Separation of reaction mixture after ethanolysis of rapeseed oil

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Abstract

Various effects on the separation of raw reaction mixture after the ethanolysis of rapeseed oil were investigated. Water addition, initial temperature of separation, centrifugation, ionic compound addition and time effects affecting concentrations of potassium, free glycerol and yield of the ester phase were found out. Centrifugation has the most positive effect. Finally, correlation between concentrations of potassium and free glycerol was found out.

1 Introduction

Biodiesel is the mixture of esters of high fatty acids and low molecular alcohol. It is produced by transesterification of triglycerides included in vegetable oils and animal fats. Glycerol is formed as a by-product. There are several methods of transesterification. Alkaline, acid or enzymatic catalysis are possible. There is also a method without using of the catalyst whereas alcohol reacts in a supercritical state [1]. An alkaline catalysis is the most effective and the most widely used method [2]. Such transesterification proceeds at gently temperature and pressure conditions. But the side reaction, the saponification of oil, decreases the yield of biodiesel [3].

Methanol is the most widely used alcohol for the transesterification; nevertheless the other alcohols can also be used. One of them is ethanol which is low-toxic and can be produced from renewable resources. These are the advantages in comparison with methanol. A lower reactivity is a disadvantage because of its longer carbon chain [4]. On equal conditions, ethanol reacts slower than methanol [5]. The more difficult separation of the rising emulsive mixture into upper ester phase and bottom glycerol phase is the next step of the alkaline-catalysed ethanolysis. Glycerol phase contains glycerol, soaps (potash soap or soda soap), alcohol and other substances. Formation of a gel mixture was observed too [6].

Emulsions are heterogeneous mixtures of two and more immiscible or limited miscible liquids which can be stabilized by emulsifier, in this case by soaps. Emulsions may be destabilized by many methods: spontaneous sedimentation, coagulation via electrolytes with polyvalent ions, addition of ion compound, warming-up, centrifugation and application of electric field [7], [8]. Separation of the emulsion after alkaline-catalysed transesterification is accelerated by optimal addition of water [9]. But a part of esters still remains in the glycerol phase after separation [10].

The equation (1) is the Stokes' law of the settling velocity of particle (u – settling velocity of particle, r – radius of particle, η – dynamic viscosity of fluid, ρ – density of particle, ρ_0 – density of fluid, g – acceleration of gravity):

$$u = \frac{2r^2}{9\eta} \cdot (\rho - \rho_0) \cdot g \qquad (1)$$

2 Materials and methods

2.1 Research strategy

The conditions of ethanolysis (see procedure 2.4) were chosen so that the conversion of the oil was more than 98 %. The rate of separation of ester and glycerol phase was monitored via determination of concentrations of potassium (*K*) and free glycerol (*fg*) and the relative yield of ester phase (*Y*, defined as ratio of real and theoretical yield). Maximum allowed values by European norm EN 14214:2003 are 5 $mg \cdot kg^{-1}$ for alkali metals and 0.02 wt-% for free glycerol. Note that norm for fatty acids ethyl esters does not exist and data can be compared only with the mentioned norm for fatty acids methyl esters.

The used separation methods were chosen to be as simple as possible: adding small quantity of water, increasing of the initial temperature of separation, addition of ionic compound (KCl water solution), time effect and centrifugation.

2.2 Chemicals

Readily available quality chemicals were used. Cold-pressed, filtrated rapeseed oil, free of erucic acid (acid number 0.95 mg $KOH \cdot g^{-1}$, water content 600 ppm and density 0.920 $g \cdot cm^{-3}$, RPN Slatiňany), Absolute alcohol (water content 0.12 %), Potassium hydroxide p. a. (purity 90 %), Carbon dioxide (for food processing industry), potassium chloride, all CZ production.

2.3 Apparatus

The first spheric flask (1000 ml volume) equipped with orifices for a paddle-shaped stirrer (2 paddles 3x1 cm), pH-electrode, cooling/heating attachment and thermometer was used as the reactor. The deethanolisation proceeded in the second spheric 1000 ml stirred flask joined to the water pump.

Separations in gravitational field proceeded in a thermostated glass cuvette (30 ml volume, 3x2x5 cm) inserted into the UV-VIS spectrophotometer (Spekol 11, Carl Zeiss Jena). The spectrophotometer was set for transmittance measuring at 570 nm [9].

Thick-walled test tubes (60 ml volume) were used for centrifugation experiments. The centrifuge had 20 cm diameter and maximal 10 000 rpm.

2.4 Procedure

The procedure of transesterification is described in the Czech patent [11]. 450 g of rapeseed oil was put into the first reaction vessel and thermostated to the reaction temperature 25°C. Then 225 ml of ethanol with 5.15 g of dissolved KOH was added and this time was considered as the start of the reaction (i.e. molar ration ethanol to oil 6:1, amount of catalyst 1.14 % relative to oil). After 4.5 hours, the reaction was stopped via neutralisation of the catalyst by gaseous CO_2 dosed into the reaction mixture (potassium carbonate was formed from KOH, neutralisation was checked by pH-electrode). Then the reaction mixture was put into the second flask and excess of ethanol was evaporated for 40 min at 80°C and pressure 10 kPa. Raw reaction mixture (RRM) was formed by this process.

Approximately 20 grams of RRM were dosed into a cuvette for experiments in the gravitational field. Then the cuvette was inserted into the thermostated extender (temperature was adjusted according to experiment conditions) and RRM was stirred by a propeller stirrer (1 cm diameter) until constant value of transmittance. Then the chosen quantity of water or KCl solution (according to experiment conditions) was added into cuvette and the mixture was stirred until constant value of transmittance. The amount of water (or KCl solution) was defined in milligram per gram of RRM ($mg \cdot g^{-1}$). After reaching of constant transmittance, the stirrer was switched off; the cuvette was taken from the extender and spontaneous sedimentation started. During this sedimentation, spontaneous cooling from initial temperature of separation to laboratory temperature (25 °C) took place. After certain time (according to experiment conditions), samples were taken to determine concentrations of potassium and free glycerol and yield of biodiesel in the ester phase, see 2.5 (analytical methods).

For centrifugation experiments, water was added directly into the second flask (see the procedure of transesterification). Approximately 30 g of RRM were weighed out into two thick-walled test tubes. The first one was used for separation in the gravitational field, the second one for centrifugation (3500 rpm, time of centrifugation 25 min). Then samples of ester phase were analyzed.

Suitable statistical functions for fitting experimental data were searched. Requirement was the simplicity of function (exponential, linear etc.) and R^2 value (coefficient of determination or square of a correlation coefficient) as high as possible.

2.5 Analytical methods

The concentration of potassium (potassium ions) ions was determined by the method of flame photometry (Flame photometer 410, Sherwood) with the help of a calibration curve. Calibration solutions were prepared by mixing of a small amount of very concentrated ethanolic KOH solutions into the biodiesel matrix without potassium ions. Biodiesel matrix was prepared by washing of biodiesel by citric acid water solution.

Concentration of free glycerol in ester phase was determined by HPLC - conditions are stated in [12].

The yield of ester phase (biodiesel) was determined as ratio of experimental mass of ester phase and RRM divided by theoretical masses of ester phase and RRM, provided that all water in the system is included in the glycerol phase. Theoretical mass of the ester phase was calculated on condition of total conversion of used oil (molar mass 879 $g \cdot mol^{-1}$) in the form of triglycerides.

$$Y = \frac{\dfrac{m_{ester\ phase}}{m_{RRM}}}{\dfrac{m_{ester\ phase}^{theoretical}}{m_{RRM}^{theoretical}}} = \frac{\dfrac{m_{RRM} - \left(m_{glycerol\ phase} - m_{addition}\right)}{m_{RRM}}}{89{,}87} \qquad (2)$$

3 Results and discussion

3.1 Effect of quantity of water addition

Initial temperature of separation was 34°C and sedimentation took 20 hours at these experiments. Then concentrations of potassium and free glycerol in ester phase were determined (Fig. 1). They decrease with the amount of added water. Exponential functions are suitable for the fitting of experimental data. Both exponential curves have similar shapes due to the similar values of exponent (–0.0775 and –0.0919). The functions limit to the value of the absolute term of the exponential function. Both concentrations can be reduced approximately ten times by water addition in comparison with the separation without water addition. The addition of water is the most effective up to approximately 54 $mg \cdot g^{-1}$.

The principle of the effect of water addition is not known. There is a similarity with the water washing of biodiesel that is often used as a purification process after the separation of phases.

3.2 Effect of initial temperature of separation

The separation was carried out using constant amount of water (54 $mg \cdot g^{-1}$) and sedimentation time (20 hours).

Concentrations of potassium and free glycerol increase with increasing initial temperature of separation (Fig. 2). Exponential functions were suitable as the statistical models again. They limit to the certain values of concentrations (6.16 $mg \cdot kg^{-1}$ of potassium and 0.0352 % of free glycerol) in the range of low temperatures (approximately from 34°C below). The curves have similar shapes again (values of exponent 0.511 and. 0.557).

The yield of ester phase (biodiesel) increases with increasing initial temperature of separation (Fig. 3). The dependence can be simulated by the linear function. Effect on yield is positive, but on the other hand higher initial temperature of separation increases concentrations of potassium and free glycerol in the ester phase. The effect of initial temperature of separation is then very disputable.

The explanation of this effect is difficult. Increasing of the biodiesel yield is probably caused by decreasing amount of ethyl esters in the glycerol phase. It was determined that the amount of ethyl esters in glycerol phase reaches to 30 % (in agreement with [10]).

The exact explanation of increasing of potassium and free glycerol concentrations in ester phase was not found out. It is probably connected with potassium soaps in GP because concentration of free glycerol depends on concentration of potassium ions or soaps, respectively (see 3.6).

3.3 Effect of ionic compound addition

In this case, aqueous solutions of KCl (54 $mg \cdot kg^{-1}$) with various concentrations of potassium chloride were added to RRM instead of pure water. Initial temperature of separation was 34°C and sedimentation time was 20 hours.

The results are presented in Tab. 1. Higher concentrations of KCl slightly increase the biodiesel yield but concentration of potassium in it increases significantly. Therefore the effect of the addition of KCl water solution is negative.

The mentioned negative effect may be caused by the solubility of KCl in biodiesel (biodiesel contains small amount of water, approximately 500 ppm).

3.4 Effect of time

The separation was tested at constant addition of water (54 $mg \cdot kg^{-1}$) and initial temperature of separation (34 °C).

Exponential declines of the potassium and free glycerol concentrations are evident (Fig. 4). In this case, it is necessary to use the second order exponential decay to fit the data. The curves have similar shapes again. The highest decrease of concentration of both components is reached during the first hour of sedimentation. After 20 hours, rate of separation is decreasing and after next approximately 40 hours it is almost finished at the investigated conditions.

The rate of separation of phases is caused by three factors. The first is the difference between the densities of phases, which is the driving force of sedimentation (see equation 1) of non-miscible liquid phases. This difference is limited by the composition of phases. The maximal difference of densities is 0.38 $g \cdot cm^{-3}$ which corresponds to densities of biodiesel (0.88 $g \cdot cm^{-3}$) and pure glycerol (1.26 $g \cdot cm^{-3}$). But in real cases, the glycerol phase contains other substances which significantly decline the density of glycerol phase, e.g. ethanol (0.79 $g \cdot cm^{-3}$) and water (1.00 $g \cdot cm^{-3}$). In the result, the difference of densities is always less then the maximum value.

The second factor is the relative high kinematics viscosity of ester phase (approximately 4.5 $mm^2 \cdot s^{-1}$ at 40°C), because the kinematics viscosity declines the rate of separation in accordance with Stokes' law.

The third factor is the coagulation of particles of glycerol phase formed in the ester phase. This process is inhibited by emulsifiers in the mixture, which are soaps and probably diglycerides and monoglycerides. These glycerides are the intermediates of transesterifications of triglycerides (monoglycerides are mentioned as emulsifiers and surfactants, e.g. in [13]). Longer time interval enables more particles of glycerol phase to form coagulates. In some cases separation of phases does not proceed at all [14].

3.5 Effect of centrifugation

The centrifugation process for biodiesel separation (time 25 min, 3500 rpm, centrifuge diameter 30 cm) was compared with spontaneous sedimentation (sedimentation time 20 hours). Initial temperature of separation was constant 34°C and amount of water addition was 54 $mg \cdot kg^{-1}$.

The results in Tab. 2 show that the centrifugation is the best and fastest method for separation of ester and glycerol phase from RRM. Decreasing of concentrations of potassium and free glycerol, small increasing of yield and the reduction of process total time are clearly positive. But the centrifugation process demands more equipment and cost. Concentration of potassium is under the norm value at four from six experiments. Concentration of free glycerol limits to norm value only. The yield of biodiesel is mostly 93 %.

The centrifugation accelerated separation significantly although time of separation was shortened. It depended on the conditions of centrifugation indeed; in our case centrifugal force was approximately 510 times greater than gravitation force.

3.6 Correlation between concentrations of potassium and free glycerol

The similar shapes of the curves of concentrations of potassium and free glycerol refer to a correlation between them. Figure 5 shows, that it is the linear dependence without an absolute term. The dependence can be explained as the stabilisation effect of potash soaps on the low-concentrated emulsion of glycerol in ester phase. Higher concentration of free glycerol is not possible without higher concentration of potash soaps. The similar result is known in the case of methanolysis of rapeseed oil [15].

4 Conclusion

Various effects on the separation of raw reaction mixture were investigated. The separation was monitored by determination of concentrations of potassium and free glycerol in the ester phase and the yield of ester phase, which depend on separation conditions. The water addition decreases concentrations of potassium and free glycerol. The optimum water concentration is 54 mg of water to 1 g of raw reaction mixture. The effect of initial temperature of separation is very disputable. Higher temperature increases the yield of ester phase but also concentrations of potassium and free glycerol. Addition of inorganic ions such as aqueous solutions of KCl increases the potassium and free glycerol concentrations in biodiesel. The sufficient gravitate separation of phases is finished after 40 hours at investigated conditions. The centrifugation has obviously positive effects. It increases the yield and decreases concentrations of potassium and free glycerol. Recommended conditions to fulfil the concentrations of potassium and free glycerol specified by the European norm and high yield of biodiesel are: water addition 54 mg of water for 1 g of raw reaction mixture, centrifugation (25 min, 3500 rpm, centrifuge diameter 20 cm) and initial temperature of separation 34°C.

The correlation between concentrations of potassium and free glycerol is linear. Ester phase is probably the relatively stable low-concentrated emulsion of glycerol in ethyl esters stabilized by potassium soaps.

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Conflict of interest statement

The authors have no conflict of interest.

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