ANALYSIS OF THE QUALITY PARAMETERS OF SELECTED MOTOR BIOFUELS, TAKING INTO ACCOUNT THE CURRENT REQUIREMENTS OF THE WORLDWIDE FUEL CHARTER

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Abstract

The paper presents an evaluation of the various quality parameters of biofuels used to power diesel engines and engines, including the current findings in this regard made to the Scientific Committee for the Affairs of the World Wide Fuel Charter.

Characterizes the requirements for ethanol and methyl esters of fatty acids, presented in addition to the fourth edition of WWFC, published in March 2009. Characterized the basic problems of storage, distribution, and operation of FAME and ethanol as a first-generation biofuels. Also presents the basic operating conditions resulting from the research for these fuels.

Presents the future prospects of biofuels for motor set in the Roadmap for Biofuels for Transport, developed by the International Energy Agency, including fuels derived from syngas, using solar energy ("solar fuels") and furan derivatives. Characterized the need for changes in the classification of biofuels and make them permanent division of *conventional biofuels (previously used) and the preferred biofuels in the future – advanced biofuel. Also presents general guidelines for the biorefinery. The possibilities of performance in the application bioDME as a biofuel for diesel engines.*

Keywords: conventional biofuels, advanced biofuels, Worldwide Fuel Charter, requirements for bioethanol and biodiesel, bio-dimethyl ether (DME)

1. Introduction

Biofuels began to be produced in the late 19th century, when ethanol was derived from corn and Rudolf Diesel's first engine ran on peanut oil. Until the 1940s, biofuels were seen as viable transport fuels, but falling fossil fuel prices stopped their further development. Interest in commercial production of biofuels for transport rose again in the mid-1970s, when ethanol began to be produced from sugarcane in Brazil and then from corn in the United States. In most parts of the world, the fastest growth in biofuel production has taken place over the last 10 years, supported by ambitious government policies.

Support policies for biofuels are often driven by energy security concerns, coupled with the desire to sustain the agricultural sector and revitalise the rural economy. More recently, the reduction of CO2 emissions in the transport sector has become an important driver for biofuel development,

particularly in countries belonging to the Organisation for Economic Cooperation and Development (OECD). One of the most common support measures is a blending mandate – which defines the proportion of biofuel that must be used in road-transport fuel – often combined with other measures such as tax incentives. More than 50 countries, including several non-OECD countries, have adopted blending targets or mandates and several more have announced biofuel quotas for future years.

There is considerable debate on how to classify biofuels. Biofuels are commonly divided into first-, second- and third-generation biofuels, but the same fuel might be classified differently depending on whether technology maturity, GHG emission balance or the feedstock is used to guide the distinction. In this paper we used a definition based on the maturity of a technology, and the terms "conventional" and "advanced" for classification. The GHG emission balance depends on the feedstock and processes used, and it is important to realise that advanced biofuels performance is not always superior to that of conventional biofuels.

Conventional biofuel technologies include well-established processes that are already producing biofuels on a commercial scale. These biofuels, commonly referred to as first-generation, include sugar- and starch-based ethanol, oil-crop based biodiesel and straight vegetable oil, as well as biogas derived through anaerobic digestion. Typical feedstocks used in these processes include sugarcane and sugar beet, starch-bearing grains like corn and wheat, oil crops like rape (canola), soybean and oil palm, and in some cases animal fats and used cooking oils.

Advanced biofuel technologies are conversion technologies, which are still in the research and development, pilot or demonstration phase, commonly referred to as second- or third-generation. This category includes hydrotreated vegetable oil (HVO), which is based on animal fat and plant oil, as well as biofuels based on lignocellulosic biomass, such as cellulosic-ethanol, biomass-toliquids (BtL)-diesel and bio-synthetic gas (bio-SG). The category also includes novel technologies that are mainly in the research and development and pilot stage, such as algae-based biofuels and the conversion of sugar into diesel-type biofuels using biological or chemical catalysts.

A wide variety of conventional and advanced biofuel conversion technologies exists today. The current status of the various technologies and approaches to biofuel production is summarised in Tab. 1.

	Advanced biofuels						Conventional biofuels
	Basic and applied			Demonstration	Early commercial		Commercial
Bioethanol				Cellulosic ethanol			Ethanol from sugar and starch crops
Diesel-type biofuels	Biodiesel from microalgae; Sugar- based hydrocarbons			B _{tL} diesel (gasification) $+FT$	Hydrotreated vegetable oil		Biodiesel (by transesterification)
Other fuels and additives	Novel fuels (e.g. furanics)		Biobutanol, DME, Pyrolysis-based fuels	Methanol			
Biomethane				Bio-synthetic gas			Biogas (anaerobic digestion)
Hydrogen	All other Gasification Biogas novel fuels with reforming reforming						
				Liquid biofuel			Gaseous biofuels

Tab. 1. Commercialization status of main biofuels technologies

2. The current requirements of Worldwide Fuel Charter for ethanol and biodiesel

Rapid growth in the use of ethanol and biodiesel prompted the WWFC Committee to address the need for more information about these important renewable fuels. As with conventional gasoline and diesel fuel, biofuel quality must match the needs and capabilities of engine and vehicle technologies, especially as these technologies become more advanced to meet ultra-clean emission standards. The purpose of the Worldwide Fuel Charter is to promote high quality and harmonized fuels on a global basis, considering the need for optimum engine and vehicle performance and durability and for the cleanest possible operation of engine and vehicle technologies.

The use of ethanol and biodiesel fuels is important to help extend supplies of gasoline and diesel fuel. As renewable fuels, they have the potential to help reduce emissions of greenhouse gases. Proper formulation also can help assure lower emissions of conventional pollutants. The key to achieving low emissions is to sustainably produce good quality blendstocks and to blend and distribute the finished fuels in a way that preserves their quality when they reach the consumer. Good ethanol and biodiesel quality are fundamental to its continued success as a fuel.

Ethanol is one of these fuels that is viable and in use today as a direct gasoline additive as well as a feedstock for making ether gasoline additives. Other promising renewable blendstocks for gasoline include bio-ethers (e.g., ethanol tertiary butyl ether (ETBE) and tertiary amyl ethyl ether (TAEE)) and bio-alcohols (e.g., biobutanol).

Given the wide variation in performance and measurement methods of biofuel blends at different blend levels, Worldwide Fuel Charter guidance focuses on the quality of the blendstock used to make finished biofuel blends, rather than on the finished fuels themselves. Specifically, to guide blenders who produce and use 100% biodiesel and diesel fuel blendstocks to make finished 5% biodiesel blends (or 100% ethanol and gasoline blendstocks to make finished 10% ethanol blends). The resulting finished fuels should continue to meet the recommendations contained in the WWFC for the various categories of market fuels.

The recommended limits are specifically established for anhydrous 100% ethanol (E100) blendstock intended for blending with petroleum-based gasoline to make a blend containing a maximum of 10% ethanol by volume (E10) suitable for use in vehicles with spark ignition engines. Higher level blends (greater than $E10$) are suitable for use only in vehicles designed for such fuel, such as "flexible fuelled" vehicles, and ethanol used for higher blends may require different limits. The finished ethanol-gasoline blends (up to 10% ethanol), as well as the finished petroleum-based gasoline, should continue to meet the requirements of the appropriate gasoline category in the Worldwide Fuel Charter.

Ethanol fuel blends must have uniform properties throughout to ensure a consistent quality. High speed injection blending is generally preferred to splash blending as a means to ensure uniform quality throughout the final fuel blend. Local regulations may require certain additives (e.g., denaturant requirements). Maintaining good fuel quality requires good housekeeping practices throughout production, distribution, blending and storage. All parties handling ethanol and its blends should watch for condensation and phase separation; fuel contaminated with water should not be sold to consumers. Blenders and retailers are advised to change filters regularly.

Ethanol-gasoline blends, especially those above 10% ethanol, must be properly labelled at the dispenser to enable the consumer to determine the fuel's compatibility with the engine or vehicle manufacturer's fuel recommendations and warranty statements. Tab. 2 contains the requirements for bioethanol fuel.

Denaturant – limits are determined by national or local regulation. Where a local government requires producers to denature the fuel ethanol, the only permitted denaturants are gasoline (conforming to PN-EN 228 or ASTM D4814); ethyl tert-butyl ether (ETBE); methyl tert-butyl ether (MTBE); tert-butyl alcohol (TBA); isobutanol (2-methyl 1-propanol); and isopropanol (2-propanol). Any or all of these denaturants may be used alone or together, except that isobutanol and isopropanol separate easily from solution, so it is advisable to use them in combination with another denaturant. The final gasoline-ethanol blend should also meet PN-EN 228 or ASTM D4814.

pH is not defined for non-aqueous solvents, and all pH-like measurements in non-aqueous solvents are purely empirical measurements defined by the measuring equipment and details of the test procedure. As a consequence, such methods are expected to return different results on the same sample.

Given the known potential for ethanol to absorb water, suppliers shall ensure that water does not contaminate the ethanol fuel under the expected range of climatic and fuel distribution conditions. Most current production vehicles with spark ignition engines are compatible with gasoline containing up to 10% ethanol but some manufacturers offer vehicles for use with high level ethanol blends, such as those containing 85% ethanol.

Biodiesel is viable and in use today, along other promising alternative diesel fuels such as renewable diesel fuel (hydrotreated vegetable oil - HVO) and biomass-to-liquid (BtL) fuels.

The recommended limits are specifically established for 100% biodiesel (B100) blendstock intended for blending with petroleum-based diesel fuel to make a blend containing a maximum of 5% biodiesel by volume (B5) suitable for use in vehicles with compression ignition engines. Higher-level blends may require different specifications, labelling, and other controls to

adequately protect consumers. Finished biodiesel (diesel fuel blends), as well as finished petroleum based diesel fuel, should continue to meet the requirements of the appropriate diesel fuel category in the Worldwide Fuel Charter.

Biodiesel quality changes over time due to the inherent nature of the fuel. Oxidation reactions begin to affect the fuel as soon as the biodiesel is created. Storage conditions, especially temperature, exposure to water, and exposure to oxygen, which is naturally present in ambient air, influence the rate of oxidation. Antioxidant additives can help slow this degradation process and improve fuel stability up to a point. Their effectiveness depends on their addition to the biodiesel during or as soon after production as practical. The overuse of antioxidants can lead to the additional formation of sludge. Thus, care must be taken in choosing the antioxidant type and amount for maximum effectiveness. It is also critical for biodiesel blendstocks to meet the limits specified in this guidance. After blending, distributors and retailers should avoid storing blends for excessive time periods or under adverse conditions, and they should monitor the blends, quality at least until the fuel is transported or sold.

Biodiesel fuel and biodiesel fuel blends must have uniform properties throughout, to ensure a consistent quality both prior to and after blending. High speed injection blending is preferred to splash blending as a means to ensure uniform quality throughout the final fuel blend. The blending process and confirmation of uniform properties is very important, especially when splash blending is used. Blenders and consumers should check with their suppliers and request confirmation of feedstock and finished product uniformity. Tab. 3 contains the requirements for biodiesel fuel.

3. Conventional biofuels used today

Sugar- and starch-based ethanol **–** In the sugar-to-ethanol process, sucrose is obtained from sugar crops such as sugarcane, sugar beet and sweet sorghum, and is subsequently fermented to ethanol. The ethanol is then recovered and concentrated by a variety of processes.

The conversion process of starch crops requires an additional step, the hydrolysis of starch into glucose, which requires more energy than the sugar-to-ethanol route. The overall economic and environmental efficiency of starch-based processes are heavily influenced by the value of coproducts such as dried distiller's grains with solubles and fructose.

The costs of production from sugar and starch are very sensitive to feedstock prices. Efficiency could be improved and costs lowered through use of more effective amylase enzymes, decreased ethanol concentration costs and enhanced use of co-products.

Conventional biodiesel – Biodiesel is produced from raw vegetable oils derived from soybean, canola, oil palm or sunflower, as well as animal fats and used cooking oil. These oils and fats are converted to biodiesel using methanol or ethanol. Vegetable oils are sometimes used as untreated raw oils, but this is not recommended due to the risks of engine damage and gelling of the lubricating oil. Co-products of biodiesel production, mainly protein meal and glycerine, are important to the overall economics of the process. The profitability of conventional biodiesel production is also sensitive to feedstock prices.

Biogas – Biogas can be produced through anaerobic digestion of feedstocks such as organic waste, animal manure and sewage sludge, or from dedicated green energy crops such as maize, grass and crop wheat. Biogas is often used to generate heat and electricity, but it can be also upgraded to biomethane by removing $CO₂$ and hydrogen sulfide (H₂S), and injected into the natural gasgrid. Biomethane can also be used as fuel in natural gas vehicles.

4. Applied current and future advanced biofuels

Cellulosic ethanol – Bioethanol can be produced from ligno-cellulosic feedstocks through the biochemical conversion of the cellulose and hemicellulose components of biomass feedstocks into fermentable sugars. The sugars are then fermented to ethanol, following the same conversion steps

¹ This limit may unnecessarily preclude certain feedstocks. Some engine technologies may need a more stringent limit.

² For temperature at or below -20 °C, viscosity should be at or below 48 mm²/s to avoid, potentially dangerous loads on the fuel injection pump drive system.

as conventional biofuels. Cellulosic ethanol has the potential to perform better in terms of energy balance, GHG emissions and land-use requirements than starch-based biofuels. The first largescale plants demonstrating this technology are now coming into production.

Advanced biodiesel – Several processes are under development that aims to produce fuels with properties very similar to diesel and kerosene. These fuels will be blend able with fossil fuels in any proportion, can use the same infrastructure and should be fully compatible with engines in heavyduty vehicles. Advanced biodiesel and bio-kerosene will become increasingly important to reach this roadmap's targets since demand for low-carbon fuels with high energy density is expected to increase significantly in the long term. Advanced biodiesel includes:

- Hydrotreated vegetable oil (HVO) is produced by hydrogenating vegetable oils or animal fats. The first large-scale plants have been opened in Finland and Singapore, but the process has not yet been fully commercialised,
- Biomass-to-liquids (BtL) diesel, also referred to as Fischer-Tropsch diesel, is produced by a two-step process in which biomass is converted to a syngas rich in hydrogen and carbon monoxide. After cleaning, the syngas is catalytically converted through Fischer-Tropsch (FT) synthesis into a broad range hydrocarbon liquids, including synthetic diesel and bio-kerosene.

Other biomass-/sugar-based biofuels – In recent years, several novel biofuel conversion routes have been announced, such as the conversion of sugars into synthetic diesel fuels.

These include:

- the use of a micro-organisms such as yeast, heterotrophic algae or cyanobacteria that turn sugar into alkanes, the basic hydrocarbons for gasoline, diesel and jet fuel,
- the transformation of a variety of water-soluble sugars into hydrogen and chemical intermediates using aqueous phase reforming, and then into alkanes via a catalytic process,
- the use of modified yeasts to convert sugars into hydrocarbons that can be hydrogenated to synthetic diesel.

Bio-synthetic gas – Bio-SG is biomethane derived from biomass via thermal processes. The first demonstration plant producing biomethane thermochemically out of solid biomass started operation in late 2008 in Güssing, Austria.

The deployment of natural gas vehicles (NGV) has started to grow rapidly, particularly during the last decade, reaching shares of 25% and more of the total vehicle fleet in countries including Bangladesh, Armenia and Pakistan. These vehicles can also be run on biomethane derived from anaerobic digestion or gasification of biomass.

Algae as biofuel feedstock – Algae have been cultivated commercially since the 1950s, mainly for the pharmaceutical industry, but only recently gained attention as a potential source of biomass. Algae promise a potentially high productivity per hectare, could be grown on non-arable land, can utilise a wide variety of water sources (fresh, brackish, saline and wastewater), and potentially recycle $CO₂$ and other nutrient waste streams. However algae cultivation faces several challenges, related to availability of locations with sufficient sunshine and water, required nutrient inputs, and oil extraction.

The most anticipated biofuel products appear to be high-quality diesel and jet fuel analogues, since few alternatives exist to replace these fuels. However, cultivation of algae and extraction of the oil is currently expensive. Optimisation of algal strains, concerns over unwanted or adverse effects due to contamination, and scaling up production remain significant challenges to the development and commercialisation of algae-based biofuels, and require more basic R&D efforts than other advanced biofuel routes. Commercially viable production of biofuel from algae will depend on effective strategies to generate high-volume, low-value biofuel along with high-value co-products.

Bio-Dimethyl ether (DME) can be produced from methanol through the process of catalytic dehydration or it can be produced from syngas through gasifying lignocellulosic and other biomass feedstocks. Production of DME from gasification of biomass is in the demonstration stage, and the first plant started production in September 2010 in Sweden. Often the production of methanol and

DME is combined in one process. Research on the application of DME as an automotive fuel has only started recently. In the past, DME derived from fossil fuels, was mainly used as a substitute propellant for chlorofluorocarbons (CFCs) in spray cans. Bio-DME is a suitable diesel engine fuel due to its low-self-ignition temperature and high cetane number (55). However, DME cannot be blended with fossil diesel and its volumetric energy content is much lower, approximately half that of diesel. Retrofitting diesel engines for the use of DME is relatively simple.

Although DME does not corrode metals, unlike bioethanol and biomethanol, it may affect certain kinds of plastics, elastomers and rubbers after some time. DME is gaseous at ambient temperature, but it is a liquid if the pressure is above 5 bars or the temperature is below –25°C. It is likely to be used as a liquid at 5–10 bar. Transport storage and distribution of DME is similar to that of LPG. The main challenges for further development of bio-DME are similar to those of Fischer-Tropsch liquids and biomethanol. The synthesis gas is produced by a high-temperature gasification, which is already used for coal gasification. Biomass has different properties than coal and, therefore, several process changes are necessary. First, the biomass pre-treatment and feeding need a different process, because milling biomass to small particles is too energy-intensive.

Moreover, small biomass particles can also aggregate and plug feeding lines. Pre-treatment processes like torrefaction or pyrolysis (which produces a liquid oil) could be developed to overcome these problems. Second, due to the higher reactivity of biomass (compared to coal) the gasification temperature might be decreased, resulting in higher efficiencies, but this will require different gasification and burner design. Third, the ash composition in biomass is different from that in coal, which results in different ash and slag behaviour, which is an important factor in the gasifier and still needs to be studied thoroughly. This ash and slag behaviour is also important for the cooling of the syngas, for which innovative development is desired.

Bio-DME is a common aerosol propellant in the domestic personal care industry. However, recent advances have made DME a prime candidate as an alternative fuel. Beyond its use as a propellant, DME has been confirmed as a safe fuel for vehicles as well as a source of power production and domestic gas replacement. Due to the raw material utilized for bio-DME production, its use does not release sulphur oxides, mercury, or nitrous oxides. This is especially important when considering that conventional fuels, including diesel, release immense amounts of air pollutants, greenhouse gases and acid rain producers. This trait is widely sought in attempt to reduce pollution.

Biobutanol can be used as a fuel in an internal combustion engine. It has a greater energy density (29.2 MJ/l) and is more similar to gasoline than ethanol, and could thus be distributed through existing gasoline infrastructure. Biobutanol can be produced by fermentation of sugar via the acetone-butanol-ethanol (ABE) process using bacteria such as *Clostridium acetobutylicum*. Demonstration plants are operating in Germany and the US and others are currently under construction. Biobutanol can be produced from the same starch and sugar feedstocks that are used for conventional ethanol. In addition, sugars can also be derived from lignocellulosic biomass, using the same biochemical conversion steps required for advanced ethanol production.

Solar fuels – Biomass can be gasified to syngas using heat generated by a concentrating solar plant, thus potentially improving the conversion efficiency and providing higher GHG emission savings. More demonstration plants and further research is needed to make the process more efficient and allow for commercial-scale operation. Another technology that could evolve as a process to produce liquid transport fuels is the splitting of water or $CO₂$ to hydrogen or carbon monoxide, which can then be turned to liquid fuels via a catalytic progress. This process is currently in the laboratory stage and considerable R&D efforts on a larger-scale are needed to support further development of solar fuels as part of the transport fuel mix in the longer term.

Fuels from hydrothermal processing – Biomass can be processed in a liquid media (typically water) under pressure and at temperatures between 300–400°C. The reaction yields oils and residual solids that have a low water content, and a lower oxygen content than oils from fast pyrolysis. Upgrading of the so-called "bio-crude" is similar to that of pyrolysis oil. Pyrolysis oil can be

produced by fast pyrolysis, a process involving rapidly heating the biomass to temperatures between 400–600°C, followed by rapid cooling. Through this process, thermally unstable biomass compounds are converted to a liquid product. The obtained pyrolysis-oil is more suitable for longdistance transport than for instance straw or wood-chips. As a by-product, bio-char is produced that can be used as solid fuel, or applied on land as a measure of carbon sequestration and soil fertilisation. The oil can be processed in ways similar to crude oil, and several research efforts are currently undertaken to upgrade pyrolysis oil to advanced biofuels.

Biorefineries – The biorefinery concept is analogous to the basic concept of conventional oil refineries: to produce a variety of fuels and other products from a certain feedstock. The economic competitiveness of the operation is based on the production of high-value, low-volume coproducts in addition to comparably low-value biofuels. Biorefineries can process different biomass feedstocks into energy and a spectrum of both intermediate and final marketable products such as food, feed materials and chemicals. Two main categories can be defined: energy-driven biorefineries, which include biofuel plants, and product-driven biorefineries, which focus on producing food, feed, chemicals and other materials and might create power or heat as a co-product.

A biorefinery can consist of a single unit, for instance a paper mill that produces pulp and paper and generates electricity from processing residues. It can also be formed by a cluster of single facilities that process by-products or wastes of neighbouring facilities. Biorefineries can potentially make use of a broader variety of biomass feedstocks and allow for a more efficient use of resources than current biofuel production units, and reduce competition among different uses of biomass.

5. Conclusion

The demand for liquid energy carriers for transport results in the search for new materials and processing technologies. So far, it was considered that biofuels produced from conventional agricultural industry resources would be able to supplement and eventually replace the need for combustion engines. However, we found that there is an ethical use of agricultural products for energy because of rising malnutrition humanity ("food competition"). Whether the production of biofuels based on known technologies for the processing of vegetable oils and the production of dehydrated alcohol-distilling ethanol does not show the projected reduction of GHG emissions, mainly carbon dioxide, which show a cycle analysis LCA. The use of these fuels in modern internal combustion engines for power and combustion systems designed and constructed taking into account the properties of hydrocarbon mixtures composed respectively causes the deterioration of the operational performance of these engines. Thus, taking into account the possibility of a relatively safe operation, and the main socio-political, Committee of the Worldwide Fuel Charter, permitted the use of mixtures of gasoline-ethanol and diesel-FAME in modern internal combustion engines, strictly specifying quality requirements and test methods for these fuel components.

Working principle of spark ignition engines and compression ignition is known and unchanged for many years. The automotive industry accepted fuel for these engines containing hydrocarbon mixtures composed, respectively, regardless of their origin. In terms of correct and reliable operation of the engine is not an important origin of these hydrocarbons, but only their properties corresponding to excitations of these engines. Practical considerations make the need for a radical narrowing of the number of species of fuel so that the user of the vehicle was simple and clear choice. Therefore, the European Biofuels Technology Platform, and later the International Energy Agency advocate the abandonment of biofuels share the so-called generations. Instead, suggest breakdown of conventional biofuels and future, while narrowing their species.

Promising raw material for obtaining biofuels are actually synthetically derived hydrocarbon mixtures from waste biomass (BtL processes), or of waste substances (processes WtL). Sometimes, it is proposed to define these processes as processes of XTL. The raw material for production of

liquid energy carriers for transport may then be any kind of waste or unused raw material for other purposes, subject to appropriate groups of hydrocarbons (the mixture must comply extortion posed by an increasingly demanding structurally and operationally, internal combustion engines).

Liquid energy carriers can be obtained in the processes carried out in biorefineries in a nearly waste-free. Moreover, it is believed that the waste carbon dioxide and water vapour as a greenhouse gas can be a raw material for production of synthesis gas, the method of processing the mixture of hydrocarbons are identified and implemented. Such processes, using solar energy have already been conducted in laboratory scale, giving rise to research into the production of solar fuels

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