# AN EFFECT OF THE SHARE OF CSME AND RME BIOCOMPONENTS ON THE CETANE NUMBER AND DISTILLATION TEMPERATURES OF BIOFUELS

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**Summary**. The objective of the research was to estimate the effects of the mixtures of diesel oil with CSME and RME biocomponents on ignition properties of type B fuels. The tests were carried out with the use of a fuel analyzer Irox Diesel produced by Grabner Instruments. The methodology and the used device made it possible to estimate the cetane number and distillation temperatures T90 and T95. The cetane number of biofuels containing RME biocomponent ranged from LC = 52.1 for B0, i.e. pure diesel oil, to LC = 54.8 for B40, i.e. the fuel with 40% content of RME biocomponent. In the case of biofuels containing CSME biocomponent the value of the cetane number also increased as the amount of the bio-additive increased. The cetane number ranged from LC = 52.1 for B0, i.e. pure diesel oil, to LC = 52.1 for B0, i.e. pure diesel oil was 333°C, and T95 was 348°C. An increase in the amount of the biocomponent resulted in an increase in distillation temperature. Distillation temperatures T95 for B40 biofuels with the addition of CSME and RME are 386°C and 392°C, respectively. To sum up, we can state that the use of a biocomponent affects an increase in both the cetane number and T90 and T95 distillation temperatures. The ignition properties of CSME biofuel are comparable with those found for RME biofuel.

Key words: biodiesel, biofuels, RME (Rapsed Methyl Ester), CSME (Cameli Sativa Methyl Ester), cetane number, distilling temperatures.

#### INTRODUCTION

One of the key directions of combustion engine development is the reduction in  $CO_2$  emission, the gas being known to contribute to the so-called greenhouse effect. According to the guidelines drawn up by the European Automobile Manufacturers' Association (ACEA), by 2010 the average emission of this compound, determined by the NEDC test, should be decreased from the current 140g/km to 120g/km. In such a situation the car average fuel consumption should be decreased from about 5.8dm<sup>3</sup> to 5.0dm<sup>3</sup> per 100 km. One of the methods for improving the  $CO_2$  balance is the use of alternative fuels to power car engines, because of the  $CO_2$  closed cycle.

Until now, the EU member-countries have been developing biofuels, for road transport vehicles, with varied effects. However, the year 2010 is approaching, so all the EU countries will be obliged, under penalty of a fine, to use in transport at least 5.75% of biofuels and biocomponents.

This is so, because every EU member-country is obliged to follow the instructions contained in the so-called White Book published in 2001, and in the Directive 2003/30/WE.

In Poland, intensive development of biofuels began with the act on biocomponents and liquid biofuels, which was passed by the Parliament of the Republic of Poland on August 25, 2006 (Law Gazette, 06.169.1199 of September 25, 2006). The act has been in force since January 1, 2007.

So far, in Europe and Poland the main bio-substitute for diesel oil has been Biodiesel RME (rape oil methyl esters). However, because of rising prices of agricultural products, new raw materials for biofuel production are searched for. Around the world, research on obtaining biofuels from other raw materials, including waste products, are carried out. At the same time, more and more attention is to be focused on the prospects for new generation biofuels. The biofuels obtained with the use of current technologies have been called the first generation fuels. The biofuels obtained from non-food materials, sub-standard or past their sell-by date products will be the second generation biofuels [1]. The first generation biofuel technologies are expected to be developed for another ten years, however, since 2010 petrol stations should offer, beside fuels and first generation biofuels, new fuels with the addition of second generation biocomponents [2]. The second generation biofuels will include bioethanol, obtained from cellulose and lignocellulose, synthetic fuels produced from synthetic gas, hydrocarbon biofuels BTL and MT, DME, methanol, H, and hydrocarbon fuels obtained by the process of thermal conversion and hydroconversion of vegetable oils and animal fats [1, 2]. Considering the fact that the second generation fuels are not available vet, all the time alternative raw materials for the first generation biofuels are prospected for. One of the plants whose oil can be used for Biodiesel production is false flax. False flax (Camelina sativa) is an oilseed plant with both winter and spring forms. From the point of view of botany, it is classed among dicotyledonous cruciferous plants. Considering the fact that its requirements as to the quality of soil are small, it can be grown on rather poor soils. False flax is also planned to be grown in cogeneration, to get both oil and honey with excellent medicinal properties. This plant is considered to be a very good substitute for rape, especially in regions with lower class soils, i.e. worse than soil class III. That is why the production of fuels of Biodiesel CSEM type can be a great chance for agricultural development in such regions. However, we lack thorough research into physicochemical properties of CSEM. The most important parameters of biofuels for compression-ignition engines, determining the ignition properties and characteristics of combustion and heat production rate, include: cetane number, cetane index and distillation temperature. In the literature, however, no results of research works on the determination of the above CSME parameters are available. That is why this subject has been taken up in the present work. The paper presents the results of the research aimed at determining the effects of the mixtures of diesel oil with Biodiesel of CSME and RME (for comparison purposes) types, on the ignition properties of type "B" fuels.

In Table 1 a typical composition of fatty acids contained in false flax oil and rapeseed oil is presented. Considering the significance and the amount of fatty acids contained in vegetable oils, the major acids are: oleinic acid, linolic acid and linolenic acid.

Oil types					
major acid content of false flax oil		major acid content of rapeseed oil			
fatty acid	share %	fatty acid	share %		
Oleic acids C <sub>18:1</sub>	12,5	Acids Oleic C <sub>18:1</sub>	62 (72)		
Linoleic acids C <sub>18:2</sub>	18	Acids Linolenic C <sub>18:2</sub>	20 (10)		

Table 1. Typical composition of fatty acids contained in false flax oil and rapeseed oil

Linolenic Acids C <sub>16:3</sub>	36	Acids Linolelaidic C <sub>16:3</sub>	10
Erucic acids C <sub>22:1</sub>	3,5	Acids erukowy C <sub>22:1</sub>	0,5
Other acids, not determined	30	Other acids, not determined	7

Analyzing the composition and amount of fatty acids contained in the above-mentioned plants we can state that in terms of the fuel value, the composition of fatty acids in rapeseed oil is much more favourable. First of all, the oleinic acid content of this oil is about five times higher compared with false flax oil, and as we have found, the higher oleinic acid content, the higher the calorific value of oil and RME. From among the 19 tested rape cultivars, the highest calorific value, 37.9MJ/ kg, was found for Contact oil containing more than 70% of oleinic acid [3]. Rapeseed oil contains much less, i.e. 20%-30% (v/v), undesirable linolic and linolenic acids, whereas in false flax oil the percentage of these acids exceeds 50%. In biofuels the content of linolic and linolenic acid esters should be as low as possible as both the acids show a tendency toward rapid oxidation, which deteriorates the biofuel quality. That is why RME containing a large amount of these acids should be supplemented with a greater amount of antioxidants to ensure good stability. The addition of extra antioxidants increases the cost of the biofuel. Out of concern for good oxidative stability of esters, the standard for biofuels of Biodiesel type, EN 14-214 (EN 14103), specifies that the maximum linolic acid ester content must not exceed 12% (w/w). CSME does not meet the requirements of EN 14103 as regards the maximum admissible amount of linolic acid esters because false flax oil contains about 35% of linolic acid.

The results obtained from the Author's personal studies show that from 1 hectare of false flax field we can get about 1,000-2,000 kg of seeds from which about 400-700 dm<sup>3</sup> of oil can be produced.

#### Properties of the major fatty acids

*Oleinic acid* (cis-9-octadecenoic acid) is a monounsaturated carboxylic acid, its molecular formula being  $C_{17}H_{33}$ COOH. It is a long-chain acid with an 18-carbon base and a double bond between the 9<sup>th</sup> and 10<sup>th</sup> carbon atoms. The molar mass of oleinic acid is 282 g/mol, and melting point is 14°C.

*Linolenic acid\_*is polyunsaturated fatty acid, its molecule contains two double bonds. The molecular formula is  $C_{18}H_{30}O_2$  ( $C_{17}H_{29}COOH$ ). The molar mass of linolenic acid is 278.4 g/mol, boiling point is 184°C and melting point is -11°C.

*Linolic acid* is unsaturated fatty acid, its molecule has two double bonds. The molecular formula is  $C_{18}H_{32}O_2(C_{17}H_{31}COOH)$ . The molar mass of linolic acid is 280.4g/mol, boiling point is 230° C and melting point is -5°C.

#### AIM AND SCOPE OF RESEARCH

The objective of the research was to estimate the effects of mixtures of diesel oil with the biocomponents CSME and RME (the latter for comparison purposes), on ignition properties of type B fuels. The base fuel for type B biofuels was diesel oil from the BP concern. Biodiesels of CSME and RME type were produced in a GW-10 reactor belonging to the Małopolskie Centre of Renewable Energy "Bio-Energy". Methyl alcohol was used for transestrification, KOH (potassium hydroxide pure p.a.) being a catalyst. Using the model for transestrification of oils with methanol, the mole ratio of methanol to oils was determined. During the tests, taking into account the excess

of methanol, the mole ratio of methanol to oil was 8:1. After separation of the glycerol phase, the esters were subjected to a process which was to improve their quality so that the obtained Biodiesel met the quality requirements of the standard EN-14214. The excess of methanol was distilled, while the rest of the catalytic mixture was neutralized with water acidified with acetic acid.

The biofuel of Biodiesel type is composed of vegetable oil methyl esters. The transestrification process is carried out so as to break heavy and large molecules of triglycerides, which compose vegetable oil, into three ester particles and one glycerol particle. Rapeseed oil contains 95% of triglycerides. A typical, model triglyceride consists of two oleinic acids and one linolic or linolenic acid. Figure 1 presents a triglyceride model, typical for rapeseed oil.



A big triglyceride particle is broken down into three small ones of which two particles of oleinic acidnd one of linolic acid are obtained by methanol application during the transestrification process. Glycerol will be formed from the residue marked with "A" symbol plus three OH groups obtained from methanol particle breakdown.



In result of triglyceride transestrifictaion we obtain three particles of fatty acid methyl esters (RME) and one particle of glycerine



Fig. 1. Triglyceride model, typical for rapeseed oil

Investigation into physicochemical properties of type B biofuels with the addition of CSME and RME

Studies aiming at a determination of the effect of the amount of CSME and RME biocomponents on the main parameters responsible for ignition properties of type B biofuels, were carried out with the use of the fuel analyzer Irox Diesel produced by Grabner Instruments (Fig.2). The methodology and the used device made it possible to estimate the cetane number and distillation temperatures T90 and T95. As the analyzer Irox Diesel can estimate physicochemical properties of biofuels containing up to 40% (v/v) of a biocomponent, the biofuels were tested from B0 to B40. The value at the letter B means the volumetric share of the biocomponent in the mixture with diesel oil. For example type B20 biofuel is the fuel containing 20% (v/v) of a biocomponent in the mixture with diesel oil. Altogether, 18 biofuels were tested. Nine of them were mixtures of diesel oil with CSME and the other nine biofuels were mixtures of diesel oil with RME.



Fig.2. Test stand with the fuel and biofuel analyzer Irox Diesel

### METHODS

Menstruation in fuel analyzer Irox Diesel is based on methodology of menstruation of infrared absorption in infrared scope from 2,7 to 15,4 $\mu$ , in a Fourier spectrometer (based on Fourier transform analysis). The obtained spectrogram of this characteristic - dactyloscopic area is correlated with spectrum table for different concentration of the analyzed substances. Menstruation chamber possessing small width in direction of transmission (for Irox Diesel is 0,1 mm), is situated in front of infrared rays beam. Intensity of rays is measured after they pass the chamber with the tested sample inside it and without the sample. The measured absorption for the given wave length tells about the concentration of a tested component. Compounds that raise the cetane number possess two distinctive absorbent maxima 1275cm<sup>-1</sup> and 1635cm<sup>-1</sup> (accordingly 7,8 $\mu$  i 6,11 $\mu$ ). To determine cetane number, cetane index, distillatory characteristics exactly is not possible out of spectrum. However, with the use of complicated mathematical models (differently from what it was in the case of a menstruation) we can anticipate those values. The method to determine those parameters is based on an estimation of the basis of spectrum and on calculation of mathematical models. Usually, the method of coefficients analysis or multilinker regression is applied to correlate the obtained spectrum or absorption straight with cetane number, cetane index, distillatory characteristics. It is difficult to introduce additional volumes into the coefficients' analysis method and the correlation of components and concentrations is not completely clear. Irox Diesel is using cluster analysis together with the method of multilinker regression. Into such a model other volumes can be easily introduced, in order to determine better dissolved compounds - saturates.

### RESULTS AND DISCUSSION

First, with the use of the analyzer Irox Diesel, physicochemical properties of the base diesel oil were determined. The obtained results are presented in Table 1.

Parameters	Value	Individual
Total aromatics	28,1	%
Total polyaromatics	1,4	%
Cetane number	52,1	-
Cetane index	51,3	-
Т 90	333	°C
Т 95	348	°C
Ethylesther	0	%
Methylesther	0,1	%
Biodiesel	0,1	%
Density	843	g/dm <sup>3</sup>
Temperature	21,2	°C

Table 1. Physicochemical properties of basic diesel oil from BP Group

The test results presented in Table 1 show that the base diesel oil meets the quality requirements for diesel oil as per PN-EN 590:2006. The value of the cetane number was in accordance with the value declared in the quality certificate given when purchasing the diesel oil.

Fig. 3. shows the results of tests, determining the effect of the share of the RME biocomponent in the mixture with commercial diesel oil produced by the PB concern, on the cetane number.



Fig. 3. Estimation of the effect of the biocomponent RME share of the mixture with diesel oil on the cetane number of the composed fuels

As Fig.3 shows, the value of the cetane number of biofuels containing the RME biocomponent increases as the share of the bio-additive grows. The cetane number ranged from LC = 52.1, for B0, i.e. pure diesel oil, to LC = 54.8 for B40, i.e. biofuel containing 40% of the RME biocomponent. As we might expect, the lowest LC value was found for pure diesel oil. The difference between the highest and the lowest LC values is LC = 2.7, which is about 5.2%.

Fig. 4. presents the values of the cetane number estimated for biofuels containing the CSME biocomponent.



Fig. 4. Estimation of the effect of the biocomponent CSME share of the mixture with diesel oil on the cetane number of the composed fuels

We can see that as in the case of biofuels with RME, an increase in the percentage of the CSME biocomponent results in an increase in the value of the cetane number. The cetane number ranged from LC = 52.1, for the type B0 biofuel, i.e. pure diesel oil, to LC = 54.2 for B40.

The results of the research have confirmed that an addition of FAME to diesel oil increases the value of the cetane number, thus improving the self-ignition properties of the fuel. The results have also shown that self-ignition properties of the mixtures of diesel oil with CSME obtained from false flax oil are similar to those of biofuels containing the RME biocomponent.

Distillation properties are considered as another parameter which is helpful when evaluating the ignition properties and which, beside the cetane number and the cetane index, affects the course of the combustion process. Too high temperatures at the beginning of distillation deteriorate self-ignition properties of fuel. In turn, too high temperatures at the end of distillation may prolong the combustion process. The determination of the temperature that should be applied to distil off 95% (v/v) of fuel is of special importance and that is why it has been specified in the requirements for compression-ignition engine fuels (EN ISO 590). The temperature of distillation of this portion of fuel, determined in accordance with EN ISO 3405, should be lower than  $360^{\circ}$ C. As the analyzer Irox Diesel makes it possible to estimate the temperatures T90 and T95, i.e. the temperatures needed to distil off 90% and 95% (v/v) of fuel, respectively, such testing was carried out on fuels with the addition of CSME and RME. Fig. 5 presents the values obtained for temperatures needed to distil 90% (v/v) of biofuels with CSME and RME biocomponents.



Fig. 5. Assessment of distilling temperatures T90 of biofuels containing RME and CSME biocomponent

On the basis of the data presented in Fig.3 we can state that generally as the share of both the biocomponents increases, the temperature of distillation increases as well. The temperature needed to distil 90% (v/v) of base diesel oil is 333°C. However, the distillation temperatures for B40 biofuels are significantly higher. In the case of biofuel containing the CSME biocomponent the distillation temperature exceeds  $372^{\circ}$ C, for biofuel with the RME biocomponent it is more than  $383^{\circ}$ C.

Fig. 6 presents the results of tests aiming at the estimation of T95 distillation temperatures for the examined fuels.

From Fig. 6 it appears that the temperature needed to distil 95% (v/v) of base diesel oil is  $348^{\circ}$ C. As in the case of T90 temperature estimation, an increase in the percentage of the biocomponents in the mixture with diesel oil also resulted in an increase in distillation temperature. The distillation temperatures for B40 type biofuels are:  $386^{\circ}$ C for biofuel with the addition of CSME and  $392^{\circ}$ C for biofuel with the addition of RME.



Fig. 6. Assessment of distilling temperatures T95 of biofuels containing RME and CSME biocomponent

## CONCLUSIONS

As we might expect, the lowest LC value was found for pure diesel oil. The difference between the highest and the lowest LC values is LC = 2.7, which is about 5.2%.

To sum up, we can state that the addition of a biocomponent affects an increase in T90 and T95 distillation temperatures. The addition of more than 12% of a biocomponent makes the distillation temperature increase above the upper limit recommended for diesel oil.

From the carried out research works we can draw a practical conclusion that the new testing method (Irox Diesel analyzer) can be used do determine LC in control tests or when rapid measurements are needed. Such an analyzer can surely be useful in mobile laboratories that verify the quality of fuels in small biofuel plants, fuel warehouses or petrol stations.

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## OKREŚLENIE WPŁYWU UDZIAŁU BIOKOMPONENTÓW CSME I RME NA LICZBĘ CETANOWĄ I TEMPERATURY DESTYLACJI BIOPALIW

**Streszczenie.** Celem badań było oszacowanie wpływu mieszanin oleju napędowego z biokomponentami typu CSME i RME na własności zapłonowe paliw typu B. Badania przeprowadzono przy użyciu analizatora paliwowego Irox Diesel firmy Grabner Instruments. Zastosowana metodyka oraz urządzenie pozwoliły na oszacowanie liczby cetanowej oraz temperatur destylacji T90 i T95. Liczba cetanowa biopaliw zawierających biokomponent RME zawierała się w przedziale od LC = 52,1, dla B0 czyli czystego oleju napędowego i rosła, by osiągnąć wartość LC = 54,8, dla B40, czyli biopaliwa zawierającego 40% biokomponentu RME. Wartość liczby cetanowa jiopaliw zawierających biokomponent CSME również rosła wraz ze wzrostem bio dodatku. Liczba cetanowa zawierała się w przedziale od LC = 52,1 biopaliwa typu B0 czyli czystego oleju napędowego do LC = 54,2 dla B40. Temperatura T90 potrzebna do oddestylowania 90% (v/v) bazowego oleju napędowego wynosiła  $333^{\circ}$ C, natomiast T95 wynosiła  $338^{\circ}$ C. Wraz ze wzrostem ilości biokomponentu rosła również temperatura destylacji T95 biopaliw typu B40 przyjmują odpowiednio wartości  $386^{\circ}$ C dla biopaliwa z dodatkiem CSME oraz  $392^{\circ}$ C dla biopaliwa z dodatkiem RME. Reasumując można stwierdzić, że zastosowanie dodatku biokomponentu podwyższa zarówno liczbę cetanową i temperatury destylacji T90 oraz T95. Własności zapłonowe biopaliwa CSME są porównywalne z odpowiednimi dla RME.

Słowa kluczowe: Biodiesel, biopaliwo, RME (estry metylowe oleju rzepakowego), CSME (estry metylowe oleju lnianki), liczba cetanowa, temperatury destylacji.