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PETROLEUM TECHNOLOGY QUARTERLY

**REFINING
GAS PROCESSING
PETROCHEMICALS**

SPECIAL FEATURES

**HEAT MANAGEMENT
CARBON CAPTURE**

When MTBE outscores ETBE for bioenergy content

If MTBE is produced from biomethanol, its bioenergy content as a fuel additive will be counted twice, according to EU biofuels regulations

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Despite improvements in engine technology and fuel efficiency, total CO₂ emissions from road transport fuels continue to grow every year. We must reduce our global dependency on the use of fossil energy.

Over the past decade, we have seen an increase in the use of biodiesel as an alternative to diesel, with ethanol being used as a biocomponent in gasoline, either in ethyl tert-butyl ether (ETBE) or through splash blending. Although these biofuels are made from renewable resources, the past few years have seen increasing concern over sustainability issues, such as deforestation, indirect land use change and competition with food. These issues are driving legislators to insist on the use of “better” biofuels made from more sustainable feedstocks. For biodiesel, alternative oil feedstocks include algae, jatropha and used cooking oils. Much effort is similarly going into the research and development of cellulosic ethanol. But there are other solutions. One such alternative sustainable fuel, biomethanol, is already commercially available in large volumes.

Biofuel generations

The development towards more sustainable biofuels has been described by some as second-generation biofuels to distinguish between traditional biofuels and those with more environmentally friendly attributes. In the EU’s Renewable Energy Directive (RED), however, there is no mention of the term. And to make matters more confusing, some of the latest

developments are now described as third- or fourth-generation biofuels.

Even though there is no clear definition of these different generations, a number of specific characteristics are typically mentioned in reference to second-generation biofuels: feedstock sustainability; innovative technology; similar fuel properties; and reduction in GHG emissions. These help to distinguish between different biofuels and demonstrate that biomethanol does, indeed, qualify as a “better” biofuel.

What makes a second-generation biofuel?

Feedstock sustainability

Biofuels were introduced as an important part of the solution to reducing the use of fossil energy sources and limiting the effects of global warming. But with growing volumes of ethanol and biodiesel being blended in the fuel pool, there also came concern over the potential negative effects some biofuels themselves might have on the environment.

Although many factors have an impact on the agricultural sector, when food prices shot up in 2008 many analysts were quick to blame biofuels as the main cause. Deforestation, change in land use and child labour are but a few of the other negative trends blamed on biofuels. As a result of these concerns, there is increasing pressure on biofuel producers to start using more sustainable feedstocks.

Article 17 of the RED lists sustainability criteria that biofuels need to fulfill to be taken into account for:

- Measuring compliance with the

requirements of the RED concerning national targets

- Measuring compliance with renewable energy obligations
- Eligibility for financial support for the consumption of biofuels and bioliquids.

An exception is made for biofuels made from waste and residues. These only need to comply with the sustainability criteria described in paragraph 2 of the same article, which deals with GHG emissions.

One such feedstock is crude glycerine, the raw material for producing biomethanol. Crude glycerine is a processing residue from biodiesel production and the oleochemical industry, and is recognised as such in Annex V.C.18 of the RED:

“Wastes, agricultural crop residues...and residues from processing, including crude glycerine (glycerine that is not refined), shall be considered to have zero life-cycle greenhouse gas emissions up to the process of collection of those materials.”

Innovative technology

Another common denominator in discussions about “better” biofuels is the use of innovative production technologies to convert sustainable feedstocks into biofuels. Typical examples include Fischer-Tropsch, hydrogenation processes and biomass gasification.

Biomethanol production is based on the original methanol production process, which converts natural gas (CH₄, methane) into methanol. Here, three stages — steam reforming, synthesis and distillation — produce 99.85% pure methanol.

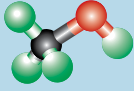
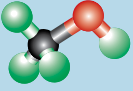
Formula		
	Methanol	Biomethanol
Purity	>99.85%	>99, 85%
Feedstock	Natural gas	Crude glycerine
Well to wheel CO ₂	-	~ 70%

Figure 1 Methanol and biomethanol are identical

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 (CO₂) and hydrogen (H₂). 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 (denser fractions) are removed from the main stream. The outcome is 99.85% pure methanol.

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 glycerine. It is not possible to feed liquid glycerine to the reformer directly. It first has to be converted to the gas phase. The glycerine is purified and evaporated in a process patented by BioMCN.

The crude glycerine contains several impurities, mainly water, sodium and potassium salts, and a certain amount of undefined organic components. These have to be removed, since the glycerine feedstock to the evaporation unit has to have a high purity level with a low chloride and sulphur content. The glycerine 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 glycerine can be used in fermentation units to produce biogas for generating green electricity (so also contributing to the reduction of CO₂ emissions).

The purified glycerine is heated

and fed to an evaporator, which is optimised to prevent early glycerine degradation. Glycerine vapour is fed to the existing steam reformer, just like natural gas in the original process.

In the reformer, as with natural gas, the glycerine is split into syngas (the reformer can also be fed with a mixture of biogas and natural gas). When converting a significant amount of glycerine, the CO/CO₂ 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 glycerine produces no components other than those expected in a conventional syngas mixture. Hence, methanol synthesised from natural gas and biomethanol produced from glycerine are chemically identical. So (apart from expensive C₁₄ analysis) it is not possible to identify whether a methanol molecule has a natural gas or glycerine origin. As for performance and applications, there is no difference whatsoever.¹

BioMCN has a total methanol capacity of 1 million tonnes, of which currently 200 000 tonnes have been converted to biomethanol.

Similar fuel properties

Even though biodiesel and ethanol are used in blend formulations, or even to fully replace fossil diesel and gasoline respectively, they do not have exactly the same properties as their fossil counterparts. They can differ in terms of cloud point, acidity or energy content. Ideally, a “better” biofuel should have properties very similar to those of its fossil counterpart.

Biomethanol is chemically identical to regular methanol made from natural gas (Figure 1). As such, it can be used to convert any existing methanol application into a bioalternative. Like ethanol, biomethanol has a lower energy content and is more acidic than gasoline. However, this does not have to be an issue, because the relevant question should be: “What makes an ideal fuel?” The answer may surprise some (see Table 1).

Ideal fuel properties	
Ideal property	Low carbon number alcohols vs gasoline
1. High octane index	Much better – RON and MON
2. High heat of vapourisation (latent heat)	Significantly higher
3. Low stoichiometric air-fuel ratio (AFR)	Much lower
<i>2 & 3 combined: reduces cycle temperature</i>	
4. High specific energy ratio	Higher
5. High flame speed	30–50% higher
<i>Improves EGR tolerance</i>	
6. High molar ratio of reactants to products	Higher
<i>More work, less heat rejection</i>	
7. Low combustion temperature	Lower
<i>Reduces heat rejection</i>	
8. Low carbon number	Yes
9. Good gCO ₂ /MJ	Better than gasoline
10. Liquid at STP	Yes
<i>Minimises oxygen displacement</i>	

Table 1

Courtesy: James Turner, Lotus Engineering

Reduction in GHG emissions

Another objective of the RED is the reduction of GHG emissions. Depending on the type of feedstock used and the energy input to produce a biofuel, the average well to wheel reduction of GHG emissions is very different. The RED has set clear targets for reducing GHG emissions, and in future those biofuels that do not meet the lower limits will no longer be included in the bioenergy targets.

According to paragraph 2 of article 17, biofuels can only be taken into account for compliance with the requirements of the directive if GHG savings are at least 35%. From January 2017, the savings will have to be at least 50%, and for new installations that start production after 1 January 2017, emissions savings will have to be at least 60% from January 2018.

For biomethanol made from crude glycerine, the current GHG savings are already around 57%, and after some further process optimisations the emissions savings are expected to even exceed 70% later this year.

Biomethanol in fuel applications

Biomethanol meets all the requirements of a second-generation biofuel. So how can it be used most efficiently to contribute to renewable energy targets?

- **Option 1: Biodiesel** To produce biodiesel, 10% methanol is added to 90% vegetable oil in an esterification process, resulting in 90% biodiesel and 10% crude glycerine. This allows for a perfect closed-loop system (see Figure 2). But, because the RED considers biodiesel to be of 100% bio-origin, there is no immediate benefit to replacing the existing methanol unless it helps to improve CO₂ emissions reduction potential or when required by specific national legislation

- **Option 2: Bio-DME** Di-methyl ether (DME) can be used in diesel engines, as liquified petroleum gas (LPG) is used in gasoline engines. In Europe, DME is still primarily used as a propellant in spray cans, while China is advancing its use as an energy product

- **Option 3: Biohydrogen** Even though the use of hydrogen as

engine fuel has been investigated for many years, so far it can hardly be called a commercial breakthrough. Despite attractive low tailpipe emissions, most hydrogen produced today is still made from natural gas. An alternative and sustainable way of producing (bio)hydrogen is by converting biomethanol into biohydrogen. Since the use of hydrogen as a transportation fuel is currently limited to demonstration projects, a more immediate short-term opportunity is to use biomethanol in direct methanol to hydrogen fuel cells (DMFCs) as battery replacements in laptop computers and mobile phones

- **Option 4: Biogasoline** In 1979, the New Zealand government decided

- **Option 6: Bio-MTBE** When the first biofuels mandates were implemented, one solution chosen by several refineries was to switch existing methyl tert-butyl ether (MTBE) facilities to produce ETBE. A drawback of this switch is that output is limited to either a fossil oxygenate (MTBE) or a bio-oxygenate (ETBE).

With biomethanol, the same plant can produce both a regular (fossil) oxygenate as well as a bio-oxygenate without having to make changes. This enhances flexibility and enables refineries to choose the option with the highest return.

In Europe, about 4 million tonnes of oxygenates are blended every year. In today's market, bio-MTBE is therefore the best option for

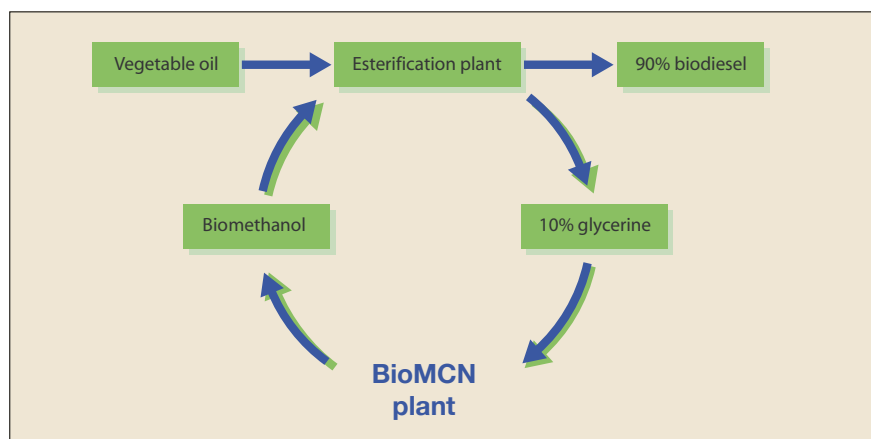


Figure 2 Biomethanol can be produced in a perfect closed loop

to build a commercial 14 500 bpd plant in Montunui, owned 75% by the New Zealand government and 25% by Mobil. The resulting gasoline has properties very similar to those of regular gasoline made from crude oil. The plant started up in 1985 and operated successfully for around ten years until its conversion to chemical-grade methanol production²

- **Option 5: Direct blending (M85)** Just as they consume E85 (85% ethanol, 15% gasoline), flexifuel vehicles can run on M85 (85% biomethanol, 15% gasoline). This is a very efficient way of using the bioenergy content of biomethanol while maintaining as much of the CO₂ reduction potential as possible. However, the use of high alcohol blends in Europe is currently still limited

adding biomethanol to existing fuel formulations while still meeting the requirements of the Fuel Quality Directive (EN228).

MTBE

Despite the clear benefit of MTBE in reducing emissions and thus contributing to better air quality, it was the centre of much negative attention in the 1990s when high levels of MTBE were found to be contaminating Californian groundwater. This was caused by leaking underground storage tanks and spills due to overfilling.

Groundwater contamination involving gasoline is not new. MTBE has attracted attention to this problem because it has become a widely used gasoline component, with several specific properties that distinguish it from other gasoline

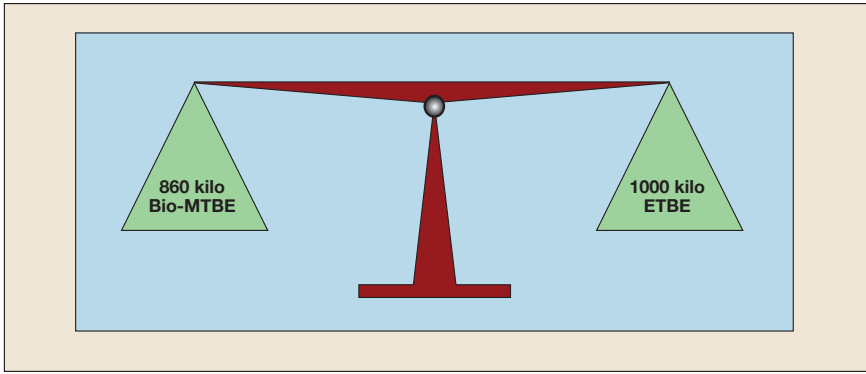


Figure 3 Administratively, only 860kg of bio-MTBE are needed to replace a tonne of ETBE

ingredients such as benzene and toluene:³

- MTBE is more soluble in water than other gasoline components, so in certain conditions it tends to spread faster and further through the soil, creating a halo effect around the spill
- MTBE has a very low taste and odour threshold that is noticeable at low concentrations
- MTBE biodegrades more slowly and therefore may appear to persist in the environment for longer.

These properties highlighted the fact that there were problems with underground storage releasing gasoline into the groundwater, but also made MTBE stand out from the other contaminants. Its strong smell and taste are easy to detect, and resulted in it becoming the scapegoat of a much more serious problem, which has led some states to ban MTBE.

Several reports have demonstrated that the incidence of serious groundwater contamination by MTBE, both in the US and Europe, is in fact low. Nevertheless, it has led to many misconceptions and prejudices against MTBE. These are largely unfounded because it has been demonstrated that the environmental and health

impact of MTBE is comparable, with the exception of certain minor variations, with that of ETBE and tert-amyl methyl ether (TAME).

MTBE has undergone a full EU risk assessment study for both health and environmental effects. The results were published in the *Official Journal of the European Union* on 4 December 2001. Both health and environmental effects are evaluated, together with the potential for exposure, to assess the overall risk that a substance may present. This process led to a formal decision by the EU that MTBE is not classified as carcinogen, mutagen or reproductive toxin.⁴

The presence of MTBE in groundwater is certainly not inherent to the product itself, but can clearly be attributed to careless handling. Banning MTBE does not solve the underlying problem of gasoline leakage and may create a false sense of security, as contamination could go undetected much longer.

MTBE has delivered significant air quality benefits by reducing harmful exhaust emissions. As long as the issue of groundwater contamination is avoided through proper handling and storage, the public need not be denied the proven benefits of MTBE, which can now

be further extended when MTBE is made from biomethanol.

Bio-MTBE and bottom line results

To encourage the development and use of more sustainable biofuels, RED Article 21.2 specifies that the energy content of biofuels made from a sustainable feedstock be counted twice towards operators' targets:

"For the purposes of demonstrating compliance with national renewable energy obligations placed on operators and the target for the use of energy from renewable sources in all forms of transport referred to in Article 3(4), the contribution made by biofuels produced from...residues...shall be considered to be twice that made by other biofuels."

According to Annex V.C.18 of the RED, crude glycerine is labelled as a residue from processing. This means the bioenergy content of biomethanol, which is made from crude glycerine, will be counted twice no later than the implementation of the Directive in December 2010.

In December 2009, well in advance of this RED implementation deadline, the Dutch parliament accepted an amendment to national legislation to implement the so-called double counting measure with immediate effect. An important element of the legislation is the verification protocol, which describes how producers and consumers of these "better" biofuels have to demonstrate compliance with the rules and regulations of the amendment to be allowed to count the bioenergy content twice.

One tonne of biomethanol contains 20 GJ of bioenergy. When counted twice, the same volume is then reported to have 40 GJ of bioenergy. In comparison, bioethanol contains 27 GJ of bioenergy. In other words, 1 tonne of biomethanol can (administratively) replace 1.5 tonnes of bioethanol (see Table 2).

To fully appreciate the impact of the higher bioenergy content of biomethanol, the production process of bio-MTBE has to be compared to that of ETBE, an alternative bio-

Bioethanol vs biomethanol energy contents

	Actual energy content		Administrative energy content	
	Energy content by weight (lower calorific value, MJ/kg)	Energy content by weight (lower calorific value, MJ/l)	Energy content by weight (lower calorific value, MJ/kg)	Energy content by weight (lower calorific value, MJ/l)
Bioethanol	27	21	27	21
Biomethanol	20	16	40	32

Table 2

oxygenate. (Bio-)MTBE is produced through the chemical reaction of (bio)methanol with isobutylene, whereas for ETBE ethanol is used as an alternative to methanol. The addition ratios are very different, though. Whereas MTBE contains ~36% methanol, ETBE contains ~45% ethanol.

To confuse matters further, the energy contribution of these alcohols relative to their total energy content is also lower than their volumetric share. The RED contributes 37% of the energy content of ETBE (36 GJ/tonne) to ethanol (versus 45% in volume), and only 22% of the energy content of MTBE (35 GJ/tonne) to biomethanol (versus 36% in volume). From these figures, the real and administrative bioenergy content of both oxygenates can be calculated and compared (see Table 3).

In other words, despite the fact that biomethanol has a lower bioenergy content than ethanol, and bio-MTBE contains less biomethanol than ETBE contains ethanol, the double counting rule results in a 16% higher (administrative) bioenergy content for bio-MTBE.

For every tonne of ETBE blended today, only 860kg of bio-MTBE is needed to achieve the same amount of bioenergy (see Figure 4). This is what makes bio-MTBE an interesting product for refineries to comply with the biofuel mandates in their respective countries.

To meet their biofuel obligations, refineries have various options. Replacing fossil fuels with E85 and B100 (100% biodiesel) would be the easiest from an operational point of view, but so far demand for these products is too low to meet the necessary targets.

Solutions will therefore have to be found within the existing fuel specifications as laid down in the Fuel Quality Directive (EN228). This currently allows for a maximum of 15% oxygenates and 5% ethanol, provided the finished gasoline product stays within specific limits (eg, oxygen content and vapour pressure, RVP).

This has resulted in a more or less common approach in Western Europe, where ~5% oxygenate

Administrative bioenergy for ETBE, MTBE and bio-MTBE					
	Alcohol, %	Isobutylene, %	Energy per tonne, GJ	Bioenergy, %	Bioenergy per tonne, GJ
ETBE	45.1	54.9	36	37	13.3
MTBE (fossil)	36.4	63.6	35	0	0
Bio-MTBE (2nd gen)	36.4	63.6	35	22	7.7 x 2 = 15.4

Table 3

(ETBE or MTBE) is first blended at the refinery. This blend is better known as Blending Oxygenate Basestock (EuroBOB). Even though the exact composition can differ between refineries or as a result of blend cost formulations, all EuroBOBs have in common that up to 5% ethanol can be added afterwards at the rack or depot to formulate the finished gasoline product that is sold at the petrol station (EN228, Euro 95).

Depending on the current strategy to meet biofuel objectives, refineries can benefit in different ways from the higher energy content of bio-MTBE:

- **Option 1: Maintain** By replacing current ETBE volumes with bio-MTBE, the bioenergy content of the EuroBOB goes up. This gives a refinery the choice of blending less ethanol at the depot to replace it with less expensive gasoline components, or continuing to blend the same amount of ethanol to sell gasoline with a higher biocontent while staying within the limits of the EN228 specifications
- **Option 2: Reduce** If the objective is to sell EuroBOB gasoline with the same bioenergy content as its ETBE counterpart, bio-MTBE allows the amount of bio-oxygenate to be reduced, thus creating room to blend other less expensive gasoline components
- **Option 3: Increase** Even though bio-MTBE has a higher bioenergy content than ETBE, the overall

energy content of ETBE is slightly higher. If a refinery requires the same amount of energy contribution from the oxygenate component, about 3% more bio-MTBE needs to be added. This results in an even higher bioenergy content contribution than option 1, with the same alternative options at the depot. Table 4 summarises these options.

Conclusion

MTBE is known to make an important contribution to reducing GHG emissions. Now that it can be made from biomethanol, the overall emissions during its lifecycle are reduced even further. And, because biomethanol is made from crude glycerine, the bioenergy content counts twice. This enables refineries and gasoline blenders to reformulate their gasoline composition to give the best balance between bioenergy on the one hand and cost on the other.

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The higher energy content of bio-MTBE makes for versatile production at refineries			
Scenario	Refinery	Biocontent (per tonne oxygenate)	Blend impact
Current	X% ETBE	13.32 GJ	
Maintain	X% bio-MTBE	15.44 GJ	+16%
Reduce	0.86X% bio-MTBE	13.32 GJ	=
Increase	1.03X% bio-MTBE	15.90 GJ	+19%

Table 4