Application of chromatography to the analysis of quality of RME type biofuels obtained from pure, fresh rapeseed oil and from the waste (previously fried) oil of the same origin

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Summary. Efficiency of RME production process from waste (previously fried) oil during transesterification with methanol in the presence of KOH (as catalyst) is a function of many variables. In the dissertation it is shown that by proper control of appropriate amount of catalytic reaction substrates as well as thermal conditions and suitable period of process time it is possible to obtain conversion efficiency of waste rapeseed oil similar to the conversion efficiency obtained for pure rapeseed oil. Investigations also confirmed that, from that waste oil, it is possible to obtain RME having physical and chemical properties similar to biodiesel manufactured from pure rapeseed oil. Therefore, the quality of biofuel on the basis of RME obtained from properly treated waste oil may have similar properties to the RME produced from pure (not used for frying or cooking) rapeseed oil.

Key words: biodiesel, biofuels, RME (Rapeseed Methyl Ester), gas chromatography, diesel engine

INTRODUCTION

World norms and directives determine the sort of biofuels that are to feed our engines in short term and long term perspective. Up to 2020 these biofuels or biocomponents used for feeding compression-ignition engines are going to be pure biofuels of plant origin or commixtures of such biofuels and derivatives.

The world's best known biofuel is Biodiesel FAME (Fatty Acid Methyl Esters). Taking into account different climate and soil conditions, biofuels of different origins are going to dominate on particular continents [4, 5, 7, 8].

Among basic parameters determining particular biofuel usefulness for feeding self-ignition engines is the arrangement of fatty acids in FAME [9, 14, 15]. Research shows that in FAME, the more oleic acid there is, the more energy in the biofuel [16, 13]. Biodiesel fuel can be a stand-alone one or can be used as bio-component for diesel [2].

PURPOSE AND SCOPE

After the analysis of knowledge the author stated that the results of studies found in the specialist literature on the possibility of manufacturing RME biofuels from waste oils show that this kind of material may be suitable for biofuel production. However, after in-depth analysis, it appears that the results of individual properties and characteristics of RME are considerably different. The aim of this study was then to determine the effect of thermal influence during frying on the quantity and quality of RME.

At the first stage of the research pure rapeseed oil and the waste (after frying) one was analyzed by gas chromatography. The idea was to check how the structure of fresh oil was changed after frying. The aim of studies was to show, whether quantity and participation of fatty acids was changed after exposure to heat during frying. Another research idea was also to confirm or deny claims presented by other researchers - e.g. Pharma Cosmetic - that pyrolysis causes thermal decomposition of fatty acids to acrolein (C_3H_4O) and/or whether the thermal conversion may cause changes in mutual content and composition of fatty acids. At this stage of research it would be very important to determine the range of change (in %) of unfavourable compounds in the structure of the fresh oil in comparison to the waste one. Chromatographic analysis covered the identification of fatty acids in the range of decanoic acid, C10:0 to nervonic acid C24:1. The scope included all the fatty acids that can potentially occur in rapeseed oil.

RESEARCH METHODOLOGY

Transesterification process. For rapeseed oil transesterification methanol was applied, because it is inexpensive and efficient in the process of transesterification [1, 12]. A catalyst in this chemical reaction was KOH (Potassium hydroxide pure p.a.). Methanolysis was used as the catalyst KOH as it is one of the most efficient catalysts [3, 6, 11]. Transesterification was a one-stage process, at both times between the temperatures of 330- 340K.

Determination of fatty acid esters in the above-mentioned oils were carried out in accordance with PN-EN ISO 5508 standard using a multi-gas chromatograph of Thermo TRACE GC Ultra type. Figure 1 shows the test stand for gas chromatography analysis.

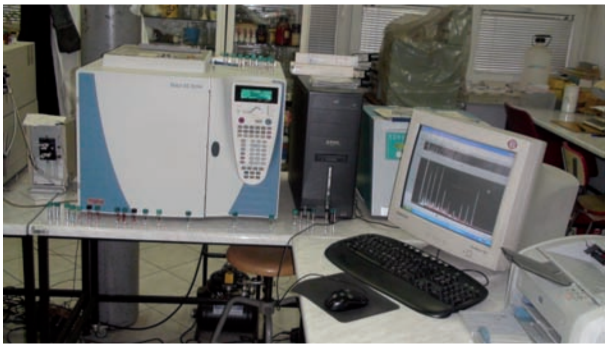

Fig. 1. The test stand equipped with a multi-channel gas chromatograph from Thermo TRACE GC Ultra type

The integration of chromatography was established to be such that the peaks from the capric acid methyl ester ($C_{10:0}$) went up to the peak of the lignoceric acid methyl ester ($C_{24:0}$) and nervonic acid methyl ester ($C_{24:1}$). Based on the received marked information below are the formulas of the contents of "C" esters:

$$C = \frac{\left(\sum A\right) - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100\%,$$

where:

$\sum A$ – the entire surface peaks of methyl esters from C_{10} to $C_{24:1}$,

A_{EI} – surface peaks representing heptadecanoic acid methyl ester,

C_{EI} – used concentrated dilution of heptadecanoic acid methyl ester; in milligrams per milliliter,

V_{EI} – the volume of the used dilution of heptadecanoic acid methyl ester, in milliliters,

m – mass of the sample, in milligrams.

Esters were produced in the reactor designed and built by the author of this article. This appliance as the only one in Europe is able to produce Biodiesel RME with a full glycerin phase of two hours.

RESULTS OF ANALYSIS

Figures 2 and 3 show RME Biodiesels chromatograms, on which you can observe the number and size of peaks identifying individual esters of fatty acid.

Table 1 shows the results of chromatographic analysis determining the number and composition of fatty acids in the produced RME and - for comparison - in B100 Biodiesel taken from the fuel station BLISKA.

The data in Table 1 show that all the biofuels - due to total amount of fatty acid esters in the RME - meet requirements of EN 14214 standard. Both the biodiesels had similar fatty acid participation. It is worth mentioning that no fatty acids changes occur during transesterification. Both biodiesels consist of the same amount of fatty acid esters as the quantity and number of fatty acids present in oil used as raw material for RME manufacturing. Comparing the number and participation of fatty acids present in RME produced from both oils with the results of RME tests from fuel station „BLISKA", one may conclude that they are identical.

SUMMARY AND CONCLUSIONS

On the basis of studies concerning physical and chemical properties of RME obtained from pure and waste

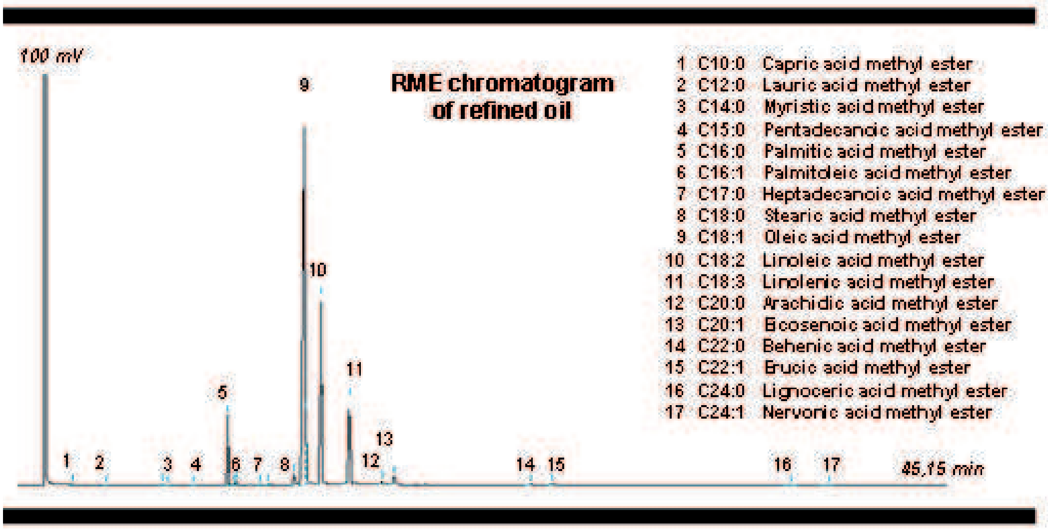

Fig. 2. Chromatogram of RME Biodiesel produced from pure, refined rapeseed oil

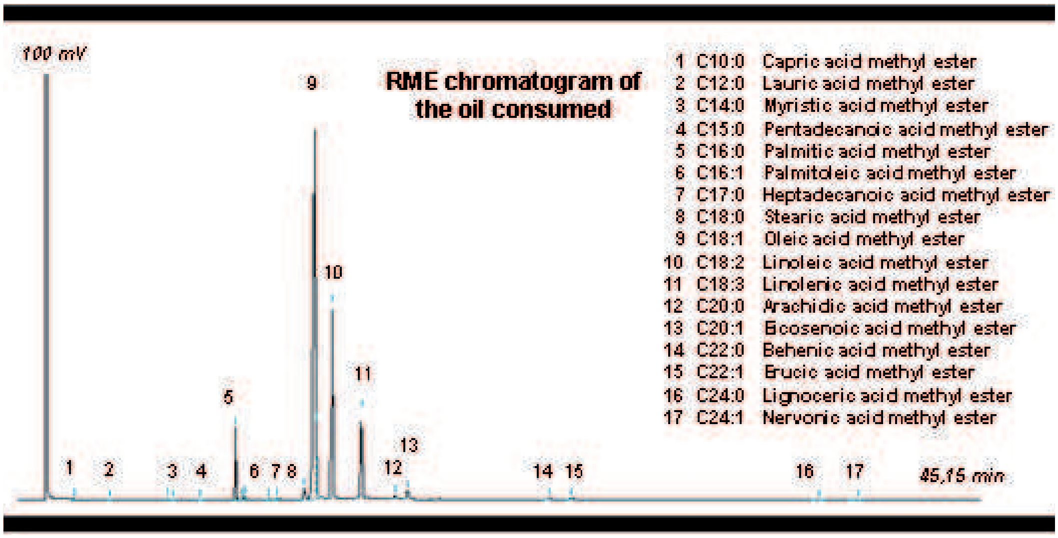

Fig .3. Chromatogram of RME Biodiesel obtained from waste (previously fried) rapeseed oil

Table 1. Composition of fatty acids in the produced biofuels in comparison to B100 Biodiesel from fuel station BLISKA

The name and participation of fatty acid % (m / m)	Chemical formula	Biodiesel from pure rapeseed oil	Biodiesel from waste (fried) rapeseed oil	RME biodiesel from the fuel station BLISKA / *
Capric acid methyl ester	C10:0	0,012	0,016	-
Lauric acid methyl ester	C12:0	0,011	0,014	-
Myristic acid methyl ester	C14:0	0,051	0,064	0,052
Pentadecanoic acid methyl ester	C15:0	0,019	0,024	0,023
Palmitic acid methyl ester	C16:0	4,263	4,759	4,486
Palmitoleic acid methyl ester	C16:1	0,186	0,202	0,265
Heptadecanoic acid methyl ester	C17:0	0,037	0,41	0,112
Stearic acid methyl ester	C18:0	1,482	1,387	1,808
Oleic acid methyl ester	C18:1	58,076	58,171	60,912
Linoleic acid methyl ester	C18:2	19,966	19,812	19,252
Linolenic acid methyl ester	C18:3	9,438	8,892	8,984
Arachidic acid methyl ester	C20:0	0,507	0,457	0,646
Eicosenoic acid methyl ester	C20:1	1,240	1,176	1,721
Behenic acid methyl ester	C22:0	0,239	0,225	0,365
Erucic acid methyl ester	C22:1	0,236	0,279	0,909
Lignoceric acid methyl ester	C24:0	0,096	0,063	0,129
Nervonic acid methyl ester	C24:1	0,112	0,101	0,187
The degree of identification of fatty acid methyl esters		Σ =99.99 % (m/m)	Σ = 100.00 % (m/m)	Σ = 99.85 % (m/m)

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(fried) rapeseed oil, we can conclude that, in general, the two biofuels are characterized by similar properties. RME produced from waste oil was characterized by composition and participation of fatty acids similar to biofuel obtained from pure oil. The investigations showed that during frying at high temperatures fatty acids were stable and only slightly (up to 2%) changed their structure. This is very valuable information because the properties of FAME type [Fatty Acid Methyl Esters] biofuels depend largely on the amount of individual fatty acids esters in FAME. Further detailed studies have shown that the following properties of RME obtained from waste oil are identical: the value of the heat of combustion, calorific value, initial point of distillation and distillation temperatures range of up to 90% v/v of biodiesel. However, the temperature of final distillation point is unfortunately higher for biofuels from waste oil. RME produced from waste oil has also a slightly worse rheological properties.

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ZASTOSOWANIE CHROMATOGRAFII DO ANALIZY JAKOŚCI BIOPALIW TYPU RME UZYSKANYCH Z OLEJU CZYSTEGO ORAZ ZUŻYTEGO

Streszczenie. Sprawność procesu produkcji RME z zużytego (posmażalniczego) oleju w procesie transestryfikacji metanolem wobec katalizatora KOH jest funkcją wielu zmiennych. Wykazano, że sterując odpowiednią ilością substratów katalitycznej reakcji oraz warunkami termicznymi i długością czasu procesu, można uzyskać sprawność konwersji dla zużytego oleju rzepakowego zbliżoną do sprawności uzyskiwanej dla czystego oleju rzepakowego. Badania potwierdziły również, że można uzyskać z oleju posmażalniczego RME o zbliżonych własnościach fizyko-chemicznych do Biodiesla uzyskanego z czystego oleju rzepakowego. W związku z tym jakość biopaliwa RME z zużytego oleju może mieć zbliżone własności do RME wyprodukowanego z czystego (nieprzepracowanego) oleju rzepakowego.

Słowa kluczowe: biodiesl, biopaliwo, RME (Estry metylowe oleju rzepakowego), chromatografia gazowa, silnik wysokoprężny.