

## EXAMINING THE QUALITY OF CUSTOM PRODUCTION'S BIOFUELS

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### Abstract

In relation to the scantiness of stores and the constantly increasing demand for energy, societies are forced to seek alternative energy sources. Biofuels that is fuels produced of biomass are one of them. The most important biofuels are bioethanol (produced from sugar cultivations and cereal crops, used with petrol) and biodiesel (ester produced mainly of vegetable oils; serves as the substitute or the addition to diesel). The esters of vegetable oils production requires using appropriate apparatus which enables to produce esters with parameters defined in very exacting legal norms about the quality of such fuel.

In the paper were described results examining the quality of esters and mineral oils made with the use highly specialist, new generation's apparatus which fulfil the conditions defining in the relevant norm. Results of those surveys are showing that using simple methods in production such biofuel doesn't let for getting the product with parameters defined by the law.

Applying fuel with lowered standard parameters influences on observed cases of improper functioning of fuel apparatus in engines with self-ignition, mainly in case of high pressure systems (e.g. Common Rail).

**Keywords:** biofuels, examinations and quality standards, custom production

### 1. Introduction

As the world resources of oil and other fossil fuels are diminishing and since the man is totally reliant on mechanisms they fuel, there appears the need to find a substitute which would be renewable and at the same time would enable these mechanisms to function well. In the last few years a lot has been said about technologies which can produce renewable energy. Solar collectors, wind farms, biogas or biofuels are more and more often used to produce energy. Figure 1 shows what part of energy consumed in certain countries is obtained from renewable sources now and what results are expected for 2020.

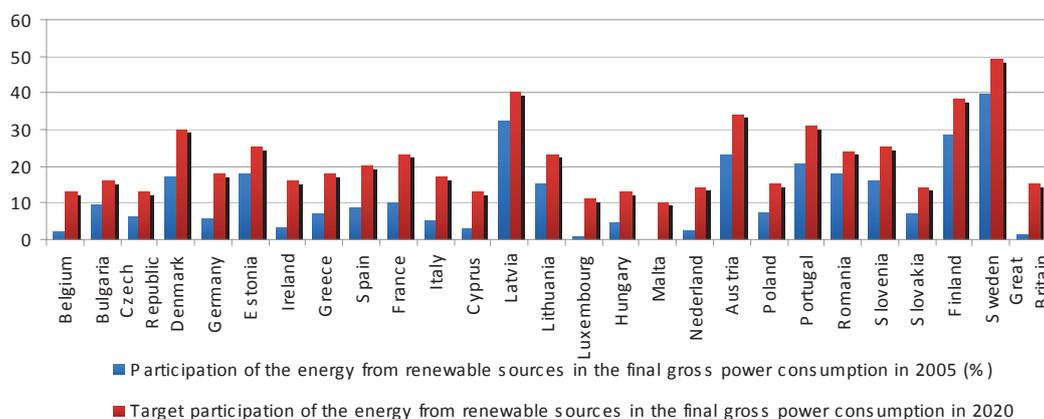


Fig. 1. Domestic general objectives within the scope of the participation of the energy from renewable sources in the final gross power consumption in 2020 [1]

Biofuels are fuels derived from biomass. Among the most important biofuels there are: bioethanol (derived from sugar and corn plantations, used together with gasoline) and biodiesel (derived mainly from vegetable oil, used as a substitute for or an addition to diesel oil).

Statistical data show that more and more crude oil is extracted and used in Poland (Fig. 2).

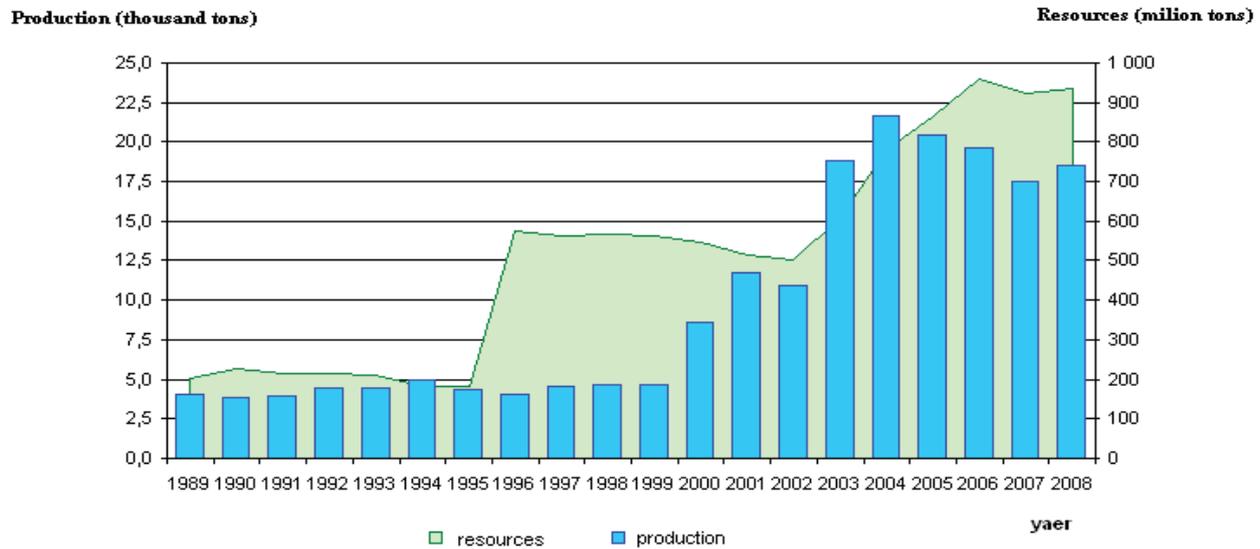


Fig. 2. Resources and getting petroleum in Poland in years 1989-2008 [14]

Such tendency is caused, among other things, by a growing number of mechanical vehicles. As statistics show [8], since 2002 we have been observing a constant increase in their number, from 315.8 thousand in 2002 to 952.5 thousand in 2008 – it is an increase by about 301.62%.

A constant increase in the demand for fuels forces people to look for such solutions that make it possible to use vehicles despite oil resources diminishing. The search for alternative ways to energise engines is prompted by societies who demand ecologically friendly politics (limiting exhaust emission, heat emission, greenhouse gases emission, etc.). In June 2010, the European Commission defined the conditions which will be followed in certifying biofuels. The EU's stand is as follows: "In the years to come, biofuels are the main alternative to petrol and diesel used in transport, which produces more than 20% of the greenhouse gas emissions in the European Union. We have to ensure that the biofuels used are also sustainable. Our certification scheme is the most stringent in the world and will make sure that our biofuels meet the highest environmental standards. It will have positive effects also on other regions as it covers imported biofuels" [13].

## 2. Laws on testing the properties of liquid biofuels

The issue of norms concerning producing and distributing biofuels in Poland is still open to discussion. Polish law in this respect is not unified and in some cases evens self contradictory. These are the basic acts:

- The Biocomponents and Liquid Biofuels Act of 25 August 2006 (based on the Biocomponents used in Liquid Biofuels and Liquid Biofuels Act of 2 October 2003),
- The Minister of Economy Regulation of 22 April 2010 on the methods of liquid biofuels quality testing,
- The Minister of Economy Regulation of 22 January 2009 on the quality requirements for liquid biofuels,
- The Fuel Quality Monitoring and Control Act of 25 August 2006.

The first of these acts provides basic definitions in the filed of biofuels, such as:

- biocomponents – bioethanol, biomethanol, ester, dimethyl ether, pure vegetable oil and synthetic hydrocarbons,

- ester – methyl ester or ethyl ester, fatty acids derived from biomass,
- bioethanol – ethyl alcohol made from biomass, including bioethanol contained in ethyl *tert*-butyl ether or *tert*-amyl methyl ether,
- biomethanol – methyl alcohol made from biomass, including biomethanol contained in methyl *tert*-butyl ether or *tert*-amyl methyl ether,
- liquid biofuels:
  - a) engine gasolines containing more than 5.0% of biocomponents or more than 15.0% of ethers mentioned in point 4,
  - b) diesel oil containing in its capacity more than 5.0 % of biocomponents,
  - c) ester, bioethanol, biomethanol, dimethyl ether and pure vegetable oil – as self-contained biofuels,
  - d) biogas – gas derived from biomass,
  - e) biohydrogen – hydrogen derived from biomass,
  - f) synthetic biofuels – synthetic hydrocarbons or mixtures of synthetic hydrocarbons made from biomass and constituting self-contained fuels [11].

The regulation on methods of testing the quality of biofuels provides guidelines for entities planning to start research in the field of determining the uniformity of the already existing fuel's parameters with Polish and European norms [10], which are enumerated and specified in the next regulation, i.e. of 22 January 2009 on the quality requirements for liquid biofuels [9]. This document divides biofuels into:

- esters constituting self-contained fuel used in vehicles, tractors as well as machines not used on roads, equipped with Diesel engines adapted to burn this liquid biofuel;
- diesel oil containing 20% of esters used in vehicles, tractors, as well as machines not used on roads equipped with Diesel engines adapted to burn this liquid biofuel.

Each of these fuels has been provided by the legislator with different parameters, different methods to establish these parameters and different limits for these parameters. Numbers in Tab. 1 pertain to ester as a self-contained fuel (B100) and as an additive to Diesel oil (B20). This table presents also the norms which illustrate particular tests.

### 3. The tested samples description

Esters production is not particularly difficult. There is no need to have a special laboratory since having the right equipment and components needed in the process of esterification one is able to produce this biofuel. However, without the appropriate equipment it is difficult to arrive at such parameters of fuel quality as to match the conditions set in regulations.

In order to test the quality of biofuel from non-standard production process (non-refinery) the following samples were tested:

- Palm ester,
- Waste cooking oil,
- Fish oil,
- Waste cooking fatty acids,
- Rapeseed fatty acids.

These biofuels were produced by a company which owns simple equipment which, still, does not have negative influence on the quality of its produce.

Tests included also ethyl esters produced by a field esterification plant of the Mechatronics Chair. It is presented in Photo 1 and 2. These esters were produced in 2006 and for three years were stored in glass bottles of 1 litre capacity in a shaded place. Thus one can expect here results different than those got when freshly produced fuel is tested.

To compare results, biofuels produced by companies specialising in the field were tested Diesel oil with 20% ester content (B20) and 100% ester (B100).

Tab. 1. Quality requirements and norms for liquid biofuels

B100	Norm	B20	Norm
Fatty acids methyl esters content			
Min 96,5%	PN-EN 14103	20 ± 1%	PN-EN 14078
Density of ester in 15°C			
860-900 kg/m <sup>3</sup>	PN-EN ISO 12185 PN-EN ISO 3675	820-860 kg/m <sup>3</sup>	PN-EN ISO 12185 PN-EN ISO 3675
Viscosity of ester in 40°C			
3.5-5.0 mm <sup>2</sup> *s	PN-EN ISO 3104	2.00-4.5 mm <sup>2</sup> *s	PN-EN ISO 3104
Flash point			
Min 101°C	PN-EN ISO 3679	Above 55°C	PN-EN ISO 2719
Sulphur content			
Max 10 mg/kg	PN-EN ISO 20884	Max 10 mg/kg	PN-EN ISO 20884
Carbon Residue			
Max 0.3 %	PN-EN ISO 10370	Max 0.3 %	PN-EN ISO 10370
Cetane Number			
Min 51	PN-EN ISO 5165	Min 51	PN-EN ISO 5165
Water content			
Max 500 mg/kg	PN-EN ISO 12937	Max 300 mg/kg	PN-EN ISO 12937
Solid pollutants content			
Max 24 mg/kg	PN-EN 12662	Max 24 mg/kg	PN-EN 12662
Corrosion behaviour			
Corrosion Level 1	PN-EN ISO 2160	Class 1	PN-EN ISO 2160
Acid value			
Max 0.5 mg KOH/g	PN-EN 14104	Max 0.2 mg KOH/g	PN-EN 14104
Cold filter plugging point			
Max 0°C, max -10°C max -20°C	PN-EN 116	Max 0°C, max -10°C max -20°C	PN-EN 116
Sulphate ash content		Incineration residue	
Max 0.02 %	PN-ISO 3987	Max 0.01 %	PN-EN ISO 6245
Oxidation stability in 110°C		Cetane Index	
Min 6 h	PN-EN 14112	Min 46.0	PN-EN ISO 4264
Iodine value		Oxidation resistance	
Max 120 g iodine/100g	PN-EN 14111	Max 25 g/m <sup>3</sup>	PN-ISO 12205
Linolenic acid methyl ester content		Lubricity	
Max 12.0%	PN-EN 14103	Max 460 µm	PN-EN ISO 12156-1
Polyunsaturated fatty acids methyl esters (with no fewer than four double bonds) content		Distillation range: 1. distils up to 250 °C 2. distils up to 350 °C 3. 95 % (V/V) distils up to	
Max 1%	XXXX		
Methyl alcohol content		1. <65 % 2. Min 85 % 3. Max 360°C	PN-EN ISO 3405
Max 0.2%	PN-EN 14110		
Monoacylglycerol content		The last of the enumerated legal acts contains general definitions relating to fuels and rules of using biofuel propelled cars which undergo traffic code (e.g. quality control). Goals which are achieved through this act concern: people's health and natural environment protection, car users' safety, ensuring economic interests of consumers and working against introducing to the market fuels which do not fulfil quality requirements set by the state [12].	
Max 0.8%	PN-EN 14105		
Diacylglyceride content			
Max 0.2%	PN-EN 14105		
Triacylglyceride content			
Max 0.2%	PN-EN 14105		
Free Glycerol Content			
Max 0.02%	PN-EN 14105 PN-EN 14106		
Glycerol content			
Max 0.25%	PN-EN 14105		
Group 1 metals content (Na + K)			
Max 5.0 mg/kg	PN-EN 14538		
Group 2 metals content (Ca + Mg)			
Max 5.0 mg/kg	PN-EN 14538		
Phosphorus content			
Max 4.0 mg/kg	PN-EN 14107		

#### 4. The tests

The tests were carried out in Biofuels Quality Monitoring Laboratory in Mechatronics Chair of Warmia and Mazury University. This laboratory had been equipped with basic machines necessary to determine parameters essential in evaluating the quality of liquid biofuels. Chosen samples underwent the following tests: oxidation stability in 110°C, group 1 metals (Na + K) content, group 2 metals (Ca+Mg) content, phosphorus content, viscosity in 40°C, flash point, sulphur content. The tests were carried out on the basis of European norms which describe the whole procedure for every determination.

*Determination of the content of elements*, both group 1 and 2 metals as well as phosphorus were carried out in the ICP emission spectrometer [2, 4]. The emission spectrometry method used here means evoking emission spectrums for particular elements' atoms, which originate as a result of an electron dropping from a higher energy level to a lower one. This technique measures the energy emitted by an atom falling from an excited state back to its ground state. The number of photons which are emitted is proportional to the number of atoms of a given element which are in the sample. In order to excite the sample it is necessary to atomise it (i.e. 'decompose' it into free atoms and ions). The content of elements is determined by comparing the emission of a single element in the solution of the test sample dissolved in kerosene (for group 1 and 2 elements) or xylene (for phosphorus) with the emission of standards at the same wavelength. The norms provide the rules of determining the content of elements.

*Determination of the content of sulphur* was carried out in a wavelength dispersive X-ray fluorescence spectrometer [5]. It is an analyser used to determine the total content of sulphur in fuels. The analyser is based on monochromatisation of radiation and the system of monochromatic dispersion of fluorescence X-ray wave. The Roentgen lamp emits radiation of 5.373Å (0.5373 nm) wave-length, which passes through the monochromator. So prepared radiation enters the sample and when reflected by sulphur atoms contained in the sample the rays pass through one more monochromator and then through the detector. The intensity of the sulphur rays is measured with an appropriate sensor and transformed into sulphur concentration in the sample [mg/kg] by means of comparison with the test sample in the calibration process. The test sample of fuel is not diluted. The sample in the measuring cuvette is exposed to primary radiation from the Roentgen lamp. The norm PN-EN ISO 20884 describes the correct procedures for this test.

*Determining flash point* was conducted with equilibrium method in the tester with the closed cup, in which the space above the product is covered with a special cover [7]. The tester is a 'flash, no flash' testing tool, i.e. it determines ignition point in 0°C - 300°C temperature range. The flash point is the lowest temperature in which a liquid heated in normalized conditions exudes enough vapours to create with air a mixture ignited when the flame comes close. Ignition limits depend on many factors, among which the following are most essential: chemical makeup of the vapours of the substance, pressure, oxygen concentration, concentration and kind of neutral gases, the shape of the space surrounding the area in which ignition will occur, the position of the flame. The test is undertaken in line with the European norm PN-EN ISO 3679.

*Determining the oxidation stability in 110°C* is a test which is performed in order to check the durability of a fuel and its resistance to oxidation [3]. A stream of cleaned air passes through the sample whose temperature is raised to a certain level (110°C). Volatile compounds freed from the sample in the oxidation process together with the air pass through to the container with distilled or demineralised water and equipped with an electrode to measure conductivity. The electrode is connected with the measuring and registering unit. It indicates the end of induction period the moment conductivity starts to rise dramatically. The increased rise is caused by dissociation of volatile carboxylic acids which are created in the process of oxidation and are absorbed in water. Rancimat is used in this test; it is a machine to measure oxidation stability. The method of passing a stream of air through the sample was used.

*Determining the viscosity in 40°C* was performed using a thermostatic water bath and a calibrated capillary viscometer [6]. The test measures the time in which a constant capacity of water flows under the influence of gravity through a capillary of a calibrated viscometer in repeatable conditions in known and strictly controlled temperature. Kinematic viscosity is calculated multiplying the measured time of flow by a viscometer calibration constant. The test was performed in line with the regulations of the European norm PN-EN ISO 3104.

## 5. Results

*Phosphorus content results.* The test was performed with 213.618 nm wavelength. Determination was carried out in the temperature of surroundings, about 20°C. Phosphorus content in all samples was within the range set in the norms. The results are presented in Tab. 2. In order for the biofuel quality to be concordant with the norms, phosphorus content cannot exceed 5.0 mg/kg.

*Elements (Na, Ca, K, Mg) content results.* Determination was carried out in the temperature of surroundings, about 20°C. In order for the biofuel quality to be concordant with the norms, group 1 elements (Mg+Ca) and group 2 elements (Na+K) content cannot exceed 5.0 mg/kg. The results are presented in Tab. 2. It can be read there that only biofuels which were produced from waste cooking oil contain forbidden quantities of these elements. It might be caused by too large an amount of these elements in the products which were cooked in these oils. In all tested esters the results were within limits.

*Sulphur content results.* The test was performed with 0.5373 nm wavelength. After the samples underwent X-rays, in most of those from non-standard production sulphur content considerably exceeded the allowed values. Only palm ester would be fit for use if only this parameter was considered. Table 2 presents the detailed results. In order for the biofuel to be concordant with the norms, sulphur content cannot exceed 10.0 mg/kg.

*Flash point results.* The measurements for every ester were stopped at 120°C, with the atmospheric pressure around 1010 hPa. The measurements show that for all the tested fuels the flash point exceeds 101°C. The results are presented in Tab. 2.

*The results of oxidation stability at 110°C.* Determination was carried out in 20°C. The undertaken tests showed that none of the fuels which underwent oxidation matches the norms. The time in which the samples oxidised is definitely shorter than the one assumed by the legislators (according to the Regulation of the Minister of Economy [9] the minimal oxidation time should be 6 hours). It means that the fuel is not durable and it is not fit to be stored for a long time. The samples reached the results close to those of ethyl ester stored in little quantity for four years in a glass container at room temperature (in such conditions one can talk about autooxidation of a fuel). To test diesel oil with 20% ester content a different method is used. The results of exposing the samples to the operation of a stream of air are presented in Tab. 2.

*The test results of viscosity in 40°C.* Determination was carried out in 20°C. The test was carried out in a bath with water of 40.05°C. Before the test the samples were warmed to 40°C. Analyzing the results, one can notice that three out of five tested samples from non-standard production do not come within the limits set by the norms. In all these cases viscosity is higher than suggested by the legislator (according to the norms viscosity should remain within the 3.5-5 mm<sup>2</sup>\*s<sup>-1</sup> range). It can be noticed that a four-year ethyl ester also does not match the limits of the norm – its viscosity is too low.

## 6. Summary

The tested biofuels of non-standard production do not match the conditions set up by the norm. It means that they could not be allowed to be used in vehicles. The fact that they do not match the conditions of the norm, apart from legal consequences of using the fuel of forbidden low quality, may result in malfunctioning of vehicles as well as toxic fumes emission (e.g. too high sulphur content).

Tab. 2. Results of conducted examinations, achieved in the Laboratory of Examining Biofuels Quality in Mechatronic Faculty UWM

Tested sample	Sulphur content [mg/kg]	Group I and II metals content [mg/kg]	Phosphorus content [mg/kg]	Flash point [°C]	Oxidation stability [h]	Viscosity [mm <sup>2</sup> *s <sup>-1</sup> ]
Palm ester	2.88	Ca: 0.157 Mg: 0 K: 0.407 Na: 0.954	P: 0.087	Over 120	4.56	7.48
Waste cooking oil	23.29	Ca: 0.113 Mg: 0 K: 0.110 Na: 0.056	P: 1.911	Over 120	0.72	4.98
Rapeseed fatty acids	26.205	Ca: 5.662 Mg: 0.818 K: 10.616 Na: 0.641	P: 1.293	Over 120	3.36	11.07
Fish oil	10.73	Ca: 0 Mg: 0 K: 0 Na: 0	P: 0.053	Over 120	0.68	4.27
Waste cooking fatty acids	19.885	Ca: 3.533 Mg: 0.107 K: 10.979 Na: 0.015	P: 1.942	Over 120	1.53	13.68
Ethyl esters	6.95	Ca: 0.107 Mg: 0.0637 K: 0.000 Na: 0.385	P: 2.342	Over 120	0.60	2.98
B20	3.98	XXXXXX	XXXXXX	Over 120	XXXXXX	4.48
B100	2.8	Ca: 0.9 Mg: 0.8 K: 0.542 Na: 0.826	P: 2.523	Over 120	Over 6h	4.53

 - results not in norms

 - results in norms

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