We are IntechOpen,
the world's leading publisher of
Open Access books
Built by scientists, for scientists

6,900
Open access books available

186,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

CLARIVATE ANALYTICS
BOOK CITATION INDEX
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Biofuels in Storage and Operating Conditions

Krzysztof Biernat

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/59802

1. Introduction

In most countries, the term "biofuels" tends to be reduced only to fatty acid methyl esters (FAME), which are derived from rapeseed oil. "Biofuels" also include mixtures of FAME with diesel oil which are generally, though incorrectly, termed "biodiesel", and ethyl alcohol, termed "bioethanol", which is added to motor spirits. Biofuels are also generally and completely wrongly considered to emit no carbon dioxide (CO_2) from the combustion process into the atmosphere. When evaluating the environmental hazards which may result from the use of biofuels, one should take into consideration total emissions along the whole train: starting from plant growing, through the production of fertilizers and fertilization, use of agricultural machines and equipment, transportation, processing and, finally, combustion processes taking place in engines. That train of processes is defined as "well to wheel" (WtW). It is a sum of WtT ("well to tank") and TtW ("tank to wheel") components, hence it is possible to evaluate the values of WtW. It should be kept in mind at the same time that carbon is the basic energy-carrying element which is present in chemical compounds of biofuels. Therefore, when examining CO_2 emissions in the WtW cycle and comparing them with the amounts of CO_2 absorbed in the photosynthesis process by the plants which make feedstocks for the production of biofuels, the energy balance of the currently available biofuels turns out to be unfavorable. As regards the production of bioethanol, large volumes of CO_2 obtained in fermentation processes should be considered as well. Apart from that, the WtW cycle may also release other compounds into the environment, for instance, nitrogen and sulfur compounds, and the production of biofuels from plants which are cultivated for human/animal consumption may reduce the pool of available foodstuffs and consequently increase the prices of food produce. Excessive exploitation of forest resources, leading to the complete deforestation to obtain arable land for the cultivation of other energy plants with a definitely lower CO_2 assimilation potential, may pose another environmental hazard.

Requirements concerning motor spirits according to currently applicable standards in 150 countries worldwide were summarized in the report "2013 Worldwide Fuel Specification", issued by the International Fuel Quality Center.

2. Classification of biofuels

With regard to their state of matter, in Europe and in US, liquid biofuels are defined as liquid and gaseous fuels for internal combustion engines, obtained from biomass. According to the European Directive (2009/28/WE), biomass means "the biodegradable fraction of products, waste and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste".

The Directive 2009/28/EC provides a definition for biofuels but it does not specify ithe respective grades or classes of the materials. That approach results from technological developments in biomass processing (BtL processes) as well as from the search for new raw materials for the production of biofuels and alternative fuels (WtL processes). Both those groups of processes are expected to ensure lower emissions arising in production processes and from the product use (LCA and WtW analysis). Thus, taking into consideration the provisions of said Directive and our own experience, gained from our research program, the following definition of biofuels is proposed: "Biofuels comprise liquid and gaseous transportation fuels, obtained from biomass or from waste substances, as well as from processes which directly or indirectly utilize waste carbon dioxide of natural and/or industrial origin".

Having in mind the historical track for the manufacture of biofuels, and meaning to promote the advancements in the second-generation and higher-generations biofuels (so-called "advanced biofuels"), it would be advisable – within the efforts intended to expand the use of biofuels – to define the raw materials and processes which would make it possible to include those biofuels into the energy carrier groups with doubled or even higher contributions to the National Index Targets, compared with other biofuels. The prospective processes have already been defined and adopted by the European Biofuel Technology Platform, Strategic Research Agenda, and they will be incorporated into the "Biofuel for Transport Roadmap" developed by the International Energy Agency.

Several supplementary definitions for biomass have co-existed so far. According to the European definition, as provided in the Directive 2009/28/EC, biomass means the biodegradable fraction of products, waste and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste. Hence, coming out of biomass as a basic feed for the production of biofuels, the European definition involves two principal routes and corresponding conversion processes, i.e., BtL *("biomass to liquid")* with alternative BtG *("biomass to gas") processes*, and WtL *("waste to liquid")* with alternative WtG ("*waste to gas*") processes.

That Directive also added the notion of "*bioliquids*" – biomass-based liquid biofuels for use as sources of energy other than in transportation, including power generation as well as produc‐ tion of thermal energy (heat or cold). Hence, the processes which are based on biomass and yield bioliquids fall within the categories of BtE ("*biomass to energy*") and WtE ("*waste to energy*").

The basic classification of biofuels is thus based on their state of matter. Pursuant to Annex № 1 to the Commission Communication № 34 of 2006, COM(2006)34 final, biofuels were broken up into the following groups: liquids, gases, and other fuels, and the notions of first-generation biofuels and second-generation biofuels were introduced for the first time. Moreover, the notion of "synthetic biofuels" was defined as synthetic hydrocarbons or mixtures of hydro‐ carbons obtained from biomass, e.g. Syngas produced in the gasification process of forest biomass, or SynDiesel.

The European classification specifies the following biofuels from the viewpoint of their state of matter:

1. Liquid biofuels:

    • bioethanol – obtained from biomass and/or biodegradable waste fraction which can be used as E10 biofuel (10 % ethanol and 90 % gasoline) and as E85 biofuel (85 % ethanol and 15 % gasoline);

    • biodiesel – which contains methyl esters (PME, RME, FAME) obtained from vegetable oils and animal oils or waste fats and oils (e.g. waste fryer oil), which meet the standard requirements for B7 diesel oil (7 % esters and 93 % petroleum diesel oil), B30 diesel oil (30 % and 70 %, respectively) and B100 diesel oil (pure esters with properties conform‐ able with the applicable standard);

    • biomethanol – as fuel or fuel component obtained from biomass;

    • bio-ETBE, ethyl-*tert*-butyl ether – obtained from bioethanol, to be used as an antiknock agent for gasolines to improve their octane number;

    • bio-MTBE, methyl-*tert*-butyl ether – obtained from biomethanol, with the same intended use as bio-ETBE;

    • BtL – as liquid fractions and their mixtures obtained from biomass, which may be used as biofuels or fuel components;

    • pure vegetable oils – obtained by pressing, extraction or similar processes (including refining but excluding chemical modification of their compositions), which are useful as environmentally friendly biofuels for specific engine types.

2. Gaseous biofuels:

3. bio-DME – dimethyl ether, obtained from biomass, to be used directly as biofuel in spontaneous-ignition engines;

4. biogas – biofuel, obtained from biomass and/or biodegradable waste fractions, suitably purified to meet the quality of natural gas;

5. biohydrogen – biofuel, obtained from biomass or biodegradable waste fractions.

6. Other fuels derived from renewable energy sources, as biofuels which have not been listed above, obtained from the sources as defined in the Directive 2001/77/EC, which may be used to drive transport facilities.

As mentioned before, said Communication presented a basis for the classification of biofuels as the first-or second-generation materials. That division resulted from the determinant factors as discussed above and, first of all, from the assessed usefulness of fuels in present-day motor engineering, and from the availability of raw materials and their environmental impact. A formal classification of biofuels into the respective generations was published in the report "Biofuels in the European Vision, a Vision 2030 and Beyond". In the report, the materials are classified as the first-generation (or "conventional") biofuels, and second-generation (or "advanced") biofuels.

The first-generation (conventional) biofuels comprise:

• bioethanol (BioEtOH, BioEt), i.e. conventional ethanol obtained from hydrolysis and fermentation processes, from such raw materials as: cereals, sugar beets, etc.;

• pure vegetable oils (PVO) obtained from oil plant seeds in cold pressing and extraction processes;

• biodiesel which is a blend of rapeseed methyl esters (RME) or methyl esters (FAME) and ethyl esters (FAEE) of higher fatty acids from other oil plants, obtained by cold pressing, extraction, and transesterification;

• biodiesel which is a blend of methyl and ethyl esters obtained through transesterification of waste fryer oils;

• biogas obtained by treatment of humid gas from landfill facilities or from agricultural sources;

• bio-ETBE obtained by chemical processing of bioethanol.

The second-generation (advanced) biofuels include the following:

• bioethanol, biobutanol and mixtures of higher alcohols as well as their derivatives obtained from advanced lignocellulose hydrolysis and fermentation processes, where lignocellulose is obtained from biomass (excluding raw materials intended for use as foodstuffs);

• synthetic biofuels, i.e., products obtained by biomass conversion in gasification and adequate synthesis processes into liquid fuel components (BtL processes), and those produced by processing biodegradable industrial and municipal waste, inclusive of carbon dioxide (WtL processes);

• fuels for spontaneous-ignition engines, obtained by converting biomass-based lignocellulose in Fischer-Tropsch processes, inclusive of synthetic biodiesel produced by blending lignocellulose-based products;

- biomethanol obtained by lignocellulose conversion processes, inclusive of the Fischer-Tropsch synthesis, with the utilization of waste carbon dioxide;

- biodimethylether (bioDME) obtained in biomass thermochemical conversion processes, inclusive of biomethanol, biogas and synthesis gases which are obtained from biomass conversion processes;

- biodiesel, i.e., biofuel or fuel component intended for spontaneous-ignition engines, obtained from hydrofining (hydrogenation) of vegetable oils and animal fats;

- biodimethylfuran (bioDMF) obtained from sugar conversion, inclusive of cellulose, in thermo-and biochemical processes;

- biogas as synthetic natural gas – biomethane (SNG), obtained by lignocellulose gasification processes and appropriate synthesis, and by treatment of biogas collected from agricultural sources, from landfill facilities and from sewage sludge;

- biohydrogen obtained by lignocellulose gasification and further synthesis of gasification products, or from biochemical processes.

The above classification shows that first-generation biofuels after further processing may not be classified as second-generation biofuels. Hence, any downstream conversion of esters, e.g., their hydrofining, will not produce second-generation biofuels and is technically and commercially unreasonable. The idea to develop second-generation biofuels is in principle based on the assumption that they should be produced from biomass, waste vegetable oils and animal fats, and any waste organic substances which are useless for the food industry or forestry.

The European Commission Directorate-General for Energy and Transport suggested that third-generation biofuels could be defined for which the manufacturing processes may be developed and commercial implementation planned for the 2030's or later. That group would initially comprise biohydrogen and biomethanol.

Because of the need to reduce emissions of greenhouse gases (GHG), including first of all carbon dioxide, which is the critical factor of growth in the use of biofuels, the concept of third-generation biofuels was more specifically defined and the fourth-generation biofuels group was proposed. The two groups of biofuels would be classified as advanced biofuels. So, the third-generation biofuels may be obtained from processes which are similar to those which yield second-generation fuels but the feed to those processes (biomass) would be modified at the stage of its cultivation with the use of molecular biological techniques. Such modifications should be tailored to improve the biomass conversion into biofuels (biohydrogen, biomethanol, biobutanol): trees should be grown with low lignin content, plants could be cultivated with suitably built-in enzymes, etc.

The suggestion to provide a new, fourth generation of biofuels has emerged because of the need to close the balance of carbon dioxide or to eliminate its environmental impact. Hence, the fourth-generation biofuel manufacturing processes should involve CCS (*Carbon Capture and Storage*), i.e. they should capture and store carbon at the stages of raw materials and biofuel

production processes. The raw materials for that production shall involve the plants with improved (even by genetic engineering) assimilation of CO_2 during plant cultivation. The adopted technologies must capture carbon dioxide into suitable geological formations by converting it into carbonate forms or by storing it in oil and gas field pits.

Biofuels are not classified in the United States. Pursuant to NREL (National Renewable Energy Laboratory), the development and implementation of biofuel processes are planned to be implemented gradually.

According to NREL, manufacturing processes are being implemented to obtain the following biofuels:

- ethanol as a biofuel component, which is produced from cereals and cellulose obtained from agriculture and forestry;

- biodiesel, i.e., esters of higher fatty acids from vegetable oil transesterification processes, blended with petroleum diesel oil.

As regards prospective developments, the processes for further biofuels are planned:

- "Green Diesel and Jet Fuel", so-called "green diesel" and general-purpose fuel for turbine engines (chiefly as a military fuel), obtained from waste fats and oils and pure vegetable oils, which are refined in petroleum refineries to reach very low sulfur levels;

- other products of biomass fermentation processes, like: butanol, acetates (ethanates), lactates (2-hydroxypropanates), etc.;

- pyrolytic liquids from biomass pyrolysis processes, as an alternative feed for petroleum refineries or gasification processes;

- syngas obtained from biomass by the Fischer-Tropsch method, as a raw material for the production of methanol, dimethyl ether or mixed alcohols;

- "Algae-derived Fuels", fuels derived from biomass of marine algae, as sources of triglycerides for the production of biodiesel, "green diesel" and "jet" fuel, as well as raw materials for the production of hydrocarbons;

- biofuels obtained from such raw material crops as: jatropha, halophyte plants and *Camelina sativa*, to be converted into diesel oils and jet fuels;

- hydrocarbon fuels, as biofuels of a distant future, to be obtained from biological processes or biomass hydrogenation, including fuels from xtL processes.

The last of the above biofuel groups is coming more and more into prominence because of the need to significantly reduce CO_2 emissions, therefore, new methods are required for closing the CO_2 balance for that gas by finding new raw materials and new methods for their processing.

Considering the assessed potential of biomass and the need to cut down CO_2 emissions, new prospective processes are being developed in USA and in Europe, such as the following:

- biofuel production processes, including jet fuels, by growing algae in the absence of sunlight on agricultural sludge, on grass-based sludge, or on waste substances, using carbon dioxide ("SOLAZYME" process);

- plasma gasification process which involves waste biomass as well as municipal and industrial waste (BtG and WtG processes), followed by conversion of product gases into liquid biofuels (diesel oils and jet fuels) in the GtL process ("SOLENA" process, just being implemented in Great Britain and in Italy);

- processes which utilize carbon dioxide to produce energy carriers;

- complex processes for biorefineries.

Taking into consideration the previous experience and technological developments in the production of biofuels (or, more precisely, alternative fuels) from raw materials which are a waste from the viewpoint of biology and civilization (xtL processes), modern societies strive above all for reduced CO_2 emissions or for optimized balancing of CO_2 in the production and fuel combustion processes. It is assumed that, in the foreseeable future of the production and use of biofuels (alternative fuels), that such fuels should:

- be available in sufficiently high volumes;

- offer technical and energy properties which make them useful a feed to engines or heating systems;

- be cost-effective in production and sale;

- be less environmentally harmful than the fuels used to-day, through lower emissions of toxic compounds and greenhouse gases from the combustion processes;

- make the use of engines and boilers safe and cost-effective, and to enable further reductions of their operating costs;

- improve energy independence.

In view of the above, the European Biofuel Technology Platform corrected its Strategic Research Agenda for Biofuels early in 2010. That correction involved technological progress and the need to intensify efforts to reduce GHG emissions. Moreover, the following biofuel groups were defined for their specific uses:

- synthetic fuels / hydrocarbons from gasification of biomass, for application as: transportation fuels from RES (Renewable Energy Sources) for aviation engines and spontaneous-ignition engines;

- biomethane and other gaseous fuels from gasification of biomass (substitutes for natural gas and other gaseous fuels) for application as: motor fuels and in high-efficiency generation of energy;

- biofuels (bioliquids) from biomass, obtained through thermochemical processes other than pyrolysis, for application as: heating fuels, in generation of energy or, indirectly, through xTL processes, as transportation fuels;

- ethanol and higher alcohols from sugar-containing biomass, for application as transportation fuels from RES or as a component of E85 gasoline;

- hydrocarbons from biomass, obtained from saccharides, produced in biological and/or chemical processes, for application as renewable transportation fuels for aviation engines and spontaneous-ignition engines;

- biofuels obtained through the use of carbon dioxide in the production of microorganisms in biotechnological processes or from the direct synthesis of waste carbon dioxide and steam in catalyzed thermochemical processes (application in transportation fuels from RES and aviation fuels).

The above definitions include the production of biofuels which were earlier defined in SRA, such as bioDME, bioDMF and other furan derivatives, FT-diesel, HTU-diesel, as well as fuels from hydrogenation of waste vegetable oils and animal feeds which are not useful in the food industry, in HVO processes.

Regardless of the above, the International Energy Agency (IEA) has developed a Biofuel for Transport Roadmap where the need has also been included for the sustained development and reduced emissions of GHG through the utilization of carbon dioxide, among other methods. This is in conformity with the European Directive which, in its Preamble, recommends that "The Community should take appropriate steps in the context of this Directive, including the promotion of sustainability criteria for biofuels and the development of second- and third-generation biofuels in the Community and worldwide...".

Considering the principal purpose of using biofuels as fuels or fuel components, which results from the need to reduce carbon dioxide emissions, it is also reasonable to assess their potential as biofuels which can be obtained by utilization of spent carbon dioxide in the production of energy carriers for the needs of transport. The efforts made in this field may be illustrated by studies conducted in the USA, where syngas is produced from carbon dioxide and steam in a catalytic process with the use of solar energy.

Having in mind earlier experiences and research findings, a tendency in the foreseeable future should be to make biofuels as hydrocarbon blends which are obtained according to specific process routes. Those routes will enable the obtaining of alternative fuels for combustion engines while closing the CO_2 cycle. Hence, the fuels of the future should comprise:

- synthetic fuels as blends of hydrocarbons from biomass gasification and from pyrolysis processes;

- biomass-based biofuels obtained through other thermochemical processes, such as, pyrolysis, depolymerization processes and hydrogenation of biomass decomposition products;

- fuel compositions, blended with the use of hydrocarbons obtained from biomass which meet the quality requirements for motor fuels, inclusive of those obtained directly and indirectly from saccharides in biological and/or chemical processes;

- biofuels which are other derivatives of saccharides, inclusive of cellulose, which meet the requirements for motor fuels;

- biomethane and other gaseous fuels from biomass gasification processes and/or from purification processes of biogas from agricultural sources, landfill facilities and sewage sludge (substitutes of natural gas and other gaseous fuels);

- bioethanol and higher alcohols (biobutanol) and their derivatives obtained from biomass in biochemical and/or in catalytic thermochemical processes;

- biofuels obtained from carbon dioxide converted by microorganisms or from the direct or indirect synthesis which converts naturally occurring carbon dioxide in thermo-and biochemical processes;

- biofuels obtained from syngas by direct or indirect (through methanol) conversion of biomass and/or GHG;

- biofuels (HVO), obtained from hydrogenation processes of waste vegetable and animal fats.

The present knowledge and the research conducted in Polish and international R&D centers, and in the Seventh Framework Programme and the Polish and European Biofuel Technology Platforms, defined the areas of use for biofuels in transport and power engineering. Thus, the following can be considered as biofuels and alternative fuels for spark-ignition engines:

- ethanol;

- methanol;

- other alcohols (e.g.: *tert*-butyl – TBA, *sec*-butyl – SBA, isopropyl – IPA and neopentyl – NPA alcohols);

- ethers (ethyl-*tert*-amyl ether – TAEE, ethyl-*tert*-butyl ether – ETBE, methyl-*tert*-amyl ether – TAME, methyl-*tert*-butyl ether – MTBE and diisopropyl ether – DIPE);

- synthetic hydrocarbon fuels;

- biomethane;

- liquefied petroleum gas;

- hydrogen.

Within spontaneous-ignition engines, efforts are being made to obtain and implement the following alternative fuels, based principally on biomass:

- methyl and ethyl esters of fatty acids, FAME and FAEE, respectively, from transesterification processes of rapeseed oil, sunflower oil, soybean oil, and other oils;

- dimethyl ether (DME); the use of diethyl ether (DEE) is also considered;

- fuel-water emulsions (Aquazole);

- pure vegetable oils;

- synthetic hydrocarbon fuels.

The following fuels have also been taken into consideration for stationary applications:

- alcohols;

- esters of higher fatty acids;

- tall-based fuels (TPO-tall pitch oils) obtained by esterification of tall oils with ethyl alcohol or methyl alcohol, with tall oils being recovered from coniferous-tree resins (by-products from the production of sulfated cellulose and from low-temperature carbonization of wood);

- fuels from pyrolysis processes;

- pure vegetable oils;

- biogas.

3. Changes in the properties of vegetable oils and FAME in storage and motor operating conditions

A pre-condition for the use of other fuels in spontaneous-ignition engines, yet without modifying the design of such engines, is that the properties of those fuels must be adjusted to those of petroleum fuels. The basic parameters to be considered before using vegetable-based fuels are include: kinematic viscosity, density, calorific value and combustion properties. Table 1 compares some selected properties of diesel oil, rapeseed oil and fatty acid methyl ester (FAME) from rapeseed oil (RME).

Parameter	Unit	Diesel oil	Pure rapeseed oil	Methyl ester
Kinematic viscosity at 20°C	mm/sec^2	2.8...8.0	68...75	6...8
Calorific value	MJ/kg	42...43	36...38	39.4...40.6
Cetane number	-	45...50	40...50	50...55(60)
Composition of air-fuel mixture	kg/kg	14.4...14.6	2.2...13	13.4...13.8
Density at 20°C	kg/dm^3	0.81...0.85	0.9...0.94	0.87...0.89
Cloud point	°C	-16*	18	-9
Cold filter plugging point	°C	-20*	-	-10
Setting point	°C	-35*	-26	-15
Sulfur content	%	0.15	0.002	0.002
Coke content	%	0.01	0.17-0.5	0.05
Flash point	°C	40...50	200...300	130
Initial boiling point	°C	175	300	300

*-for winter diesel oil

Table 1. Selected properties of biocomponents and diesel oil

Viscosity affects the auto-ignition process through the size of fuel droplets, the shape of the injected fuel stream and how far it reaches. From that point of view, vegetable oils offer much inferior parameters as compared with those of diesel oil.

It should also be noted that the droplet size for rapeseed oil is about four times as high as that for hydrocarbon/petroleum diesel oil. What is essential, is the advantageous effect of transesterification of rapeseed oil since the average droplet size of rapeseed oil methyl esters is only twice that of diesel oil.

The calorific values of methyl esters and pure rapeseed oil are by about 12 % lower than those for the conventional hydrocarbon fuel. Combustion of biodiesel is more complete because oxygen atoms are present in the chemical molecules, and biocomponents, when added to regular diesel oil, increase its density.

The differences in the performance of standard rapeseed oil and its methyl esters are shown in Figure 1. Diesel oil has a rather wide pretty wide boiling range (180...380°C), while biofuels boil in a relatively narrow range (about 380°C). That narrow boiling range of FAME may be the reason for operating problems, especially for engine starting at low ambient temperatures. It should be stressed that vegetable-based fuels will solidify more easily at low temperatures.
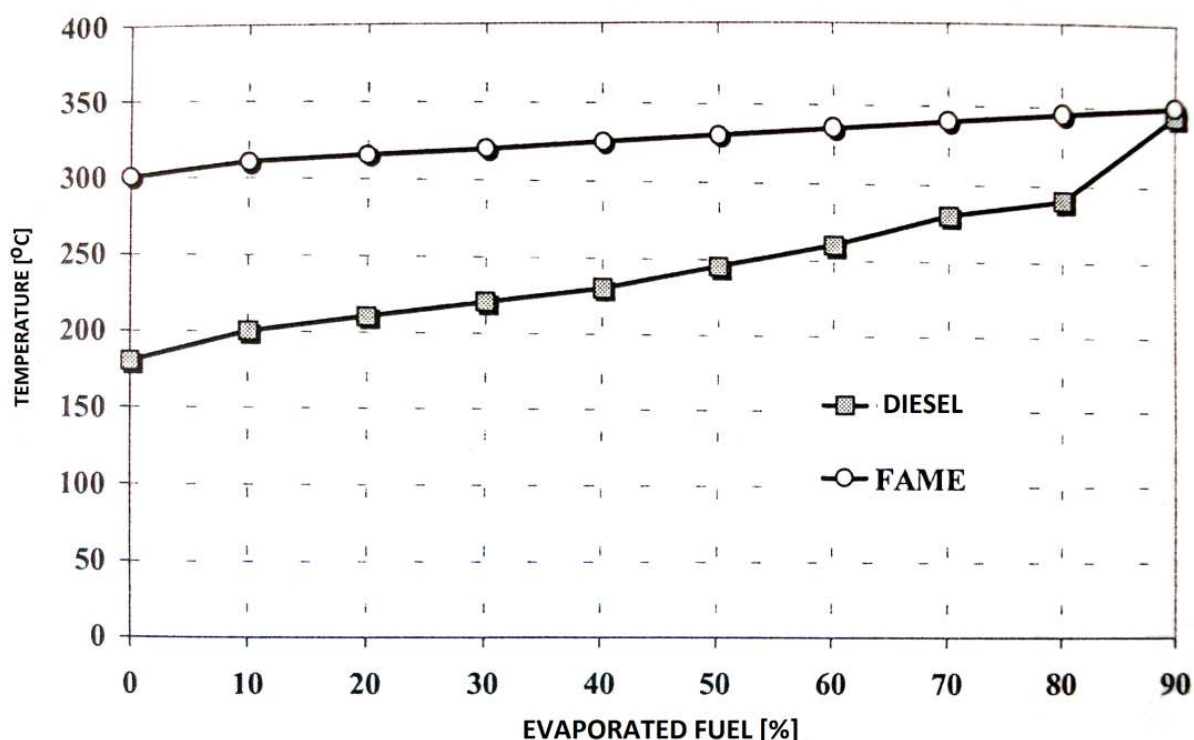

Figure 1. Boiling range for diesel oil – ON, methyl ester of rapeseed oil acids – FAME *(with consent of "Przemysł Chemiczny")*.

The cetane number is a universal comparative measure but not a physical parameter of fuels. Vegetable oil molecules have completely different chemical structures than hydrocarbon molecules of diesel oil fractions because vegetable oils are predominantly composed of fatty acid glycerine esters and are usually in the form of triglycerides. Hence, different performances may be expected for both fuel types within their self-ignition delay parameters.

The cetane number (CN) for natural rapeseed oil is 37.6, while the value for rapeseed oil methyl esters falls in the range 54...58. As can be seen, the CN values are generally lower for pure rapeseed oil but are higher for rapeseed oil methyl ethers, compared with those for diesel oil. In motor tests, when those fuel types were used, no clear relation was identified between the cetane number value and the self-ignition delay. For example, the self-ignition delay time for diesel oil with a biocomponent added is shorter in a hot engine than for pure diesel oil, while it is harder to start an engine running on a vegetable-based fuel. The possibility is high that the same relationship exists between the cetane number and the self-ignition delay in engines for those fuels as for diesel oil.

In low temperature conditions inside a cylinder, at idle run, and at low engine loads, the self-ignition (spontaneous ignition, or compression-ignition) potential for vegetable oils is generally lower than that for diesel oil. At high temperatures, on the other hand, i.e., at high engine loads, the spontaneous-ignition performance of vegetable oils may be even better as compared with diesel oil, which is shown in Figure 2.
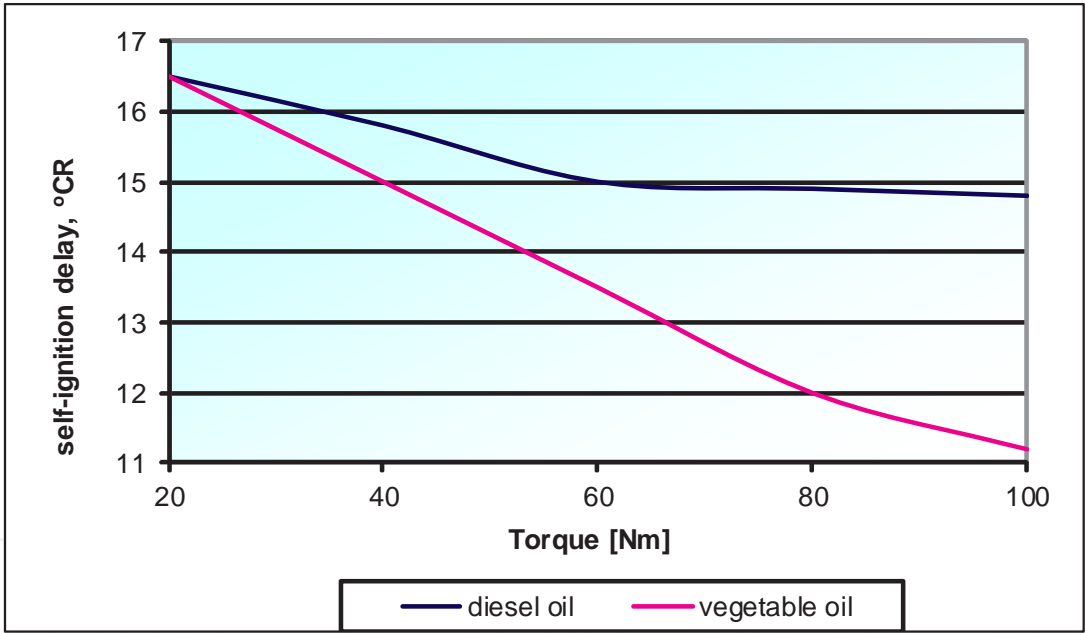
(sources J. Maćkowski, "Motor Fuels beginning of the XXI century" Publisher: Automobile Diagnostic Training Center, Katowice, 2002)

Figure 2. Effects of engine load on self-ignition delay for diesel oil and for rapeseed oil

As can be seen in Fig. 2, the self-ignition delay declines much faster for vegetable oil than for diesel oil, at increasing engine loads. When some volume of diesel oil is replaced with rapeseed oil, the self-ignition delay time will be reduced. The tests confirm that the cetane number value (as found in motor tests) gives no grounds for speculating on the self-ignition potential of vegetable-based fuels in various engine operating conditions because the effects of combustion chamber temperatures on self-ignition delays of those fuels are highly various.

Tests and measurements show that higher cetane numbers for rapeseed oil methyl esters do not provide a sound basis to expect any easier engine start when that fuel is used.

This has been confirmed by engine start tests in four farm tractors, powered with the use of methyl esters of rapeseed fatty acids. The tests failed to reveal any advantageous effect of higher cetane numbers leading to an easier engine start. A steep rise in viscosity of that fuel was also demonstrated at temperatures below-10°C, which is an additional factor affecting the engine starting properties of fuels and which in effect reduces the fuel starting charge.

A significant problem encountered in operating compression-ignition engines fuelled with FAME is that the kinematic viscosity of esters varies with temperature. The relationship is shown in Figure 3. The profile for the viscosity decrease curve indicates as well that the fuel's low-temperature properties have deteriorated. This is not expected to pose any problem in the summer or in the transition period but may lead to difficulties in engine starting or make it impossible at all in the winter. Moreover, higher viscosities are known to affect the course of fuel atomization and to cause increased injection pressures by approx. 15%, compared with diesel oil. This takes place because larger fuel drops tend to evaporate more slowly (approx. 1.5 times as slowly as diesel oil) in the combustion chamber, leading to longer initial phases of fuel self-ignition and, ultimately, to longer combustion times. An optimum solution would be to use a fuel pre-heating system (manual or automated), depending on the values shown by the temperature sensor. The solution would involve modifications in the region between the injection pump and the injectors to enable the correct engine start – as well in the fuel tank to enable the correct further operation of the unit. While the technological solution requires serious modifications, the easier way to achieve the required low-temperature properties is to simply add dedicated depressants to FAME.
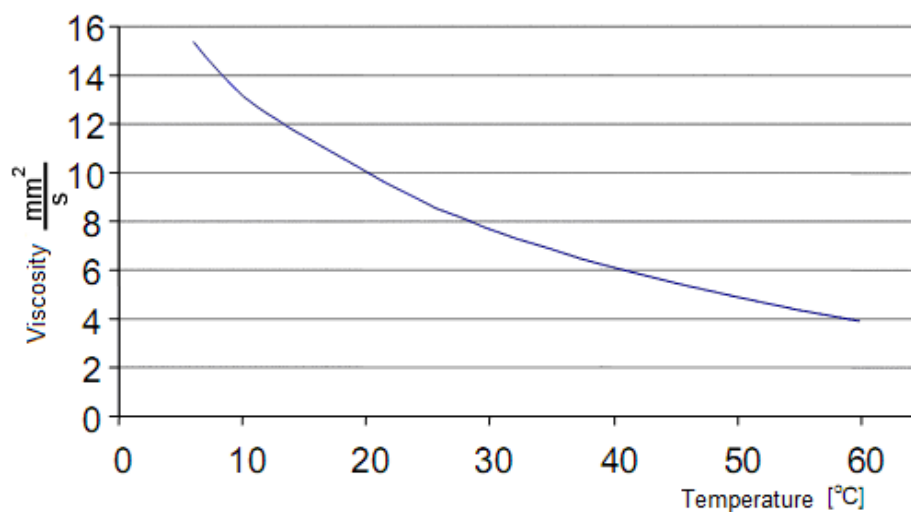

Figure 3. Effect of temperature on viscosity for FAME *(with consent of "Przemysł Chemiczny")*.

Rapeseed oil is composed mainly of fatty acid glycerine esters, in the form of triglycerides. These are mixed triglycerides, formed by reacting glycerine with saturated fatty acids: palmitic

acid ($C_{15}H_{31}COOH$) and stearic acid ($C_{17}H_{35}COOH$), and with unsaturated acids: oleic acid ($C_{17}H_{33}COOH$) and linoleic acid ($C_{17}H_{31}COOH$).

Oil fluidity increases for higher levels of unsaturated fatty acid esters, this involves lowering of oil viscosity and freezing point. Rapeseed oil has a freezing point of-26°C, which makes the material applicable also in winter conditions without any extra additives. However, for rapeseed oil, viscosity is 20 times as high as that for diesel oil, making difficulties in pumping and spraying the fuel; it may be necessary to heat up the fuel or air before feeding the fuel to the injection system. The rapeseed molecules contain oxygen and hence less air is required for fuel combustion than in the case of diesel oil. The calorific value per mass unit is thus lower than that for rapeseed oil. Rapeseed oil, on the other hand, has a higher density (by about 10 %), so that the "volumetric" calorific values are similar for both fuels.

The distillation curve profiles for vegetable oils are also connected with higher amounts of deposits in the combustion chambers and injectors. These may have an adverse effect on engine operation, causing extensive wear of the piston units. That situation results from relatively large and heavy molecules of triglycerides, as compared with diesel oil hydrocarbon mole-cules. In order to eliminate such problems, attempts have been made to eliminate glycerides from oil droplets by alcoholysis with methanol (methanolysis), followed by conversion of glycerine esters, i.e., substitution of the methyl group CH_3 instead of the glycerine group, which yields lower molecules. This method is used for manufacturing methyl esters of rapeseed oil fatty acids, which may be used directly as a fuel or as a fuel additive (5 %). The by-product from that process, glycerine, can be relatively easily separated from the ester product. The following advantages are obtained: lower fuel density and viscosity, higher volatility, and possible reduction of deposits inside the engine. The presence of esters also reduces the amount of solids and improves lubricity of diesel oils (otherwise, after elimination of sulfur from diesel oil, lubricity improvers would need to be used to prevent precision component pairs from seizing up). The use of methyl esters also has some drawbacks: high viscosity and loss of fluidity at lower temperatures, hygroscopicity and the resulting risk of extensive corrosion, potential deposits in the engine exhaust system. It is also necessary to replace gaskets and flexible tubing and to use elements made of fluorinated elastomers. The World-wide Fuel Charter which was signed by major global producers of engines and motor-cars recommends to avoid adding more than 5 % esters to conventional diesel oils. However, there are exceptions from that rule, e.g., "Skoda" and some other car manufacturers in the Czech Republic and in Germany accept the use of pure biodiesel, and "Peugeot" accepts the content of up to 30 % esters in diesel oil.

It is possible to use esters of vegetable oil fatty acids as fuels for spontaneous-ignition engines. Esters are obtained by transesterification, which involves a catalyzed chemical reaction of vegetable oil triglycerides and methyl alcohol or ethyl alcohol. Rape seeds make the most commonly used feed for the production of esters in Europe, including Poland.

Esterification processes give rapeseed oil fatty acid methyl esters (FAME), which may be used as pure esters or after blending them with diesel oils.

The FAME vegetable-based fuel is a mixture of methyl esters of rapeseed oil organic acids containing between 16 and 22 carbon atoms per molecule. The petroleum diesel oil is a mixture of hydrocarbons with boiling points from 150 to 380°C. It is produced by petroleum distillation and by secondary processing of heavy fractions (distillation residue). Diesel oils are composed predominantly of saturated aliphatic hydrocarbons and cycloalkanes with 14 to 20 carbon atoms per molecule, and of aromatic hydrocarbons. The shares of the respective hydrocarbon groups in a diesel oil product are decisive for its physico-chemical properties and affect engine performance and toxicity of exhaust gases.

Diesel oils and rapeseed oil esters are fuels obtained from different raw materials, therefore, they have different chemical compositions and different physico-chemical properties. Esters contain fewer carbon and hydrogen atoms and about 12 % more oxygen. That higher oxygen content results in lower calorific values of vegetable-based fuels. The presence of oxygen in ester molecules is favorable for the microbial growth which changes the fuel characteristics. Esters will dissolve more water than hydrocarbons, hence, biodegradability of vegetable-based fuels will be higher than that of hydrocarbons. The presence of unsaturated bonds in ester molecules leads to worse oxidation stabilities. The oxygen content in biofuels also adds some advantages: their combustibility is superior and the combustion process is more intensive and complete. This favors reduction of hydrocarbon and carbon monoxide emissions, as well as smoke level in exhaust gas, though it also increases combustion temperature and nitrogen oxide emissions. Rapeseed oil methyl esters offer higher densities and viscosities, compared with diesel oils, leading to better lubrication properties which improve the service life of fuel systems. Ester additions to low-sulfur diesel oils improves lubrication properties of the latter. The use of esters, however, may intensify deposits in the combustion chamber and fuel injectors. Esters have inferior low-temperature performance properties. They cannot be used in winter conditions unless dedicated additives are used. FAME are aggressive to rubber, to some plastics, and paint coats. Fatty acid methyl esters are miscible with diesel oils, at any proportion, which makes them useful in powering spontaneous-ignition engines.

Parameter	Value	Unit	Test method
Content of esters	96.5 min	% m/m	EN 14103
Methyl Esters of Linolenic Acid	12.0 max	% m/m	Other: ABNT NBR 15342
Methyl Esters of Poly-unsaturated Acids	1 max	% m/m	EN 14103
("/> 4 double bonds)			prEN 15779
Induction period	10 min	h	prEN 15751 or alternatively EN 14112
Iodine number	130 max	g I$_2$/100 g	EN 14111
Total acid number	0.50 max	mg KOH/g	ISO 6618 ASTM D664, D974 JIS K2501 Other: ABNT NBR 14448

Parameter	Value	Unit	Test method
Methanol	0.20 max	% m/m	EN 14110
			JIS K2536
			Other: ABNT NBR 15343
Glycerides			EN 14105
Monoglycerides	0.80 max	% m/m	EN 14105
Diglycerides	0.20 max	% m/m	ASTM D6584
Triglycerides	0.20 max	% m/m	Other: ABNT NBR 15342
Glycerol	0.02 max	% m/m	EN 14105
Free glycerols	0.25 max	% m/m	ASTM D6584
Total glycerol:			Other: ABNT NBR 15342
			EN 14105
			ASTM D6584
			Other: ABNT NBR 15342
			EN 14105/14106
			ASTM D 6584
			Other: ABNT NBR 15341
			EN 14105
			ASTM D 6584
			Other: ABNT NBR 15344
Density	Report	g/ml	EN ISO 3675
			ASTM D4052
			JIS K2249
			Other: EN ISO 12185, ABNT NBR 7148/14065
Kinematic viscosity @ 40°C	2.0-5.0	mm^2/sec	EN ISO 3104
			ASTM D445
			JIS K2283
			Other: ABNT NBR 10441
Flash point	100 min	°C	ISO 3679
			ASTM D93
Cetane number	51 min		ISO 5165
			ASTM D613
			JIS K2280
Water	500 max	mg/kg	EN 12937
Water and deposits	0.05 max	% v/v	ASTM D2709
Impurities	24 max	mg/kg	EN 12662
			ASTM D2276, D5452, D6217
Ash content	0.001 max	% m/m	ISO 6245
Incineration residue	0.005 max	% m/m	ASTM D482
			JIS K2272

| Parameter	Value	Unit	Test method
			ISO 3987
			ASTM D874
			Other: ABNT NBR 984
Ramsbottom Carbon Residue, per 100 % distillation residue	0.05 max	% m/m	ASTM D4530
Corrosion: iron	some traces max.	assessment	ASTM D665 Procedure A
Sulfur	10 max	ppm	EN 20846/20884
			ASTM D5453 /D2622
			JIS K3541-1, -2, -6 or -7
Phosphorus	4 max	mg/kg	EN 14107
			ASTM D4951, D3231
Alkali (group I) metals (Na+K)	5 max	mg/kg	EN 14108/14109, EN 14538
Alkali (group II) metals (Ca+Mg)	5 max	mg/kg	EN 14538
Trace metals	-	no willful addition	ASTM D7111

Table 2. Requirements for FAME, used as diesel additives, according to WWFC guidelines (March 2009)

The permissible duration of storage for pure esters is the subject of dedicated tests being carried out to determine the parameter. In general, it is not recommended to store pure esters for more than 12 months under typical storage conditions in closed tanks, in the absence of air or direct sunlight. It is just because of the fears for the stability of esters in long-term storage conditions that biodiesels may not be used in combat vehicles in the US army. The long-term storage of diesel-esters mixtures has not been sufficiently documented yet but it is safe to assume that their storage period is comparable to that for pure esters. As a rule, fuels should be stored in underground tanks while ground-based tanks should be provided with adequate thermal protection.

The problems faced in the manufacturing of fuel components, biofuels and final products from the middle-distillate group involve product protection issues beyond the short period of time during which the fuels are kept within the production facility. Laboratory analyses are provided to establish the acceptable fuel storage time.

4. Alcohols as fuel components

Methyl alcohol (methanol) is usually synthesized from natural gas. The first step in the production process makes use of steam reforming to convert natural gas into syngas and to adjust the CO / H_2 ratio to the required value, according to the reactions:

$$CH_4 + H_2O = CO + 3 H_2$$
$$CO + H_2O = CO_2 + H_2$$
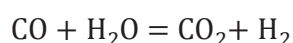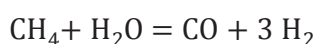
In the second step, after removal of contaminants, carbon monoxide and hydrogen are catalytically reacted to form methanol:

$$CO + 2\,H_2 = CH_3OH$$

$$CO_2 + 2\,H_2 = CH_3OH + H_2O$$
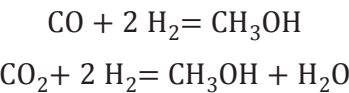
Methanol can be produced from biomass (cellulose, wood-based in most cases); it is technically feasible but not commercially viable at present. The raw material is to be converted into syngas which can be then processed into methanol. The raw material must be initially prepared by fragmentation, grinding and drying. Syngas is then obtained by gasification, i.e., by combustion in equilibrium with the supplied oxygen, to produce carbon monoxide and hydrogen, unlike in normal combustion which gives carbon dioxide and water. A portion of syngas is formed by oxidation of biomass and another portion – by steam reforming (pyrolysis). Crude syngas is then converted into methanol in the way which is similar to that for syngas, obtained from natural gas.

Methanol is frequently used in vehicles which are powered by fuel cells. As hydrogen is needed for fuel cells, it is produced just within such vehicles from methanol.

Methanol may also be used by reacting it with isobutylene to obtain methyl-*tert*-butyl ether (MTBE) – a high-octane component of gasoline.

The consumption of methanol as a propulsion agent for vehicles is relatively high, in particular that derived from biomass. Hydrocarbon emissions are high, especially for methanol obtained from natural gas. Carbon dioxide emissions for biomass-based methanol may be very low. As regards the rate of evaporation, it is low for methanol which leads to another very important advantage: its emission through evaporation is lower than that for petroleum. The storage conditions for methanol are shown in Table 3.

Storage		Safety					
		Combustion of vapor			Toxicity	Pollution of ground water	Atmospheric pollution
Weight*	Volume*	In open air	In confined space	In tank			
191	176	No risk	Risk	Very high risk	High risk	High risk	Very high risk

*) Weight and volume make the per-cent equivalent for 46 kg (~ 68 liters) of gasoline.

Table 3. Storage and safety characteristics for methanol

Alcohols may easily form explosive vapor-air mixtures within the gas space of a fuel tank at ambient temperatures. However, as regards accidents involving methanol-powered vehicles, the risk of explosion is lower than for gasoline since the rate of evaporation is lower for methanol and the fuel remains liquid. Methanol is a poison; it is toxic because of its decarbox-

ylase taking place in the human body, which produces methanal (formaldehyde). Methanol is biodegradable.

As regards alcohol-based fuels, the principal emission connected with the production of methanol comes from the energy which is used in the synthesis processes. For natural gas-based methanol, apart from emissions of methanol itself, hydrocarbons are also released in methane effluents/leakages. CO_2 emissions arising in the production process may be equal to zero when biomass is used in the conversion process since some volumes of CO_2 are absorbed by the plants in the course of their growth. The production of wood-based methanol leaves ash as the residue.

Although the properties of ethyl alcohol (ethanol) are much similar to those of methanol, the production of ethanol is usually based on biomass (crops which are rich in sugar, starch or cellulose), and less frequently on natural gas. Yeast fermentation is required for the production of ethanol. Sugar in the form of glucose occurs in a few plant species only. Raw materials are subjected to fragmentation/grinding, and then longer molecular chains in the fermented sugar are broken down by hydrolysis. The diversity of hydrolysis techniques reveals most important differences in the production methods which are required for various raw materials. The dominant content of glucose may be extracted directly from the plants and then only mild hydrolysis conditions are required. For starch crops, the enzymatic hydrolysis technology is employed. The acid hydrolysis needs to be used for cellulose.

Ethanol for industrial use is obtained through fermentation of saccharides which become available after hydrolysis of wood or from sulfite waste liquor. Synthetic ethanol is produced in chemical processes. Although the manufacturing costs for bioethanol have dropped down recently, they still remain rather high. The bioethanol production costs are strongly affected by the cost of raw material which is as high as about (60...70) % and by the volume of production. Moreover, the cost of energy which should be added is not insignificant. What is also important for the reduction of ethanol production costs is the management and disposal of the production residual materials; the general manufacturing costs can be further cut down in this way by about (15...20) %.

A few methods have been developed for the production of bioethanol which can clearly reduce production costs: they include the use of improved bacterial strains, the use of wet milling which accelerates saccharification, or the use of reverse osmosis with synthetic membranes employed for separation in order to improve alcohol recovery from the fermentation products.

Within the use of ethanol as an energy carrier, the second-generation enzymatic processes have been developed now for the production of bioethanol from such materials as straw, waste wood, etc. Such processes are reported to have been partially implemented so far.

Emissions from the ethanol production depend on the fuel consumption involved in generation of power and steam which are indispensable for the process. CO_2 emissions relating to the production may be low when biomass is used in the conversion process since some volumes of CO_2 are absorbed by the plants in the course of their growth. Emissions from the production of cellulose-based ethanol are higher than those noted for sugar-rich or starch-rich feeds since more energy is needed for the conversion of cellulose.

Ethyl-*tert*-butyl ether (ETBE), ethanol derivative, is a 100% value component of motor spirits – there is no need to employ any additional preventive measures in the logistics or use of such gasoline. The production capacity for that ether in EU countries is unfortunately limited and cannot be expanded because of the short supplies of isobutylene. Hence, most bioethanol will be added to motor spirits directly. Moreover, it can be concluded from the above considerations relating to energy that considerable volumes of motor spirits will be required to have a bioethanol content of more than 5 % (v/v). Additional protective means will be necessary in the logistics of such fuels (elimination of moisture, completely enclosed vessels, equipment and transfer processes, etc.). Moreover, such fuels should be used in dedicated vehicles only to eliminate negative environmental impacts.

In 2009, attention was brought by the automotive industry to the fact that motor spirits will have a content of anhydrous ethyl alcohol. Without changing their viewpoints on the need to restrict the use of the component, engine and car manufacturers established the quality requirements for ethanol in their guidelines (issued in March 2009). The requirements can be found in Table 4 below.

Parameter	Value	Unit	Test method
Ethanol + saturated alcohols C3-C5 (dewatered) Saturated alcohols C3-C5 (dewatered) Methanol	99.2 min 2 max 0.5 max	% m/m % m/m % m/m	EN 15721 ASTM D5501 Other: JAAS001-6.2 EN 15721 EN 15721 ASTM D5501
Water content	0.3 max	% m/m	EN 15489 ASTM E203 JIS K8101
Density	Report	kg/m^3	ASTM D4052 Other: ABNT NBR 5992
Electrical conductance	500 max	μS/m	ASTM D1125 JIS K0130 Other: ABNT NBR 10547
Inorganic chlorine	10.0 max	mg/l	EN 15484 or EN 15492 ASTM D7319, D7328 Other: ABNT NBR 10894/10895
Sulfates	4 max	mg/kg	EN 15492 ASTM D7318, D7319, D7328 Other: ABNT NBR 10894/12120
Copper	0.100 max	mg/kg (ppm)	EN 15488 ASTM D1688 modified, Method A JIS K0101 Other: ABNT NBR 10893

Parameter	Value	Unit	Test method
Organic impurities	10 max (1 max)	mg/l (% m/m)	JIS JAAS001 – 6.4
Phosphorus	0.50 max	mg/l	EN 15487 ASTM D3231
Sulfur	10 max	mg/kg or ppm	EN 15486 ASTM D5453 (< 20 ppm) JIS K2541
Heavy metals	Undetectable (traces)		Other: ICP-AES
Non-volatile matter	5 max	mg/100 ml	prEN 15691 ASTM D381 JIS JAAS001 – 6.3 Other: ABNT NBR 8644
pH	6.5-9 6-8		ASTM D6423 EN 15490 JIS JASO M361-6.10 Other: ABNT NBR 10891
Acidity	0.007 max	% m/m	EN 15491 ASTM D1613 Other: ISO 1388/2; ABNT NBR 9866
Appearance	No visible impurities		Visual inspection
Color			Visual inspection

Table 4. Requirements for ethyl alcohol employed as a gasoline additive, according to WWFC guidelines (March 2009)

5. Conclusion

The growing energy crisis and restrictions in the emissions of GHG create the need (which is also boosted by regulatory provisions) to use new types of gasoline components which are not derived from petroleum feedstocks, mainly to use biocomponents, such as ethanol, FAME, etc. The course of the oxidation (ageing) process(es) of fuels which contain those components has not been established so far. Nonetheless, applicable European documents (road maps) define the process routes for the production of new components based on lignocellulose, waste, biogas, natural gas, coal, and even syngas production processes from carbon dioxide and steam (BtL, WtL, GtL and xtL processes). The course and rate of ageing (oxidation) processes should be established also for such components and for their blends with petroleum hydrocarbons.

Because of the tendency of ethyl alcohol to form mixtures (solutions) with water at any ratios (including azeotropes), because of its oxidative and corrosive impacts, and low chemical stability of FAME's and their possible oxidation, there is a scarcity of unambiguous informa-tion indicating the permissible duration of storage and analytical methods that may be

required. As mentioned before, pure esters can probably be stored for up to 12 months if placed in tightly closed tanks/containers which are insensitive to temperature fluctuations.

Adding FAME's to the pool of fuel components and biofuels affects the fuel stability, hence, such fuels cannot be stored for long periods of time. Based on the collected data, it is evaluated that the oxidative stability of FAME after one month of storage goes down below the quality requirements in some cases, thus leading to changes in the values of other parameters. The use of improver additives makes it possible to extend the storage time up to about 8 months. Research studies are in progress on the use of tailored antioxidant packages in biofuel formulations. Our own findings indicate that the antioxidant additives which are used at present will inhibit oxidation of esters but they may at the same time have an adverse effect on the oxidation of petroleum hydrocarbons.

The above discussion shows clearly that we are facing the growing trend to modify compositions of the present-day motor fuels. Those changes result principally from the obligation being imposed on fuel manufacturers to add into fuel blends components obtained from renewable sources, with unstable compositions. Since the available resources of crude oil are becoming shorter and shorter while the fuel consumption keeps growing, it is expected that more and more alternative components will be added into fuel blends. With the components derived from various waste materials, it will be harder and harder to predict the rates of fuel oxidation processes and to define the permissible durations of storage. It was found for biocomponents used in fuels that the standard requirements for petroleum fuels and for some biocomponents are maintained. However, mixtures of those components (FAMEs) fail to meet the requirements of oxidation tests. Regardless of the above, the fuel compositions of the future must satisfy the conditions as defined in LCA, inclusive of the WtW cycle for fuels.

Author details

Krzysztof Biernat[1,2*]

Address all correspondence to: k.biernat@pimot.eu

1 Department of Fuels, Biofuels and Lubricants, Automotive Industry Institute, Poland

2 Institute for Ecology and Bioethics of CSWU, Poland

References

[1] K. Biernat, A. Kulczycki „Prognoza rozwoju biopaliw w Polsce", Krajowa Konferencja: "Rynek biopaliw w Polsce – szanse i zagrożenia" [*A forecast for the development of biofuels in Poland*, National Conference *The biofuels market in Poland – opportunities and risks*], Warsaw, April 2006.

[2] K. Biernat „Biopaliwa drugiej generacji", Krajowa Konferencja Biopaliw i Biokompo-
nentów [*2nd generation biofuels,* conference proceedings*: National Conference on Bio-
fuels and Biocomponents*], Gdańsk, October 2006.

[3] K. Biernat, J. Głąb, „Analiza wymagań technicznych, normatywnych oraz wytycz-
nych jakościowych produkcji i stosowania biopaliw w Polsce", Krajowa Konferencja
„Biopaliwa w Polsce" [*Analysis of technical and normative requirements and qualitative
guidelines for the production and use of biofuels in Poland", Conference proceedings: "Bio-
fuels in Poland" – National Conference*], Warsaw, November 2006.

[4] K. Biernat, A. Kulczycki, M. Rogulska: „Development of Alternative Fuels in Po-
land", conference proceedings "Expert Workshop on Biofuels Support in Baltic
States, Nordic Countries and Poland". Tallin, Estonia, February 2007.

[5] K. Biernat, M.Mielczarska-Rogulska, "Implementation and Properties of Biofuels and
Biocomponents", conference proceedings "European Transport in FP 7", Warsaw,
March 2007.

[6] K. Maniatis "Biofuels EU policy and recent developments", conference proceedings:
Materiały drugiego spotkania Mirror Group ETPB, Brussels, February 2007.

[7] W. Górski „Biopaliwa w normach: ISO, EN i PN" [*Biofuels according to ISO, EN, PN
standards*],, „Przemysł Chemiczny" December 2006.

[8] B. E. Kampman, L.C. den Boer, H.J.Croezen, "Biofuels under development", Publica-
tion CE No 05.4894.11, Netherlands Petroleum Industry Association, Delft, May 2005.

[9] Ethanol Guidelines, From the Worldwide Fuel Charter Committee, March 2009.

[10] Biodiesel Guidelines, From the Worldwide Fuel Charter Committee, March 2009.

[11] A. Jeziorkowski, K. Biernat, "Możliwości dostosowania współczesnych silników spa-
linowych do zasilania biopaliwami" [*Opportunities for adapting contemporary combus-
tion engines to being fuelled with biofuels*], "Przemysł Chemiczny " No. 3/2009, pp.
234-240.

[12] K. Biernat, P. Dziołak, „Bio 2,5-dimetylofuran (BioDMF) jako nowe biopaliwo drugiej
generacji" [*Bio 2,5-dimethylfuran (BioDMF) as a new 2nd generation biofuel*], Miesięcznik
Naukowo-Techniczny „Chemik, Nauka, Technika, Rynek" No. 12, December 2008
pp.657-661.

[13] K. Biernat, A. Malinowski, M. Gnat: Chapter No 4, in Monograph, Editor:. Zhen
Fang, Title: „Biofuels-Environment and Sustainability", Edition by "InTech", Decem-
ber 2012, ISBN 980-953-307-471-4: "The possibility of future biofuels production us-
ing waste carbon dioxide and solar energy".