Biomethanol as a second-generation biofuel for transportation

Biomethanol produced from by-product glycerin is a second-generation biofuel in its own right and a feedstock for other environmentally friendly fuels

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The European Union's Renewable Energy Directive (RED) has set a 5.75% biofuels target for transport fuels by 2010 (10% by 2020). These ambitious figures will bring prolonged market growth for the foreseeable future. For some years, ethanol and biodiesel have been seen as the two most viable biofuels to reduce CO_2 emissions and to reduce energy dependency in the transport sector. Recent developments have led to other alternatives, though. One of these, biomethanol, now offers petrochemical companies an attractive extra opportunity to meet the EU biofuels mandate.

Methanol (CH_3OH, methyl or wood alcohol) is the simplest of the alcohols. It is an extremely versatile and widely used chemical building block, and can produce a whole range of polymer materials, including polyolefins, polyesters, polyurethanes, phenolic resins, and acrylic paints and adhesives. It burns with a non-luminous, bluish flame. It can be used either as a fuel in its own right or as a feedstock for other environmentally friendly fuels.

Methanol is conventionally made from fossil natural gas or by coal gasification, while biomethanol is made from biogas generated exclusively from renewable and non-food crop resources. That makes biomethanol a second-generation biofuel.

Nobel Prize winner George A Olah in 2005 proposed a complete methanol economy using synthetic (or, even better, sustainable) methanol as an energy storage medium. Unlike a fuel like hydrogen, a methanol economy could use the existing gasoline infrastructure with only slight changes. When the State of California evaluated alternative fuels after recent oil price shocks, officials found that methanol "clearly stood out" as having the best widespread potential for replacing petroleum. The strongest growth in demand for methanol is currently in Asia, and most of that is in China (among other applications, as a feedstock for dimethyl ether (DME) and as a blend component in gasoline).

Making methanol from organic material is, in itself, nothing new. Its origins go as far back as the ancient Egyptians, who obtained methanol (wood alcohol) from the pyrolysis of wood. Until now, though, biomethanol production has been small scale and not economic. Dutch start-up BioMCN has, however, developed an innovative, large-scale industrial process that converts crude glycerin into biomethanol. It is almost ironic that a product which in origin is as old as the Pharaohs now qualifies as a second-generation biofuel. However, high-quality biomethanol made by

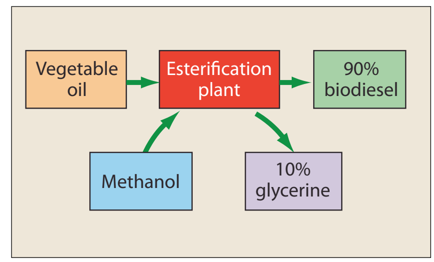


Figure 1 Biodiesel production has glycerin as a major by-product

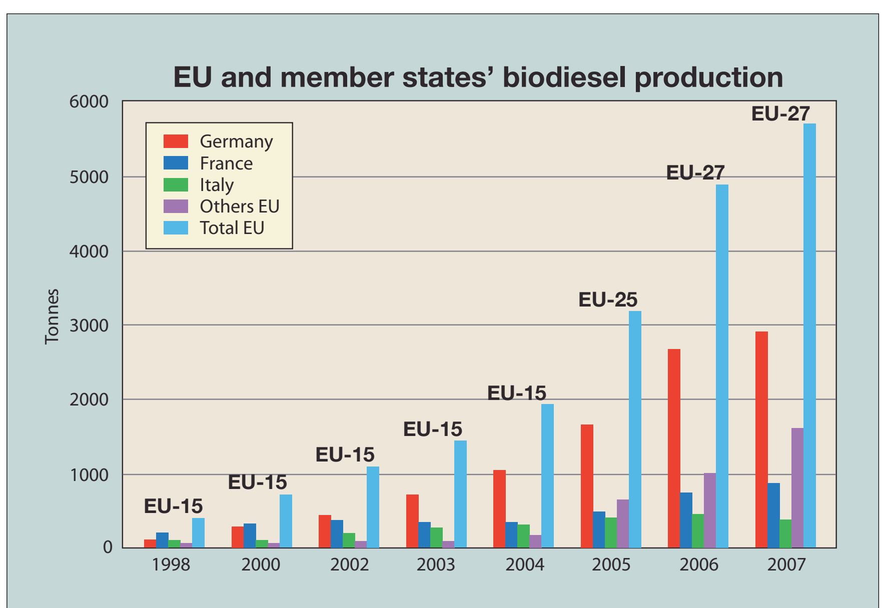


Figure 2 Growing biodiesel production brings with it huge amounts of glycerin by-product (source: European Biodiesel Board)

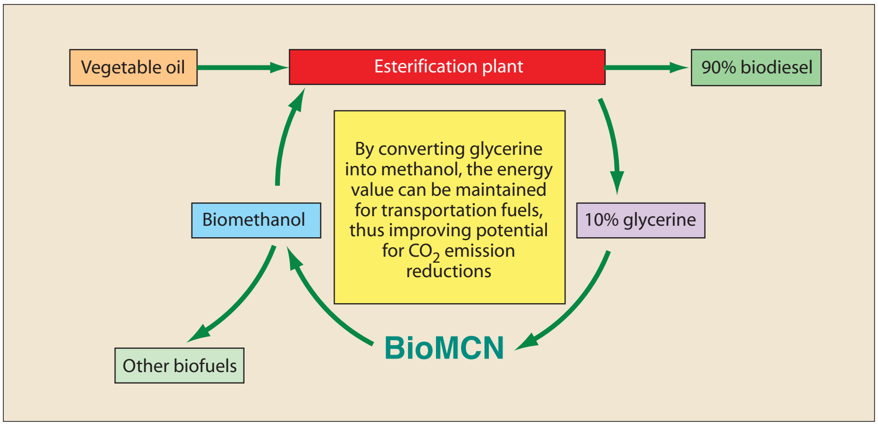


Figure 3 Converting glycerin into methanol increases the energy value and CO_2 emission reduction potential of the process

converting glycerin (itself a by-product) through a thermochemical reaction process meets all of the second-generation criteria.

Biomethanol has another advantage: besides being an excellent fuel to run combustion engines, it can also be used to make biodiesel to run diesel engines as well as a range of other sustainable fuels. And its production does not need to take valuable land otherwise used for the production of food crops.

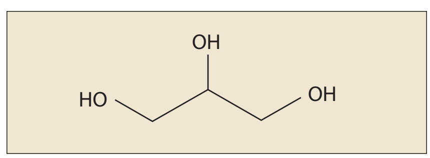
Using crude glycerin as a feedstock

Biodiesels are mono alkyl (methyl or ethyl) esters and can be used on their own or blended with conventional diesel in unmodified diesel engines. Biodiesel is now made in large-scale production from a variety of feedstocks, including palm oil, soy oil and rapeseed oil. A major by-product of biodiesel production is glycerin, and this gives it a significant advantage as a renewable feedstock: there is already a growing oversupply.

Biodiesel is commonly produced by the transesterification of vegetable oil or animal fat, exchanging one alcohol group for another. Most transesterification reactions use methanol to produce methyl esters, and these produce glycerin as a by-product. Every tonne of biodiesel manufactured produces 100 kg of glycerin (Figure 1).

Demand for diesel is increasing, and regulations worldwide will demand a corresponding increase in supplies of biodiesel. So, as biodiesel production continues to grow, crude glycerin production will increase with it. That is true not only in Europe (Figure 2), but also in the Americas and Asia, where several countries have also mandated biodiesel quotas.

Glycerin, also known as glycerol, is a colourless, odourless and viscous liquid. It is soluble in water and a sugar alcohol with the formula $C_3H_8O_3$, containing three -OH groups:



Today, much of the crude glycerin produced is purified for many different applications in the pharmaceuticals and other industries, with products ranging from toothpaste to paint. However, demand is nowhere near enough to consume the ever larger amounts of crude glycerin coming onto the market, and production is forecast to grow significantly over the coming years.

Market prices for crude glycerin are therefore rather volatile, with a tendency to fall rapidly to very low levels as soon as biodiesel production is running at higher rates of capacity utilisation. The energy potential of this crude glycerin is at the moment not being fully utilised (Figure 3), which is a waste, because converting it to biofuels could make a valuable contribution to emissions reductions.

Converting crude glycerin into biomethanol can convert its energy content into a variety of transportation fuels. That could bring 70% reductions in CO_2 emissions from each litre of gasoline saved.

The industrial process to do this has been perfected and patented by BioMCN. Founded in November 2006, BioMCN is owned by an international consortium of companies (Econcern, Teijin, NOM and ChemieInvest) and private individuals. It is the world's first company to start commercial production of biomethanol on an industrial scale. The company has already acquired two existing methanol plants in The Netherlands, with a combined capacity of approximately one million tonnes per year, which until then had been running on natural gas.

In October 2007, BioMCN received the Biofuels Technology Innovation Award for the largest contribution to new biofuels developments. A year later, in October 2008, BioMCN received the European Chemical Industry Council's (CEFIC) Responsible Care Award in the Small and Medium Enterprise (SME) category for its innovative approach.

Biomethanol production process

Biomethanol production is based on the original methanol production process, which converts natural gas (CH_4, methane) into methanol. Here, three stages — steam reforming, synthesis and distillation — produce 99.85% pure methanol.

After purification, natural gas is cracked in a steam reformer. Steam reforming mixes the methane with large amounts of steam. The methane/steam mixture flows through pipes over a catalyst and is heated to 500–850°C. After the steam reformer, the methane is split into syngas, a mixture of carbon monoxide (CO), carbon dioxide (CO_2) and hydrogen (H_2).

The syngas is cooled to an ambient temperature and compressed to close to 100 bar before it is fed to the synthesis reactor. In this reactor, the syngas components react to form methanol. This methanol contains about 17% water, which is removed by distillation.

In the distillation process, water, light alkanes and the heavy ends — the denser fractions — are removed from the main stream. The outcome is 99.85% pure methanol.

Using glycerin instead of methane as feedstock

The production process for biomethanol is no different to the production of regular methanol. What is different is the origin of the gas stream going into the methanol reformer. Instead of natural gas, the feedstock is glycerin. It is not possible to feed liquid glycerin to the reformer directly. It first has to be converted to the gas phase. The glycerin is purified and evaporated in a process patented by BioMCN.

The crude glycerin contains several impurities, mainly water, sodium and potassium salts and a certain amount of undefined organic components. These have to be removed, since the glycerin feedstock to the evaporation unit has to have a high purity level with a low chloride and sulphur content.

The glycerin is purified in a vacuum distillation process, where it can be evaporated below its degradation temperature to remove unwanted components. The organic matter (heavy fractions) that has been removed from crude glycerin can be used in fermentation units to produce biogas for generating green electricity (so also contributing to the reduction of CO_2 emissions).

The purified glycerin is heated and fed to an evaporator, which is optimised to prevent early glycerin degradation. Glycerin vapour is fed to the existing steam reformer, just like natural gas in the original process.

In the reformer, just as with natural gas, the glycerin is split into syngas

First sample of biomethanol at BioMCN

(The reformer can also be fed with a mixture of biogas and natural gas.) When converting a significant amount of glycerin, the carbon monoxide/carbon dioxide ratio in the syngas is slightly different to that of syngas produced from natural gas only, but this is of no consequence for the feed to the methanol synthesis.

Steam reforming of glycerin produces no components other than those to be expected in a conventional syngas mixture. Hence, methanol synthesised from natural gas and biomethanol produced from glycerin are chemically identical. So (apart from expensive C_{14} analysis) it is not possible to identify whether a methanol molecule has a natural gas or glycerin origin. As for performance and applications, there is no difference whatsoever.

Production capacity

March 2008 saw the successful start-up of a pilot plant producing 20 000 tonnes of biomethanol per year. In the meantime, construction of the first large production unit is well under way. The next step in the process is to fully convert both methanol production lines from natural gas to biogas. The transition will be performed in stages over the coming years, in steps of 200 000 tonnes capacity at a time. The

Placement of the purification column during the construction of a new biomethanol plant first large unit is scheduled to be operational by March 2009.

Biomethanol: a building block for sustainable fuels

Biomethanol is chemically identical to regular methanol and meets or even exceeds internationally accepted specifications published by the International Methanol Producers and Consumers Association (IMPCA). Since it is chemically identical, it can be used in the same wide range of applications for which regular methanol is used today, including production of formaldehyde and acetic acid. However, the drive to go green in most of these markets does not compare to the need for viable second-generation biofuels for transportation.

Biomethanol can be used either as a fuel in its own right or as a chemical building block for a range of fuels. The RED includes several fuels that can be made from biomethanol. These include bioMTBE, biodiesel, biohydrogen, bioDME, MTG and gasoline blends:

- Methyl tertiary butyl ether (MTBE) is used primarily as a fuel component in gasoline. Oxygenates like MTBE increase the octane rating and help gasoline to burn more cleanly. The EU biofuels mandate led to many MTBE facilities being converted to produce ethyl tertiary butyl ether (ETBE), using ethanol as the renewable component. However, MTBE is today still being produced and used in gasoline. Without needing to change anything in their processes or formulations, petrochemical companies can now easily convert a further portion of their total fuel output to meet renewable targets by simply replacing regular MTBE made from methanol with bioMTBE made from biomethanol (Figure 4)
- During the biodiesel transesterification reaction, methanol is used to produce methyl esters. Feeding back the biomethanol instead of regular methanol therefore further improves biodiesel's potential for reducing CO_2 emissions. This is of particular interest applied to those types of biodiesel where default CO_2 reduction values are below the anticipated future CO_2 reduction target of the RED
- Despite its good performance in reducing tailpipe emissions, one of the drawbacks of hydrogen is the fact that it is still today mostly made from a fossil feedstock: natural gas. One way to overcome this is by converting biomethanol into biohydrogen. Its four hydrogen atoms make methanol a very convenient way of storing hydrogen. It therefore has a high hydrogen content for its weight. This brings another advantage to converting methanol into hydrogen at point of use: it avoids the difficulties of transporting a gas like hydrogen, which needs a heavy tank pressurised to around 700 bar, or a cryogenic container at near -270ºC.

  Biomethanol can either be converted to hydrogen at the filling station or in the car itself by using direct methanol-to-hydrogen fuel cells. Other applications of direct methanol fuel cells (DMFC) include laptop batteries and mobile phones
- In Europe, DME is used primarily as a propellant in (cosmetic) spray cans. In Asia, however, DME is blended with LPG for heating and several projects have run diesel engines on DME. Tests have shown that DME is one of the cleanest fuels in terms of emission levels. When used in conventional diesel engines, soot emissions are reduced to virtually zero, even without a soot filter. DME is conventionally made from methanol. When made from biomethanol, the overall well-to-wheel performance improves even further
- Methanol to gasoline (MTG) was first introduced in the 1970s. The resulting gasoline is very similar to regular gasoline specifications, which means it can fuel existing combustion

BioMCN is converting two existing methanol plants to the biomethanol process engine designs. Using biomethanol also effectively makes the resulting gasoline renewable. And processes other than MTG can also convert biomethanol into fuels very similar to their fossil counterparts

- As with bioethanol, biomethanol can also be blended into gasoline blends. Materials used in flexi fuel vehicles (FFVs) as fuel linings and seals, for instance, are actually already typically tested with methanol to determine their resistance to corrosion.

In the US and Europe, FFV engines are optimised for a blend of 15% maximum gasoline with 85% anhydrous ethanol (E85 fuel). The ethanol content limit reduces ethanol emissions to avoid problems of cold starting at temperatures below 11ºC. Field trials with commercially available FFVs have also shown that driving on biomethanol is feasible. Driving on biomethanol in fact reduces tailpipe emissions even further than with ethanol (Figure 5).

Like most fuels, methanol is hazardous when exposed to heat or flame. It is safer than gasoline, though, being harder to ignite and releasing less heat when it burns. Although toxic, it is not as toxic to the body as conventional gasoline. If it is spilled, methanol is oxidised within days in the presence of sunlight to carbon dioxide and water. Mixed with surface water, it quickly biodegrades aerobically or anaerobically, and so should not persist in the environment. It is therefore more environmentally benign than conventional gasoline.

Biomethanol is also, in its own right, one of the best performing fuels, with properties matching or better than those of gasoline. It has, for example, a much higher octane index. It also has a significantly higher latent heat, which, combined with a relatively low stochiometric air-fuel ratio (AFR), reduces the cycle temperature. Its specific energy ratio is high, as is its flame speed, which improves exhaust gas recirculation tolerance. It also has a high molar ratio of reactants to products and a low combustion temperature, meaning less heat rejection. The carbon number is low, with good gCO_2/MJ emissions figures. And, finally, it is liquid at standard temperature and pressure.

Group Lotus remarked after tests with biomethanol: "As well as being green, the great benefit of sustainable methanol is that it would use similar engines and fuel systems to those in current cars; and sustainable methanol can be stored, transported and retailed in much the same way as today's liquid fuels such as gasoline and diesel. Sustainable methanol also possesses properties better suited to internal combustion than today's liquid fuels, giving improved performance and thermal efficiencies. And it is ideal for pressure charging (turbocharging and supercharging) already being introduced.

"Sustainable methanol is better suited to spark-ignition combustion than today's liquid fuels, delivering better performance and thermal efficiencies due to its higher octane rating, giving it better resistance to knock. As a result, it is a fuel that will benefit motorists in terms of driving experience. For example, the Exige 270E Tri-fuel is quicker to 60 mph from standstill and has a higher top speed when using 100% sustainable methanol fuel than with conventional gasoline. Sustainable methanol is also ideally suited to pressure charging, a trend already well under way as carmakers look to downsize engines to reduce fuel consumption.

"The low carbon number alcohol fuels, methanol and ethanol, give more power when burned in the engine than conventional gasoline (petrol) fuel. The performance benefits come largely from the high heats of vapourisation of methanol and ethanol, which give strong charge-cooling effects, and the increased octane ratings. There are other, secondary thermodynamic effects. Methanol's higher heat of vapourisation leads to a slightly higher performance relative to ethanol."

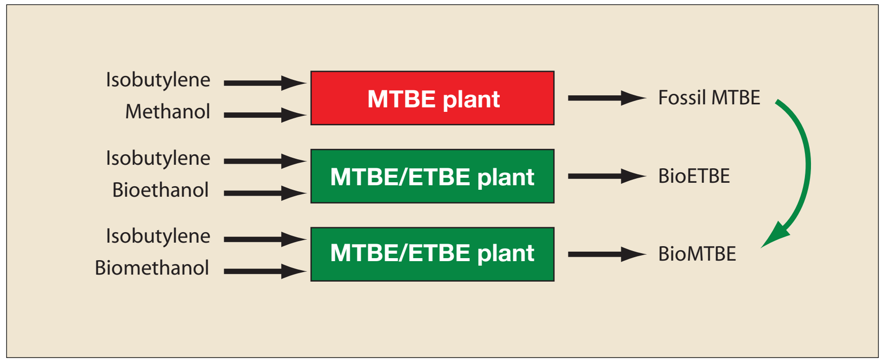


Figure 4 Biomethanol enables the use of MTBE fuel formulations as an additional way to meet the RED requirements

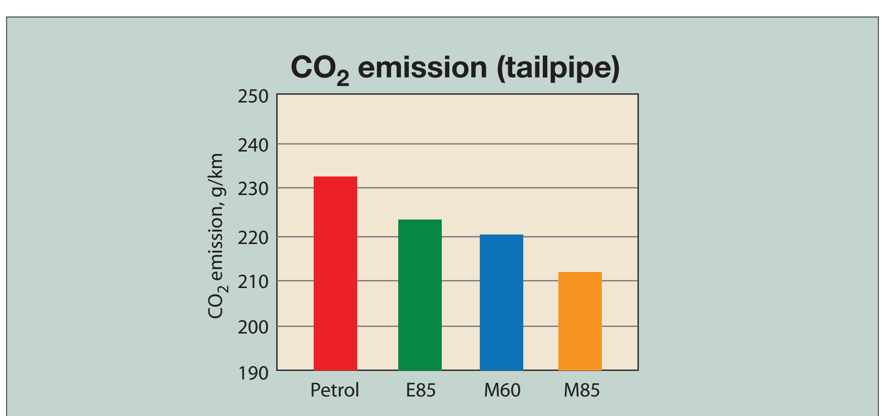


Figure 5 Tests performed with a 2.0 litre FFV engine (Euro 4) show the low CO_2 emissions when running on M85 (a blend of 85% biomethanol and 15% gasoline)

Towards a certificate of origin

Each EU member state has a different way of ensuring the RED's targets are being met. There are penalty systems, subsidies and incentives. However, the RED not only sets targets for the share of energy from renewable sources in transport fuels. Article 15 also addresses the need to meet specific targets for reductions in CO_2 emissions — for sustainability and for land use. This is where things become more complicated, because in this respect ethanol is different from bioethanol, and diesel is different from biodiesel.

And there is more. Besides gasoline and diesel (or combinations of both), the EU directive includes other biofuels such as biomethanol, biohydrogen, bioDME and bioMTBE. Meanwhile, improvements in the production processes of existing second-generation biofuels are bringing further CO_2 emissions reductions and better sustainability. That means the individual biofuels make different contributions to the EU targets.

There are many different channels to convert feedstocks to fuels. It is impossible to track individual molecules, so how can we verify that all EU targets are being met? The answer may lie in a system that has already been working for over ten years for renewable electricity: the Renewable Energy Certificate System (RECS). Instead of trying to trace the flow of individual fuel batches, a biofuel Guarantee of Origin system registers the quality and amount of biofuels entered into and taken out of the fuel system.

Bio-GOs use the same approach as the RECS to provide the necessary proof that biofuels are made from renewable resources. They also provide extra information about sustainability and CO_2 reduction: the green value becomes more transparent. Bio-GOs generate a demand pull for sustainable biofuels. All market players are involved in and benefit from the trade of green value. They ensure standardisation between different EU member states and avoid double counting. GOs can be traded across the borders of EU member states.

This system is much less bureaucratic than other options, thus reducing the overall system cost for market players and governments. Rather than waiting for a system to be enforced, the industry has the opportunity (see www.biofuelgo.org) to propose and implement a system that will work for all parties involved. The biofuelGO Association is now working with the biofuels industry to implement Bio-GO certificates. The first EU member to adopt them has been The Netherlands, which has developed a system and is now deploying it.

The Lotus Exige 270E Tri-fuel is capable of running on any mixture of gasoline, ethanol and (bio)methanol

Inputs from renewable, non-food crop sources

BioMCN is one of the founding members of biofuelGO, an initiative established to implement a pan-European system to certify information on the sustainability of a range of biofuels including biodiesel and ethanol. GO stands for guarantee of origin. It guarantees that biofuels are made from renewable resources, while providing additional information about sustainability and CO_2 emission reductions. Since biomethanol is made from biomass, it will be supplied with such a green certificate that declares the origin of the renewable resources (see Towards a certificate of origin, above).

Biomethanol has the potential to produce least-cost, carbon-neutral biofuels, with a network of biofuel production chains, conversion technologies and a choice of biomass feedstocks. This could dramatically reduce greenhouse gas emissions and improve security of supply. It also promises to avoid the problems biofuels have introduced to food production and land use.

To ensure sustainability, BioMCN uses renewable feedstocks exclusively derived from organic waste materials and crops other than for food consumption. Besides crude glycerin, organic materials like wood, wood waste, grass, algae and agricultural and other organic by-products are also being investigated as alternative feedstocks for gasification to replace natural gas.

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