

**Walter Mirabella**

ISSN 0350-350X

GOMABN 50, 3, 233-242

Izlaganje sa znanstvenog skupa/Conference paper

UDK 665.734.4 : 665.734.5 : 621.434.018.2 : 621.434.068.3

## THE ROLE OF BIO-ETHERS IN MEETING NATIONAL BIOFUEL TARGETS

### *Introduction*

*The European Union (EU) clean air strategy has consistently focused on ensuring that the correct fuel is available to enable the introduction of the next generation of clean vehicles. This has led to a harmonisation of fuel quality across the EU. By far and away the major grade of gasoline is Euro Super (95 RON; 85 MON), with Euro Regular (91 RON; 81 MON) and Euro Super Premium (98 RON; 88 MON) as niche products. Sales of Euro Regular are mostly limited to Germany and Austria, whilst those of Euro Super Premium are more widely spread across the EU. This can rightly be considered to be a single market.*

*EU fuel quality is based on Directive 98/70/EC <sup>1)</sup> and its subsequent updates. The latest of these (2009/30/EC <sup>2)</sup>) came into force in late June 2010 and Member States have until 5 Dec 2010 to transcribe it into national law. As part of this revision, the oxygen limit was increased to 3.7% and with it the maximum limit for all oxygenates. For ethers this means a rise in the permitted level from 15% to 22% in volume. However, the major innovation was the introduction of a requirement to reduce the life-cycle greenhouse gas emissions of the fuels by 6% by 2020 through the use of biofuels or improved operational efficiency. A further 4% of savings was also encouraged by a combination of the use of electric vehicles, carbon capture and storage, and emissions trading.*

*The EU began to focus on renewable energy in transport fuels in 2003 when the Biofuels directive (2003/30/EC <sup>3)</sup>) was adopted. This initial attempt to foster the development of biofuels was justified by three objectives; reduction in CO<sub>2</sub> emissions, improved security of supply and support for the rural economy. This has been recently strengthened and refined both by the aforementioned Fuel Quality directive (2009/30/EC <sup>2)</sup>), and the directive on the promotion of the use of energy from renewable sources (2009/28/EC <sup>4)</sup>). Here the emphasis is to address the climate change challenge by imposing minimum levels of renewable fuels in transport, and specifically biofuels. The “renewables” directive also sets minimum standards for the CO<sub>2</sub> reductions of individual biofuels; the so-called “sustainability criteria”.*

The two new European directives have also recognised the ability of ethers to deliver emission savings by setting default values of CO<sub>2</sub> reduction “equal to that of the ethanol production pathway used”. The European Fuel Oxygenates Association (EFOA) is pleased with this recognition, but believes that it underestimates the benefits of bio-ethers. The directives have created a surge in the use of bio-ethanol in EU gasoline. In 2008 some 29 million hectoliters<sup>5)</sup> were used a significant proportion of which was in the form of bio-ethers.

### Bio-ether Use in Europe

The introduction of the 2003 Biofuels Directive saw a major shift in EU ether production from MTBE (methyl tertiary butyl ether) to bio-ETBE (ethyl tertiary butyl ether) as it provided the oil industry with a “drop in” solution for the rapid introduction of bio-gasoline. Bio-ETBE is substantially similar to MTBE, and easier to blend than ethanol. More recently the new bio-ether TAE (tertiary amyl ethyl ether) has started to enter the market as some TAME (tertiary amyl methyl ether) producers have switched their production. As of 2008 ETBE accounted for roughly half of the fuel ethers consumed in the EU. This demand represents between 4 and 5% of the EU gasoline pool and is serviced by an extensive European production with over 50 units in 20 Member States<sup>6)</sup>. In addition there is also a strong flow of imports into the EU although this has declined somewhat in recent years<sup>7)</sup> due to the increased use of bio-ethanol. The reason for the shift to bio-ethers is quite straight forward. Not only do they remove some of the barriers associated with the introduction of bio-ethanol into gasoline, they also enhance some of its properties. Perhaps the biggest concern is the non-linear volatility behaviour of ethanol due to its loss of hydrogen bonding at low concentrations (Fig. 1).

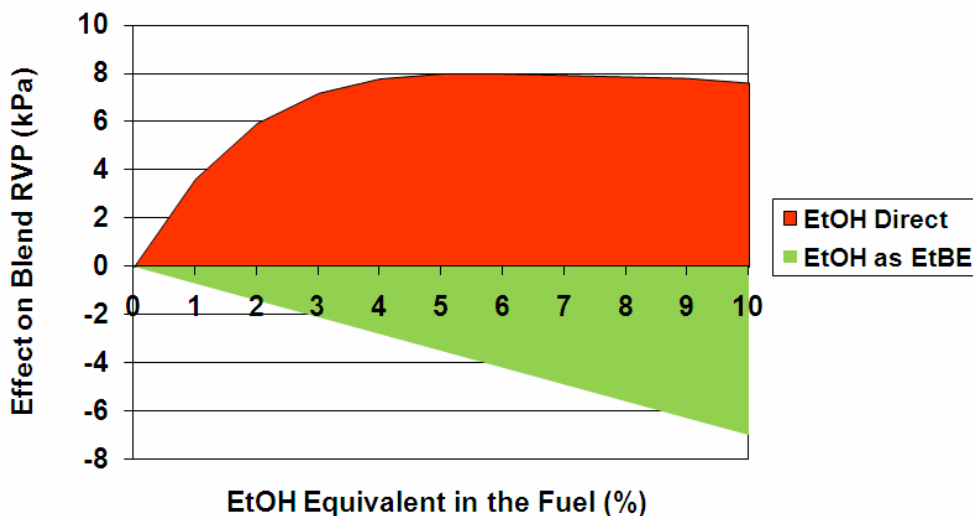


Figure 1: Volatility behaviour of ethanol (EtOH) and EtOH as EtBE

This can lead to difficulties when using shared storage facilities which contain gasoline of varying ethanol concentration. Bio-ethers, such as ETBE, behave as if they were gasoline and thus have no commingling problems. Likewise their low volatility increases the blending flexibility within the refinery. Similarly refineries with FCC and steam crackers produce mixed C<sub>4</sub> and C<sub>5</sub> olefinic streams. These highly reactive and volatile materials were historically added to gasoline. However the progressive tightening of the EU fuel quality standards has effectively removed this outlet. But they can be included if they are converted into ethers or bio-ethers.

The compatibility of bio-ethanol with both vehicle and fuel distribution systems has also been a major concern. This is particularly so in markets with a significant population of older vehicles, due not only to its known aggressivity to certain polymers and metals but also to its ability to pick up water. Bio-ethers on the other hand have been found to behave in a broadly similar fashion to gasoline<sup>8,9)</sup> (Fig. 2).

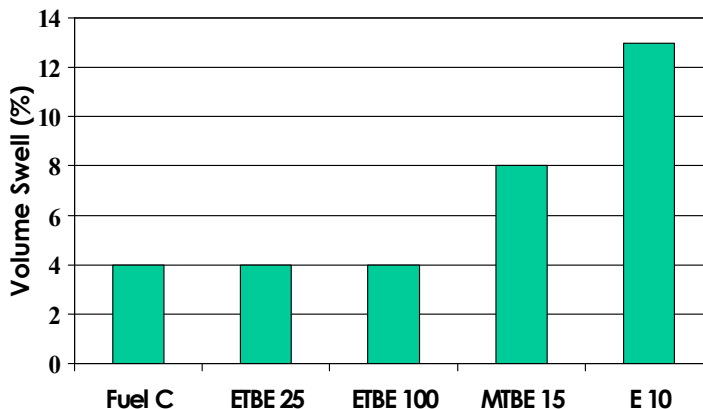


Figure 2: VITON™ a fluoroelastomer in petrol and neat oxygenates – volume swell after 168 hours at 23 °C

As regards enhancing the properties of ethanol nowhere is this more evident than with the basic property of octane number. ETBE and TAAE both have a better balance between their RON and MON values (lower sensitivity) which is economically interesting in the EU with its separate specifications. This is illustrated in Fig. 3.

Fuel ethers have been used in Europe since 1973 and bio-ethers since 1992. They have been extensively used in the existing infrastructure; service stations, pipelines and vehicles. Their compatibility with the existing car fleet is thus fully established. This is one of the reasons why they are the oxygenate of choice for the global car makers. Who in their current worldwide fuel charter state, “on the basis of emissions benefits, vehicle performance and existing regulations when oxygenates are used

ethers are preferred”<sup>10)</sup>. Coming back to the earlier comment that the CO<sub>2</sub> reduction delivered by bio-ethers is “equal to that of the ethanol production pathway used” is an underestimation. The basis for this opinion is a series of recent papers, all of which used slightly different approaches and methods but came to the conclusion that bio-ethers provided an additional benefit.

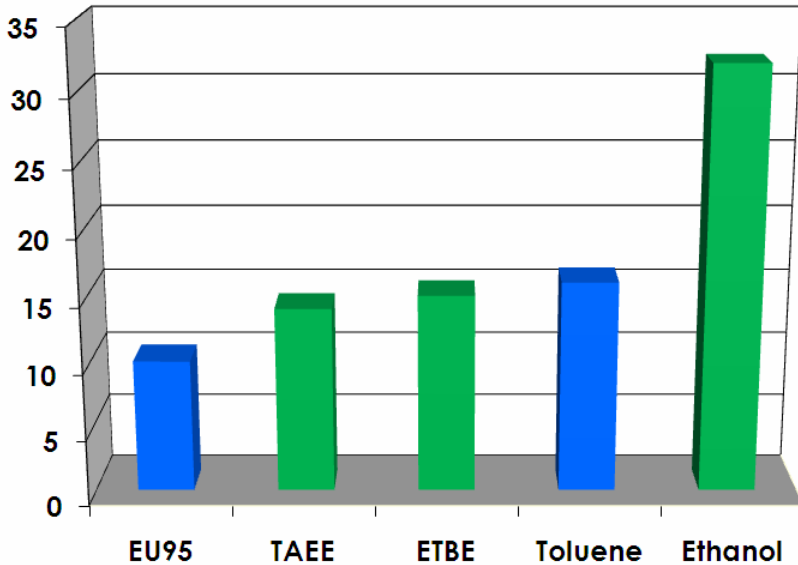


Figure 3: Octane sensitivity - balance between RON and MON values

In 2007 Hart Energy Consulting<sup>11)</sup> used a model which characterized refinery processing and blending requirements for the 2010 Western European refined products market. In the base case, the EU petrol consumption was estimated at 104.5 million tones/year with total energy of 4470 PJ/year. Also all oxygenate was assumed to be smart blended, i.e. final blends met specifications for finished petrol. While in a study conducted by CE Delft of The Netherlands<sup>12)</sup>, the calculation model was based on an average European refinery configuration with a catalytic cracker. Two scenarios were analyzed: substitution of 4.9 vol. % MTBE and other components in petrol by either 5 vol. % ethanol or an equivalent amount of ETBE, i.e. 11.7 vol. %. The greenhouse gas emissions of these scenarios were compared with each other, and with emissions of the reference situation in which no ethanol was used. In both cases, Hart Energy Consulting and CE Delft, the studies showed that ETBE offered an additional CO<sub>2</sub> saving versus ethanol. These conclusions were endorsed by the German Institute for Energy and Environment Research (IFEU). In a study<sup>13)</sup> on energy and greenhouse gas balances for bio-energy production from cereal and sugar beet commissioned by LAB e.V., the Agricultural Biofuels

Association, which represents the German ethanol industry and affiliated members they concluded that the best results by far were achieved when ethanol was processed to bio-ETBE which replaced fossil MTBE. Use of bio-ETBE was calculated as saving up to 4 times the primary energy required to produce its fossil alternative. And they recommended that the full technical potential of bio-ETBE be explored before replacing fuel by ethanol.

## Conclusions

The new EU directives on fuel quality and renewable energy have placed mandatory requirements on Member States to increase their use of biofuels over the period to 2020. This paper shows that bio-ethers offer a straightforward means of producing bio-gasoline.

Thus bio-ethers can make a key contribution to meeting national biofuels targets.

## References

- 1) Directive 98/70/EC, Official Journal of the European Communities, L350/58, 28 December 1998
- 2) Directive 2009/30/EC, Official Journal of the European Union, L140/88, 5 June 2009
- 3) Directive 2003/30/EC, Official Journal of the European Union, L123/42, 17 May 2003
- 4) Directive 2009/28/EC, Official Journal of the European Union, L140/16, 5 June 2009
- 5) Notices from Member States, Official Journal of the European Union, C225/13, 18 September 2009
- 6) European Fuel Oxygenates Association, [www.efa.org](http://www.efa.org)
- 7) Eurostat, CN codes 2909 1910 and 2909 1990
- 8) [www.dupontelastomers.com/Tech\\_info/chemicals.asp](http://www.dupontelastomers.com/Tech_info/chemicals.asp)
- 9) C. M. Shilblom, G. A. Schoonveld, R. K. Riley, R. H. Pahl, Use of Ethyl-t-butyl Ether (ETBE) as a Gasoline Blending Component, Phillips Petroleum Co., SAE 902132
- 10) World-wide Fuel Charter, 4<sup>th</sup> edition, September 2006
- 11) T. Higgins, Relative CO<sub>2</sub> savings comparing ethanol and ETBE as a gasoline component, Hart Consulting, SAE World Congress July 2008, Paris
- 12) H. Croezen, B. Kampman, The impact of ethanol and ETBE blending on refinery operations and GHG-emissions, Energy Policy 37 (2009) 5226-5238
- 13) The study (in German) can be found on the website of IFEU (Institut für Energie- und Umweltforschung Heidelberg GmbH): <http://www.ifeu.de>

UDK	ključne riječi	key words
665.734.4	biobazno etanol 20%, benzin 80% gorivo Gasohol E20	biobased ethanol 20%, gasoline 80% Gasohol E20 fuel
665.734.5	biobazno bioETBE 20%, benzinsko 80% gorivo	biobased bioETBE 20%, gasoline 80% bioether fuel
621.434.018.2	mehanički učinak benzinskog motora	gasoline engine mechanical efficiency
621.434.068.3	ispušna emisija benzinskih motora	gasoline engine exhaust emission

## Author

Dr. Walter Mirabella; e-mail: [walter.mirabella@lyondellbasell.com](mailto:walter.mirabella@lyondellbasell.com)  
European Fuel Oxygenates Association, Brussels, Belgium

## Received

6.7.2010.