

The Affection of Separation after Transesterification of Vegetable Oil

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Summary

The transesterification of vegetable oils (rapeseed and sunflower oils were used) by low molecular alcohol is the most used method of biodiesel production. A heterogeneous reaction mixture is formed by transesterification containing ester and glycerol phases. Biodiesel is gained by the sedimentation of this mixture. We have studied how separation conditions (independent variables: amount of added water, intensity and time of stirring, etc.) affect the quantity and the quality of both phases (dependent variables). The reaction mixture presents a multivariable system, therefore the statistic method Plackett - Burman was used in the planning of experiments. The multidimensional linear regression was used for the description of the relationship between independent and dependent variables. The mathematical model describing this relationship was created for both types of oil.

1 Introduction

Toxic material produced by expanding automobile transport and increasing prices of crude-oil-based fuels motivate us to search for alternative fuels. These types of fuel should be environmentally friendly, nontoxic, produced from renewable sources and relatively cheap. Biodiesel (FAME – fatty acid methyl esters) can be one of the alternatives; it is a mixture of methyl esters of higher fatty acids. It is produced from many types of crude vegetable oils (rapeseed, sunflower, soybean, etc.) including waste cooking oil and animal fats. Biodiesel does not contain polycyclic aromatic hydrocarbons, sulfur compounds and halogenides [1]. Emissions (carbon and sulfur oxides and ash) are lower from the combustion of biodiesel in the comparison with combustion of fossil-oil diesel [2, 3]. But, on the other hand, the emissions of nitrogen oxides are slightly higher [4]. Biodiesel is easily biodegradable, after 28 days is degradable 76 – 90 % of FAME in the nature [5]. It has better lubricity than diesel and its addition to diesel decreases the wearing-out of diesel engines [6]. The next advantage is that the sources of oil can be grown nearly in all countries; therefore these countries are less dependent on crude-oil imports.

Transesterification using a homogeneous basic or acid catalyst is the most widely used way of biodiesel production. Basically catalyzed transesterification is faster and more often used in the chemical industry [7]. It is possible to use guanidine carbonate as catalyst [8]. There are three newly developed methods of biodiesel production. The first of them uses heterogeneous catalysts, mostly organometallic complexes [9], variable zeolites [10] and metal oxides [11]. The easy separation of a catalyst from the reaction mixture and possibility of its replated usage are the main advantages of this method. The second method is the production of esters by supercritical methanol without a catalyst. However, this process needs a high temperature (350 °C) and pressure (20-50 MPa) [12].

The last attractive method uses enzymatic catalysts [13], but until today will produce too low a yield for low molecular alcohols.

In this paper, biodiesel is prepared by alkaline methanolysis of oil. Potassium hydroxide is used as a catalyst, see equations (1), where $R_{1,2,3}$ are hydrophobic rests of fatty acids. After transesterification, the excess of catalyst is neutralized by gaseous carbon dioxide dosed into the reaction mixture (formed potassium carbonate has no catalyst effect) [14]. The distillation of methanol from the neutralized reaction mixture is the next step in this procedure (Fig 1).

A heterogeneous raw reaction mixture (RRM) 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 quantity of other materials (unreacted oil, residuals of soaps and glycerol, etc.). The heavier bottom glycerol phase contains, besides glycerol, also potassium carbonate (the rest of the catalyst after neutralization), soaps and a small amount of methyl esters. To accelerate the separation, a suitable amount of demineralized water is added into the mixture [15].

2 Theory

2.1 Multidimensional system

The state of the final raw reaction mixture, consisting of EP and GP, depends on many independent variables. Thus, it introduces a multidimensional system. The method based on the statistical design Plackett-Burman [16] was used for planning the experiments.

The independent variables, which affect mostly the quality and quantity of the EP and GP are presented with their labels (X_i), descriptions, units and intervals of their values are in Table 1.

The power number was calculated for stirring and it is in a range from 100 (2160 rpm) to 1000 (715 rpm).

The dependent variables (Y_i) were chosen to describe the influence of independent variables: 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 : concentration of potassium ions [mg KOH/g]; Y_7 : concentration of free glycerol [wt-%].

The 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).

2.2 Statistical design of experiments

After selection of suitable independent variables (X_i), simple empirical linear model (2) was suggested for the description of dependent variables of separation Y_i .

$$Y_i = \beta_0 + \sum_{i=1}^7 \beta_i \cdot X_i \quad (2)$$

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 RME Slatiňany, Czech Republic, cold pressed, acid number 1.02 mg KOH /g, density 0.915 g/cm³ (20 °C), viscosity 36.5 mm²/s (40 °C). Sunflower oil: firm ABC Bransouze Třebíč, Czech Republic, cold pressed, acid number 2.05 mg KOH /g, density 0.918 g/cm³, viscosity 33.6 mm²/s (40 °C). 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

For experiments, two types of oils (rapeseed and sunflower) were used. Transesterification of oil by methanol (molar ratio 1:6) was carried out with a basic catalyst (0.9 wt-% of potassium hydroxide to oil) in the batch reactor. The reaction temperature was 60 °C and the reaction time 90 min. The excess of catalyst was eliminated by gaseous carbon dioxide dosed into the reaction mixture after transesterification. Then the excess methanol was evaporated. The exact procedure is described in Czech patent [14]. The RRM is formed after transesterification, neutralization of catalyst and demethanolization.

3.3 Description of experiments

At first, a sample of RRM was titrated by distilled water under turbidimetric control up to its maximum transmittance of 570 nm. The optimal amount of water needed, which is necessary for perfect and fast separation of GP from EP, was found [15].

Then a sample of RRM (22 – 24 g) was filled into a glass cuvette (optical path 2 cm) imbedded in the spectrometer (Spekol 11, Jena, BRD). The sample was stirred ca 10 min at a temperature of 30 °C and revolutions of the stirrer were 715 rpm (ω_A). A propeller stirrer (diameter 1 cm) was used and the number of revolutions of the stirrer was determined by a revolutions indicator (DZM-control, IKA, BRD). Then the aqueous solution of phosphoric acid (*acid*) was added (0.66 mol/l). The mixture was stirred to the constant value of absorbance. Then the stirrer was stopped and consequently sedimentation has started and took 20 minutes ($t_{sed A}$). After this sedimentation time, RRM was stirred again for two minutes ($t_{mix B}$) at an intensity of stirring 2160 rpm (ω_B). Then the stirrer was stopped again and consequently the separation of upper EP and lower GP has started.

After 30 minutes of separation, both phases were sampled for analyses (chap. 3.4). This is an example of experiment number 2. The conditions of all experiments carried out according to the statistic of design Plackett-Burman and twice reproduced are in Tab 2. The record of absorbance at 570 nm during experiment is depicted in Fig 2. The same statistic design of experiments was carried out for RRM prepared from the sunflower oil.

The settings of lower (-1) and upper (+1) limits of all independent variables are shown in Tab.1.

3.4 Analytical methods

All used analytical methods are described in [17].

4 Results and discussion

4.1 Resulting model

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

For rapeseed oil it holds:

$$Y_1 = 0.195 + 0.011 \cdot w \quad (0.974)$$

$$Y_2 = 0.484 - 0.484 \cdot acid \quad (0.891)$$

$$Y_3 = 18.59 - 0.73 \cdot w + 1.27 \cdot acid \quad (0.915)$$

$$Y_4 = 0.805 - 0.011 \cdot w \quad (0.982)$$

$$Y_5 = 0.4 + 0.07 \cdot w + 0.11 \cdot acid - 0.06 \cdot t_{mix B} \quad (0.908)$$

$$Y_6 = 179.6 - 43.4 \cdot acid + 33.6 \cdot \omega_A - 25.6 \cdot t_{mix A} - 47.3 \cdot t_{sed A} + 32.7 \cdot \omega_B \quad (0.966)$$

$$Y_7 = 0.357 - 0.059 \cdot w - 0.115 \cdot acid - 0.057 \cdot t_{mix A} - 0.091 \cdot t_{sed A} - 0.058 \cdot t_{mix B} \quad (0.962)$$

For sunflower oil it results:

$$Y_1 = 0.298 + 0.013 \cdot w \quad (0.863)$$

$$Y_2 = 0.761 - 0.761 \cdot acid \quad (0.949)$$

$$Y_3 = 17.70 - 0.64 \cdot w + 0.524 \cdot acid \quad (0.921)$$

$$Y_4 = 0.792 - 0.018 \cdot w \quad (0.863)$$

$$Y_5 = 0.46 + 0.05 \cdot w + 0.10 \cdot acid - 0.06 \cdot t_{mix B} \quad (0.804)$$

$$Y_6 = 155.2 - 10.6 \cdot w - 15.2 \cdot acid + 23.4 \cdot \omega_A - 12.7 \cdot t_{mix A} - 48.1 \cdot t_{sed A} + 21.3 \cdot \omega_B \quad (0.932)$$

$$Y_7 = 0.321 - 0.051 \cdot w - 0.113 \cdot acid - 0.038 \cdot t_{mix A} - 0.042 \cdot t_{sed A} - 0.032 \cdot t_{mix B} \quad (0.974)$$

4.2 Verification of the model

The founded model was verified by several independent experiments for both oils. In the mathematical model, there are seven equations and fourteen variables (seven independent and seven dependent). Therefore it is necessary to choose seven variables and to calculate the others from the model (Tab. 3). The equation for acid number (Y_5) was not considered because it is probably unreliable. Acid value has a big experimental error, because small differences in relatively small acid values (0.1-0.4 mg/g) are difficult to determine by visual determination of the equivalence point, see 3.4. After choosing and calculating all variables, the verification experiments were carried out and the predicted (calculated) and experimental values were compared (see Tab. 4). Good correspondence between values calculated from the model and values measured is shown except acid value, as expected. Nevertheless, it fulfils the Euro norm for FAME. Thus, the found linear statistic model is suitable to describe the sedimentation after alkaline methanolysis of rapeseed oil (RO) and sunflower oil (SO).

4.3 Discussion of results

The relative amounts of GP (Y_1) and EP (Y_4) depend only on the amount of added water. They increase, resp. decrease with increasing portion of water added into RRM during the separation, because water dilutes only in GP.

Amount of potassium carbonate (Y_2) in GP decreases with increasing concentration of added acid; because acid reacts with K_2CO_3 (carbon dioxide and water are formed).

Amount of soaps (Y_3) in GP decreases with increasing portion of water added (addition of water dilutes GP) and increases with increasing concentration of added acid.

Acid number (Y_5) of EP depends on three independent variables (w , $acid$ and $t_{mix B}$). Mostly, it increases with increasing concentration of acid. Addition of a phosphoric acid causes the neutralization of K_2CO_3 and soaps (CO_2 and free fatty acids are formed). Free fatty acids pass to EP and increase its acid number. The 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.

Concentration of potassium ions (Y_6) in EP increases with increasing intensity of first (ω_A) and second (ω_B) stirring. It decreases with increasing amount of acid, time of stirring A ($t_{mix A}$) and time of sedimentation A ($t_{sed A}$). Other independent variables are insignificant.

The increase of all significant independent variables decreases concentration of free glycerol (Y_7) in EP; these variables are: amount of water added, concentration of acid, time of stirring A and B, time of sedimentation A.

The concentrations of potassium ions and free glycerol in EF are relatively high, because samples for analyses were taken out after 30 minutes of sedimentation already (GP and EP were not yet separated perfectly).

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.

The relationship between dependent and independent variables of the model are similar for both types of oils; the differences are in the values of parameters β_i . The reason is that rapeseed oil and sunflower oil have different acid number and composition of triglycerides. The different acid number causes that different amount of catalyst for transesterification must be used.

5 Conclusions

The realized experiments show that the quality and quantity of ester and glycerol phases after transesterification depend on the chosen conditions of separation (amount of added water, concentration of acid, intensity and time of stirring, time of sedimentation, repeating of stirring). These dependences were mathematically expressed for two types of vegetable oil. The dependences are similar for rapeseed and sunflower oil. The found mathematical model allows calculating such conditions of separation, that the resulting biodiesel fulfils the quality requested by the European norm 14214:2003.

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Conflict of interest statement

The authors have no conflict of interest.

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Fig. 1: Transesterification of oil

Fig. 2: Time course of absorbance at 570 during the experiment described in 3.3

Fig. 1, Martin Hájek

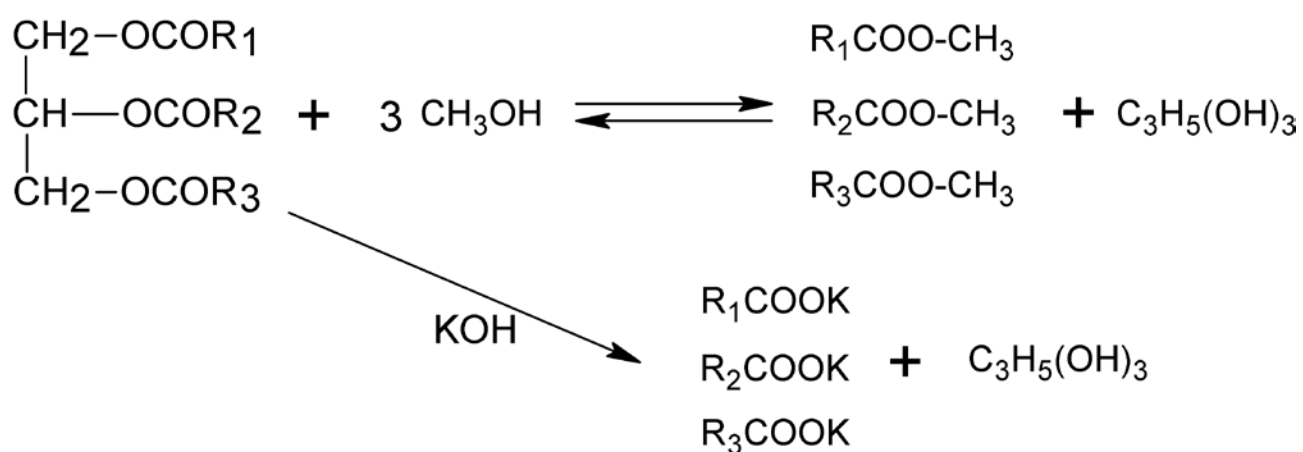


Fig. 2, Martin Hájek

