

Biodiesel preparation in batch emulgation reactor

Martin Hájek, František Skopal, Jiří Kwiecien

Department of Physical Chemistry, Faculty of Chemical Technology,
University of Pardubice, Pardubice, Czech Republic

Correspondence: *Martin Hájek*, Department of Physical Chemistry, Faculty of Chemical Technology, University of Pardubice, nám Čs. legií 565, 532 10 Pardubice, Czech Republic.

Phone: +420 466 037 053, Fax: +420 466 037 068; e-mail: martin.hajek2@upce.cz

Keywords: Biodiesel, rapeseed oil, emulgation, multivariable statistical evaluation, transesterification

Summary

The transesterification of vegetable oils (rapeseed oil was used) by low molecular alcohol is the most used method of biodiesel production. Since the reaction proceeds at the alcohol-oil interface, it is necessary to create a large interphase surface area using a special emulgation attachment. It was studied how the conditions (independent variables: molar ratio alcohol to oil, amount of used catalyst – KOH, time and temperature of reaction, intensity of stirring, revolution of emulgation attachment) affected the quality and quantity (dependent variables) of the ester phase – biodiesel. The amount of used catalyst was calculated with respect to the content of free fatty acid in oil. The statistical system of Plackett-Burman was used for experiment planning. Relationship between independent and dependent variables was found and described by multidimensional linear regression. Various statistical tests (principal component analysis, correlation matrix) were carried out, also.

1 Introduction

New types of alternative fuels to fossil fuels are being developed nowadays. These new fuels should be environmentally friendly, nontoxic, produced from renewable sources and their price must be competitive with petrol diesel. FAME (fatty acid methyl esters) is one of the alternatives; it is a mixture of alkyl-esters of higher fatty acids. The advantages of biodiesel are: Ecological fuel produced from many types of crude vegetable oils and animal fats, sources of oil can be grown in nearly all countries (therefore these countries are less dependent on crude-oil imports). Biodiesel does not contain polycyclic aromatic hydrocarbons, sulfur compounds and halogenides [1]. Biodiesel contains about 10 % of oxygen which supports burning, thus the emission of ash and smokiness are less in comparison with the combustion of fossil-oil diesel [2]. Biodiesel has better lubricity than does petrol diesel [3] but its emissions of nitrogen oxides are slightly higher [4].

The production of biodiesel can be catalyzed by homogeneous, contact or enzymatic catalyst. Homogeneous basically catalyzed transesterification is faster than the acidly catalyzed one and more often used in the chemical industry [5]. On the other hand, an acid catalyst does not cause the saponification of oil (side reaction) during the reaction [6]. The disadvantage of the homogeneous catalyst is that it cannot be reused after reaction. The advantage of a contact catalyst (e.g.: variable zeolites [7]) is its easy separation from the reaction mixture and its reusability. The other way of biodiesel production is enzymatic transesterification [8]. The production of biodiesel is possible without catalyst, also (alcohol in the supercritical state) [9].

Transesterification is affected by many parameters: molar ration alcohol to oil, time and temperature of reaction, amount of used catalyst, intensity of stirring. Oil and alcohol are immiscible, therefore a two phase system occurs during the reaction and the transesterification

proceeds on the phase boundary [10]. The creation of a large interfacial surface is necessary for the increasing of the transesterification speed (it is almost impossible without stirring). The ultrasound or mechanical emulgators are used for the creation of emulsion. Mechanical emulgators are stirrers with special attachments and very high revolutions of stirring.

In this paper, biodiesel is prepared by alkaline methanolysis of oil (potassium hydroxide as catalyst was used). The transesterification is stopped by the neutralization of the rest of the catalyst by gaseous carbon dioxide dosed into the reaction mixture (formed potassium carbonate has no catalyst effect) [11]. The distillation of methanol from the reaction mixture is the next step. The mixture is then spontaneously separated into two liquid phases – the ester phase (EP) and the glycerol phase (GP). To accelerate the separation, a suitable amount of demineralized water is added into the mixture [12]. The lighter upper ester phase contains the main product (biodiesel) and rest of unreacted vegetable oil. The heavier bottom glycerol phase contains: glycerol, potassium carbonate (the rest of the catalyst after neutralization), soaps and a small amount of methyl esters.

2 Theory

2.1 Multidimensional system

Transesterification of oils is a complicated process, which is affected by many parameters (independent variables - X_i): molar ratio methanol to oil, amount of used catalyst, time and temperature of reaction, time of emulgation before reaction, intensity of stirring (see Tab.1). The amount of catalyst was calculated according to (1) and it is used for transesterification of oil and neutralization of free fatty acids contained in the oil (determined as acid number - an_{VO}). Therefore, only the part of KOH which is used for catalyses was changed (α_{KOH}).

$$m_{KOH} = \frac{m_{VO}}{\xi_{KOH}} (\alpha_{KOH} + an_{VO} \cdot 10^{-3}) \quad (1)$$

Where: m_{KOH} is amount of used catalyst [g]; m_{VO} states the amount of vegetable oil [g]; ξ_{KOH} is the mass fraction of used KOH [-], α_{KOH} is the empiric coefficient which was changed during experiments and an_{VO} is the acid number of vegetable oil [mg KOH/g].

Following dependent variables (Y_i) were chosen to describe the influences of independent variables and to characterize EP optimally – Y_1 : yield of EP [g/g]; Y_2 : density at 15 °C [g/cm³]; Y_3 : kinematic viscosity at 40 °C [mm²/s]; Y_4 : conversion [wt-%]; Y_5 : acid number [mg KOH/g]; Y_6 : Conradson carbonization index (CCI) [wt-%] – it is the rest after total burning of biodiesel; Y_7 : flash point [°C].

Thus, it introduces a multidimensional system. To its description, statistical planning of experiments was based on the statistical design of Plackett-Burman [13], which is convenient for planning of multidimensional systems. The advantage of system is that minimum number of

experiments for description of 7 independent variables is 8 only. But on the other hand, higher number of experiments is advantage for better and more accurate statistical description.

Another method is factorial analyses; to description of 7 independent variables is necessary to perform 128 experiments (2^k ; k is number of independent variables).

2.2 Evaluation of experiments

After the selection of suitable independent variables, a simple empirical linear model (2) was suggested for the description of the dependent variables Y_i of biodiesel production (X_i are independent variables). Before statistical tests, all dependent variables have to be normalized from interval range -1 (bottom limit) to 1 (upper limit). The parameters (b_i) of the linear statistical model were determined by multidimensional linear regression in PC software QC Expert 2.5 (the least squares method was used). The statistic tests (heteroskedasticity, normality, influence points) were calculated, too.

$$Y_i = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_5X_5 + b_6X_6 + b_7X_7 \quad (2)$$

3 Material and methods

3.1 Chemicals

Rapeseed oil: firm RPN Slatiňany, Czech Republic, cold pressed, acid number 1.52 mg KOH /g, density 0.920 g/cm³ (25 °C), kinematic viscosity 36.4 mm²/s (40 °C), fatty acid composition: palmitic acid 3 wt-%, stearic acid 1 wt-%, oleic acid 64 wt-%, linoleic acid 22 wt-%, linolenic acid 8 wt-%. Potassium hydroxide pure (solid 90 wt-%). Methanol (technical). all Lach-Ner, Czech Republic. Demineralized water.

3.2 Preparation of samples

The experiments of biodiesel production were carried out in apparatus (see Fig. 1). A rustless batch reactor (volume 2 l) with stirrer and special emulgation attachment (digital Ultra Turrax[®] T25, IKA[®], Germany) was the basis of apparatus. This emulgation attachment (range: 3 400 – 24 000 rpm) created a hydrodynamic dispersion of reaction mixture. The cooler was used during transesterification, because temperature of RRM was close to the boiling point of methanol. Temperature in the reactor was set by thermostat and controlled by resistance thermometer (Pt 100).

The constant amount of rapeseed oil (880±1 g) was used for all experiments. After pouring of oil into the reactor, the emulgation attachment was switched on (22 000 rpm, ω_{emulg}) and emulgation took 25 minutes (t_{emulg}) at reaction temperature 40.7 °C (T_r). Then, the methanolic solution of potassium hydroxide (preheated to reaction temperature) was quickly added to reactor and transesterification started (amount of catalyst was calculated according (1)). After 25 minutes of the reaction (t_r), the emulgation was stopped and the reaction mixture was neutralized with gaseous carbon dioxide (ca. 1 l at 25 °C and atmospheric pressure) [11]. The distillation of methanol

(temperature 60 °C and pressure 2-3 kPa) from the neutralized reaction mixture took 30 minutes. Then, the mixture was cooled to temperature 30 °C and optimum amount of water (19 ml) was added for better and faster separation [12]. After next 15 minutes of stirring, the mixture was poured into the separation funnel and separation of ester and glycerol phases started. After perfect separation of reaction mixture to upper EP and lower GP, both phases were used for analyses (see chap. 3.4). Description is valid for experiment No.1; the others were carried out according to statistic design Plackett-Burman (see Tab.2) and reproduced.

3.3 Analytical methods

The yield of EP was defined and determined as weights ratio of EP (consists of esters and unreacted VO) to VO. The density of EP was determined by pycnometric method and kinematic viscosity by Ubelohde's viscosimeter. The CCI and flash point were determined according to method described in the EN 14214.

3.3.1 Determination of conversion

The conversion of the reaction is defined as ratio of peak area of esters in EP to standard (pure ester). The amount of esters was determined directly, without pretreatment by gas chromatograph (CHROM 5, Laboratorní přístroje Praha, Czech Republic) with a column 1200x3 mm filled with neopentylglycolamberat. The carrier gas was helium with a total flow of 36 ml/min. The injection dose was 1 µl and the peak of methylesters was detected by a flame-ionization detector. The temperatures of the injection, column and detector were 295, 218 and 180 °C, respectively [14].

3.3.2 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) with visual detection of equivalence point. The used method is described in EN 14214. The neutralization of rest of catalyst by CO₂ ensures that acid number is less than 0.5 mg KOH/g (under the EU norm). Acid number is a complementary value.

3.3.3 Determination of GP

In GP, glycerol was determined by iodometric titration. The determination of soaps and potash was carried out within one acidimetric titration by hydrochloride acid; the amount of water was determined by Karl-Fisher titration and methanol by GC [14].

4 Results and discussion

4.1 Resulting model

After the statistical evaluation, the relation between independent and dependent variables were found. Some of the independent variables were found unsubstantial during statistic testing; therefore they are not stated in the equations: e.g. emulgation before reaction (t_{emul}) and the stirring ($stir.$) do not affect any of dependent variables.

Dependent variables (Y_i) are defined in the chapter 2.1. The regression coefficients (R^2) are in the parenthesis.

$$Y_1 \text{ (yield of EP)} = 0.962 + 0.012 \cdot m.r. - 0.014 \cdot \alpha_{KOH} + 0.015 \cdot \omega_{emulg} \quad (0.967)$$

$$Y_2 \text{ (density)} = 0.878$$

$$Y_3 \text{ (viscosity)} = 4.82 - 0.15 \cdot m.r. - 0.09 \cdot \alpha_{KOH} + 0.06 \cdot \omega_{emulg} - 0.06 \cdot T_R - 0.12 \cdot t_R \quad (0.993)$$

$$Y_4 \text{ (conversion)} = 97.5 + 1.1 \cdot m.r. + 1.5 \cdot \alpha_{KOH} + 1.0 \cdot T_R + 1.4 \cdot t_R \quad (0.972) \quad (A)$$

$$Y_5 \text{ (acid number)} = 0.14$$

$$Y_6 \text{ (CCI)} = 0.031 - 0.011 \cdot \alpha_{KOH} - 0.015 \cdot T_R - 0.01 \cdot t_R \quad (0.967)$$

$$Y_7 \text{ (flash point)} = 140$$

Free glycerol and potassium ions were not determined, because their amounts depend on the separation process (not on the transesterification reaction). The water content was determined ca. 650 ppm in all experiments, because water was added to improve the separation. Therefore, the centrifugation and drying of EP is necessary to ensure that these three parameters fulfill the EN 14214. The content of methanol was measured under 0.01 wt-% in some experiments, which is in accordance with flash point.

The composition of glycerol phase (side product) was determined also in all experiments and it was approximately similar – glycerol: ca 58 wt-%; soaps: ca 18 wt-%; potassium carbonate: ca 2 wt-%, potassium hydrogen carbonate: ca 2 wt-%; water 13 wt-%; methanol 2 wt-% and the rest is ester. Small amounts of esters remain in the GP, which was published in [15] also.

4.2 Verification of the model

The model was verified by several independent experiments. It consists of four equations (A) with nine variables (four independent and five dependent); therefore five variables must be chosen and the others can be then calculated (Tab.3). Then the verification experiment was carried out (chapter 3.2) and the predicted (calculated) and experimental values of chosen variables were compared (see Tab.4). Good correspondence between calculated values (from the model) and measured values is shown. The determined linear model is thus suitable to describe this type of biodiesel preparation.

The content of glycerides was determined in the verification experiment and fills the norm – monoglycerides: 0.39 wt-%; diglycerides: 0.17 wt-% and triglycerides 0.09 wt-% (determined by GC method according to EN 14105 at Shimadzu GC-2010).

4.3 Analysis of results

Models for density (Y_2), acid number (Y_5) and flash point (Y_7) were found unsubstantial; therefore any independent variables (within changing bounds) have no influence on these three dependent variables. But fill the EN norm in all cases. The constant acid number is ensured by neutralization of catalyst by carbon dioxide (see 3.3.2) and the flash point depends on conditions of demethanolisation, which were constant in all experiments.

The yield of EP (Y_1) increases with increasing molar ratio of methanol to oil and decreases with decreasing amounts of catalyst and intensity of emulgation.

The kinematics viscosity EP (Y_3) increases with increasing molar ratio of methanol to oil and intensity of emulgation. It decreases with decreasing amounts of catalyst, temperature and time of reaction.

Conversion of oil to esters (Y_4) increases with increasing molar ratio of methanol to oil and reaction time, whereas decreases with decreasing amount of catalyst and reaction temperature.

CCI (Y_6) depends on three independent variables (molar ratio of methanol to oil, temperature and time of reaction) and decreases with increasing all of them.

The principal component analysis (PCA) and the correlation matrix were carried out in order to find out the relationship between dependent variables. The result of PCA is depicted in Fig. 2. The parameters: viscosity, density and CCI are in one group and they are in opposition to conversion, i.e. the higher conversion of oil to biodiesel means the lower viscosity, density and CCI of biodiesel. The explanation of dependences: Higher molar ratio of methanol to oil and higher reaction temperature shift the chemical equilibrium to the product (esters). The longer time of reaction, the more product forms. The usage of catalyst is necessary at these conditions (temperature, pressure) and increasing of the emulgation intensity means larger reaction surface, therefore faster reaction. More esters in the final product mean higher conversion, and therefore less viscosity and CCI (higher viscosity and CCI is caused by oil).

There is no correlation between conversion vs. yield, vs. acid number and vs. flash point. The reason of no correlation of conversion vs. yield is that the conversion depends on transesterification conditions, contrary to yield which depends also on separation conditions (part of EP remains in GP).

The correlation matrix proved the found dependences from PCA, e.g.: direct dependences of density vs. viscosity and density vs. CCI and indirect dependence between density and conversion.

5 Conclusions

The basic catalyzed (KOH) transesterification of rapeseed oil is affected by interfacial surface area of reactants. The mathematical model describing the process of biodiesel preparation was created. The found mathematical model allows calculating such conditions of preparation (molar ratio alcohol to oil, amount of used catalyst, time and temperature of reaction, etc.), so that the produced biodiesel fulfils the quality requested by the norm EN 14214:2003 except concentration of potassium, free glycerol and water. Fulfillment of these three parameters requests centrifugation and drying of the EP.

Use of this emulgation attachment shortens the reaction time by half and consumption of methanol by 10 % in comparison with biodiesel preparation without an emulgation attachment.

Acknowledgements

This work has been funded by the research project MŠMT 0021627502 of the Czech Ministry of Youth and Sport.

Conflict of interest statement

The authors have no conflict of interest.

Reference

- [1] A. K. Agarwal: Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. *Prog Energy Combust Sci.* 2007, **33**, 233-271.
- [2] Ch.-Y. Lin, S.-A. Lin: Effects of emulsification variables on fuel properties of two- and three-phase biodiesel emulsions. *Fuel.* 2007, **86**, 210–217.
- [3] M. Hess, M. Haas, T. Foglia, W. Marmer: *Energy & Fuels.* 2005, **19**, 1749–1754.
- [4] D. P. Geller, J. W. Goodrum: Effects of specific fatty acid methyl esters on diesel fuel lubricit. *Fuel.* 2004, **83**, 2351-2356.
- [5] F. Ma, M. A. Hanna: Biodiesel production: a review. *Bioresour Technol.* 1999, **70**, 1–15.
- [6] H. D. Hanh, N. The Dong, et al: Methanolysis of triolein by low frequency ultrasonic irradiation. *Energy Convers Manage.* 2008, **49**, 276-280.
- [7] J.L. Shumaker et al.: Biodiesel synthesis using calcined layered double hydroxide catalysts. *Appl Catal, B.* 2008, **82**, 120-130.
- [8] F. Yagiz, D. Kazan, A. N. Akin: Biodiesel production from waste oils by using lipase immobilized on hydrotalcite and zeolites. *Chem Eng J.* 2007, **134**, 262-267.
- [9] H. Imahara, E. Minami, S. Hari, S. Saka: Thermal stability of biodiesel in supercritical methanol. *Fuel.* 2008, **87**, 1-6.

- [10] S. Stamenkovic, M.L. Lazić, Z.B. Todorović: The effect of agitation intensity on alkali-catalyzed methanolysis of sunflower oil. *Bioresour Technol.* 2007, **98**, 2688–2699.
- [11] F. Skopal, K. Komers, J. Machek, I. Koropečký: The Czech Republic patent 289 417 (2001)
- [12] M. Hájek, F. Skopal, J. Machek: Simplification of Separation of Reaction Mixture after Transesterification of Vegetable Oil. *Eur J Lipid Sci Technol.* 2008, **110**, 347-350.
- [13] R.L. Plackett, J.P. Buman: The Design of Optimum Multifactorial Experiments. *Biometric.* 1946, **33**, 305–325.
- [14] Komers K., Stloukal R., Machek J., Skopal F.: Biodiesel Fuel from Rape Seed Oil, Methanol and KOH. Analytical Methods in Research and Production. *Fett/Lipid.* 1998, **100**, 507-512.
- [15] G. Vicente, M. Martínez, J. Aracil: Integrated biodiesel production: a comparison of different homogeneous catalysts systems. *Bioresour Technol.* 2004, **92** 297–305

Fig 1: Apparatus to preparation of biodiesel

Fig 2: Principal component analysis of dependent variables