



Report

Overview of biogas technologies for production of liquid transport fuels

Carried out by:

Danish Technological Institute
Laura Bailón Allegue and Jørgen Hinge
Kongsvang Allé 29
DK-8000 Aarhus C

Date: December 2012



Content

1	INTRODUCTION	3
2	LIQUEFIED BIOGAS (LBG)	4
2.1	Upgrading and cleaning followed by a liquefaction plant	4
2.2	Conventional upgrading technologies	6
2.2.1	Cleaning technologies	10
2.2.2	Liquefaction.....	12
2.3	Cryogenic technologies	13
2.3.1	Scandinavian GtS	14
2.3.2	Prometheus Energy	15
2.3.3	Terracastus Technologies/Acrion Technologies.....	15
3	FUEL PRODUCTION FROM BIO-SYNGAS	16
3.1	Hydrogen	17
3.2	Methanol	17
3.3	Dimethyl ether (DME)	18
3.4	Fisher-Tropsch (FT) fuels	19
4	USE OF BIOGAS AS VEHICLE FUEL IN DENMARK	19
	REFERENCES	22
	ANNEX 1	25



1 Introduction

The EU Renewable Energy Directive (RED) states that each EU Member State shall ensure that the share of energy from renewable sources in all forms of transport in 2020 is at least 10%.

Transport is the second biggest greenhouse gas emission sector, being responsible of around a quarter of EU greenhouse gas emissions. Road transport alone contributes about one-fifth of the EU's total emissions of carbon dioxide. While different sectors have been showing positive results in the previous years on emission reduction, the transport sector has shown an increase of 36% from 1990 to 2007 (Climate Action, 2011). In Denmark the transport sector accounted for 32.2% of total CO₂ emissions in 2010, the road transport being responsible for 77.5% of the total CO₂ emissions of the whole transport sector (Øresund Ecomobility, 2012).

Research and the effective development of new technologies will be the key to lower transport emissions and oil dependency issues. A priority will be on producing clean, safe, and quiet vehicles for all transport modes.

Biogas and bio-syngas as transport fuels can play an important role in the change towards a sustainable transport sector.

By removing carbon dioxide, moisture, hydrogen sulfide and other impurities biogas can be upgraded to biomethane, a product equivalent to natural gas. Biomethane can be used as compressed natural gas (CNG) in natural gas vehicles or it can be transform into a liquid energy carrier like liquefied biomethane (LBM) as well called liquefied biogas (LBG) when coming from biogas, which is analogous to liquefied natural gas (LNG). Biomethane can also be reformed to bio-syngas which is the basis for production of various fuels such as methanol, dimethyl ether, hydrogen and liquid hydrocarbons that can replace gasoline and diesel fuels.

There is considerable interest in the production of renewable liquid fuels which could be used more directly in the existing transportation fleet and could overcome the volume, range, and weight limitations imposed by compress biomethane (CBM), also called compress biogas (CBG) when coming from biogas. The use of biomethane in liquid form has special focus on long road distance transport, countries with no natural gas infrastructure and even maritime transport.

Biogas leads not only to environmental benefits such as reduced emissions of carbon dioxide and air pollutants, several additional environmental benefits can be gained (e.g. reduced emissions of ammonia and methane and nitrogen leaching). Other advantages of biogas as a transport fuel, as compared with other renewable transport options, are that its production can be localized, anywhere, urban or rural, it is not dependent on foreign markets, neither on large mono-crop production, but can be produced locally from a diverse range of organic wastes or energy crops.

The optimum use for biogas is always case specific, depending on the objectives, the feedstock, the scale and the location of the plant. In most European countries, until now, policy and incentives have favored the use of biogas to produce renewable electricity. But considering the fact that other renewable options (such as solar, wave/tidal power and wind) produce electricity directly, biogas could perhaps be better utilized in contributing to the sustainable production of transport fuel.



2 Liquefied Biogas (LBG)

Liquefied biogas has a better energy density compared to compressed biogas but still lower compared to diesel (1.7:1). However, its energy density is still better compared to liquid methanol and similar to ethanol.

The main advantages of LBG comparatively to the CBG are:

- It is a more valuable product since LBG is around 3 times more space efficient compared to compressed biogas. This means that LBG can be more easily transported on road to remote refueling stations when there is lack of natural gas grid infrastructure. For the same reason, LBG is the better option when shipping biogas overseas,
- LBG has a higher vehicle driving range, thereby, methane vehicles are getting competitive also for mid- and long distances; especially if the vehicles are also equipped with the engine technology dual-fuel, i.e. engines with compression ignition using both methane and diesel as fuel, and
- LBG can be dispensed to either LNG vehicles or CNG vehicles. The latter is made possible through liquid-to-compressed natural gas refueling station equipment which creates CNG from LNG feedstock.

Liquid natural gas is transported at relatively low pressures (e.g. 1.5 – 10 bar), but because it is a cryogenic liquid (i.e., temperatures well below -100 °C) it requires special handling.

Liquid biogas can be produced in two main ways and these are by means of cryogenic upgrading technology and conventional upgrading technologies connected to a liquefaction plant. A third alternative is to inject biomethane into the gas grid and then liquefy a part-flow at a pressure letdown station.

According with Johansson (2008), it takes around 0.8 – 1.8 kWh electricity/Nm³ clean biogas to produce LBG, which correspond to 8 – 18% of the energy content in the product. Johansson estimated the energy consumption of different alternatives and concluded that the most energy efficient ways to produce LBG are to use one of the conventional upgrading technologies; water scrubber, PSA or Coab (including heat recovery), connected with a mixed refrigerant process or to use the cryogenic GtS process (described in Chapter 2.3.1). In the last 5 years cryogenic technologies as well as small size liquefaction plants have been under constant development and it is now when the first cryogenic plants begin to run and information on commercial system is available. So Johansson data must be reviewed, but it gives a first general estimation.

2.1 Upgrading and cleaning followed by a liquefaction plant

To be able to use raw biogas as vehicle fuel it must first be cleaned and upgraded to biomethane. Cleaning means that contaminants like H₂O, H₂S, and particles and, if present, siloxanes and halogenated compounds are removed from the gas stream to avoid problems with corrosion, deposits and mechanical wear. While upgrading means that the biogas energy content is raised through removal of CO₂.

In Annex 1 typical biogas compositions as function of the main biogas sources are given.

After the cleaning and upgrading the biomethane can be transformed in LBG. There are two main working principles for biogas liquefaction, namely closed-loop or open-loop cycles.



To prevent dry ice formation and corrosion in the downstream liquefaction step, the components in the upgraded biogas need to live up to the concentrations in Table 1. LBG must also comply with the national standards for vehicle utilization or/and the vehicle manufacturer standards. If the upgrading process does not meet these requirements an extra polishing step is needed before liquefaction.

Table 1: Maximum component concentrations to be able to liquefy biogas (Johansson, 2008)

Component	Requirement
CO ₂	< 25 ppmv
H ₂ S	< 4 ppmv
H ₂ O	< 1 ppmv

There is a lack of national standards for LBG. To date the only specific standard for biomethane used as vehicle fuel is the Swedish standard SS 155438. "Motor fuels – Biogas as fuel for high-speed Otto engines". This standard contains two types: type A, for engines without lambda control and B, for engines with lambda control. Table 2 presents the details for type A (the one with most stringent requirements). At European level the European Committee for standardization created in 2011 a working group (TC 408) to set common standards on the injection of non-conventional gases, including biogas, into natural gas grids and on biogas use as vehicle fuel.

Table 2: Swedish Standard for biogas as vehicle fuel, SS 155438, type A (Johansson, 2008)

Properties:	Value:
Wobbe Index (MJ/Nm ³)	44.7–46.4
Water content max. (mg/Nm ³)	< 32
Water dew point (°C) (t = lowest average daily temperature on a monthly basis)	< t-5
CH ₄ (vol.-%)	97±1
CO ₂ +O ₂ +N ₂ (vol.-%)	< 4
O ₂ (vol.-%)	< 1
Total sulfur content, max. (mg/Nm ³)	10
Total content of nitrogen compounds (excluding N ₂) as NH ₃ , max. (mg/Nm ³)	20
Particle size, max.	1

If the biogas production and upgrading plant are situated close to the gas network one option could be to inject upgraded biogas into the gas grid and then produce LBG at a pressure letdown station.



2.2 Conventional upgrading technologies

The most common solutions for separation of CO₂ from CH₄ are:

- Adsorption: Pressure Swing Adsorption (PSA)
- Absorption: water scrubbing, physical absorption and chemical absorption
- Membrane separation: high pressure and low pressure

A brief description of these technologies is summarized in Table 3. More detailed information can be found in several reports and articles (Hullu, 2008; BC Innovation Council, 2008; Hagen, 2001; Persson, 2006; Persson, 2007; Petersson, 2009; Petersson and Welling, 2009; Beil, 2010; Ryckebosch, 2011).

Table 3: Short description of the most common upgrading technologies

<i>Adsorption:</i>
<p>CO₂ is adsorbed from the biogas stream on a material like activated carbon or molecular sieves. The most common adsorption process is the Pressure Swing Adsorption (PSA)</p> <p>– Pressure Swing Adsorption: A PSA plant consists of a series of vessels filled with adsorption material, working on 4 different phases: adsorption, depressuring, regeneration and pressure build-up. When the adsorption material is saturated in one column, the gas flow is led to the next, while reducing the pressure regenerates the saturated column, as it makes the adsorbed molecules to leave. The pressure is firstly reduced to atmospheric and then to a light vacuum. The vent from the first stage contains significant amounts of CH₄ and therefore it is sent back to the gas inlet, in order to keep the CH₄ losses low. In the second stage the vent mainly consists of CO₂ and is vented to the atmosphere.</p> <p>Before entering the adsorption column the gas needs to be dry and free from H₂S, to avoid the irreversible adsorption of the same in the adsorption material.</p> <p><i>PSA providers:</i> Acrona-systems, CarboTech, Cirmac, Guild, and Xebec/QuestAir</p>
<i>Absorption:</i>
<p>The pure physical absorption technology uses the differences in binding forces in different molecules to separate CO₂ and other compounds as H₂S from CH₄. CO₂ and H₂S are more polar and therefore more soluble in a polar absorption fluid than the non-polar CH₄. The adsorbent liquid can also react with the CO₂, driving the absorption toward completion. This process is called chemical absorption.</p> <p>– Water scrubbing: CO₂, H₂S and NH₃ are physically dissolved in water under pressure in an absorption column. Water leaving the column is enriched with CO₂, but also with small amounts of dissolved CH₄. After the column the water passes through a flashing tank, where the pressure is reduced, which releases the CH₄. The vent from the flashing is then sent back to the gas injection, reducing the CH₄ losses in the process. The water can be used just one time (single pass adsorption) or it can be reused by treating it in a desorption column where the CO₂ and other contaminants are removed (regenerative adsorption).</p> <p>In non-regenerating process, water use is approximately 150 l/Nm³ raw biogas. A hundred times less water can be consumed by a plant reusing its water, although this depends on several factors of which H₂S concentration is the most important.</p> <p><i>Water scrubbing providers:</i> Artic Nova/Biosling, ETW Energietechnik, Econet, Greenlane Biogas (Flotech group), Malmberg Water, Metener Ltd, RosRoca, Verdesis, Xebec/QuestAir.</p>



– **Physical absorption:** instead of water organic solvents are used as absorption fluid. Besides CO₂ also H₂S, NH₃ and H₂O can be separated. Solvents come in different forms and brands, including polyethylene glycol, Selexol[®], Genosorb[®]. Smaller plants can be built compared to the water scrubbing because the solubility of CO₂ is higher in these liquids than in water. H₂S is also highly soluble in organic solvents, so the higher H₂S concentration the higher temperature process is required to regenerate the solvent. Due to absorber costs and the disposal of contaminated absorber, the absorber is always regenerated. Additional drying of the upgraded gas is not necessary due to absorption of water by the organic solvent.

Physical absorption providers: HAASE, Clariant, Uop LLC.

– **Chemical absorption:** solvents as mono-ethanol amine (MEA) or di-methyl ethanol amine (DMEA) which react chemically with CO₂ are used. Amines are highly CO₂ selective, and result in minimal losses of CH₄, but they are toxic to humans and the environment and require significant energy consumption for regeneration. As in physical absorption, in chemical absorption regeneration always is carried out. The preliminary purification of the biogas is very demanding (< 6 ppm H₂S, low oxygen) to avoid corrosion, undesirable chemical reactions and higher temperatures for the regeneration.

Chemical absorption providers: AmmonGas, Biogast, BIS E.M.S. GmbH, CarboTech, Cirmac, DGE, Dreyer & Bosse, Hera, Läckeby Water Group AB, MT-Biomethan, MT-Energie, Strabag.

Membrane technology:

In a membrane separation system CO₂ and other components as H₂O, H₂S and NH₃ are transported through a thin membrane to higher or lesser extent while CH₄ is retained, due to difference in particle size and/or affinity. Two basic systems exist: gas-gas or dry membranes and gas-liquid membranes.

– **Dry membranes:** are membranes with a gas phase on both sides and the driving force is the differences in partial pressure. CO₂ permeates to the low-pressure side, while CH₄ stays under pressure. A major disadvantage of this technique is the low methane yield. Due to imperfect separation the raw gas can be purified to maximum 92% CH₄ in one step. When two or three steps are used, a gas with 96% or more CH₄ is achieved. Methane losses can be partly prevented by recirculation of a part of the permeated CO₂-enriched gas.

The membranes separate some H₂S but since H₂S is corrosive it is recommended to remove it before the process. Also, the gas needs to be compressed and dried.

Membrane providers: Air Liquide, BebraBiogas, Cirmac, DMT, Evonik, Gasrec, Haffmans, Memfoact, Terracastus Technologies.

– **Gas-liquid membranes:** Gas-liquid absorption membranes for upgrading biogas have been developed only recently and are still in research and development phase. A micro porous hydrophobic membrane separates the gaseous stream from a liquid phase. CO₂ from the gas stream diffuse through a membrane being absorbed by the liquid phase flowing in counter current. Liquid is prevented from flowing to the gas side due to slight pressurization of the gas. The removal of CO₂, carried out with an amine solution, is very efficient and biogas can be upgraded to more than 96% CH₄ in one step. The amine solution can be regenerated by heating, which releases a pure CO₂-flow which can be sold for industrial applications.

Table 4 shows some of the most relevant technical data when comparing different technologies. In practice local conditions are very different (water supply, available heat, emission limits, etc.), therefore there is not a best technical solution available on the market; all of them have their advantages and disadvantages. A deep study must be done for each specific project. Investment cost, operation costs and maintenance costs are always taken into consideration as well as plant



capacity. The operational costs are determined by the use of chemicals and by the use of energetic or physical aid streams, like heat or water, while other techniques might require electricity (pressure and/or cooling). When the installation is located near an entity that has an excess of heat, a technique that requires heat as the amine gas cleaning can be an economical relevant choice. A lot of the choices are determined by the presence or the absence of suppliers for the technology in the particular country. In Sweden, water scrubbers are used mostly. In Germany they prefer PSA and chemical scrubbing units and in The Netherlands they rather chose water scrubbers, PSA-units as well as membrane technology.

In order to make a correct comparison of investment and operation cost, the necessary costs for pre/post treatment also need to be taken into consideration, as well as the savings in useful utilization of residues. Price comparison of the 'basic installation' usually give a false picture, because one supplier integrates all process stages into a single installation, and another takes a different approach. In a report published at the end of 2008 the German Fraunhofer UMSIGT compared gas scrubbing and PSA techniques of various manufactures (Figure 1) (Petersson, 2009). The investment costs of a 500 Nm³ capacity plant were around one million euro. The scale advantages are considerable, particularly when scaling up from 250 to 500 Nm³. Today, there are commercially available plants for capacities lower than 250 Nm³/h, while also plants larger than 2000 Nm³/h are being built (Petersson and Wellinger, 2009).

Table 4: Comparison of different commercial upgrading technologies. Values are dependent on the size of the plant and the specific commercial technology

	PSA	Water scrubbing	Physical scrubbing	Amine scrubber	Membrane separation
Electricity consumption (kWh/Nm ³)	<i>kWh/Nm³ raw biogas:</i> <ul style="list-style-type: none"> • 0.23¹ • < 0.3⁵ • 0.25⁶ <i>kWh/Nm³ clean biogas:</i> <ul style="list-style-type: none"> • 0.29 – 0.43⁹ • 0.3 – 1.0 suppliers data⁴ • 0.5 – 0.6 Swedish plants data⁴ 	<i>kWh/Nm³ raw biogas:</i> <ul style="list-style-type: none"> • 0.3¹ • <0.25⁵ <i>kWh/Nm³ clean biogas:</i> <ul style="list-style-type: none"> • 0.4 (0.3 – 0.6)² • 0.3⁷ • 0.4 – 0.5⁷ With regeneration ⁴ : <ul style="list-style-type: none"> • 0.45 – 0.9 suppliers data • 0.3 Swedish plants data No regeneration ⁴ : <ul style="list-style-type: none"> • 0.45 – 0.9 suppliers data • 0.4 – 0.6 Swedish plants data 	<i>kWh/Nm³ raw biogas:</i> <ul style="list-style-type: none"> • 0.2 – 0.3¹ <i>kWh/Nm³ clean biogas:</i> <ul style="list-style-type: none"> • 0.4 (Selexol) Swedish plants data⁴ 	<i>kWh/Nm³ raw biogas:</i> <ul style="list-style-type: none"> • 0.1 – 0.15¹ • 0.05 – 0.12⁶ (Cirmac) • 0.2 – 0.25⁶ (DMT) <i>kWh/Nm³ clean biogas:</i> <ul style="list-style-type: none"> • 0.12 (LP Cooab)² • 0.15 suppliers data⁴ • 0.18⁷ 	<i>kWh/Nm³ raw biogas:</i> <ul style="list-style-type: none"> • 0.18¹ • 0.20⁶ <i>kWh/Nm³ clean biogas:</i> <ul style="list-style-type: none"> • 0.14² • 0.26⁷
Heat consumption (kWh/Nm ³) and Heat demand (°C)	None	None	<i>kWh/Nm³ raw biogas:</i> <ul style="list-style-type: none"> • < 0.2¹ 55 – 80 °C ⁸	<i>kWh/Nm³ raw biogas:</i> <ul style="list-style-type: none"> • 0.5 – 0.75¹ <i>kWh/Nm³ clean biogas:</i> <ul style="list-style-type: none"> • 0.2⁷ 100 – 180 °C ⁸	None



	PSA	Water scrubbing	Physical scrubbing	Amine scrubber	Membrane separation
CH ₄ losses (%)	2 – 4 ¹ 2 – 10 ^{2,8} 1 – 3 ⁶ 2 – 5 ⁵ 2 ⁷	1 – 2 ^{1,8} < 1 ⁵	< 2 ¹ 2 – 4 ⁵ 1 – 4 ⁸	< 0.1 ^{1,5,8} 0.1 – 0.2 ⁶	~ 2 ^{1,7} 3 – 5 ⁸ 15 – 20 ⁶ (without using residue gas)
CH ₄ recovery (%)	83 – 99 ^{1,3} < 96 ⁵ > 96 ⁸ Max. 98 ⁶ VPSA = 97 ²	< 97 ^{1,5} > 97 ^{2,8} 98.5 ⁵ 96 – 98 ⁹	93 – 97 ¹ > 97 ⁸ > 99 ⁵	97.5 – 99.5 ¹ 99.9 ² > 99 ^{3,5,8} > 99.5 ⁷ 95 – 98 ⁷	90 – 98 ¹ 82 ² 90 ^{3,5} 90 – 93.5 ⁷ 98 ¹ 96 – 98 ⁸
Pre-purification	Yes	Recommended roughly	Recommended roughly	Yes	Recommended
H ₂ S co-removal	Possible	Yes	Possible	Contaminant	Possible
N ₂ and O ₂ co-removal	Possible	No	No	No	Partial
Operation pressure (bar)	3 – 5 ¹ 4 – 7 ⁵ 6 – 8 ⁶ 4 – 10 ⁸	4 – 7 ^{1,5} 4 – 10 ⁸	4 – 7 ^{1,5} 4 – 8 ⁸	Atmospheric ^{1,5}	5 – 7 ¹ 6 – 8 ^{5,8}
Pressure at outlet (bar)	4 – 5 ¹	7 – 10 ¹	1.3 – 7.5 ¹	4 – 5 ¹	4 – 6 ¹

¹ Different companies data; ² Bekkering, 2010; ³ BC Innovation Council, 2008; ⁴ Persson, 2007; ⁵ Mezei, 2010; ⁶ Sternovem; ⁷ Jonsson, 2011, ⁸ Biomass for Energy, 2012

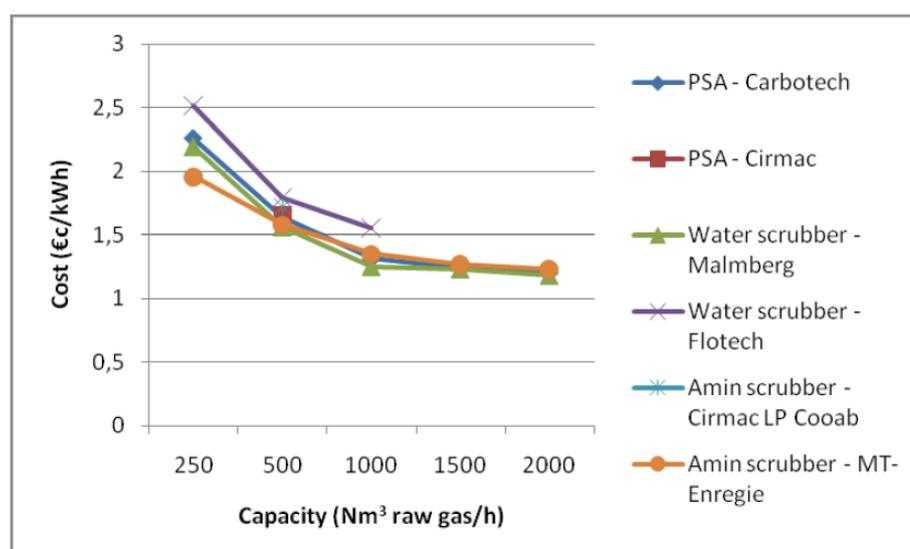


Figure 1: Common commercial upgrading technology costs (Pettersson, 2009)



2.2.1 Cleaning technologies

Apart from CH₄ and CO₂, biogas can also contain H₂O, H₂S, O₂, N₂, NH₃, siloxanes, and particles. In those upgrading technologies where CO₂ is separated from biogas, some of the other unwanted compounds are also separated. However, to prevent corrosion and mechanical wear of the upgrading equipment itself, it can be advantageous to clean the gas before upgrading.

Table 5 indicates the main cleaning technologies for different compounds. A more detailed description of these technologies can be found elsewhere (Ajha, 2010; Cline, 2002; Environment-Agency, 2004; Kohl, 1997; Krich, 2005; McKinsey, 2003; Petersson and Wellinger, 2009; Ryckebosch, 2011; Shareefdeen, 2005; Wellinger, 2000; Zappa, 2001).

Table 5: Short description of the main cleaning technologies for different biogas contaminant compounds

<i>H₂S removal:</i>
<p>Hydrogen sulfide (H₂S) is corrosive to most equipment; furthermore its combustion leads to sulfur dioxide emissions, which have harmful environmental effects. It is recommended to remove it early in the process of biogas upgrading. H₂S removal is often combined with CO₂ removal in water or alkaline scrubbers or by absorption in non-water physical solvents (see Table 3). Other common methods are:</p> <ul style="list-style-type: none">– Addition of iron salts/oxides or air/oxygen to the digester. In this way the H₂S concentration in the biogas is reduced. In the first case by formation of insoluble iron salts, like FeS, and in the second by biological aerobic oxidation of H₂S to elemental sulfur and sulfate in the reactor by <i>Thiobacillus</i> bacteria. These methods can only be regarded as a partial removal process and must be used in conjunction with another technology to go down 100 ppmv.– Adsorption in activate carbon (AC). H₂S is removed in a catalytic oxidation reaction on activated carbon, forming elementary sulfur and water. Impregnation of activated carbon using alkaline or oxide coatings, like potassium iodine or sodium hydroxide, optimize H₂S abatement with chemical adsorption. If the gas has high levels of H₂S (> 3000 ppmv), regeneration is periodically required (Wellinger, 2000). This technology is commonly used when a PSA system is used for the upgrading. Distributors of impregnated AC include: Calgon Carbon Corporation (FCA, Sulfusorb[®]), US Filter-Westates Carbon, Carmeron Carbon, etc.– Adsorption using iron oxides. Iron oxides remove H₂S by forming insoluble iron sulfide. Regeneration of the iron bed can be done with air. Typical iron oxide media are iron sponge and iron oxide pellets. Recently, proprietary iron-oxide media such as SulfaTreat[®], Sulphur-Rite[®], SOXSIA[®] and Sulfa-Bind[®] have been offered as improved alternatives.– Absorption using chelated-iron salt solutions. H₂S is oxidized to elemental sulfur by reduction of a soluble ferric chelated iron [Fe³⁺] into a ferrous chelated iron [Fe²⁺]. This can be regenerated by air stripping. Catalytic scrubbing processes on the market are for example the LO-CAT[®] and MINI-CAT[®] redox chemistry technology (Gas Technology Products-Merichem), the SulFerox[®] (Shell), the Sulfothane[®] (Biothane corporation) and the Apollo Scrubber (Apollo Environmental Systems Corp.).– Biological systems (biotrickling filters and bioscrubbers). In these systems H₂S is oxidized to sulfate or sulfur in a biological filter or reactor by microorganisms, commonly of the <i>Thiobacillus</i> genus. These bacteria are aerobic, and therefore require oxygen. Several commercial systems are available: biotrickling filters like the Biopuric process, BioSulfurex[®], BiogasCleaner[®] and bioscrubbers and bioscrubbers like the Thiopaq[®]. Normally biological methods are used in



cogeneration applications, while a second cleaning step such as activated carbon is usually required to ensure the low H₂S concentration allowed in biomethane.

Water removal:

In reaction with CO₂ and H₂S water forms corrosive acids that can damage equipment if it is not removed. The methods to remove water from biogas are generally based on separation of condensed water or chemical drying:

- **Water condensation.** Water vapor is removed by condensation and separation of the liquid water. This can be done in demisters, cyclones, moisture traps or water traps in the biogas pipe.
- **Water adsorption in a drying agent.** This drying agent can be zeolites, silica gel, aluminum oxide or magnesium oxide. The drying agent is packed in two vessels and while one is in operating mode the other one is regenerated.

Siloxanes removal:

Siloxanes can cause severe damage to engines. During combustion they are oxidized to silicon oxide (a white powder) that deposits in the downstream equipment causing damage by erosion and blockage. Most common removal methods are:

- **Adsorption on activated carbon (AC).** The most common concept is non-regenerative adsorption on fixed beds of AC or graphite. Also on the market there are fixed-bed adsorber/desorber systems working according to the principle of temperature swing adsorption. Hot air, nitrogen and/or a fraction of the purified biogas can be used for regeneration. Siloxane removal can also be achieved by the use of a fluidized adsorption bed where the media is regenerated continuously. Siloxanes can also be removed while separating hydrogen sulfide, as with the adsorption iron oxide property formulation SOXSIA[®].
- **Cooling the gas and removing water.** A 26% and 99% of removal can be achieved by cooling the gas to a temperature of -25 °C and -70 °C respectively. At -25 °C siloxanes do not significantly liquefy however, some dissolve in the condensate. Due to relatively high investment and operation cost, deep chilling is generally regarded as economically suitable only at high flow rates and elevated siloxane load.

Adsorption can also be applied, Selexol[®] being a very promising organic solvent. Biological removal of siloxanes is also being investigated.

Halogenated hydrocarbons (HHC) removal:

Halogens are corrosive and can lead to formation of dioxins and furans. HHC can be removed by **adsorption on activate carbon**. Regeneration can be carried out by heating the activated carbon to 200 °C, a temperature at which all the adsorbed compounds are evaporated and removed by a flow of inert gas. Removal of HHC by biological methods is a possibility under research.

Oxygen removal:

Small concentration of oxygen (0 – 4%) are harmless, they just dilute the energy content. But higher content can be explosive depending on the temperature. Oxygen can be partially removed by **membrane separation** and **low pressure PSA**, but the removal is expensive. Preventing the introduction of air in the biogas by careful monitoring intrusion of air in the digester or landfill gas collector is far cheaper than gas treatment.

<i>Nitrogen removal:</i>
Nitrogen is inert, being its only impact the dilution of the biogas energy content. PSA and cryogenic systems can remove nitrogen, but they are generally expensive.
<i>Ammonia (NH₃) removal:</i>
Combustion of ammonia leads to formation of nitrogen oxides. Normally NH ₃ is never a problem as it usually stays below 1ppm. NH ₃ can be removed with units filled with activated carbon and is also eliminated in some of the CO ₂ -removing units, like adsorption processes and water scrubbing .
<i>Particle removal:</i>
Biogas has to be filtered at 2 to 5 μm. Particles are removed by proven filtration technology by passing the gas through a filter pad made of stainless steel wire or through a ceramic filter pack, or alternatively using cyclone separator.

2.2.2 Liquefaction

The most common liquefaction techniques used are closed closed-loop or opened-loop cycles. In opened-loop cycles the refrigerant is a part of the feed gas and in closed-loop cycles the biogas cooling and liquefaction is attained by an external refrigerant that flows continuously in a separated circuit. These liquefaction techniques are well known and have been in use for several years in the technical gas industry, for example for the liquefaction of natural gas, but in a much larger scale than in biogas plants (Johansson, 2008).

Closed-loop systems operate using a single cryogenic refrigerant as methane or nitrogen (Nitrogen/Brayton cycle) or a mixture of these with other hydrocarbons (Mixed-refrigerant cycle). The biogas enters the process and is first cooled by the separate refrigeration process to a low temperature and thereafter expanded through either a valve or a turboexpander. This decreases both the pressure and the temperature with results in condensation of the methane (Figure 2).

The **Brayton cycle** is simple and robust but has a low efficiency since the cooling curve for N₂ does not correspond to the one for CH₄. Suppliers of this type of refrigerant process are Cryostar and Air Liquide. The **mixed-refrigerant cycle** is designed to match the cooling curve for CH₄ resulting in a continually cooled gas stream and thereby a lower energy demand. However, this process is much more complex than using a single refrigerant. A supplier of this technology is Hamworthy. They hold the licence rights to a patented

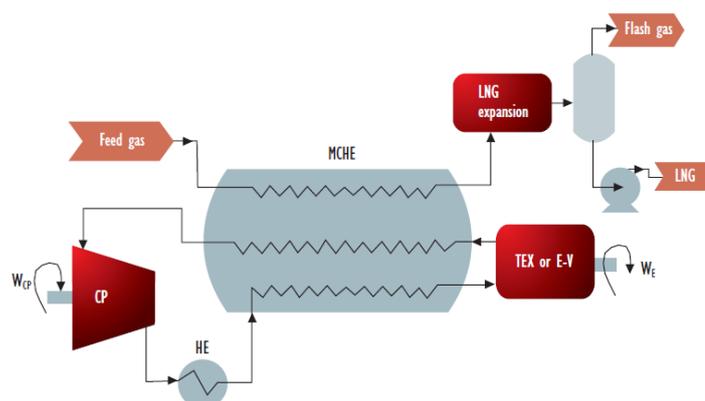


Figure 2: General scheme of a closed-loop cycle (Begazo, 2007)

MiniLNGTM technology developed by SINTEF. Other supplier is Linde BOC that holds the license of a small-scale mixed refrigerant cycle developed by GTI.

In the Lidköping Biogas plant (Sweden) the majority of the biogas is condensate using Air Liquid Brayton cycle technology. The design capacity is 12 ton LBG/day and the energy cost of liquefaction is in the vicinity of 1 kWh/Nm³ upgraded biogas, which equals approximately 10% of the energy content of the biogas. Previous to the condensation the biogas is upgraded in a water scrubber (Lidköping Biogas). The plant was inaugurated in October 2012.

Open-loop systems are based mainly on a successive compression-cooling-expansion process of the biogas. The last expansion stage is usually carried out in a turbo expander (TEX) to obtain LBG (Figure 3).

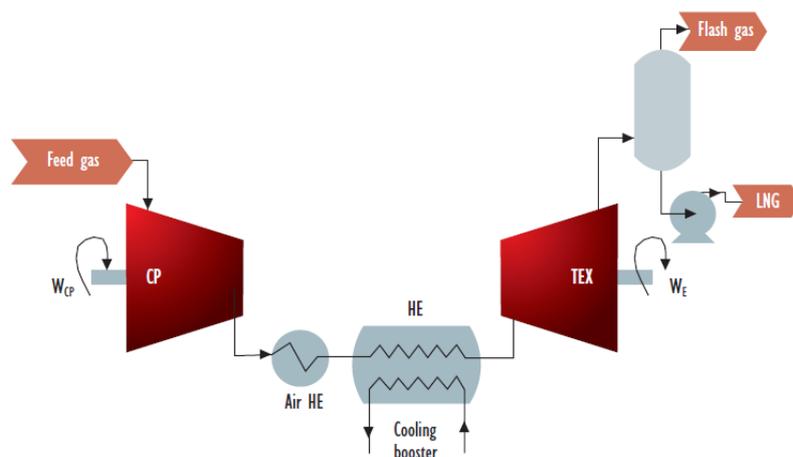


Figure 3: General scheme of an open-loop cycle (Begazo, 2007)

If the upgrading plant is situated close to the gas network one option could be to inject upgraded biogas into the gas grid and then produce LBG at a **pressure letdown station** in the gas grid with an open-loop cycle. These stations are situated where the distribution network accesses the transmission pipeline and have the function to reduce the pressure to match the requested commercial distribution pressure. Here the expansion of the gas can take place through a turboexpander. A fraction of the gas stream can then be liquefied with little or no power investment since the work taken out in the turboexpander drives the compressor (Johansson, 2008). One of these letdown systems has been developed by Idaho National Engineering and Environmental Laboratory (Begazo, 2007). This technology is in use in a demonstration plant in Sacramento, California (Johansson, 2008).

2.3 Cryogenic technologies

The cryogenic method of purification involves the separation of the gas mixtures by fractional condensation and distillations at low temperature. Because CO₂ condenses at lower pressure and higher temperatures than methane the gases can be separated. This process is of specific value when the final product is liquid biomethane. In this case, cooling for purification is synergic to further cooling to produce LBM. Suppliers of cryogenic technology are: Scandinavian GtS, Acron Technologies/Terracasatus Technologies and Prometheus-Energy.

Linde BOC has as well developed a process for the production of LBG. Linde do not sell its technology but a product, LBG, taking all the responsibility for the production. They use conventional technology followed by condensation. They have a plant at Albury landfill (U.K) through the British company Gasrec (Gasrec), commissioned in 2008 with a capacity of around 4000 ton LGB per year, and another in Altamont landfill (California) with a capacity of 1200 Nm³/h running from 2009.

2.3.1 Scandinavian GtS

The company was founded in 2007 and it is a joint venture between Scandinavian Biogas and Deutch Gastreatment Services. Scandinavia GtS has commercialized the GtS process GPP[®]. This process is implemented in 4 steps (Figure 4): gas drying, compression, gas cleaning and carbon dioxide removal. The incoming biogas is first compressed to 17 – 26 bar and subsequently cooled to -25 °C. In this step water, hydrogen sulfide, sulfur dioxide, halogens, siloxanes and other unwanted components are removed from the biogas. The gas is then led through a coalescence filter and then through a SOXSIA[®] catalyst which removes any remaining contaminants. Carbon dioxide is removed in two further stages. In the first biogas is further cooled down to between -50 and -59 °C where 30 – 40% of the carbon dioxide is removed as a liquid. In the second stage, the remaining gas stream is further cooled until -85 °C where CO₂ reaches a solid form. Three vessels are used: one is for upgrading the biogas, set at -85 °C, one is kept at intermediate temperatures (-85 °C to -60 °C) and one vessel is set at -60 °C to liquefy the CO₂. The gaseous phase is depressurized and can be injected, after odorization, into the natural gas grid. By decreasing the temperature enough to produce liquid methane, it is also possible to separate nitrogen which is an advantage when upgrading landfill gas. This is done by the addition of an extra vessel in the so call GPP[®] plus system. This is a cascade-cooling system to lower the biogas temperature to -95 °C lowering the CO₂ content even further. In 2010 a 100 Nm³ raw biogas/h GtS cryogenic plant, first of this kind, begun to produce LBG in Varberg, Sundsvall (Sweden), in 2011 a second GtS plant of 200 Nm³ raw biogas/h plant was installed in Loudden, Stockholm (Sweden). Both plants have suffered several problems. GtS have also contracted a project for LBG production in Korea in a plant of 10 million standard cubic meters of biogas per year. GtS offer plants up to 2,500 Nm³ biogas/h.

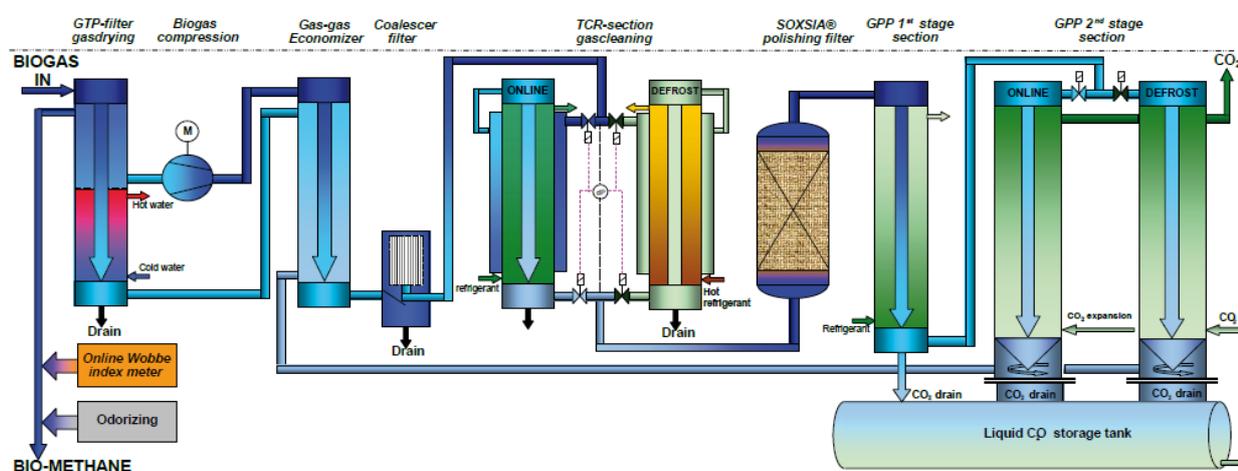


Figure 4: Overview of the GtS cryogenic upgrading process (GPP[®] of GtS)



2.3.2 Prometheus Energy

Prometheus-Energy is an American company founded in 2003, which has a technology from producing LBG integrating a gas purification and liquefaction system. Their systems are built in a modular approach as follow:

1. Pre-Purification module: Corrosive sulfur compounds, low concentrations of non-methane-organic compounds (including siloxanes) and water are removed and the gas is compressed to around 4.4 bars.
2. Bulk Purification module: Carbon dioxide is removed by freezing it while simultaneously pre-cooling methane and nitrogen.
3. Liquefaction and Post-Purification module: The purified gas is liquefied and the concentration of methane is increased by dynamic flash evaporation of the nitrogen.
4. Refrigerant module: Provides the cooling to the process through a closed Brayton N₂ cycle.

A pilot-scale plant using this technology was designed in 2000 in Victoria, B.C. Canada. Liquid methane was produced with a purity of 96%. The first commercial scale plant was built in 2006 at the Bowerman Landfill, CA, USA, in a cooperation between Prometheus and Montauk Energy Capital. The plant is designed for production of 19 m³ of liquid methane per day. They sell all the produced LBG and a part is used for fuelling a fleet of over 200 buses in the Orange County, California. To date no new Prometheus plants are under development, to the authors' knowledge.

2.3.3 Terracastus Technologies/Acrion Technologies

Terracastus Technologies founded by Volvo Technologies in 2007 holds the licensee of the cryogenic Acrion's Technology. Acrion's technology is a combination of cryogenic and conventional technology. They use a distillation column (CO₂ Wash[®]) to clean the raw gas followed by a membranes system and a liquefaction step to produce LBG. Before entering the CO₂ Wash[®] the gas is compressed, desulfurized and dried (Figure 5).

In 2005 Acrion produced LBG from landfill in a demonstration plant at Burlington County, New Jersey, USA. This project was producing around 650 – 1100 Nm³/day LBG. Acrion has several projects pending in USA, but no one has been completed yet. A liquefied biogas plant was also planned to be built on a landfill in Helsingborg, Sweden, but this project has by now been cancelled.

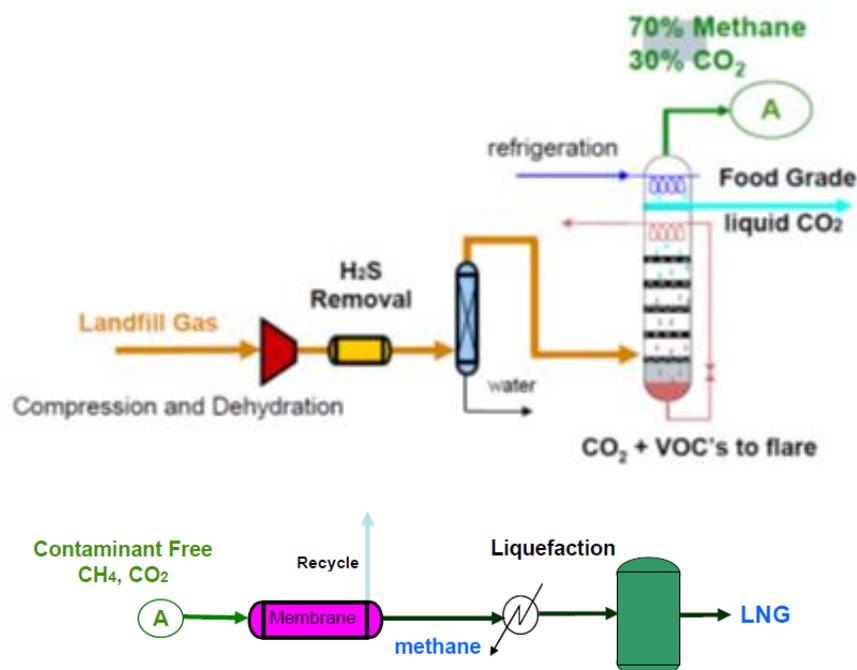


Figure 5: Acrion's process flow diagram for production of LBG (Acrion Technologies)

3 Fuel production from bio-syngas

Biomethane from biogas can be converted in syngas which is the basis for production of various fuels as methanol, dimethyl ether (DME), hydrogen, etc. (Figure 6). The main techniques for cleaning/upgrading biogas to biomethane have been described in Chapters 2.2 and 2.2.1.

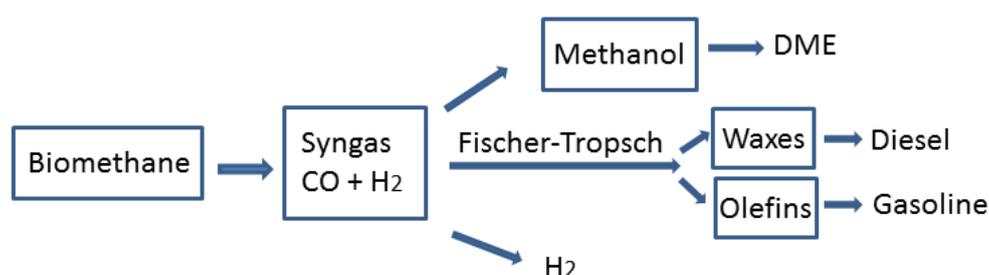


Figure 6: Schematic diagram of different fuel production from biomethane

For production of synthesis gas from natural gas (and therefore biomethane) generally three types of reforming processes exist: steam reforming (SR), partial oxidation (POX) and autothermal reforming (ATR). The most common one is the steam reforming process. Plenty of literature regarding this topic is available (Lee, 2007; Spath, 2003; Rostrup-Nielsen, 2002).

The challenge is to develop small or medium scale methane reforming plants as the existing technologies are rather devoted to process huge flows of natural gas (Czernichowski, 2006). Different research and development activities are being done in this area. This applies to current liquid fuel production process from syngas. It is expected that future technological improvements



and cost reductions in this area may provide commercial opportunities for direct conversion of biogas to liquid transportation fuels in small/medium scale production.

A very short description of the most relevant transformation technologies for manufacturing diverse vehicle fuels from methane are given in the next paragraphs.

3.1 Hydrogen

Hydrogen is produced in gas form, but as methane it can be liquefied. Liquefaction of hydrogen required large amounts of energy, moreover cryogenic transportation and storage of H₂ pose technical and economic challenges.

The current dominant technology for hydrogen production from methane is steam methane reforming. The process can be divided into the following four steps: feed pretreatment, steam reforming, CO shift conversion, and hydrogen purification. Reforming ($\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$) and shift ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) are the main reactions. The reforming reaction is highly endothermic and is favored by high temperatures and low pressures. The shift reaction is exothermic and favors low temperatures. In industrial reformers, the reforming and shift reactions result in a product composition that closely approaches equilibrium. Presently, most plants use pressure swing adsorption (PSA) after the shift conversion step, to purify the hydrogen. Using PSA, hydrogen purity greater than 99.99% can be achieved (Spath, 2003).

Today there are many licensors for the various components of the steam reforming process. A wide variety of reformer designs exists and can be used in various process configurations. Conventional steam reforming catalysts are based in NiO on a mineral support (alumina, cement, or magnesia). The high temperature shift (HTS) catalyst has an iron oxide, chromium oxide basis while the major component in the low temperature shift (LTS) catalyst is copper oxide, usually in a mixture with zinc oxide. Sulfur compounds are the main poison of reforming catalyst.

Other paths for generating hydrogen are the partial oxidation and the autothermal reforming (Spath, 2003; Liso, 2009).

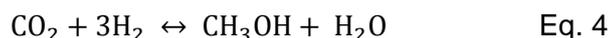
3.2 Methanol

Methanol is a promising high energy density hydrogen carrier, which through reforming can be used as a feed for hydrogen powered fuel cells or by direct conversion in DMFCs (Direct Methanol Fuel Cells). Moreover, methanol can almost directly be used as a substitute for gasoline or upgraded to DME as a substitute for diesel. Nowadays, methanol is mainly used as feedstock for chemical synthesis for the production of various compounds.

Methanol can be produced from coal, oil, natural gas or by conversion of biomass. Today, more than 75% of the methanol produced is based on a natural gas origin. Common for all resources is the intermediate production of syngas, which is synthesized into methanol. Natural gas can be replaced by biogas for the production of synthesis gas. If biogas is upgraded to biomethane then the process is exactly the same than methanol production from natural gas. This process consists on: natural gas reforming into syngas (mainly CO and H₂), methanol synthesis from the syngas and finally methanol purification in a multi-stage distillation process. A lot of literature and experience is available in methanol production from natural gas (Spath, 2003; Lee, 2007; Lögberg, 2010; Wang, 1999). Different technology suppliers can be found in Spath, 2003.



The main reactions occurring during methanol synthesis process considering steam methane reforming are:



Due to the heterogeneity of the kinetics of the biogas reforming and the methanol synthesis the catalyst selection and the operational conditions are critical. Best results are usually reported when Ni/Zn/Al catalysts are employed for steam reforming. The methanol synthesis requires lower temperatures than the biogas reforming (500 – 550 K), however higher pressures are needed (50 - 100 bar). Conventional catalysts for this second stage are Cu-based (Cu/ZnO/Al₂O₃).

As seen in Eq. 3 and Eq. 4, methanol is produced by the catalytic hydrogenation of carbon monoxide and/or carbon dioxide and the presence of carbon dioxide in the feed syngas mixture is essential. Depending on the synthesis conditions (which include reactor temperature, pressure and catalyst) this process usually aims at a (H₂-CO₂):(CO+CO₂) ratio of 2.1:1 (Majer, 2010). Conventional steam methane reforming plants when available from another nearby chemical plant may employ CO₂ injection (Wang, 1999). When CO₂ is mixed with methane, such as in the case of biogas, it can be used as a carbon source in the synthesis of methanol. However, too high CO₂ concentrations lead to slow reaction rates. Typically 2 – 8% of CO₂ is present in the syngas mixture for methanol synthesis (Lee, 2007). CO₂ can be partially purging from biogas until obtain the best molar rates (Pedersen, 2012).

Pedersen and Schultz (Pedersen, 2012) found through an equilibrium model that by supplying additional hydrogen to the methanol reactor a 50% higher CO₂ utilization is possible for steam reforming and a full utilization is possible for partial oxidation.

For syngas production from biogas, the CO₂ reforming of CH₄ or Dry Reforming of Methane (DRM) reaction has been proposed as very promising. More information about this technology can be found in Bereketidou and Goula (Bereketidou, 2012).

Further research and development in production of methanol from biogas is needed.

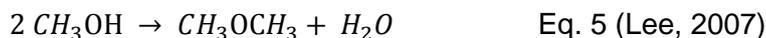
3.3 Dimethyl ether (DME)

Dimethyl ether (DME) is gaining importance as alternative fuel. DME can be used a substitute of diesel, having lower NO_x and SO_x emissions. It can also be utilized in fuel cells. Moreover it can use the existing LPG (liquefied petroleum gas) infrastructure.

Methanol serves as a direct reactant or as an intermediate in the synthesis of DME, depending on the reaction routes. In the traditional route, dimethyl ether has been produced in a two-step process where syngas (typically generated from the steam reforming of methane) is first converted



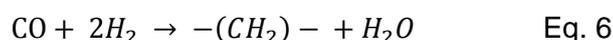
to methanol, followed by methanol dehydration over a catalyst to DME (Eq. 5) This same process can take place by generating syngas from biogas (see Chapter 3.2).



In recent years, single-state synthesis of DME from synthesis gas, in which methanol is an intermediate in the conversion of syngas to DME, has attracted a great deal of attention (Lee, 2007, Wang, 1999).

3.4 Fisher-Tropsch (FT) fuels

Fisher-Tropsch synthesis is a well-known process where hydrocarbons (C_xH_y) are synthesized from syngas. The chemical reaction that takes place under impact of a catalyst is a reaction between carbon monoxide and hydrogen. About 20% of the chemical energy is released as heat during the process, written as following (Spath, 2003):



In general, the product range includes the light hydrocarbons methane, ethane, propane and butane; naphtha; kerosene diesel fuel; low-molecular-weight wax; and high-molecular-weight wax.

The Fischer-Tropsch process is a very complicated process that requires a well-defined choice of reactors, catalysts, and operating conditions to synthesize the desired products. Even then, a mixture of compounds is obtained.

There are four main steps to produce FT products: syngas generation, gas purification, FT synthesis, and product upgrading. When using natural gas as the feedstock, many authors have recommended autothermal reforming or autothermal reforming in combination with steam reforming as the best option for syngas generation (Spath, 2003). Depending on the types and quantities of FT products desired either low (200 – 240°C) or high temperature (300 – 350°C) synthesis is used with either an iron or cobalt catalyst. The FT reactors are operated at pressures ranging from 10 – 40 bar. Low temperatures yield high molecular mass linear waxes that can by hydrocracking transformed in diesel. High temperatures produce low molecular weight olefins and by upgrading gasoline.

A comprehensive bibliography of FTS literature, including journal and conference articles, books, government reports and patents can be found in the Fischer-Tropsch Archive at www.fischer-tropsch.org.

4 Use of biogas as vehicle fuel in Denmark

Nowadays the most widespread use of biogas as vehicle fuel is as compress biomethane (CBM). But in contrast to our neighboring countries Sweden and Germany, Denmark does not use methane for vehicle transportation, neither biogas nor natural gas. In fact, today Denmark together with Albania, Montenegro and Romania are the only countries in Europe that do not have public services stations for biogas/natural gas (Øresund Ecomobility, 2012). Naturgas Fyn owns the only gas station in Denmark, together with a fleet of 14 natural gas vehicles.



This may change in a very close future as the most recent energy policies in Denmark not only support the production of biogas but also have made financially more attractive the injection of biomethane into the natural gas grid, or its use in the transport sector. The new Danish Energy Agreement 2012 – 2020 introduces a new funding scheme in which, among others, biomethane injection into the natural gas grid receives the same subsidy as electricity from biogas produced in CHP plants.

The best way of starting a socio-economic infrastructure for using biogas as fuel is by focusing in first place on the heavy traffic, as well as for example taxi fleets. Moreover, it is feared that rising oil prices will cause loss of competitive advantage for the heavy transport sector in Denmark in relation to Germany, Sweden and Eastern Europe if they have cheaper fuel alternatives. The heavy transport currently has not, as the light transport sector, alternatives such as electricity or bioethanol (Øresund Ecomobility, 2012).

In this context not only CBG but also LBG can be relevant. CBG is well suited for bus fleets or short distance transportation but for heavy duty trucks, in order to be competitive with diesel trucks, the liquefied fuel is required since its higher energy density (compared to CBM) allows getting enough driving range.

Dual-fuel technology and LBM/LNG are considered by many players as one of the first solutions that can truly compete, in the short-middle term, with the conventional diesel engines in the long distance road transportation sector. However, there are also some concerns as fuel infrastructure, emission control, and total economy that need to be overcome. In this scenario as LBM production is very limited and it is expected to continue to be relatively limited, LNG is required to secure supply of fuel. Currently Denmark has no domestic LNG terminals (Johannesson, 2011). LNG/LBM has as well a big potential as maritime fuel.

At present, biogas in Denmark is basically used for combined heat and power production and at the moment there is only one plant upgrading biogas and injecting it into the natural gas grid. This plant began to run in September 2011 in Fredericia and is producing 180 Nm³/h biomethane from a sewage plant. Nevertheless there are already several projects for building new biogas plants in the coming years, with upgrading of biogas and injection into the natural gas grid. In this line, at the beginning of 2013 the first public gas station will be established in the Skive municipality and it is expected that others will follow. Initially the Skive station will provide natural gas but in a few years it is expected that upgraded biogas will be produced in the municipality and clients should be able to fill biomethane in their cars.

Until now an important barrier for biogas and natural gas vehicles has been that this type of vehicles is subject to higher taxes than diesel vehicles. But the Danish Government has announced that this is going to change in a very near future, which would contribute greatly to the expansion of natural gas/biogas vehicles.

There are still no plans to produce LBM in Denmark at the moment, but the technology has come in the last years to commercial stage so, if conditions are favorable from an economical and/or political point of view, a fast development could take place in this area. In Sweden the first liquefied biogas production facility was open in Sundsvall in 2010 and two more have followed: Loudden in 2011 and Lidköping in 2012. At the same time a liquid biomethane infrastructure is being created. In 2010 the first public filling station for liquid methane was open in Goteborg, in 2011 it was inaugurated another filling station in Stockholm and there are plans to open more.



Regarding to the production of other liquid biofuels from biogas they will be most probably considered only in a middle-long term, as vehicle and production technologies need to be further developed and improved.



References

- Acrion Technologies. <http://www.acrion.com/>
- Ajhar M., Melin T. (2006) Siloxane removal with gas permeation membranes. *Desalination* 200:234e5
- Bereketidou O.A. and Goula M.A. (2012). Biogas reforming for syngas production over nickel supported on ceria-alumina catalysts. *Catalysis Today* 195, pg. 93-100.
- Cline, C., Hoksberg, A., et al. (2002). Biological process for H₂S removal from gas streams: The Shell-Paques/Thiopaq™ gas desulfurization process. Paper for the LRGCC, 23 –26 February 2003, Norman (Oklahoma)
- COWI (2012). <http://www.cowi.com/menu/project/IndustryandEnergy/Industry/Pages/COWIwinsFilbornaBioFuelProject.aspx>
- Begazo D.T. C., Carvalho C. E., Simões-Moreira R.J. (2007). Small-scale LNG plant technologies. *Hydrocarbon World*.
- BC Innovation Council (2008). Feasibility Study – Biogas upgrading and grid injection in the Fraser Valley, British Columbia
- Beil M. and Hoffsted U. (2010). Guidelines for the implementation and operation of biogas upgrading systems. *Biogasmax*. Project supported by the EU under RTC contract: 019795
- Bekkering J., Broekhuis A.A., van Gemert W.J.T (2010). Optimisation of a green gas supply chain – A review. *Bioresource Technology* 101, pg. 450-456
- Biomass for Energy (2012). Focus on Biomethane. Deutsches BiomasseForschungsZentrum gemeinnützige GmbH (DBFZ)
- Czernichowski A. and Wesolowska K. (2006). POX reforming of biomethane into synthesis gas for Fischer-Tropsch process. The 232nd ACS National meeting, San Francisco, Sept. 2006. Division of fuel chemistry.
- Climate Action (2011). Reducing emissions from transport. EU Directorate-General for Climate Action. http://ec.europa.eu/clima/policies/transport/index_en.htm
- Delsinne S. (2010). Biogas Safety and Regulation. Discussion document for the workshop organized on 24 November 2010 in Paris. Project 12055
- El-Fadel M., Findikakis A.N., and Leckie J.O. (1997). Environmental Impacts of Solid Waste Landfilling. *Journal of Environmental Management* 50, pg. 1-25
- Environment-Agency (2004). Guidance on Gas treatment Technologies for Landfill Gas Engines
- GPP®. Gastreatment power package of GtS. http://www.gastreatmentservices.com/index.php?option=com_content&view=article&id=31&Itemid=60&lang=en
- Hagen M., Polman, E., Myken A., Jensen J., Jönsson O., AB B. and Dahl A. (2001). Adding gas from biomass to the gas grid. Final report Contract No: XVII/4.1030/Z/99-412



- Hullu, J., Maassen J.I.W., van Meel P.A., Shazad S., and Vaessen J.M.P (2008). Comparing different biogas upgrading techniques. Final report. Eindhoven University of Technology
- Kohl, A. and Neilsen, R. (1997). Gas Purification. Golf Publishing Company, Houston, Texas. Cited in: McKinsey S.Z. (2003). "Removal of Hydrogen Sulphide from Biogas using cow-manure compost." A Thesis Faculty of the Graduate School of Cornell University
- Krich, K., Augenstein, D., et al. (2005). Biomethane from Dairy Waste: A Sourcebook for the Production and Use of Renewable Natural Gas in California. Western United Dairymen
- Johannesson S. (2011). Alternative fuels in heavy goods vehicle transport – corridor of liquefied biomethane in road transportation. Baltic Sea Region Project #26: Scandinavian-Adriatic corridor for growth and innovation. WP3, action 3.3-2. Concept for optimized heavy goods vehicle traffic
- Johansson N. (2008). Production of liquid biogas, LBG, with cryogenic and conventional upgrading technology – Description of systems and evaluations of energy balances. Master thesis. Lunds Tekniska Högskola
- Jonsson S. and Johan W. (2011). Cryogenic biogas upgrading using plate heat exchangers. Master's thesis within the Sustainable Energy System Master's program. Chalmers University of Technology. Sweden
- Lampe S. (2006). Assessment of fuel gas cleanup systems for waste gas fueled power generation. EPRI, Palo Alto, CA. 1012763
- Lee S., Speight J.G, Loyalka S.K. (2007) Handbook of Alternative Fuel technologies. CRC Press, 2007.
- Lidköping Biogas. <http://www.lidkopingbiogas.se/eng/>
- Liso v., Nielsen M.P., Kær S.K. (2009) Reforming processes for micro combined heat and powersystem based on solid oxide fuel cell. Proceedings of SIMS 50. Scandinavian Simulation Society, 2009.
- Lögdberg S. and Jakobsen H.A. (2010). Natural Gas Conversion: The Reforming and Fischer-Tropsch Processes. TKP 4145 Reactor technology. <http://www.nt.ntnu.no/users/jakobsen/TKP4145/NaturalGasConversion.doc>.
- Majer S. and Gröngröft A. (2010). Environmental and economic assessment of biomethanol for the biodiesel production. German Biomass Research Centre (DBFZ).
- McKinsey, S. Z. (2003). Removal of Hydrogen Sulfide from Biogas using cow-manure compost. A Thesis Faculty of the Graduate School of Cornell University
- Mezei S. (2010). Options for upgrading digester biogas to pipeline quality. Flotech
- Naskeo Environment (2009). Biogas Composition. http://www.biogas-renewable-energy.info/biogas_composition.html
- Øresund Ecomobility, Transportens Innovationsnetværk (2012). Potentiale og barrierer for biogas og naturgas til transport i Danmark.



- Pedersen T.H, Schultz R.H. (2012). Technical and economic assessment of methanol production from biogas. Master's thesis within Thermal Energy and Process engineering. University of Aalborg, Denmark.
- Persson M. (2007). Biogas upgrading and utilization as vehicle fuel. European Biogas Workshop. The future of biogas in Europe III
- Persson M., Jönsson O. and Wellinger A. (2006). Biogas Upgrading to Vehicle Fuel Standards and Grid Injection. IEA Bioenergy. Task 37
- Petersson A. (2009). Modern technologies of biogas upgrading. Citation from Urban W., Girod K., Lohmann H.(2008) Technologien und kosten der biogasaufbereitung und einspeisung in das erdgasnetz. Ergebnisse der markterhebung 2007-2008. Fraunhofer UMSICH
- Petersson A. and Wellinger A. (2009). Biogas upgrading technologies-developments and innovations. IEA Bioenergy. Task 37
- Rostrup-Nielsen J.R. (2002). Syngas in perspective. Catalysis Today 71, 243-247.
- Ryckebosch E., Drouillon M. and Vervaeren H. (2011). Techniques for transformation of biogas to biomethane. Biomass and Bioenergy 35, pg. 1633-1645
- Rasi S. (2009). Biogas composition and upgrading to biomethane. Jyväskylä studies in biological and environmental science 202
- Spath P.L. and Dayton D.C. (2003). Preliminary Screening – Technical and Economic assessment of synthesis gas to fuels and chemicals with emphasis on the potential for biomass-derived syngas. National Renewable Energy Laboratory. NREL/TP-510-34929.
- Shareefdeen, Z. and Singh, A. (2005). Biotechnology for odor and air pollution control. Springer
- Sternovem. Committee for Green Gas. From biogas to green gas. Upgrading techniques and suppliers. 2ETPNG0840
- Wang M.Q. and Huang H.S. (1999). A full fuel-cycle analysis of energy and emissions impacts of transportation fuels produced from natural gas. Center for Transportation Research, Argonne National Laboratory.
- Wellinger A. and Lindberg A. (2000). Biogas upgrading and utilization. IEA Bioenergy. Task 24
- Zappa, L. P. (2001). "Options in Odor Control." Water & Wastewater Products 1(1): 38



Annex 1

Main composition of biogas from different sources

Table 6: Main composition of biogas from different sources

Components	Municipal waste	Wastewater	Agricultural/ Animal waste	Waste from agrofood industry	Landfill
CH ₄ (vol.-%)	50 – 60 ²	61 – 65 ¹ 60 – 75 ² 55 – 77 ³ 55 – 65 ⁶	55 – 58 ¹ 60 – 75 ² 50 – 70 ³ 60 – 70 ⁶	68 ² 50 - 75 ³	47 – 57 ¹ 45 – 70 ³ 40 – 70 ⁴ 35 – 65 (avg.45) ⁵ 45 – 55 ⁶
CO ₂ (vol.-%)	34 – 38 ²	36 – 38 ¹ 19 – 33 ² 30 – 45 ³ 35 – 45 ⁶	37 – 38 ¹ 19 – 33 ² 30 – 50 ³ 30 – 40 ⁶	26 ²	37 – 41 ¹ 35 – 40 ³ 30 – 60 ⁴ 15 – 50 (avg.40) ⁵ 30 – 40 ⁶
N ₂ (vol.-%)	0 – 5 ²	< 2 ¹ < 1 ^{2,6}	< 1 ² < 1 – 2 ¹ < 3 ³		< 1 – 17 ¹ < 3 ³ 3 – 5 ⁴ 5 – 40 (avg.15) ⁵ 5 - 15 ⁶
O ₂ (vol.-%)	0 – 1 ²	< 1 ¹ < 0.5 ²	< 1 ¹ < 0.5 ²		< 1 ¹ < 0.2 ³ 0 – 3 ⁴ 0 – 5 (avg.1) ⁵
H ₂ O (vol.-%)	100% (saturated at digester exit temperature) ³	100% (saturated at digester exit temperature) ³	100% (saturated at digester exit temperature) ³	100% (saturated at digester exit temperature) ³	100% (saturated at digester exit temperature) ³
H ₂ (vol.-%)					0 – 5 ⁴
CO (vol.-%)					0 – 3 ⁴
H ₂ S (ppm)	70 – 650 ²	700 – 2800 ² 150 – 3000 ³ 63 ⁶	2100 – 7000 ² 32 – 169 ¹ 3 – 1000 ¹	280 ² < 21,500	36 – 115 ¹ 10 – 200 ³ 0 – 20.000 ⁴ < 100 ⁵ 15 – 427 ⁶
Aromatic (mg/m ³)	0 – 200 ²				30 - 1900 ⁴
Ammonia			50 – 100 ² mg/m ³		5 ppm
Halogenated compounds (mg/m ³)	100 – 800 ²				1 – 2900 ⁴
Benzene (mg/m ³)		0.1 – 0.3 ¹	0.7 – 1.3 ¹		0.6 – 2.3 ¹
Toluene (mg/m ³)		2.8 – 11.8 ¹	0.2 – 0.7 ¹		1.7 – 5.1 ¹
Siloxanes (ppmv)		2 – 15 ³ 1.5 – 10.6 ⁶	< 0.4 ⁶		0.1 – 3.5 ³ 0.7 – 4 ⁶
Non-methane organics (% dry weight)					0 – 0.25 ³
Volatile organics (% dry weight)					0 – 0.1 ³

¹ Delsinne, 2010; ² Naskeo Environment, 2009; ³ Lampe, 2006; ⁴ El-Fadel, 1997; ⁵ Persson, 2006; ⁶ Rasi, 2009.