Ethanolysis of rapeseed oil – distribution of ethyl esters, glycerides and glycerol in ester and glycerol phase

Michal Černoch, Martin Hájek*, František Skopal

Martin Hájek, Department of Physical Chemistry, Faculty of Chemical Technology,

University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic,

martin.hajek2@upce.cz

Keywords: biodiesel, transesterification, ethanolysis, separation, distribution

* corresponding author

Abstract

The distribution of ethyl esters, triglycerides, diglycerides, monoglycerides and glycerol between the ester and glycerol phase was investigated after the ethanolysis of rapeseed oil at various reaction conditions. The determination of these substances in the ester and glycerol phases was carried out by the GC method. The amount of ethyl esters in the glycerol phase was unexpectedly high and therefore the possibility of the reduction of this amount was investigated.

The distribution coefficients and the weight distributions of each investigated substance were calculated and compared mutually. The distribution coefficients between the ester and glycerol phase increase in this sequence: glycerol, monoglycerides, diglycerides, ethyl esters and triglycerides. Soaps and monoglycerides in the reaction mixture cause a worse separation of ethyl esters from the reaction mixture. The existence of a non-separable reaction mixture was observed also, and its composition was determined.

1 Introduction

Recently, the world importance of biodiesel production significantly increased. The admixture of fatty acid methyl esters (FAME) into fossil diesel fuel is one of the ways how to fulfil the mandatory biofuels share in the total motor fuels market in EU countries [EU, 2009]

Using of fatty acid ethyl esters (FAEE) is also possible because it has some advantages: ethanol is less toxic in comparison with methanol and can be produced from renewable materials and FAEE has higher combustion heat in comparison with FAME [Knothe, 2008]. On the other hand, ethanol has lower transesterification reactivity in comparison with methanol [Issariyakul et al., 2007] caused by longer carbon chain [Nimcevic et al., 2000].

The biodiesel production proceeds by transesterification of vegetable oils or animal fats. Alkaline, acid or enzymatic catalyses or non-catalyst processes are possible [Warabi et al.,

2004]. But the alkaline catalysis is the most effective and widely used method [Meneghetti et al., 2006]. The forming of the by-product, soaps, is the disadvantage of using of NaOH or KOH catalysts. The heterogeneous reaction mixture after transesterification contains many substances: fatty acid methyl or ethyl esters, triglycerides, diglycerides, monoglycerides, glycerol, methanol or ethanol, soaps and small amounts of other substances [Mittelbach and Remschmidt, 2004]. The subsequent separation of the reaction mixture by sedimentation into ester and glycerol phases is an important step of the biodiesel production process.

Papers concerning the biodiesel production are focused on the transesterification process and its improvement. The microwave [Azcan et al., 2008], ultrasound assistance [Santos et al., 2009] and hydrodynamic cavitation [Ji et al., 2006] represent improving methods, new kinetic models are searched [Stamenkovic et al., 2008], theoretical studies [Asakuma et al., 2009] and various optimization methods are used. But only few papers inform about the important separation of the phases after transesterification and distribution of substances between them [Di Felice et al., 2008], [Zhou and Boocock, 2006a].

In this work, the distribution of ethyl esters (EE) and triglycerides (TG), diglycerides (DG), monoglycerides (MG) and glycerol (G) between ester phase (EP) and glycerol phase (GP) after the ethanolysis of rapeseed oil was observed. The ethanolysis was carried out with KOH catalyst, CO_2 was used to stop the reaction, excess of ethanol was evaporated and reaction mixture was separated by sedimentation in the gravitational field.

2 Materials and methods

2.1 Apparatus

The double-walled laboratory reactor IKA® LR 2000 with volume of 2 litres was used. A toothed disc stirrer served as the main stirrer. High-performance disperser T-25 digital ULTRA-TURRAX® with maximal speed of 24000 rpm was installed into the reactor. The reactor was joined to thermostat and to the vacuum produced by a water pump.

2.2 Chemicals

Cold-pressed rapeseed oil, free of erucic acid (acid number 0.6 mg $KOH \cdot g^{-1}$, water content 600 ppm and density 0.920 $g \cdot cm^{-3}$, produced by RPN Slatiňany, Czech Republic), absolute ethanol (water content 0.12 %), potassium hydroxide p. a. (purity 90 %), carbon dioxide (for food processing industry).

2.3 Procedure of experiments

The constant amount of rapeseed oil (900 g) was put into the reactor; catalyst (KOH) was dissolved in ethanol and both liquids were thermostated separately to the reaction temperature. Then the disperser in the reactor was switched on, the solution of KOH in ethanol was quickly added and this time was considered as the start of the reaction. The main stirrer was set to 200 rpm during the transesterification process because of the satisfactory heat transfer and the prevention of reaction mixture overheating (the disperser produces high amount of heat). After chosen reaction time, the reaction was stopped by the neutralisation of the catalyst by gaseous CO_2 dosed into the reaction mixture until pH fell to a minimum value (approximately after 5 minutes) [Skopal et al., 2001]. Potassium carbonate and potassium bicarbonate were formed from KOH. Then the excess of ethanol was evaporated from the reaction mixture (deethanolisation) for 40 min at 80°C and pressure approximately 3 kPa. After cooling down to 25°C the reaction mixture has been separated for 24 hours to EP and GP by gravitation in a separatory funnel.

21 experiments with various reaction conditions were carried out. The experimental range of the reaction conditions (the reaction temperature *T*, the reaction time *t*, the weight ratio of catalyst to oil *C*, the molar ratio of ethanol to oil *MR* and the rotations of disperser *Ro*) is shown in Table 1 and our design of experiments is shown in the first part of Table 2. The experiments 1–8 are based on the Plackett-Burman design [Isaakson, 1970], the experiments 9–17 are additional experiments and they all originate in our previous work [Černoch, 2009].

The experiments 18–21 are verification experiments from the mentioned work which may slightly overpass the experimental range of the reaction conditions.

2.4 Analysis of ester phase

The contents of MG, DG and TG were determined by GC method according to the FAME norm (EN 14105); the norm for FAEE does not exist. The Shimadzu GC-2010 with a flame ionization detector was used. Free glycerol was determined by the HPLC method [Hájek, 2006].

The content of ethyl esters in the EP was calculated as the difference of 100 % minus the sum of content of glycerides and glycerol (in wt-%), providing that the concentrations of other substances in the EP are insignificant.

2.5 Analysis of glycerol phase

The samples of the GP had to be acidified before analysis by concentrated H_3PO_4. Thereby soaps were transformed into fatty acids and the GP was separated into a lighter non-polar phase (esters, glycerides, fatty acids and other non-polar substances) and a heavier polar phase (glycerol, water, potassium salts and other polar substances). The separation of phases was accelerated by water addition and warming up (80°C).

Then the non-polar phase was analyzed by the same GC method as the EP. The example of non-polar phase chromatogram is shown in Figure 1. Chromatograms of the EP and non-polar phases are similar. Then the concentrations of glycerides in the GP were calculated from known weights of formed non-polar phase and the used GP.

The concentration of ethyl esters was determined by GC method together with the determination of glycerides in one analysis: The peak of ethyl esters was identified in the chromatogram of the non-polar phase (Figure 1) and the sample of the EP with the lowest amount of admixtures was used as the standard for the calibration curve.

Soaps in the GP were determined by acidimetric titration [Kwiecien et al., 2009] (amount of soaps in the EP is insignificant). Glycerol in the GP was determined by the iodometric method after the oxidation by HIO_4 [Jureček, 1957].

3 Results and discussion

3.1 Measured data

Obtained data (the weights of phases and the concentrations of investigated substances) are shown in Table 2. The experiments 5, 8, 9 and 14 are problematic concerning the phase separation and they are not taken into account in the next sections (more about this problem in the section 3.4).

In the EP, the concentrations of ethyl esters are higher than 97.0 wt-% and the concentrations of glycerides are low, as expected (more information about effects of reaction conditions on ethyl ester forming are shown in the previous work [Černoch, 2009]. TG has the lowest concentration (0.010–*0.*449 wt-%), DG slightly higher concentrations (0.231–0.956 wt-%) as well as MG but with less variability (0.502–0.944 wt-%). The concentrations of glycerol are low, too (0.065–0.299 wt-%). The experiments 1, 6 and 17 are characterized by very low weight of the gained EP (less than 600 g which correspond less than 65 % of theoretical yield) which results in the high weight of the GP.

In the GP, the concentrations of ethyl esters are unexpectedly high. In some experiments (1, 5, 13, 15 and 17) they reached 50 wt-%, which caused significantly higher amounts of the GP (thereby a low amount of the EP) and their lower viscosity. This type of the GP was not stable and the part of ethyl esters separated spontaneously after several days. The GP with ethyl ester concentrations below 50 wt-% were more stable; only a small part of ethyl esters separated from it after several weeks. Higher amount of ethyl esters in the GP causes the decrease of the concentrations of glycerol only up to the 24 wt-%. These experiments are characterized mostly by higher temperature and amount of catalyst which increase undesirable

saponification of oil. Total amount of KOH catalyst can react by saponification under the reaction temperature of 60 °C within ethanolysis of rapeseed oil [Černoch, 2009]. The formed soaps cause a deterioration of the subsequent phase separation (more detailed explanation is in section 3.3).

The concentrations of glycerides in the GP are low; TG has the lowest concentrations again, MG has significantly higher concentration in comparison with TG and DG.

3.2 Distribution coefficients and weight distributions

We formulated following variables which represent the distribution between the EP and GP. The distribution coefficients of each investigated substance are calculated as the ratio of the weight concentration in the EP to the concentration in the GP [%/%]. The weight distributions are calculated as the ratio of the weight of the substance in the EP to the weight of the substance in the GP [g/g]. The higher value of the distribution coefficient (or the weight distribution) means that the higher amount of the substance passes to the EP. Relation between these values is given by (1):

$$weight\ distribution = distribution\ coefficient \cdot \frac{weight\ of\ \ EP}{weight\ of\ \ GP} \qquad (1)$$

In the case of the biodiesel production, the weight of the EP is higher than the weight of the GP and thereby the weight distribution value is always higher than the appropriate distribution coefficient value. The ranges of the distribution coefficient and the weight distribution of the investigated substances are shown in Table 3. The ranges are greatly wide and therefore the median values enable their better comparison and interpretation.

The distribution coefficients among the investigated substances are considered and increase in the row: glycerol, MG, DG, ethyl esters and TG. Ethyl esters and TG are present in greater quantity in the EP, whereas glycerol and MG are found in greater quantity in the GP than the EP. DG are present roughly equally in the GP and EP.

Zhou [Zhou and Boocock, 2006b] found out that up to 19.3 wt-% of glycerol from the reaction mixture remains in the EP in case of ethanolysis of sunflower oil. Our median value is only 1.6 wt-% (calculated from the median of the weight distribution of glycerol). This difference may be caused by presence of significantly different amount of ethanol in reaction mixture because Zhou did not carry out deethanolisation of the reaction mixture before separation.

We found out the significantly higher distribution of ethyl esters to the GP in comparison with Zhou's work. This may be caused by using a different catalyst. We used KOH catalyst, Zhou the ethoxide catalyst. According to [Vicente et al, 2004] using of KOH (or NaOH) caused significantly higher amounts of esters in the GP in the comparison with methoxide catalysts by transesterification of sunflower oil.

3.3 Influence of final reaction mixture composition on ethyl esters distribution

The reaction mixture has significant effect on the amounts of forming phases. Higher amount of the GP is caused by higher amount of ethyl esters in the GP. This part of ethyl esters decreases the yield of the EP. The negative effect of soaps on the separation of the EP and GP is generally known. Some authors [Vojuckij, 1975], [van Os, 1998] also mentioned MG as the important emulsification agent. The correlation between concentrations of soaps and MG in the reaction mixture before separation (S_{RM} and MG_{RM}, wt-%) with the concentration of ethyl esters in the GP after separation (EE_{GP}, wt-%) of the certain reaction mixture is present in Figure 2 and Figure 3. The squares of the correlation coefficients are low but values over 0.5 and the statistical testing indicates the significance of these correlations in the case of two influencing variables. The summation of the mentioned correlations into one linear relation gives the equation (2).

$$EE_{GP} = 4.0 \cdot S_{RM} + 14.9 \cdot MG_{RM} \qquad R^2 = 0.71 \qquad (2)$$

The figures and the equation proved that soaps and monoglycerides cause the presence of ethyl esters in the GP. But the regression analysis (R^2, residues etc.) indicates that other undetected variables may influence of the ethyl esters amount in the GP. The effect of the disperser may be one of them, as we found out in the previous work [Černoch, 2009]. The equation (2) has no constant term which predicates that no ethyl esters remain in the GP if no soaps and MG are present in the reaction mixture. The elimination of forming soaps and MG can decrease losses of ethyl esters and thereby increase the yield of the EP. These findings are probably also valid for the separation of the reaction mixture after methanolysis of oil.

The effect of soaps on the presence of methyl or ethyl esters in the GP is mentioned by several authors [Di Felice et al., 2008], [Vicente et al., 2006], [Vicente et al., 2007]. But no author observed the similar effect of MG although the practical utilization of MG as the emulgator of the mixture of the GP and non-polar compounds has been already described in [Striūgas et al., 2008].

3.4 Non-separable reaction mixtures

The formation of the non-separable reaction mixture (the reaction mixture in one pseudo-homogenous phase) after ethanolysis of vegetable oils was observed several times [Domingos et al., 2008], [Oliveira et al., 2008]. We observed also the problem of the non-separable mixtures. In our experiments, 17 reaction mixtures were easily-separable (separated phases were visible immediately or after few minutes), 2 were hardly-separable (separated phases were visible not until after few hours and the separation took several days) and 2 did not separate at all (mixture was clear and no separation tendency was observed), see Table 2. The composition (concentration of MG, DG, TG and soaps in the reaction mixture) of these non-, hardly- and easily-separable reaction mixtures is depicted in Table 4. Non- and hardly-separable mixtures are characterized by significantly higher concentrations of MG and DG in the reaction mixture in the comparison with easily-separable mixtures. Such phase behaviour

is characteristic for ethanolysis and butanolysis, not for methanolysis [Zhou and Boocock, 2006a].

The non-separable mixtures were not totally stable. They were stable and clear at 25 °C but they became turbid and separable by warming-up. They started to separate when they were stirred and warmed-up over approximately 70 °C. After switch of stirrer, the EP and GP were formed in few minutes (and then the phases could be analyzed). This effect was totally reversible – when these separated phases were cooled down (25 °C) and stirred; the non-separable pseudo-homogenous mixture was formed again after few minutes.

The physical principle of this problem was not investigated although theoretical models of the emulsion forming and the phase inversion exist [Yeo et al., 2002]. However it is not aim of our work.

4 Conclusions

The distribution coefficients and the weight distributions between the ester and glycerol phase were calculated; the distribution coefficients increase in this sequence: glycerol, monoglycerides, diglycerides, ethyl esters and triglycerides.

Soaps and monoglycerides formed by the transesterification reaction increase the amount of ethyl esters in the glycerol phase. This causes a decrease in the yield of the ester phase. Elimination of soaps and monoglycerides forming can reduce the losses of ethyl esters and thereby increase biodiesel yield.

The formation of the non-separable and hardly-separable reaction mixtures was observed. These mixtures were characterized by higher concentrations of monoglycerides and diglycerides in the comparison with the easily-separable mixtures.

Acknowledgements

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

References

Asakuma, Y., Maeda, K., Kuramochi, H., Fukui, K., 2009. Theoretical study of the transesterification of triglycerides to biodiesel fuel. Fuel. 88, 786–791.

Azcan, N., Danisman, A., 2008. Microwave assisted transesterification of rapeseed oil. Fuel. 8, 1781–1788.

Černoch, M., Hájek, M., Skopal, F., Study of effects of some reaction conditions on ethanolysis of rapeseed oil with dispergation. Bioresour. Technol. *in press* doi:10.1016/j.biortech.2009.09.033

Di Felice, R., De Faveri, D., De Andreis, P., Ottonello, P., 2008. Component distribution between light and heavy phases in biodiesel processes. Ind. Eng. Chem. Res. 47, 7862–7867.

Domingos, A.K., Saad, E.B., Wilhelm, H.M., Ramos, L.P., 2008. Optimization of the ethanolysis of Raphanus sativus (L. Var.) crude oil applying the response surface methodology. Bioresour. Technol. 99, 1837–1845.

EU, 2009. Directive 2009/28/EC of the European parliament and of the Council. Official journal of the European union. 52 (L 140), 16–62.

Hájek, M., Skopal, F., Machek, J., 2006. Determination of Free Glycerol in Biodiesel. Eur. J. Lipid Sci. Technol. 108, 666–669.

Isaacson, W.B., 1970. Statistical Analyses for Multivariable Systeme. Chemical engineering. 77, 69–75.

Issariyakul, T., Kulkarni, M.G., Dalai, A.K., Bakhshi, N.N., 2007. Production of biodiesel from waste fryer grease using mixed methanol/ethanol system, Fuel Process. Technol. 88, 429–436.

Ji, J., Wang, J., Li, Y., Yu, Y., Xu, Z., 2006. Preparation of biodiesel with the help of ultrasonic and hydrodynamic cavitation. Ultrasonics. 44, 411–414.

Jureček, M., 1957. Organická analysa II. Nakladatelství ČSAV, Prague.

Knothe, G., 2008. “Designer” Biodiesel: Optimizing Fatty Ester Composition to Improve Fuel Properties. Energy & Fuels. 22, 1358–1364.

Kwiecien, J., Hájek, M., Skopal, F., 2009. The effect of the acidity of rapeseed oil on its transesterification. Bioresour. Technol. 100, 5555–5559.

Meneghetti, S.M.P., Meneghetti, M.R., Wolf, C.R., Silva, E.C., Lima, G.E.S., Coimbra, M.A., Soletti, J.I., Carvalho, S.H.V, 2006. Ethanolysis of castor oil and cottonseed oil: A systematic study using classical catalysts. J. Am. Chem. Soc. 83, 819–822.

Mittelbach, M., Remschmidt, C., 2004. Biodiesel, the Comprehensive Handbook, 1st ed. Martin Mittelbach, Graz.

Nimcevic, D., Puntigam, R., Worgetter, M., Gapes, R., 2000. Preparation of rapeseed oil esters of lower aliphatic alcohols. J. Am. Chem. Soc. 77, 275–280.

Oliveira, L.S., Franca, A.S., Camargos, R.S., Ferraz, V.P., 2008. Coffee oil as a potential feedstock for biodiesel production. Bioresour. Technol. 99, 3244–3250.

Santos, F.F.P, Rodrigues, S., Fernandes, F.A.N., 2009. Optimization of the production of biodiesel from soybean oil by ultrasound assisted methanolysis. Fuel Process. Technol. 90, 312–316.

Skopal, F., Komers, K., Machek, J., Koropecký, I., 2001. Způsob výroby bionafty z rostlinných olejů, zejména z řepkového oleje. Czech patent CZ 289417.

Stamenkovic´, O.S., Todorovic´, Z.B., Lazic´, M.L., Veljkovic´, V.B., Skala, D.U., 2008. Kinetics of sunflower oil methanolysis at low temperatures. Bioresour. Technol. 99, 1131–1140.

Striūgas, N., Šlančiauskas, A., Makarevičienė, V., Gumbytė, M., Janulis, P., 2008. Processing of the glycerol fraction from biodiesel production plants to provide new fuels for heat generation. Energetika. 54, 5–12.

van Os, N.M., 1998. Nonionic surfactants: Organic chemistry. Marcel Dekker, Inc., New York.

Vicente, G., Martinez, M., Aracil, J., 2004. Integrated biodiesel production: a comparison of different homogeneous catalysts systems. Bioresour. Technol. 92, 297–305.

Vicente, G., Martinez, M., Aracil, J., 2006: A comparative study of vegetable oils for biodiesel production in spain. Energy & Fuels. 20, 394–398.

Vicente, G., Martinez, M., Aracil, J., 2007. Optimisation of integrated biodiesel production. Part II: A study of the material balance. Bioresour. Technol. 98,1754–1761.

Vojuckij, S.S., 1975. Kurs kolloidnoj chimii. Chimija, Moscow.

Warabi, Y., Kusdiana, D., Saka, S, 2004. Reactivity of triglycerides and fatty acids of rapeseed oil in supercritical alcohols. Bioresour. Technol. 91, 283–287.

Zhou, W., Boocock, D.G.B., 2006. Phase behavior of the base-catalyzed transesterification of soybean oil. JAOCS. 83, 1041–1045. (a)

Zhou, W., Boocock, D.G.B., 2006. Phase distributions of alcohol, glycerol, and catalyst in the transesterification of soybean oil, JAOCS. 83, 1047–1052. (b)

Figure captions:

Figure 1: Example of GC chromatogram of non-polar phase (part of GP) sample. On-column injection: 1 µl of sample, injection port temperature: 80 °C, column type: WCOT fused silica, stationary phase: VF-5ms, He total flow: 8.5 ml/min, column temperature: initial 80 °C, final 350 °C, detector temperature 360 °C.

Figure 2: Correlation between concentration of soaps in final reaction mixture before separation of EP and GP and concentration of ethyl esters in GP after separation

Figure 3: Correlation between concentration of monoglycerides in final reaction mixture before separation of EP and GP and concentration of ethyl esters in GP after separation