Combined effect of water and KOH on rapeseed oil methanolysis

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Summary

This paper deals with the effect of water and catalyst (KOH) amount on the quantity and quality of transesterification products of rapeseed oil by methanol, the methyl ester phase (i.e. yield, conversion), and the side-product, the glycerol phase (i.e. density, viscosity, the mass fraction of glycerol, esters, soaps). The dependencies were described by statistical models. The transesterification was carried out at constant reaction conditions (90 min reaction time, 400 rpm, 60 °C). Twelve experiments with the independent factors, amount of potassium hydroxide (0.65–0.9 mg per gram of oil) and total amount of water (0.24–1.42 mg per gram of oil) naturally present in the reaction components or formed by the neutralization reaction of free fatty acids and of added water. The data were analyzed by linear regression with respect to regression triplet (complex critical analysis of the model, data and regression method). The analysis resulted in a set of linear and/or quadratic models consisting of statistically proven terms at a statistical significance level of 0.05 and demonstrated that ester in the glycerol phase increases with increasing amount of soaps.

Keywords:

    biodiesel, statistical analysis, water, KOH, saponification

1 Introduction

Biodiesel is a term for a type of biofuel based on vegetable oils and animal fats. To improve the rheological and physical properties of biodiesel, the oils must be transformed by transesterification. In the transesterification reaction, glycerol in the oil molecule is substituted by a short-chain alcohol such as methanol and ethanol. To enhance the reaction rate, a catalyst or extra energy are needed. The most popular catalysis is via alkali hydroxides. The use of these catalysts has many advantages such as a low price and short reaction time, but it has serious limitations, too (Mittelbach and Remschmidt, 2004). The transesterification reaction can be slower or even stopped by the presence of water (Freedman et al., 1984). If the oil contains a significant content of free fatty acids, the relevant part of the catalyst is consumed at the start of the reaction and additional amounts of the catalyst are necessary to reach a desirable reaction rate and yield. Ma et al. (1998) investigated the different effects on the transesterification reaction and recommended to keep the water content in the oil below 0.06 wt% or to use another technology. Kusdiana and Saka (2004) compared the effect of water on the yield for three methods: acid-catalysed, alkaline-catalysed and supercritical methanol. The acid-catalyzed method was the most influenced by water and the supercritical methanol method was the most tolerant of water. Such a result is probably due to the different reaction mechanisms and the excess of methanol used in the supercritical methanol method (seven times more methanol than in other methods compared by Kusdiana and Saka (2004)).

The influence of water on transesterification in kinetical studies has been included only in a few models. For example the model by Komers et al. (2002) for room temperatures proposes a fast equilibrium among methanol, KOH, methoxide and water, and a steady state for methoxide and other intermediates. This model is able to describe almost 80% of the

variability in the experimental data. Another model (Bikou et al., 1999) was derived from measurements of ethanolysis of cotton seed oil at the boiling point of ethanol and third and first order kinetics were assumed for ethanol for the others components, respectively. The concentration of water was not included in the model, but the effect of the water is demonstrated by the trends of the obtained constants. Bambase et al. (2007), studied the NaOH catalysis in sunflower oil methanolysis and described the effects of reaction temperature, amount of catalyst, and methanol to oil molar ratio, but not the effect of water. The kinetics models of Vicente et al. (2005) and Stamenković et al. (2007) tried to include the effect of agitation and temperature dependences of kinetic constants in different stages of the reaction. The first stage is a mass transfer controlled reaction and the second is considered as a homogeneous reaction. The work by Slinn and Kendall (2009) dealt with the time course of the conversion. The reaction kinetic is influenced by rheology characteristics in the reactor and the interphase phenomena during the reaction.

The developed kinetics models pay only limited attention to water content in the reaction mixture, probably because of the complicated quantitative description of intermediates such as hydroxide and methoxide ions. In this study, we tested the effects of water and catalyst only by means of their content in the reaction mixture at chosen conditions of methanolysis of rapeseed oil. Therefore, no kinetic models, equilibrium constants and concentrations of intermediates were needed. This work extends our previous work (Kwiecien et al., 2009) dealing with the effect of the oleic acid (formed neutralisation water respectively) artificially added into the oil by a statistical enumeration of water effect and also it is extended by the effect of the catalyst amount.

2 Materials and Methods

The principle of alkali catalyzed methanolysis lies in the generation of methoxide ions by the reaction (1). These ions can react with glycerides to form methyl esters (ME).

$$OH^- + CH_3OH \underset{\leftarrow}{\rightarrow} CH_3O^- + H_2O \tag{1}$$

A part of the hydroxide ions on the left side of the equilibrium (1), that simultaneously cause the side saponification reaction and so decreases the yield of ME (biodiesel). Moreover, the created soaps make the separation of the final heterogeneous mixture to biodiesel and glycerol phases problematic. In this work, we alternated the concentration of potassium hydroxide and water in the initial reaction mixture to affect the result of the transesterification. The remaining reaction conditions were constant.

The first independent variable, the initial amount of potassium hydroxide α is defined as the starting relative mass of potassium hydroxide present in the reaction mixture, expressed as a mass of KOH lowered by the mass being saponificated by neutralisation of free fatty acids (FFA), (2). Neutralisation of free fatty acids (FFA) in the oil by KOH is considered as very fast.

$$\alpha = \frac{m_{KOH}}{m_o} - \frac{an}{1000} \tag{2}$$

where m_{KOH} is the weight of potassium hydroxide (100 %) in grams, m_o is the weight of oil in grams and an is the acid number of the oil in mg KOH/g of oil.

The second independent variable, the initial amount of water β is the starting relative mass of water in the whole reaction mixture per gram of oil, expressed as the sum of water masses present in the reaction components and formed by neutralisation reaction of FFA.

$$\beta = \frac{\sum m_{H_2O,i}}{m_o} \tag{3}$$

The contributions of water in each component $m_{H_2O,i}$ are stated in Tab. 1. The water content in the reaction components was determined by Karl-Fischer titration. The table shows, that the main part of the water amount was artificially added into the methanol.

The chosen intervals of these two variables should extend the reaction conditions normally used according to Skopal et al. (2001) and also cover the calculated values in the previous work of Kwiecien et al. (2009).

2.1 Chemicals and raw materials

Cold pressed rapeseed oil was kindly provided by RPN Slatiňany, CZ. The oil had an acid number of 0.89 mg KOH/g and a water content of 0.05 %. Potassium hydroxide was from Lachema Neratovice, CZ (84 wt% purity, 16% water, no carbonate content). Methanol was of technical grade with a water content of 0.1% (Lach-ner, CZ). Glycerol p. a. was from Lach-Ner, CZ. Deionized water was obtained through reverse osmosis (AQUL 21, Aqual). Grocery store-grade carbon dioxide was from Linde Gas, CZ.

2.2 Transesterification procedures

The 1-L round-bottomed glass batch reactor, equipped with a Heidolph® stirrer and a thermostat attachment, was charged with ~450 g of rapeseed oil and preheated to 60 °C. A methanolic solution of KOH was prepared by dissolving of the calculated amount of KOH in methanol (6:1 molar ratio between methanol and oil) and then the chosen mass of water was added to this solution according to the experimental plan (Tab. 2). The methanolic solution

of KOH was quickly added to the vigorously stirred oil (revolution speed 400 rpm) and the reaction mixture was stirred for 90 min. The reaction was stopped by gaseous carbon dioxide blown into the reaction mixture (Skopal et al., 2001) and the catalyst was neutralized with potassium hydrogen carbonate. Excess methanol was distilled off under lowered pressure (3–4 kPa), for 45 min at 60 °C. Since Hájek et al. (2008) found that a small admixture of water accelerated the separation the of ester phase (EP) from the GP, 10 g of water was added and the reaction mixture was cooled to ambient temperature and poured into a separatory funnel. Completely separated phases were analyzed.

2.3 Analytical methods

The water content was determined by volumetric Karl Fischer titration with biamperometric end-point indication using an automatic titrator 736 GP Titrino®, Metrohm, Switzerland. The glyceride content was determined by the HPLC isocratic analysis as described by Komers et al. (1998). The glycerol content in the glycerol phase (GP) was determined by HPLC equipped with a LCP 4000.1 pump, a Separon TM SGX column with a particle size of 7 µm, and a refractometric detector (RIDK 102, Laboratorní přístroje Praha). The mobile phase was deionized water at a flow rate of 0.5 ml/min. The glycerol mass fraction was calculated by a calibration curve. The density of the glycerol phase was measured pycnometrically and the viscosity at 40 °C was measured with an Ostwald's viscosimeter. Mass fractions of potassium carbonate, potassium hydrogen carbonate and soaps in GP were determined by acidometric titration with potentiometric indication and volumetric determination of carbon dioxide, according to Kwiecien et al. (2009).

2.4 Statistical analysis

Experiments were carried out on the basis of two independent factors (α, β) and statistic linear models were proposed. However, in some cases, the statistical analysis indicated the multivariate linear model as insufficient, so then a multivariate quadratic model was used. The multivariate linear model has the form (4) and the quadratic polynomial model with two variables the form (5)

$$Y = p_0 + p_1 \cdot \alpha + p_2 \cdot \beta \tag{4}$$

$$Y = p_0 + p_1 \cdot \alpha + p_2 \cdot \beta + p_3 \cdot \alpha \cdot \beta + p_4 \cdot \alpha^2 + p_5 \cdot \beta^2 \tag{5}$$

where Y is the dependent variable, e. g. the oil conversion, the yield of EP, the density of the glycerol phase; symbols p_i represent model parameters.

The regression and statistical testing were performed with respect to the regression triplet (Meloun et al., 2002) at a statistical significance level of 0.05. The regression triplet ensures reliable unbiased parameter estimates, and consists of the examination of the data, model and the regression method quality. It is based on series of various statistical tests: significance test of parameter estimates (Student t-test), residual analysis – detection of influential points, residual standard deviation, residual skewness, residual kurtosis, trends in residuals; homoskedascity of errors, normality of random errors distribution and multicollinearity. Akaike information criterion (AIC) and mean error of prediction (MEP) were used to distinguish among several models and to choose the best one.

Resulting models contain only statistically proven terms (significant parameters), and the least square method was used for finding the parameters values.

3 Results and discussion

Three parameters (dependent variables), the EP yield, oil conversion and water content were measured and the quality of the glycerol phase (GP) was described by following properties: density, viscosity, mass fractions of glycerol, potassium hydrogen carbonate, potassium carbonate, soaps and ME. Experimental data are shown in Tab. 3. Statistical models for each dependent variable are derived and the values of some parameters are discussed below. In general, if a parameter in the given linear equation (except of constant term) is negative, then the increasing factor (α, β) causes a decreasing of the dependent variable Y and vice versa. To show the significance of the individual parameters, standard deviation of each model parameter is stated at the parameter value in the equations (6) –(17).

3.1 Models of the EP yield

Biodiesel (i. e. the EP) yield is one of the economic parameters in biodiesel production, and should be as high as possible. In the case of the multivariate linear model, all terms were proved as statistically significant with a regression coefficient $R^2 = 0.9361$.

$$\text{yield[\%]} = (105.7 \pm 1.5) - (1272 \pm 175.4) \cdot \alpha - (298.5 \pm 41.4) \cdot \beta \tag{6}$$

The formula (6) expresses and quantifies the negative impact of both factors on biodiesel yield. The value of the constant term is slightly over 100%. The extrapolation of $\alpha = \beta = 0$ gives the theoretical estimate of the yield of biodiesel (105.7 %), without the saponification effect. (From material balances, the calculated value is 100.3 %).

Statistical analysis of residues of the measured data indicated an unwanted trend in residues caused by the using of the linear model. To describe the data better, the multivariate polynomial model was used. Only three terms were identified as significant (7).

$$\text{yield[\%]} = (105.3 \pm 1.632) - (1191 \pm 206.5) \cdot \alpha - (41220 \pm 7164) \cdot \alpha \cdot \beta \tag{7}$$

This model predicts the synergistic effect of water and KOH on the biodiesel yield. Although the regression coefficient ($R^2 = 0.90533$) is lower than in the case of the linear model, according to the comparison of MEP values and AIC from linear and quadratic model, this quadratic model is more suitable for the purpose of predicting values. Both models are statistically significant.

3.2 Model of oil conversion to the ME

The content of ME in biodiesel is one parameter of the norm EN 14214:2003 as the biodiesel quality indicator.

The ME content was determined by measuring the sum of mono-,di- and triglycerides, expressed as an oil conversion value. The linear model of conversion (8) was refused because of the poor correlation coefficient ($R^2 = 0.7846$) and other statistical tests (trend in residuals, number of outlying data). It is obvious, that the degree of conversion of the oil to ME depends very much on the concentration of the water in the reaction mixture, the effect of the catalyst amount is marginalized in the linear model.

$$\text{conversion}\,[\%] = (99.87 \pm 0.45) - (348.6 \pm 57.8) \cdot \beta \qquad (8)$$

Better statistical results (MEP, AIC, R^2) were obtained by multivariate polynomial modelling. The regression coefficient ($R^2 = 0.9590$) covers almost 96 % of the variability of the experimental data. Significant terms are presented in the equation (9). From the formula (9) it can be derived, that a variation of the amount of catalyst used can slightly correct the negative effect of water.

$$\text{conversion}\,[\%] = (97.76 \pm 0.30) + (41660 \pm 10080) \cdot \alpha \cdot \beta - (40340 \pm 4542) \cdot \beta^2 \quad (9)$$

According to our previous work (Kwiecien et al., 2009), no conversion decrease was observed, whereas these two models for the conversion express the opposite. That could

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mean that the simulation of higher acidity (i.e. high acid number of oil) connected with additional water formation (by neutralization) and direct addition of water into the reaction mixture behaves differently.

3.3 Model of water content in the EP

The water was added not only into the initial reaction mixture as variable β, but for better separation of phases, again after the methanol removal. Such addition can affect the water content in both phases (the EP and the GP), nevertheless, the corresponding model for water content in the EP was found (10). The regression coefficient was very low (R^2 = 0.4533) because of data dispersion and the analysis of residues predicts no possibility to obtain a more sophisticated model. Only the variable β is significant for this model, the significance of the α was not confirmed.

$$\text{water [ppm]} = (575.8 \pm 31.2) + (10520 \pm 3852) \cdot \beta \tag{10}$$

3.4 Model of density of the GP

The linear model is sufficient to describe the effect of the water and catalyst on the density of the glycerol phase. All three parameters are significant and the model (11) has a correlation coefficient $R^2 = 0.9393$. Both studied effects decreased the density of the glycerol phase, resulting in slower gravity-driven separation.

$$\text{GP density [g/cm}^3] = (1.237 \pm 0.015) - (11.35 \pm 1.79) \cdot \alpha - (4.598 \pm 0.4495) \cdot \beta \tag{11}$$

3.5 Model of glycerol mass fraction in the GP

As in section 3.4, a linear model for the glycerol mass fraction was found. Similar conclusions can be stated for this model (12), namely that the water content and the amount of KOH decrease the glycerol mass fraction in the glycerol phase The correlation coefficient for this model is $R^2 = 0.8568$.

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$$\text{glycerol}[\%] = (85.18 \pm 5.27) - (3117 \pm 648.3) \cdot \alpha - (1047 \pm 166.1) \cdot \beta \qquad (12)$$

Regarding the constant terms in equations (11) and (12) the following comments can be made. As stated previously, water and KOH cause a saponification reaction. In the absence of saponification, the constant term in the equation (12) gives the mass fraction of glycerol. The remainder would be mass fractions of water and inorganic salts. The experimentally determined density of the solution of glycerol and water (without salts) with the mass fraction of glycerol 85 % at 25 °C was 1.219 g/cm^3. The constant term in the equation (11) 1.237 g/cm^3 is close to this number.

3.6 Model of logarithm of kinematic viscosity of the GP

The experimental dependence of viscosity data of the glycerol phase on α and β at 40 °C has evidently a non-linear character. After a logarithmic transformation of the viscosity data, the dependence of the natural logarithm of viscosity vs. α, β, suitable for linear regression was obtained. The obtained model (13) has a correlation coefficient of R^2 = 0.9480. The growing kinematic viscosity of the glycerol phase has, according to our observation, a negative effect on phases separation.

$$\ln(\text{viscosity}\,[\,\text{mm}^2/\text{s}]) = (2.28 \pm 0.538) + (401.6 \pm 66.2) \cdot \alpha + (206.7 \pm 17) \cdot \beta \qquad (13)$$

3.7 Models of KHCO$_3$ and K$_2$CO$_3$ mass fractions in the GP

KHCO$_3$ and K$_2$CO$_3$ rise from neutralisation of the unreacted KOH with CO$_2$ after the methanolysis. The regression triplet revealed that linear model for data of mass fraction of KHCO$_3$ in the glycerol phase is not suitable at all. In the quadratic model, all terms containing the variable α were found as statistically insignificant. The final quadratic model is the equation (14) with correlation coefficient $R^2 = 0.9694$.

$$\text{KHCO}_3\,[\%] = (2.942 \pm 0.171) + (14980 \pm 3169) \cdot \beta^2 - (398.6 \pm 51) \cdot \beta \qquad (14)$$

Similarly to potassium hydrogen carbonate, the mass fraction of potassium carbonate in the glycerol phase depends only on the amount of water in the reaction mixture. The linear model for the mass fraction of K_2CO_3 with $R^2 = 0.8997$ was found (15).

$$K_2CO_3 \, [\%] = (1.77 \pm 0.10) - (123.9 \pm 13.1) \cdot \beta \tag{15}$$

$KHCO_3$ and K_2CO_3 are decreasing with an increasing amount of water. Their decline (which is steeper than in the case of glycerol) is caused by enhanced saponification of glycerides. Therefore, the mass fraction of soaps must grow.

3.8 Model of soap mass fraction in the GP

Analysis of the mass fraction of soaps (S) data gives the linear model (16), $R^2 = 0.9651$. With regard to the nonsignificance of the constant term, the saponification reaction proceeds only in the presence of water and KOH.

$$S \, [\text{wt.\%}] = (1534 \pm 52) \cdot \alpha + (803.6 \pm 50) \cdot \beta \tag{16}$$

3.9 Model of ester mass fraction in the GP

In the GP, there is, analogous to soaps, a variable amount of the ME. The linear model (17) has only two terms, without a constant, $R^2 = 0.9717$.

$$ME \, [\%] = (2082 \pm 33.6) \cdot \alpha + (143.6 \pm 33.4) \cdot \beta \tag{17}$$

The comparison of the previous two models (16) and (17) shows that the mass fraction of the ME in the GP depends on the mass fraction of soaps in the GP, because both components have positive coefficients in the relevant models and the constant terms are statistically zero. A strong correlation between concentrations of these two substances was found.

4 Conclusions

We have quantified the effect of water content and catalyst amount on the final product of basically (KOH) catalyzed methanolysis of rapeseed oil, at constant reaction conditions, and we obtained simple models consisting mostly of three terms. Therefore, we could avoid a much more complex reaction kinetics model necessary for the description of the influence of these two factors. The relevance of the models is limited to KOH concentrations between 0.65 to 0.9 mg/g of oil and a water content ranging from 0.24 to 1.42 mg/g of oil. Although the statistical models are not recommended to extrapolate in general, it was shown, that some constant terms such as mass fraction of glycerol or their absence (mass fraction of soap) have a meaningful physical explanation.

Nomenclature

AIC	Akaike information criterion
an	acid number
EP	ester phase
FFA	free fatty acid
GP	glycerol phase
ME	methyl ester
MEP	mean error of prediction
m_i	mass of the i
m_o	mass of rapeseed oil

p_i	parameter in equation
R^2	regression coefficient
S	soaps
Y	dependent variable
α	independent variable, amount of KOH
β	independent variable, amount of water

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