COMPARISON OF CALORIFIC VALUES OF PETROLEUM-DERIVED FUELS WITH ALTERNATIVE FULES OF VEGETABLE ORIGIN

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Abstract: *Calorific value of fuels has an essential impact on the operation quality of engines with self-ignition. The laboratory studies during which measurements of heating value and heat of combustion showed, that only the content of bioester higher than 10% influences on the decrease of these values. The drop of the heating value and the heat of combustion showed, that at the content of bioester up to 10%, the changes of these both values are statistically unessential. No changes in the quantity of ash following combustion on which combustion of oxygen in the atmosphere could have impact on, have been observed.*

Key words: *diesel oil, bio component, calorific value, heating value, heat of combustion.*

INTRODUCTION

The limited resources of fossil fuels and legal requirements in force in different countries concerning the use of biofuels, to a large extent decide on the volume of production and possibilities of biodiesel's use. At present it is the European Union that is the bigger manufacturer of that type of fuel in the world. Oil taken from rapeseed is the basic raw material in EU for production of biodiesel, in small amounts however is used for bio components' manufacturing: sunflower seed oil, , animal fats, oils from recycling or imported soybean and palm oil (Oilseeds: World Markets and Trade. 2013).
In many union countries being big producers of rapeseed (Germany, France, Italy), or in the countries of the Eastern Europe (Belarus, Ukraine) for the last 15-months there has been observed a considerable increase of rapeseed crops' area occupying at present the third place in the world's production of oils and fats. The reasons of that raw materials' popularity increase is a very high nutrition efficiency of rapeseed oil, forage efficiency – middlings, and most of all the possibility to use seeds for bio components' production, being the additive to conventional fuels (Szkudlarski et al. 2014).
Relatively low prices of crude oil last year, together with high prices of vegetable oils prevailing for the last years, may reduce the increase of biodiesel production in the near future. Moreover, the requirement of reduction up to 50 % of GHG in sowing of rapeseed designed for biomass and biofuels production, as well as the decisions of the European Parliament reducing in many countries of up to 70% of the share of biofuels and generation in the total balance of fuels, may have a reducing impact on that production.
Producers of rapeseed pin in their highest hopes concerning reduction of costs of the ran cultivations and possibility of acquiring cheaper oil upon seeding big areas with newly registered hybrid varieties. These varieties are characterized by yielding higher than the population varieties (on average for 10%) and many positive agronomic features making it possible to simplify and to make the cultivation operations cheaper in the technologies of their cultivation (Wałkowski, 2012; Ogrodowczyk and Bartkowiak-Broda, 2013). For the purposes of improving of the energy balance at the time of rapeseed production, application of effective technologies of biomass' harvesting and processing into biofuels is recommended (Borowski, Zastempowski, Kaszkowiak, 2013).
In most of the union countries, fuels with additive of methyl esters of the fatty acids are allowed to be marketed and standardized with the EU Directive and with given countries' regulations. Legal acts obligate up to 5% of biodiesel's share in diesel fuels and determine the quality requirements concerning the fuels powering engines with self-ignition (Directive 2009/28/WE).

Most of the vegetable oils which are used in food industry, do not meet the criteria of the standard DIN 51605 (Standard for rapeseed oil fuels, 2010), in which the minimum and maximum quality parameters of bio components used as fuels or additives to fuels of compression-ignition engines (Tab. 1).

Tab.1. Quality parameters for vegetable biocomponents determined in the standard DIN 51605 (own study)

Parameter [unit]	Limits	Unit
Density	910-925	[kg*m^3]
Viscosity	>36	[mm^2*s]
Heating value	<36	[MJ*kg$^-$]
Acidity	>2	[mg]
Ignition point	<101	[°C]
Pollution	>24	[mg*kg^{-1}]
Content of sulphur	>10	[mg*kg^{-1}]
Content of water	>750	[mg*kg^{-1}]

One of the criteria of fuel's quality assessment are the following: calorific value (influencing among the others the engine's power and turning moment) and the ash's mass (polluting the filters of particulate solids).

In the own studies there has been conducted the analysis of the impact of different B 100 biocomponent's percentage share in the diesel fuel of fossil origin on the calorific value and the mass of ash following the fuel's burning.

MATERIALS AND METHODS

Setting of the calorific values of the base fuel (diesel fuel), methyl esters of the fatty acids received from the rapeseed oil and the mixture of the diesel fuel with methyl esters of the fatty acids were the subject matter of the studies. The research was conducted with the use of the calorimeter KL-12Mn, burning samples of fuels in the oxygen atmosphere. The scheme of the calorimeters used for the researches is shown in figure 1.

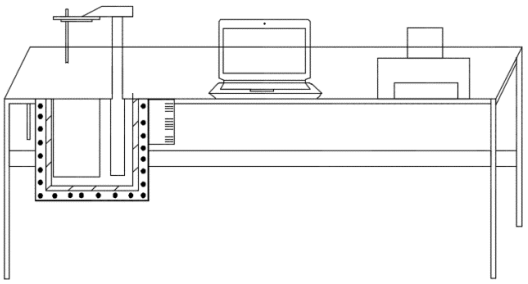

Fig.1. Scheme of the calorimeter KL-12Mn (own study)

The mixtures of the diesel fuel with biocomponent with reference to the diesel fuel and biocomponent in a clean form were tested. Proportions of samples are presented in table 2.

Tab. 2. Proportions of the tested samples (own study)

Sample I	100% Diesel fuel
Sample II	90% diesel fuel 10% methyl esters of the fatty acids
Sample III	70% diesel fuel 30% methyl esters of the fatty acids
Sample IV	50% diesel fuel 50% methyl esters of the fatty acids
Sample V	100% methyl esters of the fatty acids

Pursuant to the calorimeter's manual, tested were the samples of the weight of 1g. In order to set the mass of the ash, prior to the measurement there were tested clean and calcined melting pots for sam-

ples' burning. After each measurement, the melting pot with deposit was weighted. In the real terms, ash from the thermal process accompanies the processes of liquid fuels' combustion.
Examining of the heat of combustion, calorific value and measurement of the ash's mass was conducted in 5 repetitions for each sample. The obtained results were subject to statistical analysis with the use of the statistical software Analwar FR on the basis of Excel. The differences were verified with the Tukey's test of significance on the level of significance of 0,05. The mean values of the obtained results are presented in table 3.

RESULTS AND DISCUSSION

The volume of energy emitted at the time of thermal conversions during combustion of the mass of fuel, during complete combustion, considering condensation of water steam was determined. In table 3 there are presented the mean values of measurements of: heat of combustion, calorific value and the mass of ash for individual mixtures.

Table 3. Mean values of the heat of combustion, calorific value and mass of ash (own study)

Sample	Calorific value [MJ*kg^{-1}]	Heat of combustion [MJ*kg^{-1}]	Mass of deposit [g]
I	43,097^{a}	44,277^{a}	0,00397
II	42,199^{a}	43,779^{a}	0,00390
III	41,959^{b}	42,139^{b}	0,00113
IV	40,590^{c}	41,770^{c}	0,00140
V	37,906^{d}	39,097^{d}	0,00217
NIR	NIR (0,05)=1,006	NIR (0,05)=0,973	n. i. (nie istotne)

The obtained results were subject to the statistic analysis with the software ANALWAR FR on the basis of Excel. Both for the changes of the calorific value changes as well as for the heat of combustion, no essential changes between the fuel of 100% content of diesel fuel of fossil origin (sample I) and the mixture of the content of bio component 10% (sample II). In the remaining cases, between the sample I and V, there has been observed a statistically essential drop in calorific value for 12,1%. For the heat of combustion's parameter, the drop was also statistically essential and amounted to 11,7% between the samples I and V. However, no essential statistically differences have been disclosed for individual samples in the ash's mass.
The above dependencies are presented on the graphs 3 and 4.

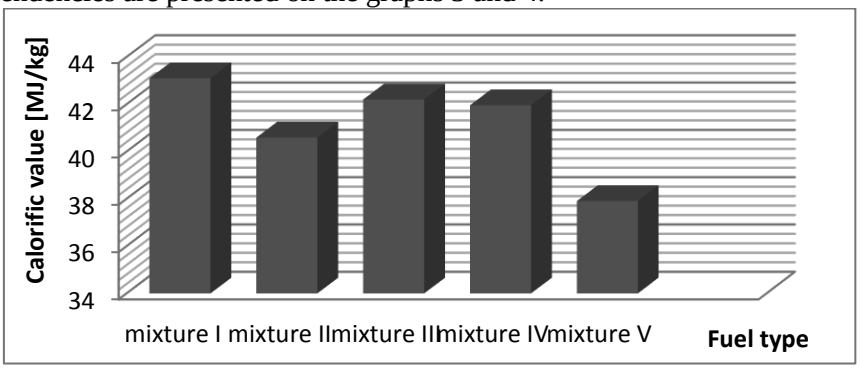

Fig.3. The set calorific value of individual samples (own study)

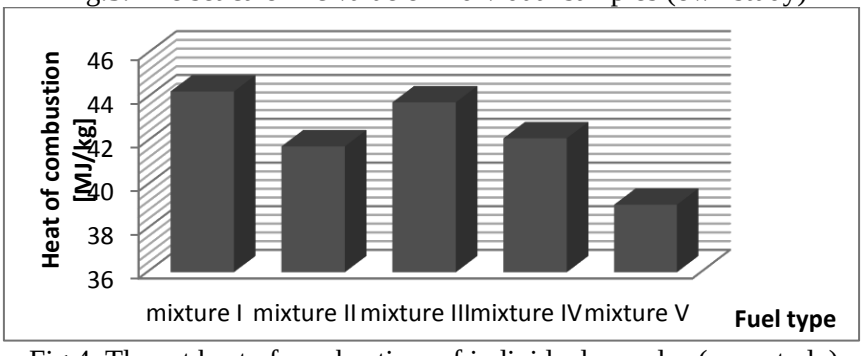

Fig.4. The set heat of combustion of individual samples (own study)

CONCLUSIONS

Addition of biocomponent B100 results in lowering of the fuel's calorific value and heat of combustion.

Essential statistical differences are visible only at the component's content in the diesel oil higher than 10%. Higher share of biocomponent results in the decrease of both the heat of combustion as well as the calorific value. The calorific value of the pure diesel oil amounts to 43,097 $MJ*kg^{-1}$, and of the methyl esters of the fatty acids to 37,906 $MJ*kg^{-1}$. The calorific value of fuel drops together with the increase of the biocomponent's content for the diesel oil and for mixtures III, IV and V and amounts respectively to 42,199 $MJ*kg^{-1}$, 41,959 MJ/kg and 40,590 MJ*kg. The differences are statistically essential. The heat of combustion of the diesel oil amounted to 44,277 $MJ*kg^{-1}$, however for the biggest proportion (sample V) it did not drop below 40 $MJ*kg^{-1}$, similar results were observed by other researchers [Jaworski, Kuszewski, Ustrzycki, 2011]. No statistically essential changes of the mass of ash remaining after all the samples' combustion were observed.

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