Methanol as a New Energy Carrier

A Forecast for the Introduction of Methanol as Energy Carrier in the Netherlands

Techniek en Toekomst
WM0908TU

August 2005

Bianca Breure (1013831)
B.Breure@tnw.tudelft.nl

1. Introduction

The scarcity of fossil fuels urges our society to look at alternative raw materials for the production of energy and chemicals. Furthermore, global warming and stricter environmental regulations forces us to look at more sustainable ways to satisfy the increasing demands of our energy-intensive society. At the moment, hydrogen is seen as a very promising energy carrier for the future. Some experts think that hydrogen will form the basic energy infrastructure that will power future societies, replacing today's natural gas, oil, coal and electricity infrastructure. The hydrogen economy vision is based on a clean and closed cycle. Hydrogen is produced from biomass or by separating water into hydrogen and oxygen using renewable or nuclear energy. The hydrogen can be used to power a fuel cell, internal combustion engine or turbine, where hydrogen and oxygen recombine to produce electrical energy, heat and water to complete the cycle. This process produces no particulates, no carbon dioxide and no pollution. However, the application of hydrogen as energy carrier also has some disadvantages. Hydrogen is a gas in normal circumstances and therefore it must be transformed into a transportable, storable and dispensable form after production. Compression or liquification is necessary, which requires a lot of energy. Furthermore, changing the current system into a system that supports hydrogen as energy carrier is a massive operation requiring very high investments.

A promising alternative for hydrogen is methanol. Methanol is a very reasonable and versatile fuel with many advantages over pure hydrogen. Methanol is a liquid at ambient conditions and could be handled and distributed with exactly the same type of infrastructure by which liquid gasoline is distributed today. It has none of the handling or materials complications that come with a pure hydrogen fuel. Furthermore, methanol is cheap and is in principle renewable when made from biomass. Also the only products of combustion are carbon dioxide and water. Therefore, when methanol is made from renewable raw materials, we can also talk of a closed cycle without the production of pollutants. Methanol can be used as a fuel to power vehicles, it can be converted to electricity in fuel cells and it is an important feed material in the petrochemical industry. Therefore methanol is one of a number of options to be seriously considers as an energy carrier for a clean and sustainable energy future.

In this report a forecast is made for the possibility of production of methanol in the Netherlands. First possible applications of methanol as energy carrier are discussed, followed by a short description of the present production of methanol and an explanation of a sustainable route for methanol production by using biomass as feedstock. Then the different feedstocks that can be used to produce methanol are discussed and the most suitable biomass feed material for cultivation in the Netherlands is chosen. Finally, an estimation is made for the amount of methanol that can be produced in the Netherlands from biomass cultivated on an area as big as the province Flevoland.

2. Applications of methanol as energy carrier

Methanol as energy carrier can be applied in different ways as a power source. It can be used in fuel cells after it has been reformed to a mixture of hydrogen and carbon monoxide, it can be directly converted to energy in fuel cells that convert methanol without reforming and it can be used as a direct fuel in vehicles.

2.1 Fuel cells as power source

Over the past decade, the interest in fuel cells as new power sources have increased tremendously. Fuel cells are energy conversion devices that transform the energy stored in a fuel into electricity and heat. The fuel is not burned in a flame but oxidized electrochemically. In a typical fuel cell, gaseous fuels are fed continuously to the anode (negative electrode) compartment and oxidant (i.e. oxygen from air) is fed continuously to the cathode (positive electrode) compartment. Electrochemical reactions take place at the electrodes to produce an electric current. A fuel cell, although having components and characteristics similar to those of a typical battery, differs in several aspects. Batteries are energy storage devices and the maximum energy available is determined by the amount of chemical reactant stored within the battery itself. The battery will cease to produce electric energy when the chemical reactants are consumed. A fuel cell on the other hand, is capable of producing energy for as long as the fuel and oxidant are supplied to the electrodes. The major applications for fuel cells are as stationary electric power plants, as motive power for vehicles and as on-board electric power for space vehicles or other closed environments [1].
Methanol can be used as a fuel in conventional fuel cells. In this case, the methanol has to be reformed to hydrogen that is converted in the fuel cell. The advantage of methanol is that it contains low energy chemical bonds and therefore it can be reformed to hydrogen at relatively low temperatures (250°C to 350°C). Other hydrocarbon fuels require reforming temperatures of 800° to 900°C [2]. Depending on the type of fuel cell (e.g. SOFC, MCFC) different electrochemical reactions take place at the electrodes. However, the overall reaction of fuel cells that use hydrogen as the fuel is the same:

$$H_2 + 1/2\,O_2 \rightarrow H_2O$$

Stationary power is the most tried and tested application of fuel cells. Fuel cell vehicles have only been developed for testing. Most car manufactures have or are working on demonstration models, but up to now no commercial fuel cell vehicles are on the market. At the moment, several research projects are under way to improve the performance and lower the costs of fuel cells.

2.2 Direct methanol fuel cell

At the moment there is also a lot of interest in the use of fuel cells as a new power source for the ever-growing number of mobile electronic devices, such as laptop computers, mobile phones and camcorders. The advantage of using a fuel cell instead of a conventional solid battery for electronic devices is that recharging will merely involve refilling with the liquid fuel and not plugging the device into an external electric supply for long periods of time. Refilling could simply be done by plugging in a new fuel cartridge. A promising fuel cell as power source for portable devices is the Direct Methanol fuel cell (DMFC). As the name implies, this fuel cell can run on a methanol-water mixture fed directly into the unit without prior reforming. The advantage of the DMFC is that one does not need complicated catalytic reforming, and storage of methanol is much easier than that of hydrogen, because it does not need to be stored at high pressures. Furthermore, the energy density of methanol is orders of magnitude greater than even highly compressed hydrogen [1]. A lot of electronic companies like Toshiba, are performing an extensive amount of research to improve the performance of DMFCs to make them more compatible with conventional batteries. Toshiba recently announced that they made the world's smallest DMFC with an energy output of 100 milliwatts [3]. The fuel cell is as long and wide as a thumb and has a total weight of only 8.5 g. According to Toshiba, this fuel cell is efficient enough to power a MP3 music player for as long as 20 hours on a single 2cc charge of highly concentrated methanol.

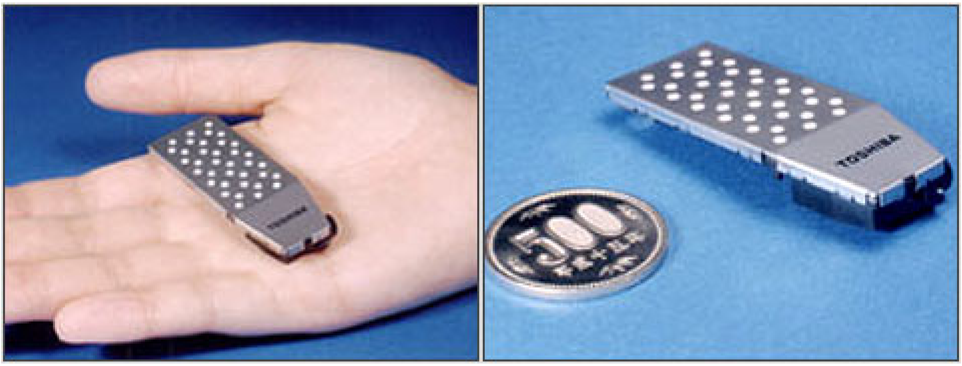

Figure 1. Direct Methanol fuel cell developed by Toshiba [3]

DMFCs consist of a polymer electrolyte and the charge carrier is the hydrogen ion (proton). Liquid methanol is oxidized in the presence of water at the anode generating carbon dioxide, protons and electrons that travel through the external circuit as the electric output of the fuel cell. At the cathode, oxygen from the air reacts with the protons that have traveled through the electrolyte and electrons from the external circuit to form water. The reactions that take place in the DMFC are thus the following:

Anode reaction: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$

Cathode reaction: $3/2\,O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$

Overall cell reaction: $CH_3OH + 3/2\,O_2 \rightarrow CO_2 + 2H_2O$

The operating temperature of the DMFC is low; cells have been tested in a temperature range from 50 to 120°C. This low operating temperature and no requirement for a fuel reformer make the DMFC an excellent candidate for very small to mid-sized applications. The low temperature operation of this fuel cell also has some drawbacks. The low-temperature oxidation of methanol to hydrogen ions and carbon dioxide requires a more active catalyst, which means a larger quantity of the expensive platinum catalyst. At the moment, an important handicap of the DMFC is the undesired methanol crossover through he membrane. Methanol is transported through the membrane to the cathode, where it is burned. This reduces the efficiency of the fuel cell [1]. Before these fuel cells can be applied as replacements of batteries still some extensive research has to be done. At the moment, research is mainly focused on increasing the efficiency of the DMFC (total efficiency is currently about 25% and the aim is to achieve 30%), miniaturizing the DMFC and extending its life. For high power application such as laptop computers and camcorders, it is necessary to enhance the cell performance further in order to compete with the lithium ion battery. The first applications are said to be envisaged for notebooks in the 50 Watt range. So far nobody developed more powerful DMFCs that could, for example, propel automobiles. This is due, in part, to the comparatively low power density of this type of fuel cell. The DMFC technology is also relatively new compared to that of fuel cells powered by pure hydrogen, and DMFC research and development are roughly 3-4 years behind that for other fuel cell types [4].

2.3 Methanol as a direct fuel in vehicles

Methanol has already been applied as a fuel for automotive applications. In the state California in the United States methanol is used as a fuel in flexible fuel vehicles (FFVs) [5]. These FFVs are specially designed vehicles that can operate on alcohol, gasoline or any combination of the two. In California, these FFVs are introduced to reduce pollution. A mixture of 85 % alcohol and 15 % gasoline can reduce hydrocarbon emissions by 30 to 40 % and up to 80 %, when pure methanol is used [11]. Methanol has also the advantage that it is safer in case of accidental fire than gasoline, because it burns cooler. The amount of energy in alcohols fuels is lower than gasoline, which will result in a shorter driving range. However, with larger fuel tanks, FFVs often have driving ranges equivalent to conventional gasoline cars.

3. Production of methanol

Methanol is a colorless and odorless liquid with the chemical structure CH_3OH. It is a commodity chemical and one of the top ten chemicals produced globally. The total world production of methanol is estimated to be 35 x 10^6 metric tonnes/year [20]. Typical world scale plants for the production of methanol from natural gas are in the range of 2000-3000 metric tonnes/day [20]. At the moment, the main application of methanol is as feedstock for producing formaldehyde; 35% of the world methanol production is used for the production of formaldehyde [14]. Furthermore, methanol is used as raw material for the production of methyl tertiary butyl ether (MTBE), a widely used additive in petrol. It is a liquid at ambient conditions, which facilitates transportation and handling. The introduction of methanol as a new energy carrier will result in an increase in the demand for this alcohol.

3.1 Conventional production of methanol

Methanol was originally recovered from wood as a by-product of charcoal manufacture and was often called “wood alcohol”. Pyrolysis (the decomposition of organic matter at high temperature in an inert atmosphere or vacuum) causes thermal cracking of the wood (or other organic material) and allows much of the wood to be recovered as charcoal. The watery condensate that is produced as a by-product of the pyrolysis, contains methanol amongst other compounds. Approximately 16 kg of methanol could be recovered per 1000 kg of air-dried wood that was carbonized [6]. Nowadays the major feedstock for the production of methanol is natural gas (and some coal and heavy petroleum fractions). This natural gas is converted to synthesis gas, a mixture of hydrogen, carbon monoxide and carbon dioxide. Now almost all of the methanol used world wide-wide comes from the processing of natural gas. In a typical world-scale methanol plant, synthesis gas is produced by steam reforming of natural gas feedstock and shift conversion of carbon monoxide to obtain the proper molar ration of hydrogen to carbon oxides [15]. Additionally, contaminants such as sulphur are removed. Methanol synthesis is then performed over copper-based catalysts at about 240 to 270°C. Because of equilibrium limitations, conversion of synthesis gas is only a few percent per pass in the catalytic reactor (the product gas contains about 5% methanol). After methanol separation, the product gas is recycled back to the reactor [15].

3.2 Production of methanol from biomass

Up to now, a lot of research has been focused on producing methanol in a more sustainable way. A promising method is the production of methanol from synthesis gas produced out of biomass. For the production of methanol from biomass generally the following steps are required:

- Gasification of the biomass to produce synthesis gas
- Gas upgrading (gas clean-up, CO-shift and CO_2-removal); to meet the requirements of the methanol synthesis
- Methanol synthesis and purification to meet the output specifications

Upgrading of the produced synthesis gas and methanol synthesis followed by purification are mature technologies. These processes are basic unit operations in the conventional methanol production process, where natural gas and coal are used as feedstock. The least developed step is biomass gasification. The gasification techniques are still at a relatively early stage of development using biomass feed, with no units operating commercially yet. The first step in the production of methanol from biomass is pretreatment of the biomass to meet the processing constraints of the gasifier. This typically involves size reduction and drying to keep the moisture contents below specific levels. The objective of the drying process is to decrease the moisture content of the fuel to a level suitable for use in the subsequent conversion process. Drying can be done via mechanical processes, thermal processes or in the open air. Mechanical drying (centrifuging, pressing) can only be used for very wet materials to be dried to a moisture content of about 50% (wet basis). Obtaining a moisture content below 50% requires thermal drying. Sizing is often performed for easy handling and easy combustion.

After the pretreatment step, gasification of the biomass takes place [18]. Biomass gasification involves heating biomass in the presence of low levels of oxygen, to prevent combustion of the biomass. The heat may be supplied by supplying oxygen to the gasifier and carrying out the partial oxidation of the biomass in the gasifier itself, or biomass, synthesis gas or char may be burned in a separate combustor and the heat transferred to the bed. If the partial oxidation is carried out in the gasifier, pure oxygen must be used to minimize the cost of compressing the synthesis gas to the pressure required for methanol synthesis, and to minimize the amount of gas, which must be purged to prevent a build-up of inerts (mainly nitrogen) in the methanol synthesis process. Above certain temperatures the biomass will break down into a gas stream and a solid residue. The gas stream contains hydrogen (18-20%), carbon monoxide (18-20%), methane (2-3%), carbon dioxide and nitrogen [19]. The exact composition of the gas stream is influenced by the operating conditions of the gasifier. The synthesis gas produced by biomass gasification also contains a range of contaminants, depending on feed and gasification process. Gas clean-up is required to prevent mechanical problems and deactivation of the methanol catalyst. Clean-up steps may include particulate removal, sulphur removal and scrubbing for chlorine compounds. Before the produced gas can be used for methanol synthesis, the gas must be further upgraded to meet the requirements of methanol synthesis. The synthesis gas produced in the gasifier has a H_2/CO ratio less than the 2.0 required for methanol synthesis. The H_2/CO ratio is increased in some cases by reforming any methane or hydrocarbons present [19]:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

and by running the water-gas-shift reaction, which trades carbon monoxide for additional hydrogen [19]:

$$CO + H_2O \rightarrow CO_2 + H_2$$

The resulting gases are sent to the methanol synthesis process, where the carbon monoxide and hydrogen are combined to produce methanol. Commercial methanol synthesis involves reacting carbon monoxide, hydrogen and steam over a copper-zinc oxide catalyst in the presence of a small amount of carbon dioxide at a temperature of 240 to 270°C and a pressure of about 70 bar [15]. The methanol synthesis reaction is equilibrium controlled and excess reactants must be recycled to obtain economic yields.

$$CO + 2H_2 \Leftrightarrow CH_3OH$$

$$CO_2 + 3H_2 \Leftrightarrow CH_3OH + H_2O$$

The two methanol forming reactions are coupled by the water-gas-shift reaction [15]

$$CO + H_2O \Leftrightarrow CO_2 + H_2$$

Because the per pass conversion of synthesis gas to methanol is equilibrium limited, a recycle process is used, where the methanol is separated from the product gases, and the unconverted synthesis gas is returned to the reactor. The methanol is then purified by distillation. The major advantage of the thermo-chemical conversion processes is that they use very high temperatures (approximately 1,000ºC) to break down the biomass to simple molecules such as CO, CO_2, H_2 and H_2O. Therefore, thermo-chemical conversion processes are relatively unaffected by the detailed structure of the biomass, and are capable of using the entire feedstock (cellulose, hemicellulose and lignin).

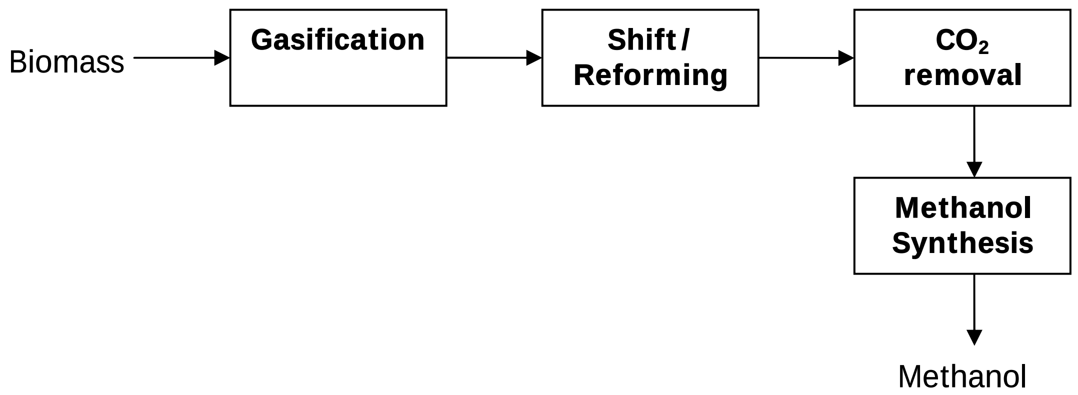

Figure 2. Thermo-chemical conversion of biomass to methanol [18]

At the moment, research is also focused on the possibility of performing biomass gasification as a two-stage process [16,17]. In the first stage, biomass is pyrolysed to yield bio-oil as main-product and gas and char as byproducts. Bio-oil is a complex aqueous mixture of simple aldehydes, alcohols and acids together with more complex carbohydrate –and lignin derived oligomeric materials. In the second step, catalytic steam reforming of the bio-oil takes place to hydrogen and carbon dioxide. An advantage of this two-stage gasification process is that bio-oil is much easier to transport than solid biomass and in this way pyrolysis and reforming can take place at different locations. The pyrolysis plants could be located at the sites where the biomass feedstock is available.

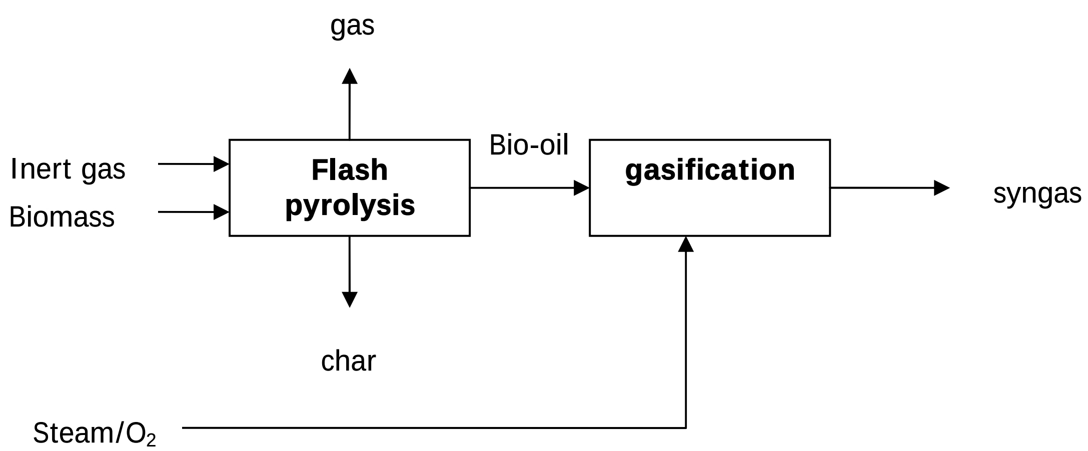

Figure 3. Synthesis gas production by a two-stage gasification process [16]

The produced oil can then be transported to the central reforming plant where synthesis gas and methanol are produced. In the fast pyrolysis process fine, low-moisture biomass particles are rapidly heated up to 500-600 °C at atmospheric pressure [16].
The vapors formed are quickly quenched to avoid secondary cracking, thus preventing a loss of product. Next to the liquid bio-oil product (70-80 wt%), some combustible gas and char is produced in the flash pyrolysis process. These can be used as fuels in the process or for local energy generation or other applications. Fast pyrolysis is a relatively new process and is not yet available for commercial application.

The advantage of the production of methanol from biomass is that when this methanol is used as a fuel and burned to carbon dioxide and water, no new carbon dioxide is added to the atmosphere. Biomass, when produced in a sustainable way, roughly emits the same amount of carbon dioxide during its plant growth as is emitted during its conversion and the combustion of products made from this biomass. The use of biomass therefore does not contribute to a build-up of carbon dioxide (an important contributor to global warming), in the atmosphere

4. Feedstock for methanol production

Considering the declining fossil fuel resources and the increasing demand for more sustainable production processes, biomass is a very good alternative as a renewable feedstock for the petro(chemical) industry and the energy sector. Biomass can be converted to products according to three general processes: biological conversion, thermo-chemical conversion and oil extraction (see figure 4). Biodiesel is mainly derived from oilseed crops through oil extraction and esterification. Ethanol can be derived from crops rich in cellulose, sugar and starch. Bio-oil, gas and heat are produced from dry matter. From figure 3, it becomes clear that for the production of methanol from biomass lingo-cellulose crops are the most suitable feedstock.

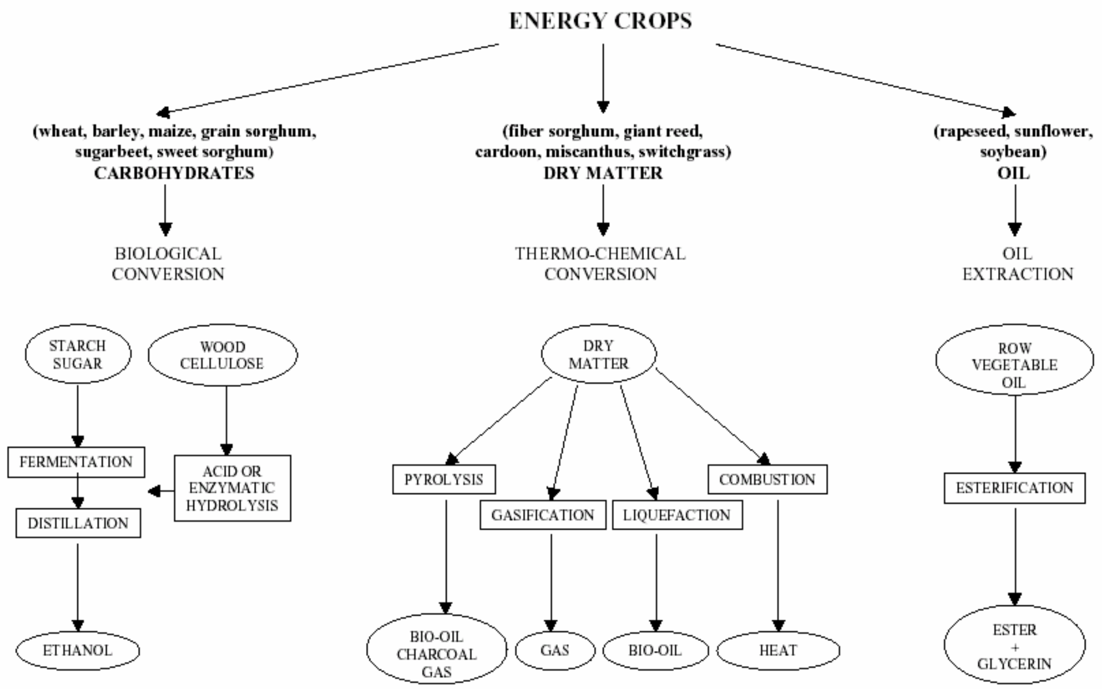

Figure 4. Main energy crops, conversion processes and available products for energy uses [7].

4.1 Feedstock requirements

An important step in the production of methanol from biomass, is the selection of an appropriate feedstock from the different crops that can be used for methanol production. For the successful placement of a crop in a certain area and the use of this crop as a feedstock for the methanol production process, it must comply with the following pre-requirements:

- The geographical and climate conditions must be suitable to grow the crop. These conditions include among others, the amount of rainfall in the area, the annual temperature profile, soil conditions and the presence of suitable nutrients.

- The energy crop cultivation must preferably result in uniform and continuous yield levels with respect to amount and quality. In this way, a more or less constant output of the crop is guaranteed, which is especially important when the crop is used as an input for an industrial production process.

- It must be relatively easy to introduce the crop in the area; it has to fit in with the existing agricultural knowledge and techniques. When an energy crop fits in well with the present knowledge and techniques of farmers, the commitment and willingness of farmers to grow the crop increases.

- The crop must result in high yield levels so growing of this crop is as little as possible in competition with the use of land for growing of crops for food production or other possible land uses (living, working, recreation etc.).

- Growing of the crop must result in a competitive income compared to the growing of traditional crops. The cultivation of energy crops must provide the farmers or landowners with an income comparable to the income obtained fro growing traditional agricultural crops. This could possible be achieved by giving them a subsidy.

- The crop must be resistant to major biotic and abiotic adversities. This reduces the input of pesticides and the probability of failing harvests

- Proper machinery must be available to harvest the crop. Ideally it should be possible to harvest the energy crops with machinery already owned by the farmers.

Because of competition for land, which can be used for wide range of goals, yield is probably after geographical and climate the main parameter for the selection of a certain crop. This is especially the case in the Netherlands, since the Netherlands is densely populated and space is scarce. For the production of methanol from the gasification of biomass lingo-cellulose crops are preferred. These lingo-cellulose crops can be further subdivided into woody crops and herbaceous crops. Wood feedstock comprises wood chips, wood powder and sawdust from ordinary forestry, short-rotation forestry, various wood residues and wood waste. Herbaceous feedstock includes specially grown energy crops and straw.

4.2 Herbaceous crops

Growing herbaceous crops for energy purposes is a relatively novel practice. The main herbaceous species currently considered in Europe for energy application are Miscanthus, red canary grass and switchgrass [8,9]. Miscanthus is a perennial crop. It is growing 2-3 metres a year after an initial period of three years. Miscanthus likes warmer climate and is restricted from the north by Denmark, southern Sweden, the UK and Ireland. Miscanthus has a great potential to be used as biomass energy crops. First of all because it can be harvested annually and has a lower moisture content when harvested compared to short rotation coppices. Furthermore, it has the advantage that growing requires lower input of fertilizers and pesticides compared to agricultural crops, while yields can reach 15 metric tonnes per hectare per year under optimum conditions [8,9]. Slightly lower maximum yields are earned from switchgrass, generally up to 10 metric tonnes per hectare per year [8]. Reed canary grass gives even lower yields, about 5-7 metric tonnes per hectare per year, but it fits well the climate conditions of Nordic countries [8]. Reed canary grass is very invasive of wetlands and is not a suitable alternative to agricultural crops on high grades of arable land. The advantage of herbaceous species is that they have a lower moisture content than wood. The disadvantage is the lower bulk density, which increases transportation and handling costs; a larger content of undesirable compounds compared to woody crops (potassium, sulphur, ash), which may cause problems during synthesis gas production.

Figure 5: Miscanthus (left), reed canary grass (center) and switchgrass (right)

Another good herbaceous crop as a feedstock for methanol production is hemp, a crop that has been traditionally grown as a fiber crop. Hemp is fast growing but an annual crop and it is more or less similar to maize. From experience, obtained in the Netherlands from hemp cultivation for pulp, the yield is 10-17 odt/ha (odt = oven dry (0% moisture) tonnes) with the best figures for clay soils [8]. Herbicide treatment is not required since the crop can successfully compete with weeds for resources, but fungi can substantially harm the crop in wet years, however this could be solved by selection and breeding [8]. From environmental point of view, hemp seems to be environmentally friendly since it requires low input of fertilizers and pesticides, has relatively high output. Standard machines could be used for sowing and the crop fits well into crop rotation. However, public perception of the crop should be taken into consideration before wider implementation of hemp in agriculture.

Aside from these herbaceous crops, residues from agricultural crops can also be used for the production of methanol. Agricultural crops that are suitable for methanol production are cereals (wheat, barley, rye). An advantage of growing cereals is that they are traditional food crops and there is a lot of knowledge of their cultivation. Another advantage of using cereals is that the straw can be used for the production of methanol, whereas the grains can be used for consumption purposes. Similar to herbaceous crops, straw usually has lower moisture content than woody biomass. However, it has a higher content of ash and problematic inorganic components such as chlorine, potassium and sulphur then the perennial grasses, which cause corrosion and pollution [9].

4.3 Woody crops

To minimize the amount of land that is required to grow woody crops, it is important that the trees that are used for the production of methanol are fast growing trees. In this way the harvest per hectare of land are maximized. Fast growing trees include poplar, willow and eucalyptus [8]. For the Dutch climate, poplar and willow are more convenient than eucalyptus that normally grows in warmer areas. Eucalypt is a very frost sensitive species and therefore cannot be grown in northern Europe. The disadvantage of growing willow and poplar is that they are not traditional agricultural crops and therefore it is expected that their introduction to agricultural practice is a long process. Willow is harvested in 2-4 year intervals, when the shots are approximately of 6 meter of height, normally in winter in order to reduce the moisture content. After harvesting, willow stumps are left to coppice and another crops grows in 2-4 years [9]. Poplar needs longer harvest intervals, 8 to 15 years [9]. Yields of short-rotation forestry can reach 10 to 15 metric tonnes per hectare per year [9]. The long crop-rotation and the risk of increased pest problems are among the barriers for the introduction of willows. With poplar the risk of pest problems is smaller as good disease resistant clones are available. However, the longer crop-rotation is a disadvantage. The cultivation of wood also has some environmental benefits compared to growing conventional annual crops, like less soil disturbance and lower fertilizer and pesticide inputs. Furthermore, good habitats are created for insects, birds and mammals and the short-rotation forests can potentially be used for recreation.

4.4 Selection of feedstock for methanol production

In general, the characteristics of the ideal energy crop are: high yield (maximum production of dry matter per hectare), low inputs, low costs, low composition of contaminants and nutrients and high pest resistance. Of course, not one crop has all these characteristics and therefore a choice must be made from the available crops to select the most optimal crop that can be cultivated in the Netherlands.

Conventional agricultural crops such as wheat, rye and barley have the advantage that farmers already know how to grow them. The problem is that these crops require higher input and annual ploughing, which leaches nitrates and other nutrients from the soil. Also the higher content of ash and inorganic components in the straw can cause problems during gasification and further production steps [10]. Like conventional agricultural crops, hemp is an annual crop and therefore more labor-intensive. However, inputs of fertilizers and pesticides are low. The main problem with hemp is also the public perception of the introduction of hemp as an energy crop.

In this perspective, perennial energy crops such as willow, poplar and Miscanthus are more interesting. Compared to traditional crops, the perennials need lower inputs are less labor-intensive and pose much less risk of nutrient leaching. Moreover, biomass from perennial crops contains lower levels of nutrients, which means more efficient use of nutrient input and better combustion characteristics [10]. On the other and, perennial energy crops are still relatively new and do not benefit from the centuries of selection and breeding associated with conventional crops. Much progress in improving yield and quality remains to be made through better breeding and crop management.

A disadvantage of the production of woody crops and Miscanthus is that converting agricultural land to produce these energy crops requires a long-term commitment by the farmer. Establishment costs are high and it will take several years before the crop yields are at their full potential. Poplar and willow are established by planting stem cuttings and Miscanthus is established by the planting of rhizomes [10]. Both techniques are labor intensive and thus costly. However, research is focused on establishing Miscanthus from seed [10]. If this is possible this will considerably reduce the establishment costs. The other perennial grasses have lower establishment cost as they are grown from seeds. The advantage of herbaceous crops over woody crops is that they result in annual yields; herbaceous crops can be harvested annually, whereas woody crops are harvested in intervals of a couple of years. With woody crops, conversion of land back to conventional agricultural crops will require significant effort due to the presence of roots. In table 1, an overview is shown with information current available for the different perennial crops.

Table 1. Overview with information currently available for perennial crops [10]

Crop	*Poplar*	*Willow*	*Miscanthus*	*Switchgrass*	*Reed canary grass*
Current typical yield t	10-15	10-15	15	10	5-7

dry mater ha^{-1}					
Establishment time	3 years +	3 years +	3 years +	2-3 years +	1-2 years
Pesticide requirements	Low	Low	Low	Low	Very low
Fertiliser requirements	Low/medium	Low/medium	Low	Very low	Medium
Agronomic knowledge	Good	Good	Reasonable	Low	Low
Establishment costs	High	High	Very high	Very low	Very low
Pest/disease problems	?	Beetle rust	None serious	None serious	Possible insect pest problems
Plantation longevity	20 years +	20 years +	20 years + ?	20 years + ??	10 years + ??
Other issues	Resistant to lodging	Resistant to lodging	Resistant to lodging	-	-

Based on the advantages and disadvantages of growing the different woody and herbaceous crops, Miscanthus seems to be the most promising energy crop for the Netherlands. As already mentioned, high yields per acre are very important in a densely populated country as the Netherlands. From all the crops suitable for cultivation in the Netherlands, Miscanthus has the highest yields. And there is scope for significant increase in yields as relatively little research has conducted on this grass. It is not unreasonable to expect Miscanthus yields of about 25 metric tones per hectare during the next 20 years [10]. Furthermore, establishment costs could also be reduced greatly when it becomes possible to grow Miscanthus from seeds. Other advantages of Miscanthus are its low fertilizer and pesticide requirements.

5. Methanol production in the Netherlands

After the selection of the optimum crop for methanol production in the Netherlands and the selection of the optimal biomass gasification process and methanol production process, an important question is: *How much methanol could possibly be produced in the Netherlands?* In this report it is supposed that an area as big as the province Flevoland is dedicated to the cultivation of Miscanthus. It is assumed that this area is suitable for growing Miscanthus and optimal yields as reported in literature can be obtained.
The area of the province Flevoland amounts approximately 97,000 hectare. All the Miscanthus, grown on this area is used for the production of methanol from synthesis gas, produced via the gasification of Miscanthus. When cultivating Miscanthus, the yield per acre amounts roughly 15 odt/hectare. Since Miscanthus can be harvested only ones a year, this amount of biomass is available in one year for the production of methanol. Miscanthus that is not used directly for the production of synthesis gas should be stored until it is used in the plant. The annual harvest of Miscanthus grown on an area of 97,000 hectare amounts 1.455 million metric tonnes of Miscanthus.

It is assumed that methanol is produced from synthesis gas produced by the gasification of biomass. This process is better developed than the relatively new two-stage gasification process with fast pyrolysis. It is estimated that for the production of methanol from cereal straw with 80% dry matter, about 2.4 metric tonnes of straw are required per metric tonne of methanol produced. Another 0.4 metric tonnes of straw are required as a fuel in the gasification process [12]. This indicates that the combined requirement for feedstock and fuel is 2.8 metric tonnes straw per metric tonne methanol produced. Assuming that similar ratios are obtained for Miscanthus, an annual harvest of 1.455 million metric tonnes of Miscanthus can result in the production of roughly 520,000 metric tonnes of methanol or equivalently 657,000 m^3 methanol. However, in this case the energy required for harvesting, transportation, pre-treatment, methanol production etc are not taken into account. If the yields of Miscanthus can be increased to 25 odt/hectare by selection and breeding, the methanol production can be increased to 866,000 metric tonnes or equivalently 1,095,000 m^3 methanol.

In the Netherlands, methanol is produced by the company Methanor located in Delfzijl. The production capacity of this plant is about 900,000 metric tonnes a year and natural gas is used as feedstock [13]. The amount of biomass that can be produced in the Netherlands by the cultivation and gasification of biomass on an area as big as the province Flevoland is about twice as small as the amount of methanol that can be produced annually by the conventional methanol plant in Delfzijl. When methanol is used as an energy carrier, the production of methanol must increase considerably. The production of methanol could be increased by converting not only Miscanthus, but also wood residues and agricultural residues to synthesis gas. In addition, it is possible to import large amounts of biomass from for example Scandinavia or the Baltic countries, where extensive forests are present. This should be the only option for producing enough methanol in the Netherlands to use methanol as a power source. The Netherlands itself is too small and too densely populated to be self sufficient in the production of its own biomass for the production of methanol used as main energy carrier.

6. Conclusion

This report has shown that methanol instead of hydrogen could be an interesting energy carrier for the future. Methanol can be used in different ways as energy source. It can be used in fuel cells for stationary electric power generation, for vehicle motive power and to produce electricity for portable electronic devices. Furthermore, it can be used as a fuel in conventional combustion engines. Methanol is also an important industrial chemical. Nowadays, methanol is mainly produced from natural gas. However, present research is focused on more sustainable routes to produce methanol. The most promising route for the production of methanol is by gasification of biomass to produce synthesis gas, that in turn is converted into methanol. In the Netherlands, the most suitable biomass for methanol production are energy crops that result in high yields per acre. Of the woody crops willow and poplar are more suitable to grown in the Netherlands, whereas Miscanthus, switchgrass and hemp are good herbaceous crops. Miscanthus is chosen as most suitable energy crop to be grown in the Netherlands, because of its high yields, low fertilizer and pesticide inputs. At the moment, establishment costs for Miscanthus are high, but this could be reduced when more research is devoted to growing Miscanthus from seeds instead of rhizomes On an area as big as the province Flevoland, 1.455 million tonnes of Miscanthus can be produced that can be converted to 657,000 m^3 of methanol. This is about half of the amount that is produced by a full-scale methanol plant. If we want to use methanol as a new energy carrier the production of methanol should be increased considerably. The production of methanol from biomass could be increased by converting in addition to Miscanthus, also agricultural and wood residues and by importing biomass from other countries.

Literature

1. Fuel Cell Handbook, US Department of Energy, National Energy Technology Laboratory, 5th Edition, Morgantown, (2000)
2. http://www.idatech.com/solutions/multi_fuel_solutions/methanol.html
3. http://www.toshiba.co.jp/about/press/2004_06/pr2401.htm
4. http://www.eere.energy.gov/hydrogenandfuelcells/fuelcells/fc_types.html
5. http://www.epa.gov/otaq/consumer/fuels/altfuels/420f00040.pdf
6. http://www.rirdc.gov.au/reports/AFT/02-141.pdf
7. P. Venturi and G. Venturi, Analysis of energy comparison for crops in European agricultural systems, Biomass and Bioenergy, 25, 235-255 (2003)
8. R. Venendaal, U. Jørgensen and C.A. Foster, European energy crops: a synthesis, Biomass and Bionenergy, 13(3), 147-185 (1997)
9. http://www.cse.csiro.au/publications/1999/biomasseconomy-99-07.pdf
10. D.S. Powlson, A.B. Riche and I. Shield, Biofuels and other approaches for decreasing fossil fuel emissions from agriculture, Annals of Applied Biology, 146, 193-201 (2005)
11. www.epa.gov/otaq/consumer/fuels/altfuels/420f00040.pdf
12. http://www.cse.csiro.au/publications/1999/biomasseconomy-99-07.pdf
13. http://www.methanor.nl/main.htm
14. http://www.ecn.nl/docs/library/report/2001/i01001.pdf
15. J.A. Moulijn, M. Makkee and A. Van Diepen, Chemical Process Technology, John Wiley and Sons, New York (2001)
16. http://egov.oregon.gov/ENERGY/RENEW/Biomass/bioenergy.shtml
17. http://bioproducts-bioenergy.gov/pdfs/bcota/abstracts/23/87.pdf
18. http://www.vtt.fi/virtual/amf/pdf/annex_iv_final_report.pdf
19. http://www.rirdc.gov.au/reports/AFT/02-141.pdf
20. tccb.tnw.utwente.nl/docs/Routes%20to%20methanol.pdf