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FACTORS AFFECTING THE RATE OF FORMATION AND THE CONTENT OF RAPESEED OIL METHYL ESTERS IN PRESENCE OF SODIUM HYDROXIDE AS CATALYST

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Studies of the transesterification reaction of vegetable oils are important in the production of biodiesel. The rapeseed oil methyl ester concentration in the rapeseed oil layer was found to be directly proportional to RME yield in experimental conditions at the time interval to 180 minutes. The coherence is described by equation $Y = 0.99147 \times C - 2.690$ ($r = 0.961$), where Y – stands for the RME yield, but C – for the RME content in oil layer. The increase of the molar ratio of methanol to oil (3.2–6.0 mol), the concentration of NaOH (0.2–1.5 weight % of oil) and the reaction temperature (from 30 to 80 ºC), caused the increase of speed of the equilibrium entrance, and the yield of RME was increased about 8.0, 7.9 and 8.2% accordingly. For the implementation of batch processes, the preferred reaction temperature is 50 ºC, the molar concentration of methanol is 4.0 mol and that of NaOH amounts to 0.5%. However, when using continuous processes, the reaction would be more efficient at higher temperature with lower quantities of catalyst and methanol.

Key words: *biodiesel, transesterification, kinetics, rapeseed oil, ester content.*

INTRODUCTION

Biodiesel is one of the most popular contemporary alternative fuels and it has the following advantages in comparison with diesel [1–3]:

1) biodiesel is produced from the renewable resources and it can be obtained from the all kinds of biomass containing long chain fatty acids or their esters;
2) biodiesel is more environmentally friendly than fossil fuel, and this is why CO_2 excreted in operation of combustion engine will cause only the insignificant greenhouse effect hence the considerable part of it is consumed in the vegetation period of the oil plant;
3) operating diesel engines with biodiesel the emission of other noxious gases is noticeably less than operating them with the fossil fuel;
4) the increase of the volume of biodiesel, the production and use of the power independence of countries with limited or unavailable fossil energy sources also increase;
5) production of biodiesel ensures the more balanced development of the national economy.

Studies of the transesterification reaction of vegetable oils are important in the production of biodiesel. Optimizing the conditions of the biodiesel extraction process it is possible to achieve the significant savings of energy resources and raw materials, thus reducing the end product cost. The decrease in the price of biodiesel will encourage the consumer interest and demand, ensuring the development of the domestic resources and production to meet the transportation requirements. The study of the influence of concentration of triglyceride, alcohol and catalyst as well as the temperature and the reaction time on the transesterification process and its optimization is a way to achieve an economic impact in biodiesel extraction [4–6]. To implement this, a systematic study of the impact of the most important factors on the reaction product yield and its level of purity is necessary. To determine the suitable reaction conditions for the extraction of rapeseed oil methyl ester (RME) from the rapeseed oil produced in Latvia, a series of experiments was conducted, using conditions characteristic of the industrial processes [7–10]. The main variables were the concentration of NaOH (0.2–1.5 weight % of oil), the molar ratio of methanol to oil (3.2–6.0 mol), the reaction temperature (30–80 ^{o}C) and the reaction time (2–180 minutes).

EXPERIMENTAL

The biodiesel was obtained using the refined rapeseed oil produced by SIA „Iecavnieks”. To determine the impact of the temperature, NaOH concentration and the molar ratio of methanol on the rapeseed oil methyl ester extraction process, an experiment plan was made in accordance with the data in the Table 1. The variable factor impact research methodology, similar to the published one, was used in the experimental study [11]. Each experimental sample of the series of experiments was obtained by extracting it (5 ml) at regular intervals (see Table 1) from the reaction mass with a specially designed disposable polyethylene pipette. The stirring speed of the reaction mass was kept constant throughout the whole series of experiments (1200 rpm^{-1}). The sampling time for the each experimental sample was measured with a stopwatch and the report was initiated when all of the necessary alkaline solution in methanol was added to the reaction mass. Time error does not exceed 5 seconds and the maximum temperature variation is ±1.0 ºC (thermostat with an accuracy of ±0.1 ºC was used). After a sample was taken, it was shaken vigorously with 30 ml of distilled water in which hydrochloric acid dissolves at a sufficient concentration to neutralize the alkaline residue to a neutral environment. This procedure ensures that the transesterification reaction stops.

After being neutralized, the emulsion was placed in the thermostat for 10 min (60 ºC) so that the layers settle. When the emulsion had settled, the upper layer of oil was separated, then within 10 minutes the remnants of water and methanol were distilled using a rotary evaporator under 900 Pa pressure at temperature of 90 ºC. To determine the RME yield, the separate experiments were carried out; preserving all the reaction conditions, but increasing the amount of rapeseed oil to 100 g (reaction was carried out in a 250 ml round-bottomed flask). RME content was determined using *Nicolet 5700 FT-IR* infrared spectrometer manufactured by *Thermo Electron Company* with *Smart multi bounce HATR* multiple reflection accessory. To develop a control method for the quantitative determination of RME in rapeseed oil and RME mixtures, *TQ Analyst* software was used. The calibration mixtures were prepared with RME content from 30 to 100% (m/m%). To determine the percentage of RME in rapeseed oil and RME mixtures, we used the algorithm of Beer–Lambert law and the spectral band at 6968.6 nm with a baseline between points 6816.6 and 7107.3 nm, similarly to the published studies [12–13].

RESULTS AND DISCUSSION

By studying the kinetics of the transesterification reaction and impact of the variable factors on the biodiesel process, we can obtain the maximum product yield with minimum consumption of the raw materials, time and energy resources [14–15]. To research the rapeseed oil transesterification process, the variable factors selected were concentration of NaOH, the molar ratio of methanol to oil, reaction temperature and time. RME content in the oil layer after the separation of reaction by-products and other impurities was selected to be the reaction process control parameter [11]. To determine whether the RME content in the oil layer adequately represents the reaction process, analysis of RME yield calculation results was performed. Since the accurate determination of the mass of oil layer is a very time-consuming procedure, complex and potentially inaccurate process, it was very important to determine whether the reaction process during a time interval of up to 180 minutes can be characterized by determining only RME content in the oil layer, which can be done quickly using the developed FTIR (Fourier transform infrared spectroscopy) method. Table 1 summarizes data on the RME content in the oil layer and the mass of this layer which have been calculated theoretically and determined experimentally in two selected points (with reaction time 60 and 180 min). The average molecular mass of the rapeseed oil used in the calculations was determined experimentally by the saponification value, considering that there were three parts of fatty acid and one part of glycerol molecules in rapeseed oil triglyceride. The calculated molecular mass amounted to 932.0 g mol^{-1} and was similar to the published value [16].

To characterize the reaction process, RME yield % should be used, which could be obtained by multiplying the mass of biodiesel layer with the RME content (%) in it and dividing by the theoretically expected yield at the corresponding rapeseed oil conversion stage (see Equation 1):

$$Y = \frac{100}{Y_{teor}} \times M \times C\,, \tag{1}$$

where Y – RME yield, %;
M – the mass of biodiesel layer, g;
C – RME content, %;
Y_{teor} – degree of rapeseed conversion to biodiesel.

As shown by Figure 1, there is a linear correlation (r = 0.961) between the RME yield and RME content in the oil layer, and the experimental points are below the line formed by the three theoretically calculated points at rapeseed oil conversion levels of 80, 90 and 100%.

Therefore an experimentally clearly demonstrated fact can be considered that the reaction process at least in the given reaction conditions can be represented only by the biodiesel content in the oil layer. To judge of the general nature or the application restrictions of the obtained linearity, additional studies are necessary, however, a linear relationship exists in the experimental conditions (see Equation 2), which allows the calculation of Y values from the experimentally determined C values.

$$Y = 0.99147 \times \mathrm{C} - 2.690\,, \tag{2}$$

where C – RME content, %;
Y – RME yield, %.

Table 1. **Design of experiments for the research of RME extraction conditions, RME content and mass of oil layer as well as theoretical parameters in the 80–100% range**

RME sampling time (min), from the start of the reaction	NaOH concentration, weight % of oil	Molar ratio of methanol to oil	Reaction temperature, °C	Ester content, %	The mass of biodiesel layer, g
		Theoretical calculation			
				80.0	100.34
				90.0	100.39
				100.0	100.43
		Experimental data			
60	0.9	3.2	60	86.4	96.0
180	0.9	3.2	60	89.6	97.1
60	0.9	3.5	60	89.0	95.4
180	0.9	3.5	60	90.8	97.5
60	0.9	4.0–6.0	60	96.5	96.1
180	0.9	4.0–6.0	60	95.9	96.8
60	0.2	4.0	60	84.1	97.4
180	0.2	4.0	60	91.3	95.4
60	0.3	4.0	60	88.3	96.3
180	0.3	4.0	60	93.5	97.0
60	0.4–0.5	4.0	60	94.2	96.3
180	0.4–0.5	4.0	60	94.8	95.5
60	0.6–1.5	4.0	60	95.7	95.9
180	0.6–1.5	4.0	60	96.8	96.0
60	0.5	4.0	30	82.6	96.8
180	0.5	4.0	30	87.9	95.1
60	0.5	4.0	40	84.5	96.9
180	0.5	4.0	40	91.7	95.2
60	0.5	4.0	50–80	93.8	96.6
180	0.5	4.0	50–80	95.4	95.4

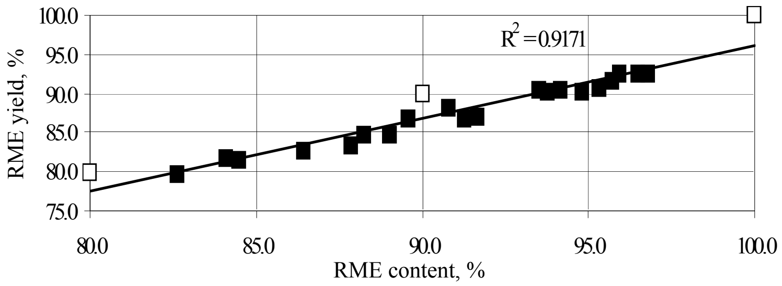

Fig. 1. Relationship between RME yield and RME content in the oil layer (□ – theoretical data; ■ – experimental data).

Using this equation, we can calculate that in the rapeseed oil conversion range of 80–100%, RME content in the layer is higher than the RME yield, and this difference does not exceed 3.47%, which practically does not change the shape of the kinetic curves obtained with the help of *C* values. The Gauss least squares method is used in these calculations and the reliability of the approximation is characterized by Pearson correlation coefficient ($r = 0.961$).

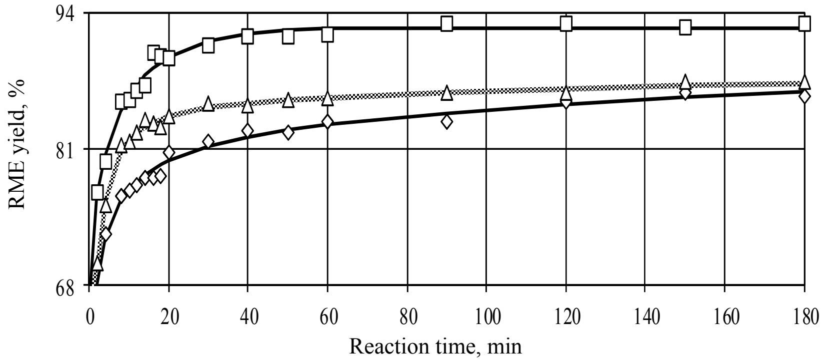

Fig. 2. The influence of molar ratio of methanol to oil (◊ – 3.2; Δ – 3.3; □ – 4.0–6.0) on the RME extraction process.

Figure 2 depicts the impact of the molar ratio of methanol on the rapeseed oil transesterification reaction process over time at 60 °C with NaOH concentration of 0.5% of oil weight. In the given conditions, with 3.2 and 3.5 mol of methanol to 1 mol of rapeseed oil, in 2 minutes the RME yield reaches ~67.8 and ~70.1%, respectively, but in time interval from 60 to 180 min it increases to ~86.1 and ~87.3%. With 4–6 moles of methanol, the transesterification reaction is fast and already in 2 minutes ~76.8% of rapeseed oil are converted to biodiesel. The reaction equilibrium is reached after ~40 minutes, producing RME yield of ~91.6 to 92.9%. As the authors point out in their studies, [17] to obtain the highest yield of biodiesel, 6.0–15.0 moles of methanol per mole of oil should be used in the reaction. However, if the concentration of methanol is increased, the crude glycerol phase does not precipitate, thus considerably hindering biodiesel extraction [18]. Our research shows that in order to produce biodiesel with high yield at a reaction time of up to 180 min, only 4.0 moles of methanol per mole of oil should be used, because, as the predominance of methanol is increased, the reaction velocity increases insignificantly and if it reaches the equilibrium, the yield remains unchanged regardless of the amount of methanol used. Using 4.0 moles of methanol, the glycerol phase precipitates very rapidly, stimulating the separation of biodiesel from the reaction mixture.

Figure 3 depicts the impact of the concentration of catalyst (NaOH) on the rapeseed oil transesterification process over time at 60 °C using 4.0 moles of methanol per mole of oil. In these conditions, with 0.2 and 0.3% of NaOH (of the oil mass), in 2 minutes the RME yield reaches ~51.0 and ~58.7%, respectively, but in the time interval from 60 to 180 min it increases to ~86.2 and ~88.8%. As the NaOH concentration is increased to 0.4–0.5 and 0.6–1.5%, the transesterification reaction is fast, and already in 2 minutes respectively ~68.8 and ~75.9% of rapeseed oil are converted to biodiesel. The reaction equilibrium, respectively, is reached after ~30 and ~40 minutes, providing the RME yield of ~89.8–91.1% and ~92.5–93.0%, respectively. As the authors point out in their studies, [19, 20] to obtain the highest RME yield with the lowest catalyst consumption, the most efficient NaOH concentration is from 0.3 to 0.5% (of the oil weight). Our research shows that when producing biodiesel, up to 180 min, the preferable NaOH concentration is from 0.4 to 0.8% because at such catalyst quantities the reaction proceeds rapidly and with the highest biodiesel yield. If the NaOH concentration is increased over 0.8%, the reaction velocity and the RME yield do not increase, but separation of biodiesel and its purification from the crude glycerol layer is more difficult, because the reaction mass contains a considerable amount of soap.

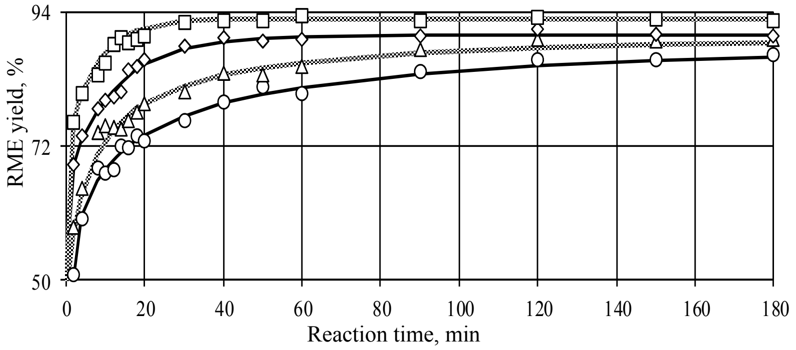

Fig. 3. The influence of NaOH concentration (o – 0.2%; Δ – 0.3%; ◊ – 04–0.5%; □ – 0.6–1.5%) on the RME extraction process.

Figure 4 depicts the impact of the temperature on the rapeseed oil transesterification process over time, using NaOH concentration of 0.5% of the oil mass and 4.0 moles of methanol per mole of oil. If the reaction is carried out at 30 and 40 °C, in 2 minutes the RME concentration in the biodiesel layer reaches ~37.6 and ~50.2%, respectively, but in the time interval from 60 to 180 min it increases to ~84.3 and ~87.7%. If the reaction is carried out at 50–80 °C, in 2 minutes the RME yield reaches ~69.8%. The reaction equilibrium is reached after ~40 minutes, producing the RME yield of ~89.6 to 91.2%. As the authors point out in their studies, [21] temperature significantly affects the equilibrium time and the yield of the transesterification reaction, since it reduces the viscosity of the reaction mixture and increases the molecular diffusion. Our equilibration times are similar to the ones indicated in the publications [22, 23], but RME yields are by 1–5% lower. This phenomenon could be attributed to the characteristics of RME extraction, purification and analytic methodology.

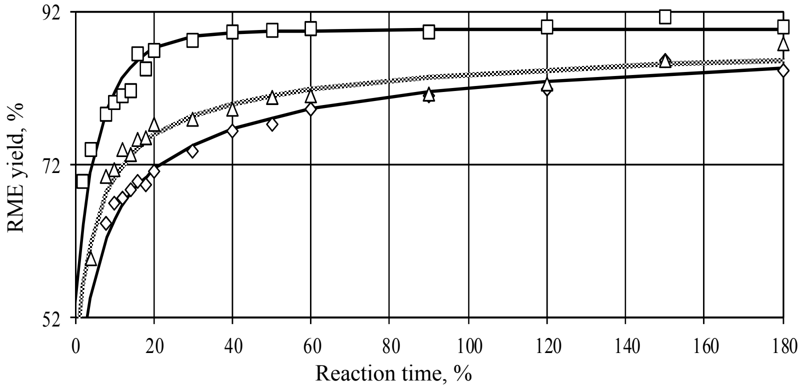

Fig. 4. The influence of temperature (◊ – 30 °C, Δ – 40 °C, □ – 50–80 °C) on the RME extraction process.

CONCLUSIONS

1. The concentration of rapeseed oil methyl ester (RME) in the rapeseed oil layer is directly proportional to RME yield in experimental conditions at the time interval up to 180 minutes. The coherence is described by equation $Y = 0.99147 \times C - 2.690$ ($r = 0.961$), where Y – stands for RME yield, but C – for RME content in oil layer. The transesterification reaction in the experimental conditions within the error limits can be adequately characterized by the concentration of RME in the oil layer without determining the mass of this layer.

2. The increase of the molar ratio of methanol to oil (3.2–6.0 mol) causes the increase of speed of the equilibrium entrance, and increase of yield of RME of about 8.0%.

3. The increase of NaOH concentration (0.2–1.5 weight % of oil) causes the increase of speed of the equilibrium entrance and yield of RME of about 7.9%.

4. The increase of the reaction temperature (from 30 to 80 ^{o}C) causes the increase of speed of the equilibrium entrance and yield of RME of about 8.2%.

5. For the implementation of batch processes, the preferred reaction temperature is 50 ºC, the molar concentration of methanol is 4.0 mol and the NaOH concentration is 0.5%. However, when using the continuous processes, the reaction would be more efficient at higher temperature with lower quantities of catalyst and methanol.

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RAPŠU EĻĻAS METILESTERU IEGŪSANAS REAKCIJAS ĀTRUMU UN ESTERU SATURU IETEKMĒJOŠIE FAKTORI

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KOPSAVILKUMS

Augu eļļu pāresterificēšanas reakcijas pētījumiem ir liela nozīme biodīzeļdegvielas ražošanā. Optimizējot biodīzeļdegvielas iegūšanas procesa apstākļus, iespējams panākt ievērojamu energoresursu un izejvielu ekonomiju, samazinot gala produkta izmaksas. Samazinoties biodīzeļdegvielas cenai, pieaugtu arī patērētāju interese un pieprasījums, nodrošinot vietējo resursu izmantošanas un ražošanas attīstību transporta vajadzībām. Triglicerīda, spirta un katalizatora koncentrācijas, kā arī temperatūras un reakcijas laika ietekmes izpēte uz pāresterificēšanas procesu un tā optimizācija ir viens no veidiem, kā radīt ekonommisko efektu biodīzeļdegvielas iegūšanā. Lai noskaidrotu rapšu eļļas metilesteru (RME) iegūšanas reakcijas apstākļus no Latvijā ražotas rapšu eļļas, veikti eksperimenti, par pamatu izmantojot rūpnieciskajiem procesiem raksturīgus apstākļus. Darbā noskaidrots, ka eksperimenta apstākļos laika intervālā līdz 180 min RME koncentrācija rapšu eļļas slānī ir tieši proporcionāla RME iznākumam. Sakarību raksturo vienādojums $Y = 0{,}99147 \times C - 2{,}690$ (r = 0,961), kur Y – RME iznākums, bet C – RME saturs eļļas slānī. Izpētīts, ka, palielinot metanola molāro attiecību pret rapšu eļļu (no 3,2 līdz 6,0 moliem), NaOH koncentrāciju (no 0,2 līdz 1,5 masas % no rapšu eļļas) un reakcijas temperatūru (no 30 līdz 80 ^{o}C), palielinās līdzsvara iestāšanās ātrums un RME iznākums attiecīgi pieaug par 8,0, 7,9 un 8,2%. Periodisku procesu realizācijai ieteicamā reakcijas temperatūra ir 50 ^{o}C, metanola molārā koncentrācija 4,0 M un NaOH koncentrācija 0,5%. Izmantojot nepārtrauktus procesus, reakciju efektīvi būtu realizēt augstākā temperatūru ar zemākiem katalizatora un metanola daudzumiem.

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