

# Dimethyl ether (DME)

Lab scale

**Bench scale** 

**Pilot Plant** 

monstration

Production

# Introduction

Dimethyl ether (typically abbreviated as DME), also known as methoxymethane, wood ether, dimethyl oxide or methyl ether, is the simplest ether. It is a colourless, slightly narcotic, nontoxic, highly flammable gas at ambient conditions, but can be handled as a liquid when lightly pressurized. The properties of DME are similar to those of Liquefied Petroleum Gas (LPG). DME is degradable in the atmosphere and is not a greenhouse gas.

See page two for Production Process.

# **Applications**

Due to its good ignition quality, with a high cetane number, DME can be used in diesel engines as a substitute for conventional diesel fuel. However, compared to diesel fuel DME has a lower viscosity (insufficient), and poor lubricity. Like LPG for gasoline engines, DME is stored in the liquid state under relatively low pressure of 0.5 MPa. This helps to limit the number of modifications required to the engine. Still, some slight engine modifications are necessary, primarily relating to the injection pump and the installation of a pressure tank, similar to that for LPG. The fuel line must also be adapted with specific elastomers.

DME in diesel engine burns very cleanly with no soot.

The infrastructure of LPG can be used for DME. As part of the FP7 project BioDME, under the leadership of the Volvo Group, DME production is being optimized, especially for use as a transport fuel.

# **European Projects on DME**

**BioDME** - Production of DME from Biomass and utilisation as fuel for transport and for industrial use. Funded by 7th Framework Programme and Swedish Energy Agency.

# Molecular Formula

$$C_2H_6O / CH_3OCH_3$$

# **Comparison of Fuel Properties**

Property	DME	Diesel
Density at 20 °C [kg/l]*	0.67	0.83
Lower heating value [MJ/kg]*	28.4	43.1
Cetane number*	60	50
Fuel equivalence*	0.59	1
GHG [gCO <sub>2</sub> eq/ MJ]**	Waste wood DME: 5	
	Farmed wood DME: 7	

Source: FNR 2012. \* Median values are used for simplification. Please refer to the standards for ranges. \*\* Directive 2009/28/EC, total for cultivation, processing, transport and distribution

# Utilization

Substitute for diesel fuel; transportation fuel; power generation fuel; domestic gas

# **Relevant fuel regulations**

EN590 (diesel fuel)

# Main feedstocks

Forest products, agricultural by-products, organic waste, energy crops, black liquor

# **Scale of Production**

Demonstration scale

# **Production process**

DME is primarily produced by converting natural gas, organic waste or biomass to synthesis gas (syngas). The syngas is then converted into DME via a two-step synthesis, first to methanol in the presence of catalyst (usually copper-based), and then by subsequent methanol dehydration in the presence of a different catalyst (for example, silica-alumina) into DME.

The following reactions occur:

2H<sub>2</sub>+ CO ⇔ CH<sub>3</sub>OH

 $2CH_3OH \iff CH_3OCH_3 + H_2O$ 

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CO+H_2O \iff CO_2+H_2
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Alternatively, DME can be produced through direct synthesis using a dual-catalyst system which permits both methanol synthesis and dehydration in the same process unit, with no intermediate methanol separation, a procedure that, by eliminating the intermediate methanol synthesis stage, the licensors claim promises efficiency advantages and cost benefits.

Both the one-step and two-step processes are commercially available.

DME can also be converted itself into olefins and synthetic hydrocarbons.

#### **Major stakeholders**

Volvo Group, Sweden

Chemrec, Piteå, Sweden

Haldor Topsøe, Kgs. Denmark

Preem, Sweden

Total, France

# State of the Art

The DME demonstration plant in Piteå, Sweden, which was put into operation in 2010, is the only gasification plant worldwide producing high-quality synthesis gas based on 100% renewable feedstocks. The raw material used is black liquor, a high-energy residual product of chemical paper and pulp manufacture which is usually burnt to recover the spent sulphur.



BioDME plant with DME log truck in foreground © Chemrec 2011

#### **Further information**

Up-to-date information on Diemethyl ether DME R&D&D is available on the Euorpean Biofuels Technology Platform website **www.biofuelstp.eu**.



# Ethanol

Lab scale

**Bench scale** 

**Pilot Plant** 

Production

# Molecular Formula



#### **Comparison of fuel properties**

Origin	Ethanol	Petrol
Density at 20 °C [kg/l]*	0.79	0.74
Lower heating value [MJ/kg]*	26.7	43.9
Octane number*	>100	92
Fuel equivalence*	0.65	1
GHG [gCO <sub>2</sub> eq/ MJ]**	Sugar beet ethanol: 33	
	Farmed wood ethanol : 20	
	Wheat straw ethanol: 11	

Source: \*FNR 2012. Median values are used for simplification. Please refer to standards for ranges. \*\* Directive 2009/28/EC, total for cultivation, processing, transport and distribution

#### Utilization

Substitute for petrol; petrol blend component; feedstock for petrol additive ETBE

#### **Relevant fuel regulations**

EN 228, EN 15736

#### Main feedstocks

Sugar and starch from agricultural crops, (sugar cane, cereals, sugar beets); lignocellulosic biomass (forestry residues, agricultural residues, energy crops)

#### **Scale of Production**

Industrial production for first-generation ethanol and pilot-plant/demonstration scale for second generation (cellulosic) ethanol

#### Introduction

Ethanol, also known as ethyl alcohol, pure alcohol, grain alcohol, or drinking alcohol, is often abbreviated as EtOH. EtOH is a light alcohol and is a volatile, colourless, flammable liquid with a characteristic odour. EtOH burns with an almost invisible flame and is biodegradable.

Without proper conditions, EtOH attracts water while stored. Another important feature of EtOH is the formation of an azeotropic mixture with water.

See pages 2 & 3 for Production Process, State of the Art and Applications.

#### **Major stakeholders**

The major bioethanol stakeholders in the EU are listed below:

Abengoa Bioenergy, Spain

Tereos, France

CropEnergies, Germany

Cristal Union, France

Agrana Group, Austria

Verbio, Germany

Agroetanol, Sweden

Industria Meridionale Alcolici, Italy

AlcoBioFuel, Belgium

N.prior bioenergy, Germany

Chemtex, Mossi & Ghisolfi Group, Italy

DONG Energy, Denmark

Abengoa Bioenergy, a biofuels subsidiary of the Abengoa group, is the European leader of fuel bioethanol production. In 2011, its production capacity was equal to 3125 millions of litres, 1,500 of which was distributed on the EU market. In the fiscal year 2011/2012, the French industrial group Tereos registered a total production capacity of 543 Ml while the German group CropEnergies reached a total production capacities of 692 Ml/yr.

# Ethanol

# **Production process**

EtOH is a naturally widespread chemical, produced by ripe fruits and by wild yeasts or bacteria through fermentation. Ethanol from biomass can be produced from any feedstock containing appreciable amounts of sugar or materials that can be converted into sugar. Fermentation (biotechnology) is the predominate pathway for EtOH production. Biomass can also be converted to EtOH via biotechnological and thermochemical pathways.

# **Biochemical pathways**

The most common raw materials are sugar cane and corn, and in temperate climates also sugar beet, wheat or potatoes. The overall fermentation process starting from glucose is:

# $C_6H_{12}O_6 \iff 2 C_2H_5OH + 2 CO_2$

Naturally, the underlying biochemical processes are much more complicated. Adapted yeasts, for example *Saccharomyces cerevisiae* are used and fermentation can be carried out with or without the presence of oxygen. With oxygen some yeasts are prone to respiration, the conversion of sugars to carbon dioxide and water. As EtOH is a toxin, there is a limit to the maximum concentration in the brew produced by the yeasts. This results in a high energy demand for EtOH purification by distillation.

In industrial processes an efficiency of about 90 to 95 % of theoretical yields can be reached. But, unmodified yeast will only convert sugars with 6 carbon atoms. As sugars with 6 carbon atoms are only a part of the biomass the overall conversion efficiency is much lower. To enable the use of a wider range of biomass components, processes that also convert sugars with 5 carbon atoms are under development. Larger compounds in biomass (cellulose and hemicellulose) must first be broken down into fermentable sugars and lignin, which is currently not a candidate feedstock for EtOH.

# **Other pathways**

Non-biotechnological methods for production of EtOH have been developed. EtOH from chemical conversion routes is called synthetic ethanol. The most common chemical process for EtOH production is the acid-catalyzed hydration of ethylene:

# $C_2H_4 + H_20 \iff C_2H_5OH$

Ethylene is obtained from petrochemical feedstocks. Phosphoric acid is mostly used as a catalyst.

EtOH can also be produced from synthesis gas through chemical synthesis. In addition, certain microorganisms are able to digest synthesis gas to produce ethanol.

See page 3 for State of the Art and Applications.

# **EC-funded projects on ethanol**

**BIOLYFE** - Demonstrating large-scale bioethanol production from lignocellulosic feedstocks

**NEMO** - Novel high-performance enzymes and micro-organisms for conversion of lignocellulosic biomass to bioethanol

**DISCO** - Targeted DISCOvery of novel cellulases and hemicellulases and their reaction mechanisms for hydrolysis of lignocellulosic biomass (FP7)

**BABETHANOL** - New feedstock and innovative transformation process for a more sustainable development and production of lignocellulosic ethanol

**PROETHANOL2G** - Integration of biology and engineering into an economical and energy-efficient 2G bioethanol biorefinery

**HYPE** - High efficiency consolidated bioprocess technology for lignocellulosic ethanol

**KACELLE** - Demonstrating industrial scale second generation bioethanol production – Kalundborg cellulosic ethanol plant

**FIBREETOH** - Bioethanol from paper fibres separated from solid waste, MSW

LED - Lignocellulosic ethanol demonstration

**PROCETHOL 2G** - Cellulosic Ethanol Pilot Plant (funded by public and private partners in France)

**BABILAFUENTE** - Project for the production of 200 Million Litres of Bioethanol in Babilafuente (SalamanTHOLca) from Cereals and Lignocellulose

# Ethanol

# **State of the Art**

Global bioethanol production in 2011 has been estimated at 84.6 Bl. The United States is the leading producer with 52.6 Bl (62%), while Brazil produced 21.1 Bl (25%). The EU-27, with a production of 5467 Ml (4.6%), ranks third behind these two majors producers.

As an alternative to using sugar- and/or starch-based biomass, R&D is focused on advanced processes that use lignocellulosic materials as feedstocks. These processes have the potential to increase the variety and quantity of suitable feedstocks, including cellulosic and foodprocessing wastes, corn stovers and cereal straws, as well as dedicated fast-growing plants such as poplar trees and switch-grasses. Advanced processes include biomass pre-treatment to release cellulose and hemicellulose, hydrolysis to fermentable 5- and 6-carbon sugars, sugar fermentation, thermal conversion of solid residues and non-hydrolysed cellulose, and distillation of ethanol to fuel grade. In order to provide better conversions, new pretreatment schemes and innovative enzymatic processes have been investigated.

One of the more sophisticated solutions is the so-called "lignocellulosic feedstock biorefinery (LCF biorefinery)" which uses lignocellulosic biomass, for example wood from short rotation forestry or energy crops like Triticale. Besides EtOH, in theory, a broad range of intermediate chemicals could be produced from a LCF biorefinery.

Today in Europe some pilot or demonstration plants are running or are being commissioned.

Due to significant investments in funding by the EU and by industry the technology for production of lignocellulosic biomass to EtOH is available, but a proper regulatory framework is needed to promote and support technology deployment at commercial scale.

#### **Applications**

Low-percentage ethanol-gasoline blends (E5, E10) can be effectively used in most conventional spark-ignition engines with no technical changes, while modern flexifuel vehicles (FFV), which can run on any gasoline-EtOH mixture up to 85% EtOH (E85), are made with just a few modifications during production. The use of alcohol fuels, such as ED95, in heavy duty applications is also implemented on a limited scale.

EtOH has a series of technical advantages as a fuel for spark-ignition engines. First, EtOH has a very high octane number. This gives the fuel a strong resistance to knock which translates into the possibility of optimizing the engine by increasing compression ratio and advancing spark. Second, EtOH has a high heat of vaporization, enabling an air-cooling effect. This enhances the filling efficiency, partly offsetting its lower energy content per litre. Finally, the presence of oxygen in the ethanol molecule provides a more homogeneous fuel-air mix formation and permits low-temperature combustions with a consequent decrease in unburned or partially burned molecule emissions (HC, CO, and NOx).

Despite these advantages, some negative properties have also to be considered. Firstly, the oxygen content leads to an increase in the fuel volumetric consumption and, due to its ability to oxidize into acetic acid, causes compatibility issues with some materials used in the engine, such as metals or polymers. Ethanol may also contain metallic ions and other impurities that enhance aggressiveness towards materials. Secondly, the high latent heat of vaporization can cause running difficulties in cold conditions, especially cold start. Finally, EtOH leads to azeotropes with light hydrocarbon fractions and can cause volatility issues. It is miscible with water, which can cause demixing issues when blended with hydrocarbons, and implies acetaldehyde emissions.

#### **Further information**

Up-to-date information on ethanol is available on the European Biofuels Technology Platform website www.biofuelstp.eu



# Fatty Acid Methyl Esters (FAME)

Lab scale

Bench scale

**Pilot Plant** 

**Biofuel Fact Sheet** 

# Introduction

Fatty Acid Methyl Esters (FAME) are esters of fatty acids. The physical characteristics of fatty acid esters are closer to those of fossil diesel fuels than pure vegetable oils, but properties depend on the type of vegetable oil. A mixture of different fatty acid methyl esters is commonly referred to as biodiesel, which is a renewable alternative fuel. FAME has physical properties similar to those of conventional diesel. It is also non-toxic and biodegradable.

Some properties of biodiesel are different from those of fossil diesel and for correct low temperature behaviour and for slowing down oxidation processes biodiesel requires a different set of additives than fossil diesel. Impurities, such as metals, in FAME must be limited for use as a motor fuel.

See page two for Production Process and State of the Art.

# **EC-funded projects on FAME**

ALGFUEL - Biodiesel production from microalgae

**ECODIESEL** - High efficiency biodiesel plant with minimum GHG emissions for improved FAME production from various raw materials

**SUPER METHANOL** - Reforming of crude glycerine in supercritical water to produce methanol for re-use in biodiesel plants

**InteSusAl** - Demonstration of Integrated & Sustainable enclosed raceway and photobioreactor microalgae cultivation with biodiesel production and validation

**AllGas** - Industrial Scale Demonstration Of Sustainable Algae Cultures For Biofuel Production (BioDiesel and BioGas)

**BioFAT** - Microalgae to biofuel demonstration

# **Applications**

Tests have been undertaken by motor manufacturers in the European Union on blends with diesel oil up to 5-10 %, or at 25-30 % and 100 % pure. These have resulted in guarantees for each type of use. Modifications (seals, piping) are required for use at 100 % pure. The use of biodiesel as a low-blend component in transport fuel (up to 7 percent in Europe for the time being according to EN 590) does not require any changes in the distribution system, therefore avoiding expensive infrastructure changes.

# Molecular Formula CH<sub>3</sub>(CH<sub>2</sub>)nCOOCH<sub>3</sub>

# **Comparison of Fuel Properties**

	FAME	Diesel
Density at 20 °C [kg/l]*	0.88	0.83
Lower heating value [MJ/kg]*	37.1	43.1
Viscosity at 20 °C [mm <sup>2</sup> / s]*	7.5	5.0
Cetane number*	56	50
Fuel equivalence*	0.91	1
GHG [gCO <sub>2</sub> eq/ MJ]**	Rape seed biodiesel: 46 Waste vegetable or animal oil	
	biodiesel: 10 Palm oil biodiesel (process not specified): 54	

Source: FNR 2012. \* Median values are used for simplification. Please refer to the standards for ranges. \*\* Directive 2009/28/EC, total for cultivation, processing, transport and distribution

# Utilization

Substitute diesel; transportation fuel; power generation fuel

# **Relevant fuel regulations**

EN14214 (Biodiesel specification), ASTM D 6751, EN590

# Main feedstocks

Oil seeds (rape, sunflower, soy, palm), used cooking oil, waste animal fat

# **Scale of Production**

Industrial scale

# **Production process**

FAME is produced from vegetable oils, animal fats or waste cooking oils by transesterification. In the transesterification process a glyceride reacts with an alcohol in the presence of a catalyst, forming a mixture of fatty acids esters and an alcohol. Using triglycerides results in the production of glycerol.

Transesterification is a reversible reaction and is carried out by mixing the reactants. A strong base or a strong acid can be used as a catalyst. At the industrial scale, sodium or potassium methanolate is mostly used. The following reaction occurs:

The production of biodiesel is relatively simple from a technical standpoint, also allowing the construction of small decentralised production units without excessive extra costs. This limits the need to transport raw materials long distances and permits operations to start with modest-sized installations.

Rapeseed, sunflower, soybean, palm oils, UCO and animal fat are the most common raw materials being used for the production of biodiesel. Using methanol in the transesterification process has the advantage that the resulting glycerol can be separated simultaneously during the transesterification process. When using ethanol during the process the ethanol needs to be free of water and the oil needs to have a low water content as well to achieve an easy glycerol separation.

The end products of the transesterification process are raw biodiesel and raw glycerol. After a cleaning step biodiesel is produced. The purified glycerol can be used in the food and cosmetic industries, as well as in the oleochemical industry. The glycerol can also be used as a substrate for anaerobic digestion.

#### State of the Art

Industrial scale production of biodiesel for use as a transport fuel has taken place in Europe since 1991.

Global biodiesel production in 2011 was 18,826 Mtonnes. The leading producer was the USA with 2,800 M tonnes of biodiesel produced, followed by Germany with 2,780 M tonnes and Argentina with 2,427 M tonnes. Globally, 2011 has seen significant FAME output growth of around 2.5 M tonnes (growth rate 16%), bringing worldwide production to a record high (F.O. Lichts, Vol.10, Is.14).

# **Major stakeholders**

Some of the major biodiesel stakeholders in the EU are listed below:

Diester Industries, France ADM Biodiesel, Germany Biopetrol Industries, Switzerland Verbio, Germany Cargill, Germany Ital Green Oil Italy Bioenergética Extremeña, Spain Acciona Energia, Spain Gate, Germany Biofuels Corporation, United Kingdom Novaol, Italy Natural Energy West, Germany

With the inauguration in 2008 and 2009 of four new facilities and a total of 10 facilities, Diester Industries remains the largest producer of biodiesel in the EU in 2009 with a production capacity of 2,250 MI/yr, only in France. ADM Biodiesel, a German subsidiary of the American group Archer Daniels Midland (ADM), runs three production plants in Germany with a total production capacity of 1,130 MI/yr. The American group owns biodiesel plants also in Brazil, India, Indonesia and the United States. Its global production capacity is about 1,700 MI/yr. The Swiss group Biopetrol Industries is also one of the leaders of the European biodiesel market, its biodiesel production is done in Germany in Schwarzheide (220 MI/yr) and in Rostock (170 MI/yr), and since 2008 in the Netherlands in Rotterdam (450 MI/yr). The German company Verbio is active in both biodiesel and bioethanol markets. It owns two biodiesel production facilities in Germany, in Schwedt (280 MI/yr) and Bitterfeld (230 MI/yr). According to the EBB (European Biodiesel Board), the production capacity of biodiesel in the EU exceeded 23,500 MI in 2008, with a total of 276 production facilities.

# **Further information**

Up-to-date information on methanol from biomass R&D&D is available on the Euorpean Biofuels Technology Platform website **www.biofuelstp.eu**.



# Methanol from biomass

Lab scale

**Bench scale** 

**Pilot Plant** 

monstration

Production

#### Introduction

Methanol, also known as methyl alcohol, wood alcohol, or wood spirits, is often abbreviated as MeOH. It is the simplest alcohol, and is a light, volatile, colourless, flammable liquid with a distinctive odour. At room temperature it is a polar liquid. MeOH is miscible with water, petrol and many organic compounds. MeOH burns with an almost invisible flame and is biodegradable. Without proper conditions, methanol attracts water while stored. Methanol is a safe fuel. The toxicity (mortality) is comparable to or better than gasoline. It also biodegrades quickly (compared to petroleum fuels) if spilled.

See page two for Production Process.

#### State of the Art

MeOH has grown into one of the largest chemical synthesis feedstocks. Key uses include production of formaldehyde, MTBE/TAME (petrol additives), acetic acid, DME and olefins and direct use as a petrol blend component.

In 2007 the world production of MeOH amounted to 40 million tonnes with a forecast compound annual growth rate of 4.2 % for the period 2008-2013 excluding captive production for the methanol-to-olefins (MTO) route. Today, methanol from biomass is produced through gasification of glycerine, a by-product of biodiesel production, by BioMCN in the Netherlands. The thermochemical conversion of syngas to methanol is well known from fossil feedstocks and the basic steps are not different for biomass. The main issue faced is the economic feasibility of gasification of biomass at elevated pressures and conditioning of the raw synthesis gas.

In the past there was some small-scale production of methanol from biomass. In 2004 the German company Choren Industries GmbH produced methanol from wood using its Carbo-V process. In the Chemrec AB pilot plant in Piteå, Sweden about 6 tons per day of methanol is used as an intermediate in the production of BioDME. While the biochemical route through methanothrophic bacteria is still in an early state of development the conversion of biogas to methanol has been proven at bench scale. ZSW has proven that methanol could be produced from biogas at a decentralised level.

# Applications

Low-percentage methanol-gasoline blends (up to 3 % as per current EU standard EN228) can be effectively used in conventional spark-ignition engines with no technical changes, the use of alcohol fuels in heavy duty applications is being investigated by motor manufacturers.

#### **Molecular Formula**

CH<sub>4</sub>O

# **Comparison of Fuel Properties**

Property	Methanol	Petrol
Density at 20 °C [kg/l]*	0.79	0.74
Lower heating value [MJ/kg]*	19.7	43.9
Octane number	>110	92
Fuel equivalence	0.48	1
GHG [gCO <sub>2</sub> eq/ MJ]**	Waste wood methanol: 5	
	Farmed wood methanol: 7	

Source: \*FNR 2012. Median values are used for simplification. Please refer to standards for ranges. \*\* Directive 2009/28/EC, total for cultivation, processing, transport and distribution

#### Utilization

Chemical feedstock, petrol blend component

Relevant fuel regulations

EN 228

Main feedstocks Natural gas, coal, biomass

# Scale of Production

Industrial scale

#### **Projects on methanol**

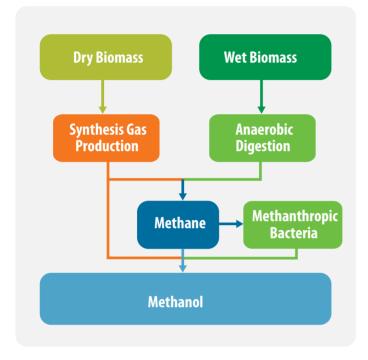
**SUPER METHANOL** - Reforming of crude glycerine in supercritical water to produce methanol for re-use in biodiesel plants (FP7-212180)

MTO/OCP Project - Methanol-to-olefins/olefin cracking process (€45m project funded by Total)

# Methanol from biomass

# **Production process**

In nature MeOH is produced via anaerobic metabolism by many bacteria. It is also formed as a by-product during the ethanol fermentation process. MeOH also occurs naturally in many plants, especially in fruits. MeOH is mainly synthesized from natural gas, but also from coal, mainly in China and South Africa. Biomass can be converted to MeOH via thermochemical and biotechnological pathways as shown in the following diagram.



# **Thermochemical pathways**

The thermochemical conversion paths to MeOH are basically the same as for fossil feedstocks, such as coal or natural gas.

The biomass is gasified and the resulting synthesis gas, a mixture of CO,  $H_2$  and  $CO_2$ , is adapted to the quality requirements of MeOH synthesis.

During synthesis the following reactions occur:

 $CO + 2H_2 \iff CH_3OH$ 

 $CO_2 + 3H_2 \iff CH_3OH + H_2O$ 

 $CO_2 + H_2 \iff CO + H_2O$ 

The formation of MeOH is exothermic and is favoured by high pressures and low temperatures. For reasons of process simplification, investment cost reduction and energy consumption reduction, alternatives are under development, which could also be used for MeOH from biomass

Direct oxidation of Methane:  $2CH_4 + O_2 \iff 2CH_3OH$ 

Liquid-phase oxidation of Methane

Conversion through monohalogenated methanes

# Some major methanol stakeholders in the EU

Chemrec AB, Sweden VärmlandsMethanol AB, Sweden BioMCN B.V., Netherlands B.T.G. BIOMASS TECHNOLOGY GROUP BV, Netherlands Choren Industries GmbH, Germany Karlruhe Institute for Technology (KIT), Germany ZSW, Germany DECHEMA, Germany Technical University of Vienna, Austria Technical University of Graz, Austria

# **Biochemical pathways**

One biochemical route is via methane formation by anaerobic digestion. This process is well developed due to the rise of biogas production from municipal waste or landfill sites. The biogas has to be cleaned to obtain a gas with high methane content and MeOH is then produced from the methane as described above.

Recently a genuine biochemical route using methanothrophic bacteria has been investigated. For example, bacteria such as *Methylococcus capsulatus* will convert methane to MeOH if methane is the only available resource.

# **Further information**

Up-to-date information on methanol from biomass R&D&D is available on the Euorpean Biofuels Technology Platform website **www.biofuelstp.eu**.



# Liquid, synthetic hydrocarbons

Lab scale

Bench scale

Pilot Plant

Demonstratio

Production

### Introduction

Hydrocarbons are organic compounds consisting of hydrogen and carbon. There are many sub-groups: paraffins, such as alkanes, alkenes, alkynes, naphthenes, such as cycloalkanes, and aromatics, such as xylene and benzene, as well as many other related compounds consisting of hydrogen, carbon, nitrogen and sulphur.

Hydrocarbon fuels produced from biomass are called biofuels. When the fuels are produced via extensive processing, such as the XtL routes, they are generically called synthetic fuels.

See page two for Production Process and Applications.

#### State of the Art

Currently, there is no large-scale production of BtL fuels in Europe. The research project OPTFUEL, led by the Volkswagen Group, aims at demonstrating the production of BtL-based fuels made from wood and wood residues. In the OPTFUEL project fast growing biomass like willow or poplar are used as feedstock. The development of BTL production technology is still in progress and is not yet competitive.

CHOREN Industries Ltd. developed the so-called Carbo-V process, which is a three-stage gasification process resulting in the production of syngas:

- low temperature gasification
- high temperature gasification
- endothermic entrained bed gasification

After gas conditioning the Fischer-Tropsch process is then used to convert the synthesis gas into a crude product which is further processed using hydrocracking into products such as the automotive fuel SunDiesel<sup>™</sup>.

Currently, a pilot plant for a novel production process, the socalled bioliq-process, is underway at the Karlsruhe Institute of Technology (KIT). The bioliq pilot plant will cover the process chain required for producing customized fuels from residual biomass, dry straw or wood. Furthermore, the integrated process chain enables production of both fuels and chemicals. The concept combines decentralized production of an energy rich intermediate product "bioliqSynCrude" and centralized processing into products with final industrial-scale refinement.

# **Molecular Formula**

 $C_x H_y$  (general),  $C_n H_{2n+2}$  (alkanes)

# **Comparison of Fuel Properties**

	BtL**	Diesel
Density at 20 °C [kg/l]*	0.76	0.83
Lower heating value [MJ/kg]*	43.9	43.1
Viscosity at 20 °C [mm <sup>2</sup> / s]*	4.0	5.0
Cetane number*	>70	50
Fuel equivalence*	0.97	1
GHG [gCO <sub>2</sub> eq/ MJ]*	n.a.	

Source: FNR 2012. \* Median values are used for simplification. Please refer to the standards for ranges. \*\* Figures based on FT.

#### Utilization

petrol, diesel, aviation fuel, marine fuel, Chemicals (naptha)

# **Relevant fuel regulations**

EN 590 (diesel fuel) ASTM D7566 (50% FT fuel in Jet-A1)

#### Main feedstocks

Energy crops and trees, agricultural food and feed crops, agricultural crop wastes, wood wastes and residues

# **Scale of Production**

Pilot test stage

# Liquid, synthetic hydrocarbons

# **Production process**

A wide variety of hydrocarbon components are blended together to make fuels according to the specifications appropriate for cars, trucks, trains or aeroplanes.

Liquid, synthetic hydrocarbons (XtL) can be used in petrol, diesel, aviation fuel and marine fuels. To what extent depends on their properties, which result from the specific manufacturing process and subsequent downstream processing. XtL is the generic abbreviation for synthetic liquid hydrocarbons. To distinguish between the different raw materials; the abbreviations CtL (Coal to Liquid), GtL (Gas to Liquid) and BtL (Biomass to Liquid) are used. BtL is produced in a four-step-process:

#### 1. Gasification – to produce raw syngas:

 $C_xH_vO_z + AOa \rightarrow CO + H_2 + CO_2$ 

Exact reactions are multifold, e.g. any sulphur becomes  $\rm H_2S$  and COS

#### 2. Syngas conditioning - to achieve correct gas quality:

 $CO + H_2O \iff CO_2 + H_2$ 

and removal of  $CO_2$ , and any  $H_2S$  and COS

#### 3. Synthesis via a type Fischer-Tropsch process:

 $nCO + 2nH_2 \iff (-CH_2-)n + nH_2O$ 

or

synthesis via a Methanol-to-Gasoline process:

 $CO + 2H_2 \iff CH_3OH$ 

 $nCH_{3}OH + H_{2}O \rightarrow n/2CH_{3} - O - CH_{3} + n/2H_{2}O \iff (CH_{2})_{n} + nH_{2}O$ 

#### 4. Product preparation – to achieve desired properties:

This can range from simple distillation to complex hydroprocessing and distillation. This is followed by preparation of final fuels, which is largely a skilled blending operation.

Hydrotreated vegetable oils (HVO) are produced from vegetable oils or fats via direct hydrogenation (hydrogenolysis). It is possible to use the catalytic processes and catalysts similar to crude oil middle distillate hydro treatment, which is a commercial process. The liquid fuel is comparable to FT fuels.

# Applications

Hydrocarbon fuels are ideal for transportation applications because they have high energy content per volume or mass and, since they are mostly liquids, they can be easily transported and stored.

# **Major stakeholders**

Some major stakeholders in the EU are listed below: Volkswagen AG, Germany Renault SA, France Karlsruhe Institute of Technology (KIT), Germany Lurgi, Germany IFPEN, France NSE Biofuels Oy (Joint venture Neste Oil and Stora Enso), Finland UPM Kymmene, Finland Uhde, Germany

Their utilization as a transportation fuel requires no significant changes to the existing infrastructure and engines, because synthetic hydrocarbons can be processed to fit the current specifications. Hence they are often referred to as drop-in fuels.

# Example projects on synthetic hydrocarbons

**OPTFUEL** - optimised fuels for sustainable transport (FP7)

**BIOLIQ** - Biomass to Liquid Karlsruhe

**BioTfueL** - a French/German project aims to integrate all stages of the BTL process chain and bring them to market

**BRISK** – European research infrastructure for thermal conversion technology, which aims to overcome fragmentation in experimental facilities and foster greater cooperation R&D (FP7)

**CEA Bure Saudron** - will use foresty and agricultural residues to produce ~23000 tonnes/year of biofuel (diesel, kerosene and naptha)

**Rentech** - US-based projects focusing on syngas production and synthetic hydrocarbon technology

# **Further information**

Up-to-date information on synthetic hydrocarbons R&D&D is available on the Euorpean Biofuels Technology Platform website **www.biofuelstp.eu**.