

IMPROVING PHYSICAL PROPERTIES OF RAPE BIOFUELS

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ABSTRACT

The researches on the use of biodiesel and fuel derived from waste plastics are presented in the paper. Biodiesel and fuel obtained from waste plastics were both used as fuel components. FAME is a bio-admixture in the fuel. The catalytic cracking of polyolefin was the source of second fuel admixture. The physical properties of the analyzed components of fuel have been presented. The operational parameters of direct injection in diesel engines fuelled by tested fuel blends was set out. The preparation of the fuel mixture was also described. The concept of the diesel fuel which is made from the components of opposite physical properties could have a positive practical effect and could improve the use of biofuels.

Keywords: alternative fuel, diesel engine, fuel composition, FAME, polyolefin.

INTRODUCTION

Growing demand for fuel and energy that results from economic development, in the face of decreasing fossil fuel resources, forces the search and support for the development of biocomponents, the components obtained from the processing of plastics liquid biofuels and other renewable fuels. In the world scale, the actions aimed at promoting oil derivatives can be observed.

One of the methods of making combustion engines be more eco-friendly is to use admixtures of substances characterised by the fact that their carbon cycle runs on the earth surface. This type of fuel is generally based on plant production. In case of high compression engines processed vegetable oils are used, in case of low-compression engines alcohol made of crops and other plants is used.

In most cases the discussed additives are only one type of admixtures. The properties of such fuel are analysed and the best method of its production is searched for.

When additives to diesel fuel are used, the changes in fuel mixture physical properties are the basic problem. The changes of properties

result from the fact that both vegetable oils and their esters have higher density and viscosity than the fuel from processed crude oil.

One method to limit this phenomenon is to use other admixtures of lower density and viscosity than petroleum derivative fuels together with vegetable additives. One example of such an additive is fuel from polyolefin wastes [6, 7].

European Union undertook legislative actions aimed at increasing the share of biocomponents in the market of fuels used in transportation. In accordance with an EU directive, aimed at increasing the share of non-petroleum derivatives the production of fuel fractions from polyolefin wastes is becoming more and more common in the last few years. They have the highest share in the stream of waste plastics.

The fuel obtained from plastic wastes (polyolefin) can also be called ecological fuel as it is produced in a recycling process from plastics and helps achieve the complete elimination of plastic wastes storage in the landfills.

Therefore, using both types of fuels to make alternative fuels for high compression engines may increase significantly the share of admixtures which stimulate the ecological effect.

PHYSICAL-CHEMICAL PROPERTIES OF THE ANALYSED FUELS

Physical and chemical properties of the following fuels were analysed: Verva diesel fuel from Orlen, FAME biodiesel (methyl esters of fatty acids) and the fuel from polyolefin wastes from plastics POC (obtained in a catalytic cracking) [4]. FAME fuel was based on rape oil.

It should be emphasised that presently the commercial fuel (e.g. Verva) contains c.a. 3-5% of FAME admixture, however, in the analyses it was considered as a basic fuel.

The properties of the basic fuel are presented in Table 1, according to producer's information [1].

POC fuel used in the analyses is produced in the process of catalytic cracking of polyolefin, primarily foil and plastic bags [9]. The cracking installation consists of a reactor and distillation column. 6 m³ reactor is made of steel (except for the agitator) and placed on a furnace with burners. The reactor is equipped with a dispenser that allows constant dosage of the material (in the amount of 30-50 kg) and appropriately selected mixture of ingredients that play the role of a catalyst (aluminium and other metals).

Rectification column (filled with rings) is equipped with two condensers that receive two fractions: gas and liquid, and a set of thermoelements (to measure the temperature inside the reactor and at the top of the column). The system also covers a cooling tower and the nitrogen supply installation. Nitrogen spread on the surface of the cracked plastic make the input mix. It runs through the whole installation, what significantly increase the safety of the process. Installation productivity is from 200 to 400 dm³/h of liquid hydrocarbons.

The mixture of different hydrocarbons is obtained as a result of polyolefin cracking. It contains a mix of saturated, unsaturated and branched hydrocarbons, with significant predomination of the latter ones. Gaseous and liquid products are obtained at temperature at the top of the column reaching 50 to 200 °C, and from 200 to 315 °C.

Table 2 presents selected properties of biodiesel fuel (FAME) and the fuel obtained from plastics (POC).

The fraction from lower boil temperature range contains hydrocarbons from C6 to C14. The fraction from higher boil temperatures

Table 1. Specification of diesel oil used in the analysis, according to PN-EN-590 and ZN/ITN-ORLEN/NF-229/2004 [1]

| Item | Analysed properties | Units | Value | Requirement, acc. to the norm |
|------|--|--------------------|--------|-------------------------------|
| 1 | Density at 15°C | kg/m ³ | 837 | min. 820, max.845 |
| 2 | Cetane number | – | 57,8 | min. 55 |
| 3 | Cetane index | – | 53,4 | min. 46 |
| 4 | Distillates to 250°C | % V/V | 33 | max. 65 |
| 5 | Distillates to 350°C | % V/V | 95 | min. 85 |
| 6 | 95%(V/V) distillates to temp. | °C | 352 | max. 360 |
| 7 | end of distillation temp. FBP | °C | – | – |
| 8 | Efficiency | % V/V | – | – |
| 9 | Kinematic viscosity at 40°C | mm ² /s | 2,89 | min. 2+max. 4.5 |
| 10 | Cloud point | °C | -5 | not standardize |
| 11 | Temp. of blocking cold filter | °C | -6 | max. 0 |
| 12 | Ignition temp. | °C | 68 | min. 56 |
| 13 | Position after coking from 10% of dist. remn. | %(m/m) | 0,01 | max. 0,3 |
| 14 | Remnants from turning into ash | %(m/m) | <0,001 | max. 0,01 |
| 15 | Sulphur content | mg/kg | 3,2 | max. 10 |
| 16 | Content of multielement of aromatic hydrocarbons | %(m/m) | 2,5 | max. 7 |
| 17 | Ad of corroding properties with copper | – | 1 | max. 1 |
| 18 | Water content | mg/kg | 75 | max. 150 |
| 19 | Solid waste content | mg/kg | 9 | max. 24 |
| 20 | Oxidation resistance, total insoluble residues | g/m ³ | 5 | max. 25 |
| 21 | Corrected diameter of wear at 60°C | µm | 204 | max. 400 |
| 22 | Spray passability decrease index | % | 85 | max. 85 |
| 23 | Cont. of methyl esters of fatty acids FAME | %(V/V) | – | max. 5 |

KJ statement:
 VERVA Diesel fuel ON B 4,8 complies with ZN-ORLEN-6:2005 and PN-EN 590:2006 and agrees with RMG as of 09-12-2008.

Table 2. Selected properties of rape biofuels FAME and POC fuel used in the analyses [4].

| Item | Analysed properties | Measured value POC | Measured value FAME |
|------|--|--------------------|---------------------|
| 1 | FAME content [%] | – | 96,8 |
| 2 | Density at 15°C [kg/m ³] | 808 | 870 |
| 3 | Cinematic viscosity [mm ² /s] at 40°C | 2,10 (at 20°C) | 4,20 |
| 4 | Sulphur content [% m/m] | 0,0125 | – |
| 5 | Ignition temperature [°C] | 62 | 180 |
| 6 | Corroding properties with copper (3h, 50°C) | No 1 | No 1 |
| 7 | Acid value [mgKOH/g] | – | 0,1 |
| 8 | Iodine value [g jod/100g] | – | 110 |
| 9 | Heat of combustion MJ/kg | 42 | – |

(200-315°C) consists of hydrocarbons from C6 to C28. It contains mainly heavier hydrocarbons, yet hydrocarbons C6 to C13 can make up to 47% [8].

As a result of the process, liquid products are obtained in broad range of temperatures. Properly cracked hydrocarbon fractions can be used as fuel oil or as an ingredient for fuel production.

RESULTS OF EXPERIMENTAL TESTS

Laboratory experiments conducted in order to verify the information provided by fuel producer. Density measurements were made for POC fuel and its admixtures with diesel fuel. The measurements were made with a densimeter and thermometer that is used to control fuel temperature. The results of measurements of mixture density are presented in Table 3.

The results show that POC fuel density is by 3.6% lower than diesel fuel density. The density of mixtures POC – rape oil changes in a linear way, with its increase for lower content of POC in the fuel admixture.

The engine tests were conducted at breakless testing equipment described in [4] and [5]. General scheme of the testing equipment is presented in Fig. 2.

The testing apparatus was prepared on the basis of a tractor Ursus C-360, which is equipped with a four-piston high compression engine

with S-4003-type direct fuel injection system. The clutch was disconnected before the engine worked without external load. Modified control system allowed for quick change of the position of control gear of the injection pump. Pneumatic wheels of the tractor allowed omitting all the problems related to suspension and engine vibrations. The external conditions and engine temperature were checked with instruments which are a typical equipment of every engine test stand.

Dynamic speed characteristics is obtained as a reply of the unloaded engine to the displacement change [3]. The engine is made to change acceleration by a change of fuel volume to the maximum value. Quick dosage disconnection caused the engine slow down. Changeable work conditions for engine were obtained, what corresponds to engine exploitation characteristics.

The tests were conducted in series for each type of fuel. Each series consisted of 15 cycles acceleration-slowing, performed for the same initial conditions, including: rotational speed (similar to neutral gear) and constant engine oil temperature and cooling agent (according to producer’s guidelines). The system was rinsed and fuel filter was changed for each change of fuel. Average course obtained in 10 closes tests were considered as representative. The results were obtained as the courses of angular acceleration in the function of rotational speed of the engine. The registered runs of the engine acceleration are presented in figures 3 and 4.

Table 3. Density of the tests fuel mixtures [8]

| Type of fuel | t [°C] | ρ [kg/m ³] | ρ [kg/m ³] at 15°C |
|--------------|--------|------------------------|--------------------------------|
| POC 100% | 27 | 800 | 809 |
| POC 50% | | 814 | 823 |
| POC 25% | | 822 | 831 |
| ON VERVA | | 829 | 838 |

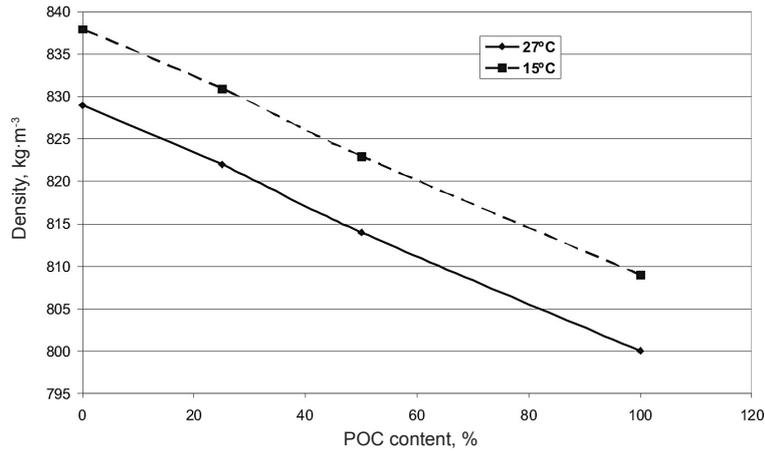


Fig. 1. Density changes in POC-ON mixtures

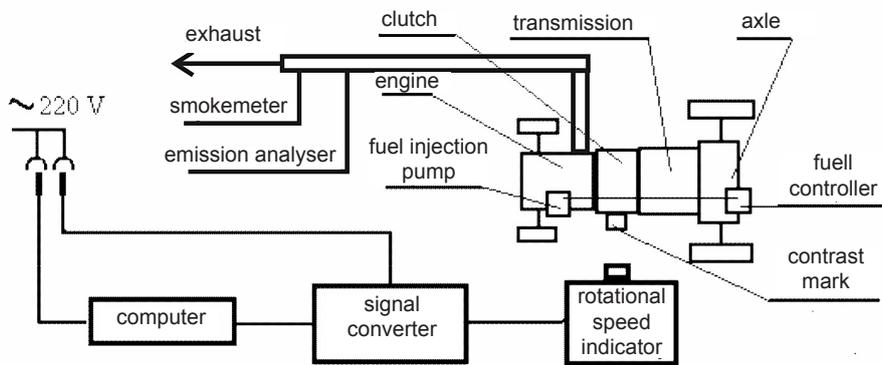


Fig. 2. General scheme of the testing equipment

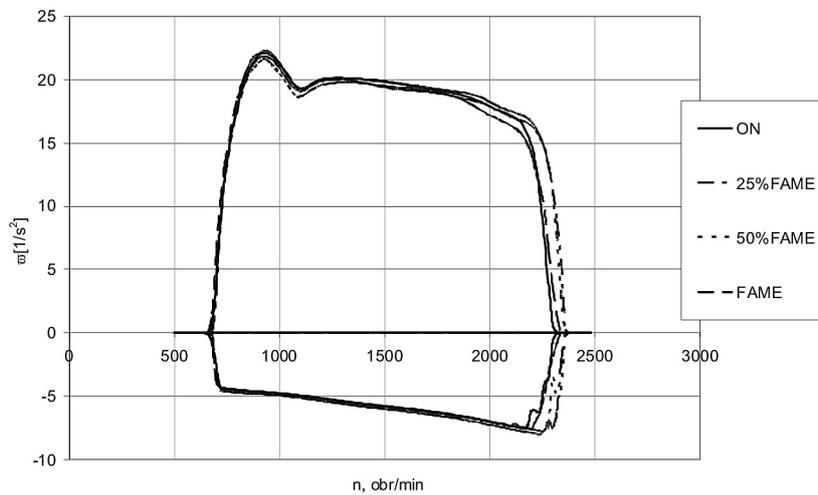


Fig. 3. Registered courses of angular acceleration for the crankshaft during free S-4003 engine acceleration for the tested FAME fuel

The obtained results show that both FAME and POC worsen engine performance. This phenomenon is typical for alternative fuels.

The composition of exhaust gases was measured with multi-gas analyser Technotest-488M, which allows to measure CO, CO₂, HC i NO_x

content in fumes. The obtained results are similar for all the tests admixtures and are presented in paper [4].

In order to measure smoke contamination optical smoke-meter Olivier D60 was used. The results show that for fuels FAME and POC, the

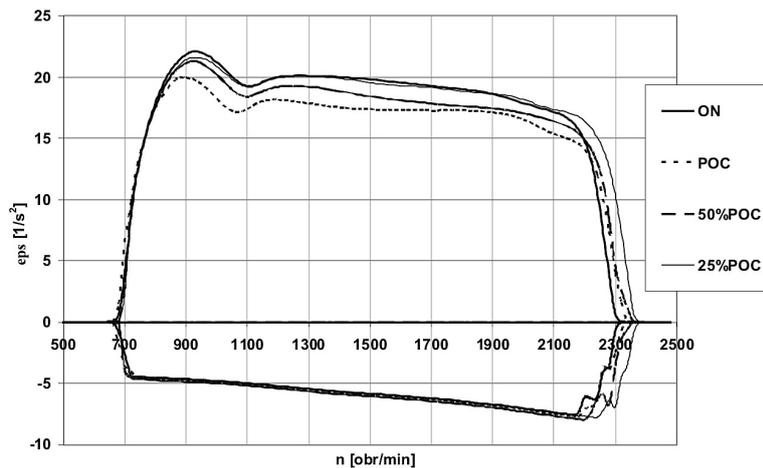


Fig. 4. Registered courses of angular acceleration for the crankshaft during free S-4003 engine acceleration for the tested POC fuel

level of contamination is significantly lower than for the diesel fuel [4].

PROCEDURE OF FUEL ADMIXTURE PREPARATION

The improvement of physical properties of biofuels concerns preparation of such a fuel admixture that does not change basic physical parameters of the basic fuel. If the defined amount of FAME biodiesel is added to the basic diesel fuel, appropriate amount of POC fuel should also be added in order to consider the density changes of the mixture. The required amount of the additive can be calculated on the basis of the mass balance or estimated on the basis of the graph from Fig. 5.

For instance: in case of 20% additive of biofuels (FAME) to diesel oil, the increase of mix-

ture density to the following value is registered:

$$y = 0,3336 \cdot 20 + 836,7 = 843,372 \quad (1)$$

then the density difference equals:

$$\Delta y = 843,372 - 836,7 = 6,672 \quad (2)$$

the necessary amount of POC additive is then:

$$x = \frac{6,672}{0,2914} = 22,9\% \quad (3)$$

Therefore, the amount of POC equals 22.9% of the amount of rape oil. It should be added to the mixture in order to avoid density changes of the mixture. The density of fuel mixture is then equal to the density of diesel fuel. In such way higher amounts of biofuels can be used, with no fear for injection condition changes, which may take place for higher fuel density. Viscosity changes and be balanced in the same manner.

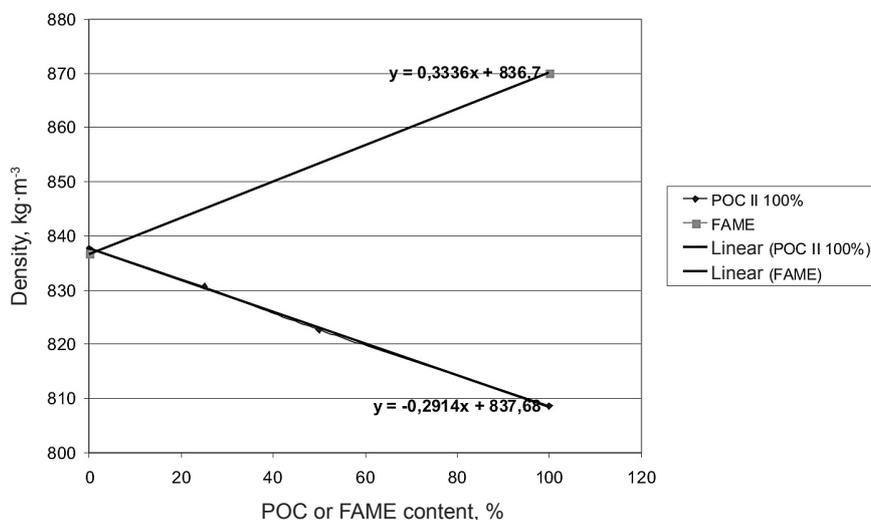


Fig. 5. Density changes of the mixture in the function of POC and FAME concentration

FAME biofuels have certain disadvantages. The major ones include the certain amount glycerine by-product that is produced in conventional process of biodiesel production. In STING process [2] the produce does not exist and the process efficiency increases (by 10-12%). Biodiesel produced in Simultaneous Reaction of Transesterification and Cracking (STING) consists of mainly methyl esters of fatty acids, diacylglycerols and monoacylglycerols. The density of STING fuel is similar to FAME density, however, they have slightly better viscosity conditions [3]

Second example: if 20% of STING fuel is added to diesel fuel, its density increases in the following way:

$$y = 0,4332 \cdot 20 + 836,7 = 845,364 \quad (4)$$

then the density difference equals:

$$\Delta y = 845,364 - 836,7 = 8,664 \quad (5)$$

the necessary amount of POC additive is then:

$$x = \frac{8,664}{0,2914} = 29,7\% \quad (6)$$

The amount of STING fuel makes 29.7% of the amount of diesel fuel. It should be added to the mixture in order to avoid density changes of the mixture. The density of fuel mixture is then equal to the density of diesel fuel.

On the basis of the mass balance, the following formula can be used to calculate the amount of POC:

$$V_{POC} = V_{BIO} \cdot \frac{\rho_{BIO} - \rho_{ON}}{\rho_{ON} - \rho_{POC}} \quad (7)$$

where:

V_{BIO} – biofuels additive in % of base fuel volume (diesel fuel),

V_{POC} – POC additive in % of base fuel volume (diesel fuel),

ρ_{ON} – diesel fuel density w kg/m³,

ρ_{BIO} – biofuels density in kg/m³,

ρ_{POC} – biofuels density in kg/m³,

However, the real content of biofuels in the admixture can be calculated from the following formula as u_{BIO} :

$$u_{BIO} = \frac{V_{BIO}}{V_{ON} + V_{BIO} + V_{POC}} \cdot 100\% \quad (8)$$

On the basis of the example, real FAME concentration in the diesel fuel mixture is will be 14%. Because the tested fuels make real solutions, after mixing them together homogenous liquid can be obtained. The literature says that the stability of mixed fuel is evaluated once every 6 months.

According to the presented procedure combinations of biofuels and diesel fuels can be made, maintaining the allowed level of permitted by law. The avoidance of physical property changes is a considerable advantage, as these changes may influence fuel injection.

The use of double additive to the fuel mixture may allow obtaining ecological fuel with properties similar to standard diesel fuel.

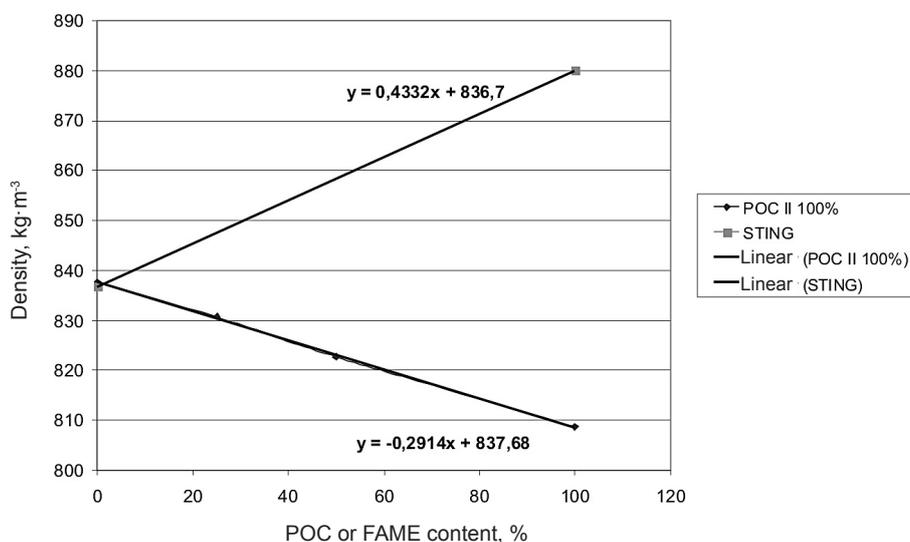


Fig. 6. The changes of mixture density in the function of changes in POC or STING concentration in he mixture

CONCLUSIONS

On the basis of the conducted analysis, the following conclusions can be drawn:

1. Designing fuel with opposing physical properties may bring positive practical effect.
2. By using multi-ingredient mixtures, it is possible to increase the percent share of additives in fuel, what boosts significantly the ecological effect, understood as the decrease of greenhouse effect and the decrease of waste management risks.
3. The evaluation of the proposed methodology requires experimental verification of the influence of such fuels on engine parts durability, lubrication properties and other aspects of combustion engine work.
4. It seems that the use of double additive to the fuel mixture may have positive influence on the use of unprocessed vegetable oils as engine fuels.

REFERENCES

1. Baczewski K., Kałdoński M. Paliwa do silników o zapłonie samoczynnym. 2004. WKŁ. Warszawa
2. Iijima W., Kobayashi Y., Taniwaki K.: Proces for non-catalytically producing biodiesel fuel without yielding by-product. US Patent No.: US 2006/0288636 A1
3. Kiernicki Z.: Simulation method of operating parameters assessment used for engine comparative analysis. *Combustion Engines*, No. 1/2008 (132), p. 73-78.
4. Kiernicki Z., Hys L., Sawa J. Chosen Properties of the Fuel Obtained from Polyolefin's Catalytic Cracking. 7th International Colloquium „Fuels 2009”, January 14-15, 2009, Esslingen – Stuttgart, pp. 227-234.
5. Kiernicki Z., Hys L., Sawa J.: Some Properties of Sting Type Fuel in Comparison to Chosen Biofuels. 7th International Colloquium „Fuels 2009”, January 14-15, 2009, Esslingen – Stuttgart, str. 219-226.
6. Masuda T., Kuwahara H., Mukai S. R., Hashimoto K. Production of high quality gasoline from waste polyethylene derived heavy oil over Ni-REY catalyst in steam atmosphere. *Chemical Engineering Science* 54 (1999). 1999, pp. 2773-2779
7. Walendziewski J., Steininger M. 2001, Thermal and catalytic conversion of waste polyolefin's. *Catalysis Today* 65 (2001), pp. 323–330
8. Zieliński J. The effect of advance angle on the operation of the Diesel fuelled with POOC fuel. Master work. 2010, Lublin University of Technology, Lublin, pp. 126.
9. www.kabex.pl