small systems , but | for very cheap plants |
| | | expensive materials | due to materials and |
| | | | high power density |
| Maximum | 3.4 MW | 45 kW | 15 kW |
| demonstrated | | | |
| stack size | | | |
| Products | H_2 and O_2 | H_2 and O_2 | H ₂ + CO (syngas) and |
| | | | O ₂ |

Table 9: Characteristics of the three main electrolysis technologies

| Installed capacity MW | 2877 |
|--|------------|
| Size of plant Nm ³ /h: | 620 |
| Price of plant, DKK.: | 12,000,000 |
| Efficiency, kwh/Nm ³ DC: | 4.64 |
| Heating value for hydrogen kWh/Nm ³ | 3.5 |
| Installed capacity MW | 2877 |
| Years of operation: | 10 |
| Operation costs, DKK/kWh | 0.01 |
| Maintenance costs, DKK/kWh: | 0.01 |
| Efficiency of hydrogen production | 0.75 |

Table 10: Input data for the analysis of \mathbf{H}_2 production cost by alkaline electrolysis

| Heat production MW/MW | 0.22 |
|--|------|
| Price of heat DKK/MWh | 236 |
| Sale of heat DKK/MWh electricity consumption | 52 |
| Oxygen production Nm ³ /MWh electricity consumption | 108 |
| Price of oxygen DKK/Nm ³ | 0.5 |
| Sale of oxygen DKK/MWh | 54 |

Table 11: Key figures for calculation of the value of the produced oxygen and heat in Figure 38



Figure 38: The cost of hydrogen produced by alkaline electrolysis based on the assumptions above taking the value of produced oxygen and heat into account. Key figures are listed in Table 10 and Table 11

| Electricity | 1.3US¢/kWh |
|--------------------------------------|-----------------------------------|
| Heat | 0.3US¢/kWh |
| Investment | 4000 \$/m ² cell area |
| CO ₂ | 2.3 \$/ton |
| Cell temperature | 850 °C |
| Heat reservoir temperature | 110 °C |
| Pressure | 1 atm |
| Cell voltage* | 1.47 V (thermo neutral potential) |
| Life time | 10 years. |
| Operating activity | 50 % |
| Interest rate | 5 % |
| Energy loss in heat exchanger | 5 % |
| CO ₂ inlet concentration | 95 % (5 % CO) |
| CO ₂ outlet concentration | 5 % (95 % CO) |

Table 12: Economy assumptions for CO production by SOEC; input to Figure 39



Details on calculation assumptions are specified in Table 12¹⁹

¹⁹ The cost of CO was converted to "equivalent price of crude oil" by converting the CO energy costs to that of crude oil on a simple heating value basis.

8 Fuel Handling, Storage and Safety

Per Sune Koustrup, Serenergy A/S

An important issue of green synthetic fuels is safety, storage and handling, which is important for setting up an efficient distribution network. Methanol is an example of a fuel where the regulations regarding safety and storage may prohibit an efficient distribution network. One way of avoiding the handling and safety issues of methanol is to sell the methanol in sealed cartridges; Smart Fuel Cell in Germany has for instance set up a distribution network based on cartridges in the 5 to 28 liter range.

8.1 Methanol

8.1.1 Safety

What happens in case of fire, human toxicity and spills are all described in the subchapter below. Furthermore, a subchapter about safe dispensing is included in this chapter.

Fire

According to an American report, gasoline-ignited fires in 1986 involving cars, buses or trucks resulted in 760 deaths, 4.100 serious injuries, and \$215 million in property damage (U.S. ENVIRONMENTAL PROTECTION AGENCY OFFICE OF MOBILE SOURCES, 1994). Projections indicate that casualties would drop dramatically if methanol were substituted for gasoline as the country's primary automotive fuel. Looking just at vehicle fires in which gasoline is the first material to ignite, a switch to methanol could save an estimated 720 lives, prevent nearly 3.900 serious injuries and eliminate property losses of millions of dollars a year. Methanol's fire safety advantage over gasoline stems from several physical and chemical properties.

Lower volatility

Methanol does not evaporate or form vapor as readily as gasoline does. Under the same conditions, exposed gasoline will emit two to four times more vapor than will exposed methanol.

Higher flammability requirement

Methanol vapor must be four times more concentrated in air than gasoline vapor for ignition to occur.

Lower vapor density

Gasoline vapor is two to five times denser than air, so it tends to travel along the ground to ignition sources. Methanol vapor is only slightly denser than air and disperses more rapidly to non-combustible concentrations.

Lower heat release rate

Methanol burns 25 % as fast as gasoline and methanol fires release heat at only one eighth of the rate of gasoline fires. These properties together make methanol inherently more difficult to ignite than gasoline and less likely to cause deadly or damaging fires if it does ignite. Methanol is the fuel of choice for Indianapolis-type race cars, in part because of its superior fire safety characteristics.

If one extrapolates the American numbers from 1986 to Danish numbers in 2010 one will get a reduction in traffic fatalities of 14, a reduction in serious traffic injuries of 73 and a reduction in property damage of

approx. 3.5 mill Euros per year. In order to understand the proportions it should be mentioned that there were 309 traffic fatalities in Denmark in 2009 and 4,967 serious injured (Vejdirektoratet, 2010). A swift from gasoline to methanol is therefore estimated to reduce the number of Danish traffic fatalities with 4 - 5 % and the number of serious injured by 1 - 2 %. In Table 13 the numbers for USA, 1986 and the extrapolated Danish numbers for 2010 are seen. In reality, a shift from gasoline to methanol is expected to result in fewer saving, due to improved gasoline security since 1986.

| | USA | DK |
|----------------------------------|-------|-----|
| Death | 760 | 14 |
| Seriuos injuries | 4,100 | 73 |
| Property damage | | |
| (1986 \$ for USA, 2010 € for DK) | 215 | 3.5 |
| No. of inhabitants (July 2009) | 307 | 5.5 |

Table 13: Estimated reduction due to use of methanol instead of gasoline

Fire regulation

Table 14 shows the fire regulations for both USA and Europe.

| NEDA 20 class | Definition | Examples of |
|----------------|---|------------------|
| NI FA SU Class | | energy carriers |
| Class IA | Flash Point less than 22.8 °C; Boiling Point less than 37.8 °C | DME |
| Class IP | Flash Point less than 22.8 °C; Boiling Point equal to or greater than | Gasoline, |
| Class IB | 37.8 °C | Methanol |
| Class IC | Flash Point equal to or greater than 22.8 °C, but less than 37.8 °C | 60/40 Methanol |
| Class II | Flash Point equal to or greater than 37.8 °C, but less than 60.0 °C | Diesel fuel |
| Class IIIA | Flash Point equal to or greater than 60.0 °C, but less than 93.3 °C | Home heating oil |
| Class IIIB | Flash Point equal to or greater than 93.3 °C | Lubricating oils |

Table 14: Methanol fire classification according to USA regulation (NFPA 30) (National Fire Protection Association , 2010)

For Europe, flammable liquids included in Class 3 are included in one of the following packing groups:

- Packing Group I, if they have an initial boiling point of 35 °C or less at an absolute pressure of 101.3 kPa and any flash point, such as dimethyl ether or carbon disulfide
- Packing Group II, if they have an initial boiling point greater than 35 °C at an absolute pressure of 101.3 kPa and a flash point less than 23 °C, such as gasoline and acetone
- Packing Group III, if the criteria for inclusion in Packing Group I or II are not met, such as kerosene and diesel.

Human toxicity

Methanol's properties and toxicity are well understood (Malcolm Pirnie, Inc., 1999). According to the extensive literature reviewed for this study, methanol is neither mutagenic nor carcinogenic. Human exposure to methanol can occur via the inhalation, ingestion or dermal contact pathways. Inhalation of methanol vapors can cause irritation of the mucus membranes, dizziness, nausea, headaches and blurred vision if exposure at high levels occurs. While inhalation is the most common route of exposure to the body, ingestion represents the most serious acute health hazard due to the much higher volume of methanol which can be ingested relative to the volume which can be inhaled. The effects of ingestion follow the same pattern described for inhalation. With respect to dermal contact, methanol readily absorbs

into the dermal layer with repeated exposure causing eczema, redness and scaling. However, the current evidence shows that acute toxic effects on humans and some animals from methanol only occur at high doses (> 10 mg/l). The U.S. Department of Energy considers gasoline to be "overall" more hazardous to human health than neat (i.e., pure) methanol.

"The U.S. Department of Energy considers gasoline to be "overall" more hazardous to human health than pure methanol" (Malcolm Pirnie, Inc., 1999).

Spills

A large release of methanol to the surface water, soil or groundwater has the potential to adversely impact the surrounding environment (Malcolm Pirnie, Inc., 1999). Once released into surface waters or the subsurface environment, the fate of methanol depends on numerous environmental factors including: the nature and quantity of the release, and physical, chemical and biological characteristics of the impacted media. Various reports summarize estimates of possible methanol half-lives (the time required for 50% reduction in concentration) (see Table 15) in various environmental media. In the atmosphere, methanol will be photo oxidized relatively quickly; the half-life ranges between 3 and 30 days. In soil or groundwater, rapid biodegradation is expected with the half-life ranging from 1 to 7 days. Finally, in surface water following a pure methanol spill, methanol is expected to disappear quickly; half-lives are reported between 1 and 7 days. The half-lives are compared to reported half-lives for benzene to illustrate the relatively rapid degradation of methanol. Based on data summarized in Table 15, regardless of the release scenario, methanol appears unlikely to accumulate in the soil, air, surface water or groundwater.

| | Methanol half-life | Benzene halflife |
|---|-----------------------|---------------------|
| Environmental medium | (days) | (days) |
| Soil | | |
| (Based upon unacclimated grab sample of aerobic/water suspension from groundwater aquifers) | 1-7 | 5-16 |
| Air (Based on photooxidation half-life) | 3-30 | 2-20 |
| Surface water | | |
| (Based upon unacclimated aqueous aerobic biodegradation) | 1-7 | 5-16 |
| Groundwater | | |
| (Based upon unacclimated grab sample of aerobic/water suspension from groundwater aquifers) | 1-7 | 10-730 |

"Methanol appears unlikely to accumulate in the soil, air, surface water or groundwater." (Malcolm Pirnie, Inc., 1999)

 Table 15: Estimated half-lives of methanol and benzene in the environment

Methanol will quickly biodegrade, and therefore natural attenuation is likely to be an effective and inexpensive remediation strategy in most soil, groundwater and surface water scenarios.

"Relative to gasoline, methanol is safer and more environmentally benign." (Malcolm Pirnie, Inc., 1999).

Safe dispensing

On 3 December 2001 it was announced that the Methanol Fuel Cell Alliance (consisting of DaimlerChrysler, Xcellsis, BASF, Methanex, BP and Statoil ASA) had entered into a development contract with Identic AB, Sweden. By the terms of the agreement, Identic should develop a new refueling mechanism for methanol-powered fuel cell vehicles. Identic should further develop this refueling mechanism to create a system for safely dispensing methanol. A prototype system was installed in a DaimlerChrysler Necar 5 fuel cell vehicle, which was then tested and demonstrated by the California Fuel Cell Partnership in 2002. To facilitate the introduction of methanol as a widely used fuel, Identic has developed a SVR system for methanol in cooperation with the Methanol Fuel Cell Alliance – here installed in DaimlerChrysler Necar 5 Fuel Cell Vehicle.



Figure 40: The old and the new dispensing system for the NECAR 5

8.1.2 Strategic Energy Stocks

On the Danish harbors there are strategic stocks of gasoline and diesel for the equivalent of 90 days of consumption in the transport sector. The energy content of methanol is only half that of gasoline, but since the energy-conversion efficiency in a HTPEM system compared to a modern diesel powered vehicle is so much higher, the strategic stocks will last the same 90 days equivalency. This is not possible with e.g. hydrogen as an energy carrier.

8.1.3 Distribution and Tank Stations

Legislation concerning Road Transportation of Methanol/DME

In Europe the ADR agreement concerning the international carriage of dangerous goods on road applies (UNECE, 2008). The Danish legislation is based on the ADR convention. Three different packaging groups exist. Packing groups are used for the purpose of determining the degree of protective packaging required for Dangerous Goods during transportation.

Tank stations

The following text differs between small methanol stations and full size methanol stations.

Small methanol stations

A 1,000 I tank (that can hold 4,440 kWh in the form of 1,000 I methanol) costs 1,700 DKK. This is equal to an investment price of 0.38 DKK/kWh. The tank is approved for methanol use and can be delivered in 3 working days all over Denmark. In comparison, a hydrogen refueling station which e.g. contains 20 kg of hydrogen (667 kWh) is assumed to costs 500,000 DKK. This is equal an investment price of 750 DKK/kWh. By using these assumptions it is assumed that a hydrogen station is almost 2,000 times more expensive than a methanol station per kWh of storage. On top of these prices one has to include dispensers etc. and the fact that refueling can occur faster using liquid methanol than high pressure hydrogen. A hydrogen



dispenser can easily cost 20,000 DKK, whereas a methanol dispenser can be bought for less than 500 DKK. This is a difference of a factor 40. A 1,000 I tank suitable for methanol is shown in the picture to the right.

If one assumes that diesel tanks for farmers can be used with very minor modifications, then one can acquire a total tank station for only 7,375 DKK²⁰. This system holds 1,172 kWh of energy in the form of 60% methanol (440L * 4.44 kWh/L pure methanol * 0.60). This is equal to an investment cost of 6.3 DKK/kWh.

Private diesel tanks have to be inspected in order to be legal. It is likely that methanol stations, no matter the size, have to be inspected once a year to be legal in the future as well. For farmers it normally makes economical sense to have their own tank station if they use diesel to the equal of 60,000 km in a car. If the consumption is that high or higher a popular way of doing it for farmers will be to a 1,200 l diesel tank from a diesel distribution company.

Full size methanol stations

In (EA Engineering, 1999) it was investigated what it would cost to make a 10,000 gallon double-walled storage tank, two hose dispenser, 20 vehicle per hour capacity methanol tank station.

These are the results:

| \$62.400 |
|----------|
| \$56.000 |
| \$19.174 |
| \$30.711 |
| |

It is assumed that there are 3,000 tank stations and > 2 mill cars (2007) in Denmark. It further assumed 1/3 of the places one will use underground storages, 1/3 of the places one will refurbish/clean an existing tank and 1/3 of the places one will re-tank the inner liner. If so, then the total costs will be approx. 37,000 USD/station * 5.6



²⁰ http://www.tankshop.dk
USD/DKK * 3,000 tanks = 622 mill DKK, which is equal to 113 DKK per Dane.

A recent study estimates the cost of building a hydrogen infrastructure (McKinsey & Company, 2010). The report states that an investment of 3 bio EUR (22 bio. DKK) is required to support an infrastructure of 1 mill cars. Therefore, it is concluded that a hydrogen infrastructure in orders of magnitude is more expensive than a similar methanol infrastructure. In other words, it is possible to erect 75 methanol refueling stations for each hydrogen refueling station.

9 Fuel Quality and Specifications

9.1 DMFC

Jacob Bonde, IRD

The DMFC units produced by IRD have relatively strict demands to the purity of the methanol used. Typically the system is fed by approx. 100% methanol, which is diluted internally in order to provide the optimal operating concentration for the direct methanol fuel cell. In general, the system should be operating on pure methanol without any traces of metal ion's and other organic compounds. IRD has however identified several organic and inorganic species that influences the system performance. The effects of these compounds range from membrane poisoning/dissolution to catalyst poisoning and dissolution. We have found that especially the life time is extremely sensitive to the different impurities. We have until know identified the following unwanted impurities and have set preliminary specifications as:

99.9% MeOH

< 1 ppm Cl, S, Al, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Zn

< 100 ppm Aromatic compounds, hydrocarbons, olefins up to C12.

9.2 HT-PEMFC

Morten Sørensen and Per Sune Koustrup, Serenergy

Impurities

For use with HT-PEM reformer systems from Serenergy, the methanol has to comply with the standard "IMPCA Methanol Reference Specifications" from the International Methanol Producers & Consumers Association (IMPCA)²¹. It is especially important that the non-evaporable residue has to be lower than 0.1 PPM, to limit deposits in the system.

Fuel properties

Reformed Methanol Fuel Cell (RMFC) systems can preferably use a pre-mix of 60 % methanol and 40 % demineralized and de-ionized water (on a volume basis). This mixture is advantageous as an energy-carrier compared to pure methanol for four reasons:

- 1) This fuel is safer from a fire perspective than pure methanol
- 2) This fuel is cheaper to transport as a result of the lower flammability (20% per I, but also 38% less energy per I)

²¹ http://www.impca.eu/en/specs/specsjan2008.pdf

- 3) No water-condenser is needed (cost, weight, efficiency)
- 4) 1 bipolar-plate per cell instead of 2 \rightarrow a lower cost per kW is possible



Figure 41: Methanol flashpoint as a function of methanol/water content (Methanex Corporation, 2006)

When methanol and water are mixed the molecules mix and the blend becomes denser. The relation between the original volume of methanol and water before mixing and the finale volume is seen in Figure 42. The original volume of water does not appear, but it is 100 minus the original volume of methanol before mixing. This means that one can actually carry almost 4 % more energy in one liter of 60/40 methanol than one should think.



Figure 42: Final volume when methanol and water are mixed at 25 °C (Methanex Corporation, 2006)

10 Concept Catalog

Several plant concepts were derived during the project. The concepts are shown in Appendix 3. The figures show a brainstorm of different concepts devised in the project. The concepts are not thought through and may not be realizable.

11 Concept Selection

Jesper Lebæk, Danish Technological Institute

Based on plenum discussion amongst the project partners²² with origin in the previously presented technologies, it was decided to focus on two technology concepts. These two chosen technology concepts are based on technologies in which Danish companies have key competencies. The Danish business potential is therefore significant for both concepts. The two concepts are presented below:

11.1Methanol/DME Synthesis based on Electrolysis Assisted Gasification of Wood



The technology concept is graphically presented below.

Figure 43: Scenario 1: Methanol/DME production plant

The concept is unique in the sense that oxygen derived from SOEC electrolysis is used as oxidizer in the gasification process and that the plant is integrated with a central biomass-fired power plant. Moreover, a unique feature of the SOEC and the present concept is that the hydrogen produced from the electrolyzer is used to adjust the M-ratio for an optimal methanol synthesis. The amount of hydrogen needed in the methanol synthesis reaction is also what governs the size of the electrolyzer. Using oxygen derived from electrolysis, the downstream gasification gas benefits from being free of nitrogen. When using ambient air in a gasifier, there is a significant risk of creating nitrogen oxides (NO_x) and the bulk mass of the inert nitrogen gas that is to be carried through the remaining process steps, makes the subsequent components more expensive and makes the gas clean-up processes more difficult and expensive. Pure oxygen in a gasifier also increases the gasifier temperature and subsequently lowers the content of tar and other unwanted components in the gasification gas (Dimitri Mignard, 2008).

The plant is expected to be placed in the vicinity of a biomass fired central power plant, in order to extract steam from the biomass boilers to the SOEC and potentially also to add steam to the gasifier in order to adjust the C/H ratio. It is however also possible to operate the SOEC in a thermo-neutral state, meaning that the excess heat from the process is used to generate the inlet steam. Furthermore, it is advantageous

²² GreenSynFuels project meeting at the Confederation of Danish Industry in Copenhagen, 15th of April 2010

to have the plant in connection with a district heating network, in order to achieve payment for the excess process heat; this can have a significant effect on the resulting methanol/DME price (Lasse R. Clausen, 2010; Weel & Sandvig, 2007). Due to the plant size, only underground storage is a viable option for the possible storage of oxygen and hydrogen generated from the SOEC (Lasse R. Clausen, 2010). Underground storage is deemed unrealistic by the project group and is not considered an option.

Description of Process Scenarios:

There are several scenarios in which the technology concept can be operated – below three basic and fundamental operating scenarios are described. All scenarios are based on the assumption that the gasifier should be operated at the nominal load (1000 t wood/day):

SOEC at full load operation

In this case the SOEC is operated at given number of hours during the year according to obtainable power spot price, see Figure 1. This means that the plant operation is dictated by the electricity market price.

Hybrid mode 1: SOEC periodic shutdown

In this case the SOEC shuts down, as the previous case, according to the electricity market price. However, by installing an oxygen generation plant, shift reactor and a CO2 scupper, the gasifier can be operated without production of hydrogen and oxygen from the SOEC. This means that in periods of high electricity prices the SOEC shuts down and methanol is produced solely from biomass gasification.

Hydrid mode 2: SOEC part load operation

In this case the SOEC is operated in part load operation when the electricity price is high. When the price is high the electrolyzer is controlled by the oxygen demand of the gasifier, which is about 1/3 of the rated capacity when controlled by the demand of hydrogen to the methanol synthesis reaction.

The above described concepts and more are analyzed further in the Phase II chapter.

11.2Methanol/DME Synthesis based on Biogas Temporarily Stored in the Natural Gas Network

The technology concept is graphically presented below.



The concept is based on a traditional biogas plant situated in the vicinity of natural gas pipeline. Here, the biogas is upgraded/purified, so that it can be pumped into the domestic natural gas pipeline in Denmark. Hereafter, the biogas/natural gas mixture is extracted at a central large scale synthesis plant, where methanol or DME is produced. This offers some good possibilities, as the natural gas network can be used for storage of the gas, and makes it possible to produce methanol at large cost-effective plants, while at the same time the biogas can be produced local at smaller biogas plants. The gas clean up can be done with SOEC and further increasing the value of the biogas, and evening out production and consumption at the electrical grid, see section 5.2.3 for more information regarding this. This concept is also in very good coherence with the recent strategy report from Energinet.dk, the Danish TSO, called "Gas I Danmark" (Energinet.dk, 2010).

11.3 Concept Selection Summary

Both of the selected technology concepts feature large scale synthesis facilities. This is a clear choice from the project group. Large scale synthesis plants are well-known and the techno-economical estimations will therefore be more accurate for this part of the concept. This does however not mean that smaller decentralized plants are not found interesting. Given the time and economical frame of the project, it was decided to focus on concepts in which knowledge of the technology components was readily available within the project team members.

Therefore concepts are chosen, in which Danish companies hold key competencies within the technology components, the concepts therefore also possesses business potential for Danish companies if the concept plant should be realized. The concepts, with special emphasis on the gasification concept, can operate in a future market with highly fluctuating electricity production and prices. Most importantly the concepts both hold the potential of producing green synthetic fuels that can be used in a future green transportation sector, in which fuel cells operation on methanol will play a pivotal role.

The concepts presented in Section 11.1 and Section 0 also illustrate the project partners that are responsible for the individual technology components.

12 Discussion on Basis of Phase I

The focus in this report is to a large extent on methanol, due to the higher focus on this fuel within the project partners. Compared to pure hydrogen, methanol has distributional and storage advantages, as it can be stored relatively simple in plastic containers, and can be distributed, with minor adjustments, through the existing infrastructure. This has a large effect on how much potential the fuel has. Ammonia is highly corrosive and needs higher temperatures in order to be reformed into hydrogen, so methanol is also here preferable for use in fuel cells, especially for PEM-based cells. DME can relatively easily be produced from almost the same base as methanol, so this production is also taken into phase II of the project. From the concepts chosen the most non-proven technology component is clearly SOEC. Therefore special care must be taken when analyzing this component in relation to the techno-economical calculations.

13 Summary on Basis of Phase I

The following section summarizes Phase I of the GreenSynFuel project. The Phase I section is the foundation for Phase II of the project, in which specific plant/process configurations are analyzed and examined.

The biomass potential is divided into wood, straw and biogas. Concerning wood, the political scene calls for more forest areas for recreation and plans to almost double the forest area from 13 % today till 25 % in 2089. This does not promote further use of Danish wood for energy purposes, but there is also a possibility for importing wood from other countries.

Some of the production of straw is not used and is left on the fields. The potential here is evaluated to be rather constant, so the surplus depends on other uses for the straw. The amount of straw which was not used in 2008 amounts to approximately 2 mill tons out of a total production of approximately 5.6 mill tons. A recent decision from DONG Energy has been made to increase the consumption of wood pellets and reduce their consumption of straw by approx. 25% from 5-600,000 to 580,000-480,000 tons. The reason is that the Studstrup CHP plant is converted into using wood pellets, which eliminates the possibility of using straw. This may also increase the excess straw in the near future.

In Europe, the biogas potential in 2020 was 166 mill tons, and 5.9 mill tons are used at the moment. Biogas can be produced from either manure (1/5), byproducts and waste (1/5) or energy crops (3/5). The production of biogas from manure enhances the use of the product for agricultural use. There is enough agricultural land in Europe to both produce food and some energy crops for biogas. In Denmark, about 75 % of the biogas is produced from animal manure; the rest is produced from waste from different processes and from energy crops. The theoretical production from all domestic animal manure in Denmark counts up to 16.5 PJ per year.

Research within thermal gasification has been going on for some decades with many success stories but also some failures. The world syngas production is increasing and in 2007 the production of syngas from large plants was 56,000 MW_{th}. Approximately 24 % of the syngas is made in Europe.

The gasification plants have different setups with different pros and cons. Especially with regards to tar and NO_x generation. With the use of pure oxygen instead of air in the gasification process, large advantages can be assumed due to low NOx production and possibilities of higher gasification temperatures and low tar production.

Biogas plants can be divided into rather small scale farm scale plants and the larger scale centralized plants. Pig farms have the largest potential for farm scale plants due to good quality manure for biogas production and they also need heat for buildings. There is a number of biogas plants in Denmark, but the production has ceased since 2001 due to the lack of financing and low political incentives. Centralized plants with delivery of manure from multiple farms suffer from the high transportation costs and from complaints from the community in search of suited placement. The plant has to be able to deliver heat to a community, and have access for transportation of manure. Biogas could be added to the natural gas grid, but plant upgrades are needed in order to make this possible. The cost for this is assessed to 1.09 DKK/m³, whereas the price for sending biogas directly to a CHP plant amounts to approx. 0.1 DKK /m³_{CH4}.

Electrolysis can act for regulating power in the electricity system by using electricity when the consumption is higher than the production, and the electricity price is low. In Denmark, this scenario will usually also mean that electricity is largely produced by RE (wind mills) and some decentralized production. Production of hydrogen has largely been done by reforming of natural gas due to a lower price. SOEC electrolysis is capable of producing hydrogen from water (steam) and CO from CO₂. SOEC is still under development, but has a large potential due to high efficiency and cheap materials.

Methanol is classified as a hazardous chemical, which produces some challenges. With regards to safety, methanol is both safer and more unsafe compared to other fuels depending on which properties are looked at. The U.S. Department of energy regards methanol for less dangerous than gasoline, despite the fact that digestion of methanol is lethal for human beings. In a fire, methanol is less dangerous than gasoline. In the case of spills methanol reacts faster than gasoline into not dangerous compounds. Reformed Methanol Fuel Cell (RMFC) systems can operate with higher efficiencies than gasoline and diesel engines, and hereby reduce the energy end CO2 release. Methanol has a lower energy density than most other liquid fuels. For RMFC systems, a mixture of 60%_{vol} methanol and 40%_{vol} water is used. Most methanol in Denmark originates from Norway and is shipped into Esbjerg, Denmark. Methanol can be stored and distributed close to that of gasoline and diesel. Diluted methanol can probably be transported as diesel due to its low flammability limit.

Phase II

1 Introduction

In Phase I of the projects two technology concepts were chosen based on the baseline description presented in the previous chapter Introduction. It was chosen by the project group to focus primarily on concept 1): Synthesis of methanol/DME from large scale gasification of wood (1,000 tons/day), using pure oxygen from electrolysis as oxidation source. This technology concept will be analyzed thoroughly in the following chapter.

2 Mass and Energy Balance

Below, the mass and energy balance for each of the components in the chosen concepts are presented.

2.1 Gasification Technology selected for this Case Project

For this project we have chosen to exemplify a possible gasification technology by using a pressurized bubbling fluidized bed gasifier (BFB) from Carbona.



Figure 45: Principle of a pressurized bubbling fluidized bed gasifier (BFB) from Carbona

2.1.1 Fuel Properties

The fuel of choice in this project is wood pellets; the technical specifications of wood pellet are presented in Table 16. The basis for the plant concept calculations is a daily throughput of 1,000 tons wood pellets.

| Fuel type: | Wood pellets |
|---------------------|---------------------|
| Moisture: | 5.0 wt% (dry basis) |
| Ash: | 1.1 wt% dry basis) |
| Lower Heating Value | 19.0 MJ/kg (dry |
| (LHV): | basis) |

Table 16: Gasifier fuel properties

2.1.2 Mass and Heat Balance

The mass and energy balance for the gasifier is presented in Table 17. As the gasifier is pressurized at 10 bar, CO_2 is used to pressurized the inlet biomass feed, as seen in Figure 45. Moreover, bed material are continuously added at the feed line. Steam and oxygen is added at the bottom of the gasifier.

| INPUT | | OUTPUT | | | | | |
|-----------------|-----------|------------------|------------------|----------------|--------------|------------------|------------------|
| | Mass flow | Chemical Heat | Sensible Heat | | Mass flow | Chemical Heat | Sensible Heat |
| | [kg/s] | [MJ/s] | [MJ/s] | | [kg/s] | [MJ/s] | [MJ/s] |
| Biomass | 11.57 | 207.5 | 0.0 | Product gas | 17.36 | 178.9 | 25.3 |
| Bed material | 0.10 | | 0.0 | Bottom ash | 0.08 | 0.1 | 0.0 |
| Oxygen | 3.03 | | 0.5 | Fly ash | 0.25 | 4.1 | 0.2 |
| Steam | 2.58 | | 0.9 | Heat losses | | | 0.3 |
| CO ₂ | 0.40 | | 0.0 | | | | |
| Total IN | 17.69 | 208 | 3.9 | Total OUT | 17.69 | 208 | 3.9 |

Table 17: Gasifier mass and heat balance

2.1.3 Composition of Product Gas at Gasifier Outlet

Table 18 shows the gas composition at the gasifier outlet. This gas composition therefore constitutes the basis for the system mass and energy balances presented in section 2.2.

| Pressure | 10 | bara |
|-------------|------|---------|
| Temperature | 850 | °C |
| CO | 26.7 | vol% |
| CO2 | 20.0 | vol% |
| H2 | 28.6 | vol% |
| H2O | 16.4 | vol% |
| CH4 | 7.5 | vol% |
| O2 | 0.0 | vol% |
| N2 | 0.1 | vol% |
| H2S | 65 | ppmv |
| COS | 8 | ppmv |
| NH3 | 823 | ppmv |
| HCN | 10 | ppmv |
| HCI | 15 | ppmv |
| C2H6 | 2278 | ppmv |
| C2H4 | 1685 | ppmv |
| C6H6 | 2219 | ppmv |
| C7H8 | 30 | ppmv |
| C10H8 | 401 | ppmv |
| C14H10 | 115 | ppmv |
| CxHy | 77 | ppmv |
| TOTAL | 100 | vol% |
| | | |
| H2/CO - | 1.07 | mol/mol |
| ratio | | |

Table 18: Gas composition at gasifier outlet

2.2 System Mass and Energy Balance (Sankey Chart)

Using a Sankey Chart, the system mass and energy balance for an energy system can be displayed. For reasons of comparison, two gasification concepts were analyzed:

- 1) Traditional plant Gasification without electrolysis
- 2) Novel concept SOEC assisted methanol synthesis based biomass gasification.

Below, the mass flow is displayed for the two concepts above using a Sankey chart. Both plant concepts are based on the gasification data presented in section 2.1.

2.2.1 Traditional Plant

To provide a basis for comparison, a traditional methanol production based on biomass gasification was analyzed. Downstream of the gasifier, the syngas is filtered, next the tar and methane are reformed in the tar reformer. The tar reformer is heated using the purge gas from the synthesis reactor. After the tar reformer, COS is hydrolyzed into H2S and is removed in a H2S wash process. The H2S wash is followed by a shift reactor and a CO2 wash. The syngas is then compressed to 60 bars and directed to the methanol synthesis reactor.





2.2.2 Novel Concept

Using a Sankey chart, the system mass and energy balances are displayed in Figure 47. In the SOEC assisted gasification concept the production of electrolysis unit is controlled by the balancing of the stoichiometric ratio of the methanol synthesis process, therefore hydrogen from electrolysis is added to adjust the ratio. The produced hydrogen is added after the H_2S wash, omitting the shift reactor and the CO_2 wash. Therefore, more CO_2 is exploited in the process. The oxygen used in the gasifier is produced by the SOEC in excess quantities. The tar reformer is in this case also heated by the purge gas from the methanol synthesis reactor.

Excess heat is recuperated using production of steam at two pressure levels, 120 and 38 bar. The high pressure steam is overheated to 520 °C. Electricity is produced in two counter pressure steam turbines with an assumed isentropic efficiency of 85 %. The remaining excess heat between 60 and 90 °C is used for district heating. The SOEC is operated in thermo-neutral state, i.e. excess heat is used to generate and superheat the feed of steam.



2.2.3 Comparison of Key Parameters

The following table displays a comparison between the key parameters of the two methanol plant concepts. In Table 19 the energy and electricity balance is shown.

| Energy | Flows [MW] | Traditional Plant | Novel Concept |
|-------------------------|-------------------|-------------------|---------------|
| | Wood | 207.5 | 207.5 |
| JTS | SOEC, Electricity | - | 141 |
| INPL | Electricity | -3.8 | -5.6 |
| | TOTAL | 203.7 | 342.9 |
| TS | Methanol | 120.6 | 242.7 |
| TPU | District heating | 46 | 37 |
| NO | TOTAL | 166.6 | 279.7 |
| q | Compressors | 7.3 | 8.1 |
| y rs an ers | Oxygen production | 3.8 | 0 |
| ctricit duce sume | Expanders | -14.9 | -13.7 |
| Ele pro con | Net electricity* | -3.8 | -5.6 |

 Table 19: Plant energy and electricity balance

 * This is excluding electricity to the SOEC

A comparison of the plant efficiencies is shown in Table 20. As can be seen, the SOEC-assisted plant is superior to a traditional plant in terms methanol output efficiency. Although the total resulting system efficiencies are similar, a SOEC-assisted plant is better at converting the input energy into the primary output, which is methanol.

| Efficiencies [%] | Traditional Plant | Novel Concept |
|-----------------------------|-------------------|---------------|
| Methanol Efficiency | 59.2 | 70.8 |
| District Heating Efficiency | 22.6 | 10.8 |
| TOTAL | 81.8 | 81.6 |

Table 20: Plant efficiency comparison

A traditional plant does however exploit the excess heat better than the SOEC-assisted concept. The daily district heating production can be seen in Table 21, along with the methanol production and the electrical consumption per day. As can be seen the methanol production is approximately doubled when using SOEC-produced hydrogen to adjust the C/H stoichiometric ratio in the methanol synthesis reaction, see section 6.1.2 in the previous chapter.

| Daily production [-] | Traditional plant | Novel concept |
|-----------------------------------|-------------------|---------------|
| Methanol [Ton/day] | 523 | 1053 |
| District heating [MWh/day] | 1104 | 888 |
| Electricity consumption [MWh/day] | -91.2 | 3249.6 |

Table 21: Daily plant production and consumption

2.2.4 Plant Carbon Efficiency

In the near future biomass is going to be a limited resource. The amount of biomass that can become available for the generation of bio-energy fuels will be physically and economically constrained towards 2030 (K. Hedegaard, 2008). Therefore, upgrading of biomass, with other renewable energy sources such as wind, will become very relevant in the future. In that context, it is relevant to introduce carbon efficiency as a measure of how well a given plant is to preserve carbon in the process. The carbon efficiency was calculated for the two concepts presented in section 0 and 2.2.2 is **42** % for the traditional concept and **84** % for the SOEC concept.

As can be seen, adding electrolysis to a gasification plant significantly improves the carbon efficiency. This is mainly due to the better utilization of the CO2 as hydrogen is added in the synthesis reaction. In the traditional gasification concepts, large amounts of CO2 are removed in order to adjust the C/H ration for the methanol synthesis reaction.

3 Economical Analysis

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The economic analysis is to a large extent based on the calculation method used in the work of Mignard and Pritchard (Dimitri Mignard, 2008). The method is simple and relies on summation of capital expenses CAPEX and summation of the operational expenses OPEX, to calculate the yearly production cost price of the fuel produced. "Never before has humanity faced such a challenging outlook for energy and the planet. This can be summed up to five words: More energy, less carbon dioxide"

(Jeroen van der Veer – Chief Executive, Royal Dutch Shell, Shell Energy scenarios to 2050)

Therefore the production cost of bio-methanol based on gasification of biomass in combination with variable degrees of green hydrogen from electrolyzers will be analyzed. The hydrogen should obviously origin from renewables. In this analysis renewable hydrogen originating from wind power, via either alkaline electrolysis or Solid Oxide Electrolysis Cells (SOEC) are assumed.

The result will be that one can transform our sparse biomass to gaseous or liquid energy carriers that can be used in transportation instead of burning the precious biomass in stoves and/or power plants. The output energy content of methanol can be doubled by coupling with hydrogen from electrolysis of water.

The price of the methanol produced will be expressed in USD/barrel of oil-equivalents based on the conversion numbers given in (Energistyrelsen, 2010)²³. This equivalent number includes the costs associated with oil refining, thus the numbers given throughout this section should be interpreted as:

At the calculated USD per barrel value green methanol will become cheaper than conventional gasoline seen from a cost per energy unit perspective.

3.1 Introduction to Method

The method is based on the mix of gasification and electrolyzer technologies to provide a means for green methanol production, conversion of renewable electricity to green methanol and in some case also regulating power to extent the amount of renewable electricity, which can be put into the grid. There are many unknowns but the two overall scenarios, which need to be addressed, are:

- 1. The technology potentials
- 2. The wind energy penetration in the energy system.

3.2 Technology Scenarios

For detailed overview of the components used in the different scenarios please refer to appendix 1 and 2.

The following technology selection scenarios are analyzed:

- **Gasification only:** Methanol from oxygen gasification of wood pellets only.
 - This scenario builds upon a plant consisting of a traditional plant layout, as seen in Figure 46 including gasification, oxygen generator, gas clean up, water gas shift and methanol

²³ Currency conversion used: 1.3 USD/EUR

synthesis. In this scenario the C-to-H ratio is less than the ideal relation and therefore CO2 will be purged from the process.

- **Balanced SOEC**: Methanol from mixed hydrogen from electrolysis and oxygen gasification of wood pellets.
 - In this scenario the optimal balanced mix of C-to-H ratio is obtained by mixing hydrogen with the gasified and cleaned up gasification products, as seen in Figure 47. Oxygen from the electrolyzer is fed to the gasification unit, thereby omitting the oxygen generator and the water gas shift reactor due to the ideal C-to-H mix. This means that the process will only release negligible amounts of CO2, as all carbon is consumed in the process to create methanol.
 - The main plant components in the layout include gasification, gas clean up, electrolyzer and methanol synthesis.
- **Turn down SOEC/Alkaline**: Methanol from mixed hydrogen from electrolysis and oxygen gasification of wood pellets.
 - This is a similar scenario as the previous, however the control strategy here is to turn down electrolyzer to 1/3 of the rated capacity when the electricity price is too high. This is coherent to the amount of oxygen needed to feed the gasification unit. This gives the ability to use the plant actively as regulating power towards the grid. This would make sense in future scenarios where high percentage of wind energy penetrates the energy system.
 - The main plant components in the layout include gasification, gas clean up, water gas shift reactor, electrolyzer and methanol synthesis.

3.2.1 Wind Penetration and Electricity Price Scenarios

Wind power penetration will have a large effect on which of the above scenarios will be ideal, as the electricity price variations will become larger with more wind power integrated to the energy system. DTU Risø has previously analyzed the impact of larger amounts of electricity in the grid. The work by Jørgensen et al. (Claus Jørgensen, 2008) resulted in the model (shown in Figure 48) for accumulated electricity price per hour during a year.



Figure 48: Average spot price of electricity cumulated as function of hours per year

The model has only been used in terms of the relative price over the year and has following been normalized by the average predicted spot prices (61/82 EUR/MWh respectively 2010/2025) at the

consumer (company) given in (Energistyrelsen, 2010). This results in the following cumulated average electricity cost per year:

| Year: | 2010 | 2025 | 2025 |
|-------------------|--------|--------|---------|
| Wind penetration: | 20% VE | 50% VE | 100% VE |
| Hours per year: | | | |
| 1000 | 25 | 13 | 0 |
| 2000 | 36 | 30 | 3 |
| 3000 | 41 | 43 | 18 |
| 4000 | 44 | 53 | 31 |
| 5000 | 45 | 59 | 44 |
| 6000 | 47 | 62 | 56 |
| 7000 | 50 | 66 | 62 |
| 8000 | 53 | 71 | 72 |
| 8760 | 61 | 82 | 82 |

As shown, three different wind penetration scenarios have been chosen. The current status is 20% wind penetration in 2010, whereas 50% and 100% is chosen for 2025, even though only 27% is expected in 2025 by Energistyrelsen (Danish Energy Agency, 2010). The reason for this is to show how the combination of gasification and electrolysis to produce methanol can positively affect the ability to incorporate additional wind power beyond 2025. It is chosen not to calculate a 2050 scenario, as no future energy prices were published for this year in (Energistyrelsen, 2010); furthermore, economic plant predictions on this time scale will be highly unpredictable.

3.2.2 Assumptions

The design size of the plant was chosen to be equivalent to 1,000 tons of gasified biomass per day. This corresponds to a thermal input power of biomass of approx. 200 MW (heating value: 17.5 GJ/ton). The size of the plant was chosen to be in this, rather larger, paradigm, as this is equivalent to a conventional Danish coal power plant. One reason is that the economics of scale are for some of the components (in particular the gasification unit and the synthesis reactor) very significant. The other reason is to obtain combined heat and fuel (CHF) capability, which makes the plant location ideal around larger cities. For heat production is assumed that the excess heat can be sold as district heating at prices given in (Energistyrelsen, 2010).

3.2.3 CAPEX

Regarding CAPital EXpenditures (CAPEX) the structure and methodology of Mignard et al. (Dimitri Mignard, 2008) is used. Experts in the design of methanol plants assessed the credibility of the structure and methodology of the Mignard paper and judged it to be high. Most numbers have been estimated based on knowledge of the project group members. Some numbers has been increased and others have been decreased. The total sum is however close to that of Mignard et al. For further information, see appendix 1 and 2.

The capital expenditures are depreciated over a 20 year horizon with 10% interest rate to compensate for the risk associated with the plant. It is expected however, that the SOEC stack (1/3 the cost) needs to be replaced every 5 years, whereas most of the system components (2/3 the cost) will last for most of the 20 years.

Therefore the capital cost is estimated to be twice the SOEC system costs. An annual 1% maintenance cost of the electrolyzer unit is included in the OPEX calculation below. The alkaline electrolyzer unit is expected to last for the full 20 years with smaller maintenance costs during the period. An example of the distribution of CAPEX cost of one of the analyzed scenarios is shown in Figure 49.

3.2.4 **OPEX**

The inputs for Operating EXpenditures (OPEX) are based on the Danish report "Forudsætninger for samfundsøkonomiske analyser på energiområdet" (Energistyrelsen, 2010). The most important inputs are the price of renewable electricity as a function of wind penetration rate and as a function of operating hours per year. For further information, see appendix 1 and 2.

The maximum number of operating hours per year is calculated to be 8,000 h as maintenance periods (760 hours annually) needs to be incorporated. Figure 50 shows an example of the OPEX cost distributions in the "Turn Down SOEC and 2025, 50% Wind" scenario.



Figure 49: Total CAPEX cost distribution (341 MEUR) in the "Turn Down – SOEC" scenario



Figure 50: Annual OPEX cost distribution (156MEUR/year) in the scenario "2025 - SOEC - (50% Wind)".

3.3 Results

Figure 51 shows the result plots of the two scenarios of 2010 base line and 2025 with 50% wind penetration. It is clear that the lowest methanol production costs are found in the 2010 scenario, which is no big surprise since both electricity and biomass costs are expected to be lower today. As shown in Figure 49, the electricity and biomass prices constitute more than 2/3 of the operational expenses.

Also it seems like for both SOEC scenarios it is favorable to run both the gasification unit and the electrolyzer continuously throughout the whole year. This is partly due to the significant capital costs and partly due to the relatively low uniform cost of electricity in these two scenarios. The alkaline electrolyzer, which is less efficient and more costly than the SOEC system, is not as feasible with a projected lowest manufacturing cost of 147/168 USD per barrel equivalents (2010/2025 respectively).



Figure 51: Parameter study. Number of operating hours per year vs. technology type. Left: 2025 (50% wind), Right: 2010 (20% wind)

Figure 52 (left) shows how a 100% wind scenario will affect the optimal operating point of the plant. At this wind power penetration level, the plant is more cost efficiently operated with the electrolyzer (both SOEC and alkaline) at part load (1/3) during half the operating hours. The reason for this is that the electricity price variation is much higher and therefore large periods with very high prices. Figure 52 (right) shows that the 100% wind scenario should enable marginally lower methanol cost than the 50% wind scenario (138 vs. 141 USD/barrel eq.).



Figure 52: (right) Scenario 2025 cost structure but with 100% wind penetration. (left) Scenarios where SOEC is turned down to 1/3 part of the year corresponding to the number of hours per year.

Figure 53 shows a summary of the different technology scenarios vs. the year/wind penetration. The reference case (gasification only) is also shown, which is remarkably more expensive in the 2010 scenario than both the SOEC and alkaline based systems. However, as the electricity price is expected to go up of the years from 2010-2025 alkaline seems to become too in-efficient, unless the technology is improved.



Figure 53: Comparison between cost optimal operations of gasification only, turn down SOEC and turn down alkaline scenarios measured in USD per barrel equivalents

3.3.1 Sensitivity Analysis

Table 22 shows the prioritized sensitivity of five dominated components, the table shows what the price increase (in USD/oil barrel equivalent) will be for 30 % increase on the different components of the OPEX/CAPEX calculations. It is clear that the electricity and biomass costs are the most sensitive input parameters in both the 2010 and the 2025 scenario. CAPEX also has a strong influence and the estimations of the costs may end up giving the largest on certainty. The interest rate, which is conservatively chosen to 10 %, will not contribute to large changes.

| | 2010 (20%) Wind | 2025 (50%Wind) |
|-------------------------------------|-----------------|----------------|
| Calculated price [USD/oil bar. eq.] | 141 | 120 |
| Electricity price (+30%) | + 16 | + 14 |
| Biomass price (+30%) | + 15 | + 13 |
| CAPEX (+30%) | + 9 | + 9 |
| Interest rate (+30%) | + 6 | + 7 |
| District heating price (+30%) | + 3 | + 3 |

 Table 22: Sensitivity (30% increase) of various cost parameters for the SOEC case vs. product cost expressed in USD/oil barrel equivalents.

3.3.2 CO₂ Quotas

The methanol production prices shown in the previous chapters are not corrected for CO_2 quotas as the produced bio-methanol will displace fossil fuels. In order to estimate the impact of CO_2 quotas a calculation based on the 2010 (20 % wind) turndown SOEC scenario is conducted.

It is assumed that 1 GJ of methanol replace 1 GJ of gasoline in a car. The CO_2 output from a gasoline car is according to (Energistyrelsen, 2010) 72.8 kg/GJ, using the LHV for methanol 1.62 of CO_2 is displaced for each ton of methanol. The CO_2 quota price is 105 DKK/ton CO_2 , which results in a quota price of 174 DKK/ton (23.3 EUR/ton) of methanol. From Appendix 2 a methanol production price of 426 EUR/ton was

calculated. Thus a corresponding reduction 5.5 % in the methanol production price can be assessed. This equivalent to methanol production of 113 USD/barrel equivalent.

3.3.3 District Heating Variations

Naturally, district heating cannot be supplied evenly on a yearly basis as the demand is highly seasonal dependent (winter vs. summer). Moreover, during the summer time additional costs may be added to dissipate the generated heat. Therefore, in order to estimate the impact of less district heating, it is assumed that district heating can be sold on only half of the days of plant operation. If this is implemented in the 2010 (20 % wind) turndown SOEC scenario the methanol price production is increased by 4.4 % and results in a methanol production price of 126 USD/barrel equivalents.

3.4 Conclusion

Based on the conclusions in this section, it is believed that green methanol will become cheaper than conventional gasoline when/if the oil hits 120 USD per barrel in the near future or 141 USD barrel in 2025. These figures are based on available gasification units and Solid Oxide Electrolysis Cell (SOEC). In order to realize this potential, further development of gas purification (char removal) and SOEC needs to be conducted. When the calculations are made on the already existing alkaline technology the relative oil price needs to be 147 USD based on energy input prices of 2010. It is estimated that the impact of the CO_2 quotas and district heating variations equals out as the cost analysis results presented in Figure 53.

3.5 Methanol Consumer Price

By Constituted Director, Cemtec Per Sune Koustrup

Methanol price at the pump is a result of the base production price, distribution & profits, CO_2 tax, energy tax and Value Added Tax (V.A.T). All prices will be listed in \notin/L or \notin/MT . Distribution & profits, CO_2 tax, energy tax and V.A.T. are listed according to Danish taxation rules.

Base Price

The Base Price is defined as the cost of methanol Free On Board (F.O.B) on a vessel, a train or truck(s). The company Methanex has posted prices for the European market since January 2002 (the so-called Methanex European Posted Contract Price (MEPCP)).²⁴ During the timespan from January 2002 to December 2010 prices hit a minimum in March 2002 at 125 \leq /MT and a maximum in March 2008 at 525 \leq /MT. The maximum price, when adjusted for price shocks, occurred in December 2008 at 295 \leq /MT. The average price (incl. the price shocks) was 249 \leq /MT. The current price (January 2011) is 277 \leq /MT. An average price of 250 \leq /MT (0.20 \leq /L) is defined. So is a low price of 125 \leq /MT (0.10 \leq /L) and a high price of 375 \leq /MT (0.30 \leq /L). All of these prices for methanol are based on fossil fuels and are in this section referred to as Black Methanol.

For methanol based on renewable energy the numbers from section 3.3 are used. In Table 23 one can see the low and high scenario prices for black as well as green methanol, which is referred to as Bio Methanol. All prices are converted from ℓ/MT to ℓ/I assuming a density of methanol of 0.793 kg/l.

²⁴ <u>http://www.methanex.com/products/documents/MxAvgPrice_January272011.pdf</u>

| Scenario / production method | Black Methanol | Bio Methanol |
|--|------------------------|--------------|
| Low / Tur. SOEC - 2010 @ 20 % wind | 0.10 | 0.34 |
| High / Tur. SOEC - 2010 @ 50 % wind | 0.30 | 0.39 |
| Table 23: Low and high scenario prices (€/L) | for black & bio MeOh I | FOB at plant |

It can be seen from the above table that the maximum difference between a "Low, Black methanol" Base price and a "High bio methanol" Base price is $0.39 \notin$ /L. For an improved quality of the conclusions drawn on the basis of the table it is recommended that the numbers should be cleaned for inflation according to (Energistyrelsen, 2010)²⁵.

Distribution and profits

Methanol is distributed exactly the same way as diesel and gasoline. That is – transport from plant to storage facilities on harbours using vessels, storage at harbours in huge storage tanks storing several thousands of tons at a time, distribution by trucks (normally up to 28 tons at a time) and storage in underground or above-ground tanks at petrol stations.

From a distribution cost point of view methanol burns easier than diesel but less easy than gasoline. Methanol is easy bio-degradable meaning that in the case of a huge spill the cost for cleaning up will be much less. Therefore one can assume that the insurance cost of a vessel, a storage tank and a truck carrying methanol will be less than a vessel, a storage tank and a truck carrying and/or storing diesel, gasoline or crude oil. In summary it is assumed that it costs the same to distribute one I of methanol as it costs to distribute one I of diesel or gasoline. The costs associated with distribution and profits were 24.50 DKK/GJ for diesel and 33.09 DKK/GJ for gasoline in 2008. When taking into account that prices are increasing and are 4.3 % higher in 2011 than they were in 2008, then that is equal to prices of 0.12 €/I for diesel and 0.15 €/L for gasoline (Energistyrelsen, 2010)²⁶. In the table below the low and high price scenario for distribution and profit is shown. A medium scenario is defined as an average of the low and the high scenario.

| Scenario | €/L |
|----------|------|
| Low | 0.12 |
| Medium | 0.14 |
| High | 0.15 |

Table 24: Low, Medium and High scenario prices for distribution and profits

Table 24 shows that the difference between a "Low" Distribution & Profits price and a "High bio-methanol" Distribution & Profits price is 0.03 €/L

CO2 Tax

According to "LBK nr. 889 af 17/08/2006", the so-called CO_2 -tax law (CO_2 -afgiftsloven)²⁷, there is a CO_2 tax of 0.22 DKK/I gasoline (0.03 \notin /L). Per unit of CO_2 -emission it is the same for diesel. When adjusting for a

²⁵ As listed in Table 1 of (Energistyrelsen, 2010)

²⁶ Table 4

²⁷ <u>https://www.retsinformation.dk/forms/r0710.aspx?id=17302</u>

substantially lower CO_2 -emission per l of methanol the CO_2 tax amount to 0.014 \notin /l. If the methanol is green this tax will clearly not have to be paid. Therefore two scenarios exist; one where the tax has to be paid and another where the tax does not have to be paid. See the table below.

| Scenario | €/I |
|----------------|------|
| Green Methanol | 0.00 |
| Black Methanol | 0.01 |

Table 25: Black and Green scenario for CO2 tax

Table 25 shows that the difference between a "Green Methanol" scenario for CO_2 tax and a "Black Methanol" scenario for CO_2 tax is $0.01 \notin /I$.

Energy tax

The energy tax on gasoline in Denmark is in 2011 3.789 DKK/l, equivalent to $0.51 \notin /l.^{28}$ Since the energy content of one l of methanol is 49 % of that of one l of gasoline the energy tax amounts to $0.25 \notin /l$ for methanol. Two scenarios are listed: A bio scenario where methanol is exempted from energy tax and a black scenario where the energy tax amounts to $0.25 \notin /l$, see Table 26.

| Scenario | €/I |
|----------------|------|
| Bio Methanol | 0.00 |
| Black Methanol | 0.25 |

Table 26: Black and Green scenario for energy tax

Value Added Tax

The Value Added Tax (V.A.T.) is 25 % on all goods in Denmark. The result of V.A.T. on both black and bio methanol can be seen in the tables below.

| Scenario | Base production price | Distribution and | CO2 tax | Energy tax | Part sum | V.A.T. |
|----------|-----------------------|------------------|---------|------------|----------|--------|
| | (1) | Profits | (3) | (4) | =1+2+3+4 | (5) |
| | | (2) | | | | |
| Low | 0.10 | 0.12 | 0.01 | 0.25 | 0.48 | 0.12 |
| High | 0.30 | 0.15 | 0.01 | 0.25 | 0.68 | 0.17 |

Table 27: V.A.T. for black methanol

V.A.T. for black methanol varies between 0.12 and 0.17 €/l and is primarily a result of fluctuating base production prices.

| Scenario | Base price | Distribution and | CO2 tax Energy tax | | Part sum | V.A.T. |
|----------|------------|------------------|--------------------|-----|----------|--------|
| | (1) | profits | (3) | (4) | =1+2+3+4 | (5) |
| | | (2) | | | | |

²⁸ https://www.retsinformation.dk/Forms/R0710.aspx?id=15758&newwindow=true

| Low | 0.34 | 0.12 | 0 | 0 | 0.46 | 0.11 |
|------|------|------|---|---|------|------|
| High | 0.39 | 0.15 | 0 | 0 | 0.54 | 0.14 |

Table 28: V.A.T. for bio-methanol

V.A.T. for Bio-methanol varies between 0.10 and 0.13 €/l and is also a primarily result of fluctuating base prices. From the above tables it is found that the difference between a "bio-methanol" scenario for V.A.T. and a "black methanol" scenario for V.A.T. is 0.07 €/l.

Total cost at pump

The total cost (€/I) of methanol at the pump is listed for black and bio-methanol in the tables below.

| Scenario | Base price | Distribution and | CO2 tax | Energy tax | V.A.T. | Total cost at pump | | | |
|---|------------|------------------|---------|------------|--------|--------------------|--|--|--|
| | (1) | profits (2) | (3) | (4) | (5) | (6) | | | |
| Low | 0.10 | 0.12 | 0.01 | 0.25 | 0.12 | 0.60 | | | |
| High | 0.30 | 0.15 | 0.01 | 0.25 | 0.17 | 0.85 | | | |
| Table 20. Table and other sources for Dials Marthauer | | | | | | | | | |

| Scenario | Base price | Distribution & Profits | CO2 tax Energy tax | | V.A.T. | Total cost at pump |
|----------|------------|------------------------|--------------------|-----|--------|--------------------|
| | (1) | (2) | (3) | (4) | (5) | (6) |
| Low | 0.34 | 0.12 | 0 | 0 | 0.11 | 0.57 |
| High | 0.39 | 0.15 | 0 | 0 | 0.14 | 0.68 |

Table 29: Total cost at the pump for Black Methanol

Table 30: Total cost at the pump for bio-methanol

The above listed prices are probably only meaningful to people with a very deep insight into methanol as an energy carrier. In order for ordinary people to understand the implications one has to look at a far less scientific number – methanol price per driven km.

3.5.1 Methanol Consumer Price per Driven km

The methanol price per I is one thing. What is however of significantly higher value for ordinary customers is the cost per driven km. The cost per driven km is a result of cost per I and Tank-To-Wheel (TTW) efficiency. The cost per I is listed in the section above. The efficiency of fuel cell systems is analyzed in this section.

The TTW efficiency of a fuel cell system depends on a number of factors. Some of these factors are standalone, while others influence each other in different ways. In order to narrow down the efficiency spectrum of different fuel cell types at different times it is therefore necessary to define and describe the most important of these factors and assume certain levels/numbers regarding the different factors. In the following, the main definitions and assumptions influencing the efficiency of fuel cell systems are therefore attempted listed and so are the levels regarding some of the most important factors. It should be noted that the list is not necessarily exhaustive.

Fuel cell types

First of all the different fuel cell types are defined. In the report "Alternative Drivmidler til Transportsektoren" (Cowi, 2010) one driveline is considered regarding a methanol-fueled fuel cell vehicle. It is not stated directly what kind of fuel cell technology is assumed. From a historical perspective one can however assume that the driveline is regarding to a Low Temperature Proton Exchange Fuel Cell system (LTPEMFC).

In order to include all (relevant) fuel cell technologies Direct Methanol Fuel Cells (DMFC), High Temperature Proton Exchange Membrane Fuel Cells (HTPEMFC) and Solid Oxide Fuel Cells (SOFC) should/can eventually be included in the above mentioned report.

Assumptions

1) Pure methanol as input

It is assumed that pure methanol is used. If a mix of water (H2O) and methanol (CH3OH) is used, then the system-efficiency can be slightly increased since reutilization of water will not be necessary

2) Regulated AC current as output

Regulated AC current as output is defined. If an unregulated DC current was used instead a significantly higher efficiency can be assumed.

3) A relatively low load-point

A load-point (A/cm2) of 25 % of peak-power is defined. This is so since most often cars tend to drive at relatively low average speeds. The average speed in New European Drive Cycle (NEDC) is e.g. only 34 km/hr. Furthermore the power needed to sustain a certain speed is to a large extent a result of the speed in 2nd order.

4) Beginning Of Life

The efficiency is defined as the efficiency at Beginning of Life (BOL) and after the break-in time.

5) Balance Of Plant

The efficiency number includes Balance of Plant (BOP) components such as blowers, evaporators, pumps, burners, controllers etc.

6) A "running" system in steady state

In order not to define a "drive-cycle" and in order to keep things simple a "running" system working at a 25 % workload is defined.

7) Standard conditions for Temperature and Pressure

Standard conditions for Temperature and Pressure (STP) according to the SI system (288.15 Kelvin and 101.325 kPa (1 atm)) is used.

8) Size of system (measured in kW)

The size of the FC system is defined as being of 20 kW. Heat-losses for significantly smaller systems are significantly – Especially for HTPEMFC and SOFC.

9) No heat utilization

If one utilizes some or most of the waste-heat, the electric efficiency is slightly reduced. This is due to increased parasitic losses to heat exchangers, pumps and blowers.

Even though a number of assumptions have been made, as shown above, then it is still not possible to pinpoint an exact TTW efficiency. Platinum loading (for DMFC and HTPEMFC), electrode type and design, system design, price pr. kW, expected scientific breakthrough, lifetime etc. all influence the efficiency.

Finally there is the efficiency of the electric motor(s), the efficiency of the hybridization (batteries or super caps), and the weight of the FC technology as well as the weight of the whole car. As can be seen from the

above, a long list of factors influences the cost per km. In the table below the current efficiency (2011) and the expected 2025 efficiency from methanol to regulated AC current is listed.

| Technology type | 2011 | 2025 |
|-----------------------|---------|---------|
| DMFC ⁱ | 25 – 40 | 30 – 45 |
| HTPEMFC ⁱⁱ | 30 – 40 | 45 – 55 |
| SOFC | 46 | 56 |

Table 31: Tank to regulated AC current output ⁱ Jacob Bonde, IRD Fuel Cells A/S ⁱⁱ Anders Korsgaard, Serenergy A/S ⁱⁱⁱ John Bøgild Hansen, Haldor Topsøe A/S

Depending on technology and including losses in electric motors one can assume a tank-to-wheel efficiency of roughly 35 to 40 % in 2011 and 40 to 50 % in 2025. Let us assume a 2025 TTW efficiency for:

- methanol fed fuel cell cars of 40 % (low case) or 50% (high case),
- gasoline cars of 23.5 % (Cowi, 2010) and
- hydrogen fed fuel cells of 55 %.

Let us then use the historical prices for gasoline, methanol and a future low cost for hydrogen to see the cost measured in US cents per kWh relative to each other. In Figure 54 is seen the low case.





It is seen that even when one uses a low efficiency (40 % TTW) for methanol fed fuel cells, then methanol is the cheapest energy carrier per driven km. In the figure below is seen the high case.



Figure 55: Price per driven km, 2025 (High efficiency case)

Please note that for hydrogen to be competitive (US cents/kWh), hydrogen has to be approx. 5 times cheaper than the stated 7€/kg²⁹. Please also note, that the gap between the methanol and the gasoline lines tends to broaden, thereby making methanol a more and more attractive long-term solution.

3.5.2 Well-to-Wheel – Bio-Methanol to Fuel Cell

Based on the results presented in the previous sections, a partial well-to-wheel efficiency is calculated below for a bio-methanol for fuel cell vehicle case. The efficiency of biomass to the methanol production site and the distribution efficiency from the methanol production site to the vehicle tank is not taken into consideration in calculation below. To obtain a full well-to-wheel study coordination is needed between (Cowi, 2010) and the data presented in Table 32.

As presented in Table 20, the methanol production efficiency is 70.8 % and the tank-to-wheel efficiency was estimated in section 3.5.1 to be roughly 35 - 40 % in 2011 and 40 - 50 % in 2025. Therefore, with the assumptions stated above the well-to-wheel efficiency is shown in Table 32.

| Year | Biomass to plant | Biomass to meoh [%] | Meoh to tank | Tank-to-wheel [%] | Total well-to- wheel [%] | | |
|------|------------------|------------------------|--------------|----------------------|--------------------------------|--|--|
| 2011 | N/A | 70.8 | N/A | 35 – 40 | 24.8 – 28.3 | | |
| 2025 | N/A | 70.8 | N/A | 40 - 50 | 28.3 - 35.4 | | |

Table 32: Well-to-wheel efficiencies for bio-methanol to fuel cell vehicle case

²⁹ The price of hydrogen has been converted to US cents.

4 Conclusion and Recommendation

The main purpose of the present project was to identify viable methods for the production of green synthetic fuels, which holds a significant Danish business potential. Based on modification of all-ready established Danish technology concepts, e.g. biogas and gasification, two novel plant concepts are derived that are very close of being economic and technological feasible. Although, the project group consists of members with various interests, it is managed to agree on two plant concepts for a future production of green synthetic fuels.

In the present project, several different routes for the production of green synthetic fuel have been identified. Among these to specific methanol/DME production plant concepts have been chosen by the project, as they represent potentially viable methods for a Danish-based production and they represent a significant Danish business potential. The two chosen concepts are:

- 1. Methanol/DME Synthesis based on electrolysis assisted biomass gasification
- 2. Methanol/DME synthesis based on biogas temporarily stored in the natural gas network.

It was chosen by the project group to focus primarily on concept 1), as the gasification case is the most interesting concept from a Danish perspective. The mass and energy balances for a large scale plant of concept 1) have been calculated. Furthermore, for reasons of comparison a traditional gasification concept was also analyzed. As mentioned it was decided to focus on large scale plants; therefore the designing limit was 1,000 tons wood per day as input for the gasifier.

Considering a traditional gasification plant 500 tons methanol can be produced from 1,000 tons wood (1,000 t wood = 523 t methanol). However, when adding hydrogen to adjust the equilibrium of the methanol synthesis reaction, the plant output is doubled, the plant can therefore produce 1,000 t methanol from 1,000 t wood (1000 t wood = 1053 t methanol).

Surprisingly high plant efficiencies were found, on a traditional gasification plant with oxygen input a methanol production efficiency of (η_{meoh} = 59.2 %) was found, and for the electrolysis-assisted plant a methanol production efficiency of (η_{meoh} = **70.8** %) was found. Therefore, not only can electrolysis double the production output, it can also boost the plant methanol production efficiency. The total efficiency of the two analyzed concepts was however similar (η_{tot} = **81.6** %), as district heating is better recovered in the traditional plant concept.

The economic analysis was conducted using a simple CAPEX/OPEX approach. The results of the analysis showed that if SOEC and other critical plant components were readily available today, green methanol can be produced at an oil equivalent price of **120 USD/barr. eq.** Considering the current oil price (approx. 100 USD/barrel), the feasibility gap is quite small for a green substitute. The analysis also showed that the production cost is likely to increase in the future, due to the expected increase in energy prices (biomass and electricity), even though the number of available hours of cheap spot market electricity will increase as a function of wind energy penetration to the energy system.

It was not possible to conduct a full well-to-wheel study for a bio-methanol to fuel cell case, as it was not possible to extract all the necessary data from (Cowi, 2010). Data is however provided in the present study so that the publication can be updated with more precise data for a bio-methanol to fuel cell case.

The methanol production prices found in this study should be considered along with the fact that a plant can, to some extent, be used as means of storing electricity. The plant concept can therefore assist to the ongoing plans of expanding the Danish wind energy penetration.

Based on the work presented in the present report, the project group can recommend that further work should include:

- 1. Engineering of the suggested plant concepts in order to provide precise cost estimations
- 2. The concepts presented illustrates the large potential of SOEC technology, therefore priority should be given to improving and demonstrating durability and reliability of SOEC stacks and systems
- **3.** To further improve SOEC, more fundamental work of finding better electrode materials and defining optimal structures plus research in cheap fabrication procedures for making these electrode structures of the new materials is needed
- 4. Further work should be conducted on gasification concepts, in which special attention must be directed towards handling of the syngas tar
- 5. The project group recommends that both the biogas and the gasification plant concepts are scale demonstrated, once the technological challenges mentioned in the above points are solved
- 6. It is pivotal for a future sustainable energy system that the scarce global biomass supplies are used efficiently. It is therefore recommended that future energy conversion plants are assessed with regards to their carbon efficiencies
- 7. Partial well-to-wheel data for a bio-methanol to fuel cell case has been given. It is recommended that the present publication "Alternative Drivmidler for Transportsektoren" is updated using the data supplied in section 3.5.1, in order to obtain a full well-to-wheel data for the bio-methanol to fuel cell case.
- 8. A techno-economic analysis for a 2050 scenario was not conducted in this project. It was chosen to omit this scenario as the data foundation for such a scenario is too weak. It is therefore recommended that the publication "Forudsætninger for samfundsøkonomiske analyser for energiområdet" is update and extended from 2030 to 2050, so that more accurate 2050 scenarios can be conducted.

The obtained results are coherent with the plans published by Energinet.dk in "Energi 2050 – udviklingsspor for energisystemet" (Energinet.dk, 2010) and "Gas I Danmark 2010 – Forsyningssikkerhed og udvikling" (Energinet.dk, 2010) and the new strategy by the Government "Energistrategi 2050 – fra kul, olie og gas til grøn energi" (Danish Ministry of Climate and Energy, 2011). Obtained results allows with time integration of an increasing amount of wind energy into the electric supply system.

Lastly, it can be concluded that the present report has shown that green methanol can indeed be produced at competitive prices and be used as step towards expanding the share of renewables in the energy system and especially in the transportation segment.

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Appendices

1 CAPEX Calculations

| | Scaled, conve | currency rter from | | | | | Source/ |
|---------------------------------|------------------|-----------------------|-------------|--------------------|------|-------------------|--|
| | Mignard et al. | | Traditional | ional Electrolyzer | | Hybrid (alkaline) | comments |
| Plant Component | £MM | M EUR | M EUR | | | | |
| Wood receiving and preparation: | 4,2 | 31,0 | 10,0 | 10,0 | 10,0 | 10,0 | Estimated |
| Gasification | 7,2 | 53,2 | 45,0 | 45,0 | 45,0 | 45,0 | Carbona, including piping, setup, excluding foundation |
| Acid-gas removal (downdraft) | 2,9 | 21,4 | 21,4 | 21,4 | 21,4 | 21,4 | Mignard et al. |
| Tar reformer | 2,9 | 21,4 | 22,5 | 22,5 | 22,5 | 22,5 | Estimated |
| Shift Reactor | 7,8 | 57,6 | 15,0 | 0,0 | 15,0 | 15,0 | Estimated |
| Gas cooling | 0,5 | 3,7 | 3,7 | 3,7 | 3,7 | 3,7 | Mignard et al. |
| Methanol Synthesis & purif. | 5,9 | 43,6 | 21,8 | 43,6 | 43,6 | 43,6 | 50% cost - only 50% throughput in traditional type |
| Electrolysis | 48,6 | 359,0 | 0,0 | 77,2 | 77,2 | 122,6 | 3000 DKK per 7,5 kW, Mogensen, 2x system price |
| Gas compression and expansion | 2 | 14,8 | 14,8 | 14,8 | 14,8 | 14,8 | Removed due to pressurized fluedized gas type reacto |
| Oxygen generator | 10,6 | 78,3 | 78,3 | 0,0 | 0,0 | 0,0 | |
| Utilities and offsites | 10,3 | 76,1 | 37,5 | 37,5 | 37,5 | 37,5 | Mignard et al. |
| Miscellaneous fees | 5,15 | 38,0 | 38,0 | 38,0 | 38,0 | 38,0 | Mignard et al. |
| Land | 0,5 | 4,4 | 0,97 | 0,48 | 0,97 | 0,48 | 5 acre, 50,000m2 (4x price farming land) |
| Start-up costs | 1,6 | 11,8 | 11,8 | 11,8 | 11,8 | 11,8 | Mignard et al. |
| CAPEX (1): | 110 | 814 | 321 | 326 | 341 | 386 | |

CAPEX

2 OPEX Calculations

| OPEX | Traditional | | Balanced (SO | EC) | Т | urn down (S | OEC) | Tur | n down (al | kaline) | |
|---|-------------|------|--------------|-----------------------|---------------------|-------------|--------|--------------------|------------|-----------------|------------------|
| <u>Scenario</u> | High | Low | Medium | High | Low | Medium | High | Low | Medium | High | _ |
| Operating hours per year - Electrolyzer mode | | 3000 | 40 | 00 800 | <mark>)</mark> 3000 | 4000 | 5000 | 3000 | 4000 |) 500 | 0 h |
| Operating hours per year - gasifier mode | 8000 | | | | 5000 | 4000 | 3000 | 5000 | 4000 |) 300 | 0 h |
| Average load | 0 | 342 | 4 | 57 91 | <mark>3</mark> 913 | 913 | 913 | 913 | 913 | 91 91 | 3 Tonnes per day |
| Electricity price @ 20 %VE - low price hours | 53 | 41 | | 44 5 | <mark>3</mark> 41 | 44 | - 45 | 5 41 | . 44 | 4 | 5 EUR per MWh |
| Electricity price @ 50% VE - low price hours | 71 | 43 | | 53 7 | <mark>1</mark> 43 | 53 | 59 | <mark>)</mark> 43 | 53 | 5 5 | 9 EUR per MWh |
| Electricity price @ 20 %VE - high price hours** | | | | | 61 | 63 | 67 | 61 | . 63 | 6 | 7 EUR per MWh |
| Electricity price @ 50% VE -high price hours** | | | | | 87 | 7 89 | 90 | 87 | 89 |) 9 | 0 EUR per MWh |
| Electricity consumption - Electrolyzer mode | | 406 | 5 | 42 108 | 3 406 | 5 542 | 677 | 589 | 785 | 5 98 | 2 GWh per year |
| Electricity consumption - gasifier mode | 13 | | | | 226 | 5 181 | . 135 | 327 | 262 | 2 19 | 6 GWh per year |
| Dry wood cost - 2010 | 53 | 20 | | 27 5 | <mark>3</mark> 53 | 53 | 53 | <mark>.</mark> 53 | 53 | 5 5 | 3 MEUR per yr |
| Dry wood cost - 2025 | 62 | 23 | | 31 6 | <mark>2</mark> 62 | 2 62 | 62 | 2 62 | 62 | 2 6 | 2 MEUR per yr |
| Total electricity cost @ 20 % VE | 0,7 | 17 | | 24 5 | <mark>3 30</mark> |) 35 | 39 | 9 44 | 51 | L 5 | 7 MEUR per year |
| Total electricity cost @ 50% VE | 0,7 | 17 | | 28 7 | 7 37 | 44 | 52 | 2 54 | 65 | 57 | 6 MEUR per year |
| District heating income - 2010 | -13,3 | -5,0 | -(| 5,6 -13, | <mark>3</mark> -5,C |) -6,6 | -8,3 | -5,0 | -6,6 | 5 -8, | 3 MEUR per year |
| District heating income - 2025 | -15,4 | -5,8 | -1 | 7,7 -15, - | <mark>1</mark> -5,8 | 3 -7,7 | -9,6 | 5 -5,8 | -7,7 | -9, | 6 MEUR per year |
| Catalyst and chemicals | 2,0 | 0,8 | : | .,0 2, | 0,8 | 3 1,0 | 1,3 | <mark>8</mark> 0,8 | s 1,0 |) 1, | 3 MEUR per year |
| Maintenance electrolysis | 0,0 | 0,3 | (|),4 0, | 7 0,7 | 0,7 | 0,7 | 0,7 | 0,7 | ⁷ 0, | 7 MEUR per year |
| Miscellaneous | 1,0 | 1,0 | : | .,0 1, | <mark>)</mark> 1,0 |) 1,0 | 1,0 | 0 1,0 | 1,0 |) 1, | 0 MEUR per year |
| Labour | 3,4 | 3,4 | 3 | 3,4 3,4 | <mark>1</mark> 3,4 | 3,4 | . 3,4 | 3 ,4 | . 3,4 | l 3, | 4 MEUR per year |
| Maintenance Gassifier | 0,9 | 0,3 | (|),4 0,5 | 9 0,9 | 0,9 | 0,9 | 0,9 | 0,9 |) 0, | 9 MEUR per year |
| Maintenance Remaining | 3,5 | 1,3 | : | .,7 3, | 5 1,3 | 3 1,7 | 2,2 | 2 1,3 | 1,7 | ⁷ 2, | 2 MEUR per year |
| Insurance and taxes | 2,3 | 2,3 | 2 | 2,3 2, | <mark>3 2,</mark> 3 | 3 2,3 | 2,3 | <mark>.</mark> 2,3 | 2,3 | 3 2, | 3 MEUR per year |
| Depreciation, risk and financing (10%/20yr) | 37,7 | 38,3 | 38 | 3,3 38,3 | <mark>3</mark> 40,1 | 40,1 | . 40,1 | 45,4 | 45,4 | 45, | 4 MEUR per year |
| Total costs per yr @ 50% VE - 2025 | 98 | 82 | 1 | 00 17 | 5 143 | 3 150 | 156 | 5 165 | 175 | 5 18 | 5 MEUR per yr |
| Total costs per yr @ 20 % VE -2010 | 91 | 79 | | 92 14 | 9 129 |) 132 | 136 | 5 148 | 153 | 3 15 | 9 MEUR per yr |
| | | | | | | | | | | | - |
| Equivalent oilprice (50% VE 2025) | 158 | 177 | 1 | 51 141 | 146 | 145 | 144 | 168 | 169 | 17 |) USD/barrel |
| Equivalent oilprice (20% VE - 2010) | 148 | 170 | 14 | 18 120 | 131 | 128 | 125 | 150 | 148 | 14 | 5 USD/barrel |

3 Concepts












