The Factors Affecting the Separation of the Reaction Mixture after Transesterification of Rapeseed Oil

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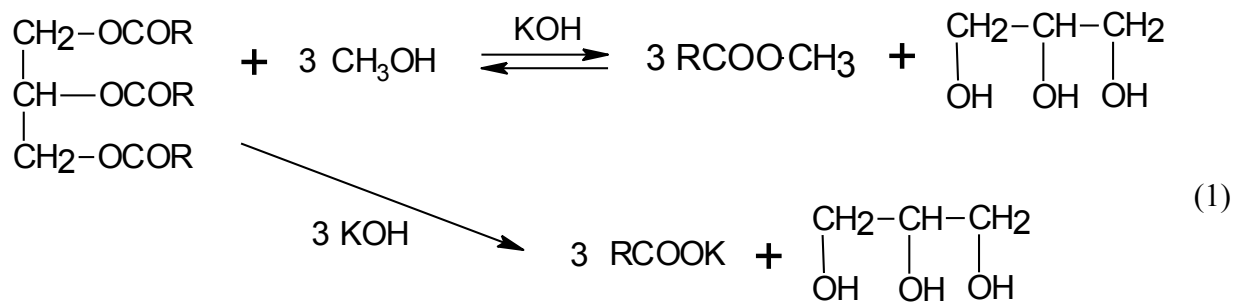
Summary

The most used method of biodiesel production is the transesterification of vegetable oils by basic homogeneous catalyst. Heterogeneous reaction mixture is formed by this process and contains two phases: ester phase and glycerol phase. From this mixture, biodiesel is gained by sedimentation. Quality and quantity of both phases are affected by conditions of sedimentation process. It was studied how conditions (independent variables: temperature of separation, amount of added water, time of sedimentation, etc.) affect the quantity and the quality of both phases (dependent variables). The statistic system Plackett - Burman was used for experiments planning. The relationship between independent and dependent variables was found and described by multidimensional linear regression. The created model allows to calculate the optimum conditions of biodiesel production so the quality of biodiesel fills the EN 14214.

1   Introduction

Deterioration of environment caused by toxic materials which are produced by expanding automobile transport and increasing prices of crude-oil-based fuels motivate us to search for alternative, environment-friendly sources of energy. Biodiesel is one of the alternatives to fuels produced from crude vegetable oils. It is a mixture of methyl esters of higher fatty acids. Biodiesel is a nontoxic ecological fuel and it is easily biodegradable [1, 2]. It is more lubricious than diesel and its addition to diesel decreases the wearing out of diesel engines [3]. Emissions of carbon monoxide, sulfur and ash are lower during combustion of biodiesel in comparison with combustion of fossil-oil diesel [4, 5]. But, on the other side, the emissions of nitrogen oxides are slightly higher [6]. Biodegradability and low air pollution are the main advantages of biodiesel.

It is possible to use all types of vegetable oils (rapeseed, sunflower, soybean, etc.) including waste oils and animal fats for biodiesel production. Transesterification using a basic catalyst is the most widely used way of production. There are three newly developed methods of biodiesel production. First of them is the preparation of esters by supercritical methanol without catalyst [7]. The second attractive method uses enzymatic catalysts for biofuels production. Disadvantages of this method are long chemical reaction time (5-8 hours) [8, 9] and low conversion. In the third method special solid catalysts based on organometallic complexes of tin, zircon [10] or ruthenium [11] are used at high temperature and pressure. Solid acid catalysts on the base of zeolites [12] are developed, too.

In this paper, biodiesel is prepared by transesterification of rapeseed oil by methanol. Potassium hydroxide is used as catalyst, see equations (1), where R are hydrophobic rests of fatty acids. After transesterification, the excess of catalyst is neutralized by gaseous carbon dioxide dosed into the reaction mixture [13] (potassium carbonate is formed).

$$\begin{array}{l} CH_2\text{-}OCOR \\ | \\ CH\text{-}OCOR \\ | \\ CH_2\text{-}OCOR \end{array} \;+\; 3\,CH_3OH \;\underset{}{\overset{KOH}{\rightleftharpoons}}\; 3\,RCOO\text{-}CH_3 \;+\; \begin{array}{ccc} CH_2\text{-}CH\text{-}CH_2 \\ | \quad | \quad | \\ OH \;\; OH \;\; OH \end{array}$$

$$\xrightarrow{3\,KOH}\; 3\,RCOOK \;+\; \begin{array}{ccc} CH_2\text{-}CH\text{-}CH_2 \\ | \quad | \quad | \\ OH \;\; OH \;\; OH \end{array} \tag{1}$$

Removal of methanol from the neutralized reaction mixture is the next step. A heterogeneous raw reaction mixture is formed by this preparation. The mixture is then spontaneously separated into two liquid phases – ester phase (EP) and glycerol phase (GP). The lighter upper ester phase contains the main product - biodiesel and small rest of other materials (limited by Euro Norm EN14214:2003). The heavier bottom glycerol phase contains, besides glycerol, also the rest of the catalyst in the form of potassium carbonate, soaps and small amount of biodiesel. To accelerate the gravitative separation, optimum amount of demineralized water is added into the mixture [14].

2   Theory

2.1   Multidimensional system

The state of the final raw reaction mixture (RRM), consisting of EP and GP, depends on many independent variables. Thus, it introduces a multidimensional system. To its description the method based on the statistical design Plackett-Burman [15] was used for planning the experiments. The composition of RRM is affected by many factors (independent variables – X_i). Following variables and intervals of their values were chosen: temperature, amount of added water or aqueous acid solution, concentration of acid, time and intensity of stirring, repetition of stirring, time of sedimentation (intervals see Tab.1). These independent variables affect mostly the separation and therefore also quality and quantity of the products, EP and GP. The stirring is one of independents variables, therefore the power number was calculated and it is in range from 100 (2160 rpm) to 1000 (715 rpm).

Following dependent variables (Y_i) were chosen to describe the influences of independent variables and to characterize optimally EP and GP: For GP – Y_1: relative amount of phase [g/g]; Y_2: amount of potassium carbonate [wt-%]; Y_3: amount of soaps [wt-%]. For EP – Y_4: relative amount of phase [g/g]; Y_5: acid number [mg KOH/g]; Y_6: amount of potassium ions [mg KOH/g]; Y_7: amount of free glycerol [wt-%].

Concentrations of free glycerol and potassium (Y_6 and Y_7) in EP depend very much on the course of sedimentation and their concentrations must fulfil the biodiesel quality norm. On the other hand, acid number of EP (Y_5) changed only slightly during experiments and, unfortunately, its determination shows a big relative error of analysis (see chap.3.4.3).

2.2 Statistical design of experiments

After selection of suitable independent variables and their intervals, simple empirical linear model (2) was suggested for the description of every chosen dependent variable Y_i describing the separation of products after transesterification

$$Y_i = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_5 X_5 + \beta_6 X_6 + \beta_7 X_7 \qquad (2)$$

The parameters β_i of the linear statistical model were determined by multidimensional linear regression in PC software QC Expert 2.5. The statistic tests (heteroskedasticity, normality, influence points) were calculated, too.

3 Material and methods

3.1 Chemicals

Rapeseed oil: firm ABC Brancouze, Czech Republic, cold pressed, density $0.922\ \mathrm{g/cm^3}$, viscosity $36.8\ \mathrm{mm^2/s}$, acid number 1.2 mg KOH /g. Potassium hydroxide pure (solid 83 wt-%). Methanol (technical). Phosphoric acid p.a. (85 wt-%), all Lach-Ner, Czech Republic. Demineralized water.

3.2 Preparation of samples

Complete procedure of biodiesel preparation is described in the Czech patent [13]. Transesterification of rapeseed oil by methanol (molar ratio 1:6) was carried out by basic catalyst (1 wt-% potassium hydroxide to oil) in the batch reactor at the reaction temperature 60 °C. The so called raw reaction mixture (RRM) is formed after transesterification, neutralization of catalyst by gaseous carbon dioxide and demethanolisation.

3.3 Description of experiments

At first, a sample of RRM was titrated by water under turbidimetric control up to its maximum transmittance at 570 nm. In this way the optimal amount of water needed for perfect and fast separation of EP and GP was found. Then a sample of RRM (20 – 22 g) was put into a glass cuvette with optical path 2 cm imbedded in the spectrometer (Spekol 11, Jena, BRD). The sample was stirred ca 10 min at constant temperature and revolutions of a propeller stirrer with diameter 1 cm (indicator DZM-control, IKA, BRD) according to the plan of experiments (see Tab.2). Then aqueous solution of phosphoric acid was added. After next 10 min of stirring (when the constant value of absorbance was reached), the stirrer was stopped and consequently sedimentation started. After 30 min, RRM was perfectly separated to upper EP and lower GP. Then both phases were sampled for analyses (see chap.3.4).

The settings of lower (-1) and upper (+1) limits of all independent variables are shown in Tab.1. All experiments were carried out according to statistic design Plackett-Burman (see Tab.2).

3.4 Analytical methods

3.4.1 Determination of relative amount of GP and EP

The relative amounts of GP and EP are dependent variables. Raw reaction mixture (mass m_{RRM}) was poured into a cuvette (ground plan 2x3 cm). After experiment and sedimentation described in 2.3, the heights of interfaces of phases (h_1 and h_2) were determined by cathetometer (Fig. 3). The relative amounts of both phases were calculated according to (4). The conditions of preparation of samples are set up so the density of EP is constant (ρ_{EP}=0.88 g/cm^3).

$$w_{EP} = \frac{\rho_{EP} \cdot 2 \cdot 3 \cdot (h_2 - h_1)}{m_{RRM}} \qquad \text{and} \qquad w_{GP} = 1 - w_{EP} \qquad (4)$$

3.4.2 Determination of K$_2$CO$_3$ and soaps in GP

The determination of both components was carried out within one acidimetric titration by hydrochloride acid (0.1 mol/l) in methanol. A couple glass electrode – saturated argentchloride electrode was used as detector. The result of this determination was a two-step titrimetric curve, where both equivalence points were evaluated by second-order derivation. It was found that carbonates were titrated to bicarbonates in the first step and bicarbonates and soaps were titrated in the second step.

3.4.3 Determination of acid value in EP

The determination was carried out by alkalimetric titration by the ethanolic solution of potassium hydroxide (0.1 mol/l) and phenolphthalein was used as an indicator. Small differences in relatively small acid values (0.1-0.4 mg/g) of individual experiments were determined. These small differences are difficult to detect by titration with visual determination of the equivalence point. Therefore this analytical method has for this purpose too great relative error. The equivalence point is possible to detect by electrode. In this paper, it was not used because the amount of consumed ethanolic solution for titration was small, therefore usage of electrode would not lead to higher accuracy of determination. In addition, the usage of the visual determination is less time consuming and is described in EN 14214. The used process of biodiesel production ensures that acid number is less than 0.5 mg KOH/g (under the EU norm). Acid number is a complementary data.

3.4.4 Determination of potassium in EP

Potassium soaps – the minor by-product - which are carriers of potassium ions, are formed by side reactions (neutralisation of free fatty acids present in the oil and hydrolysis of methyl esters

and/or oil by KOH) within this biodiesel production. The major part of these soaps passes to the glycerol phase during separation, but a slight portion remains in the ester phase.

Acidimetric titration of potassium soaps by ethanolic solution of hydrochloride acid (0.01 mol/l) was used for the determination. The potentiometric titration was used with a couple glass electrode –saturated argentchloride electrode. The amount of consumed HCl was evaluated by first-order derivation of the resulting potentiometric curve.

3.4.5 The determination of free glycerol in EP

Glycerol, the main by-product of the biodiesel production, does not pass to the glycerol phase completely, but remains in small concentration in biodiesel. To its determination in EP we used the method described in detail in [16]. This determination has two phases – extraction of free glycerol from EP into water and subsequent determination of glycerol in water solution by HPLC.

4 Results and discussion

4.1 Resulting model

After the statistical evaluation, the relationships between independent and dependent variables were found. Some of the independent variables were found unsubstantial during statistic testing, therefore they are not stated. Dependents variables (Y_i) are defined in the chapter 2.1. The regression coefficients (R^2) are in the parenthesis.

$$Y_1 = 0.168 + 0.011 \cdot m_w \qquad (0.952)$$

$$Y_2 = 0.503 - 0.503 \cdot acid \qquad (0.990)$$

$$Y_3 = 18.03 - 0.64 \cdot T_{sed} - 0.66 \cdot m_w - 1.24 \cdot t_{mix} + 0.96 \cdot op \qquad (0.977)$$

$$Y_4 = 0.832 - 0.011 \cdot m_w \qquad (0.952)$$

$$Y_5 = 0.6 + 0.18 \cdot T_{sed} + 0.07 \cdot m_w + 0.25 \cdot acid - 0.17 \cdot \omega_A + 0.05 \cdot t_{mix\,A} - 0.07 \cdot op - 0.03 \cdot t_{sed} \qquad (0.998)$$

$$Y_6 = 124.8 + 34.2 \cdot T_{sed} + 4.8 \cdot acid - 12.1 \cdot \omega_A + 25.9 \cdot t_{mix} - 26.1 \cdot op - 84.6 \cdot t_{sed} \qquad (0.999)$$

$$Y_7 = 0.257 + 0.031 \cdot T_{sed} - 0.032 \cdot op - 0.181 \cdot t_{sed} \qquad (0.985)$$

4.2 Verification of the model

The described model was verified by several independent experiments. It has seven equations and fourteen variables (seven independent and seven dependent); therefore seven variables must be chosen and the others can be then calculated (Tab.3). The equation for acid number (Y_5) was not considered because it is probably unreliable (determination of acid value has a big relative error, see 3.4.3). The verification of experiment was carried out, so that the predicted (calculated) and experimental values of chosen variables were compared. Good correspondence between measured

values and values calculated from the model is shown in Tab.4 except acid value. Acid value has a big relative error of determination; nevertheless it fulfils the Euro norm for FAME. The determined linear model is thus suitable to describe the sedimentation after alkaline methanolysis of rapeseed oil.

4.3 Analysis of results

The relative amount of GP increases (and of EP decreases) with increasing portion of water added during the separation into RRM, because water dissolves only in GP.

Amount of soaps in GP decreases with increasing temperature, amount of added water and time of stirring. Repeating of stirring increases amount of soaps in EP.

Amount of potassium carbonate in GP decreases with increasing concentration of added acid.

Acid number of EP depends on all independent variables. Mostly, it increases with increasing concentration of acid. The neutralization of K_2CO_3 and soaps (CO_2 and free fatty acids are formed) is caused by addition of a strong acid. Free fatty acids pass to EP and increase its acid number. Other independent variables affect the acid number less significantly. The used determination of acid value has a big relative error and is thus less reliable.

Amount of potassium ions in EP increases with increasing temperature of sedimentation concentration of acid and time of stirring. It decreases with increasing stirring intensity and time of sedimentation, and repeating of stirring.

The direct dependence of the free glycerol concentration in EP on increasing temperature of sedimentation and indirect dependence on repetition of stirring and time of sedimentation were found. Other respected independent variables are insignificant.

The correlation matrix was used to find out the dependence between dependent variables. A strong direct dependence between free glycerol and potassium ions concentrations in EP was found.

5 Conclusions

The realized experiments show that the quality and quantity of both phases, EP and GP, resulting after methanolysis of the rapeseed oil catalyzed by KOH and demethanolysation of the final reaction mixture, depend on the chosen separation conditions of this raw reaction mixture. The dependences were mathematically expressed. The determined optimal conditions do not describe the system completely. However it is possible to calculate such optimum sedimentation conditions from this mathematical model, so that the produced biodiesel has the quality requested by the EU norm EU 14214/2003.

Acknowledgements

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