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Effect of phase separation temperature on ester yields from ethanolysis of rapeseed oil in the presence of NaOH and KOH as catalysts

Martin Hájek *, František Skopal, Michal Černoch

Department of Physical Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic

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ABSTRACT

The effects of phase separation temperatures (5–90 °C) on losses of higher fatty acid (C_{16} and C_{18}) ethyl esters in the glycerol phase were investigated. Losses of ethyl esters produced from ethanolysis of rapeseed oil were 30–60% higher when NaOH rather than KOH was used as homogeneous catalyst. The losses decreased with an increase in separation temperature, resulting in an increase in the yield of the ester phase. The concentration of impurities (e.g. alkali metals, free glycerol and glycerides) in the ester phase increased with increasing separation temperature due reversible transesterification and reciprocal solubility of the compounds. Carbonates formed during neutralization of the catalysts are also transesterification catalysts and they cause reverse reaction. The ethyl ester bound in the glycerol phase during NaOH-mediated catalysis can be extracted by heating the separated glycerol phase to 60–90 °C. The ester yield is increasing with increasing separation temperature, however with decreasing quality.

1. Introduction

In an effort to decrease carbon dioxide emissions, reduce dependence on fossil fuel and increase sales opportunities for farmers, the use of biodiesel is being promoted, and mixing of fatty acid methyl esters (FAME) into fossil diesel fuel is required by law in many countries (EU, 2009).

Biodiesel production proceeds mainly by catalytic transesterification. The most frequently used catalysts are homogeneous acid (strong mineral acids) but especially bases (KOH, NaOH) (Cvengros and Povazanec, 1996; Encinar et al., 2007). Other possible catalyst are basic or acid heterogeneous catalysts (Yonemoto et al., 2007) or enzymes (de Castro et al., 2009). There is also a method without any catalyst, where alcohol reacts in a supercritical state (Lee et al., 2009).

The most frequently used alcohol is methanol, but since it is toxic and difficult to produce from renewable raw materials, ethanol might be preferable in biodiesel production. However, ethanol has lower reactivity compared to methanol during transesterification (Dalai et al., 2007) is due to its longer carbon chain (Nimcevic et al., 2000) and transesterification takes more than 1 h.

Another problematic part of biodiesel production is the separation of the final reaction mixture into a lighter ester phase (EP) and a heavier glycerol phase (GP) (Kapilan et al., 2010; Veljkovic et al., 2010). Separation studies are usually focused only on methyl esters (Aroua et al., 2011), but the separation of ethyl esters is more complicated and losses are higher than in the case of methyl esters (Aracil et al., 2004; Ramos et al., 2007). Considerable losses of ethyl esters in the glycerol phase were shown by (Cernoch et al., 2010a). The concentration of esters in the GP varies from 15 to 50 wt.%. The current study describes chemical changes in the reaction mixture during and after separation. Transesterification of rapeseed oil was carried with NaOH and KOH catalysts. Ester losses in the GP as a function of the separation temperature were studied.

2. Methods

2.1. Chemicals

Cold-pressed filtered rapeseed oil, free of erucic acid (acid number 1.6 mg KOH g^{-1}, water content 600 mg kg^{-1} and density 910 kg m^{-3} (20 °C) was obtained from RPN Slatiňany, Czech Rebublic. Absolute ethanol (water content 0.12%), sodium hydroxide p.a. (purity 98%), potassium hydroxide p.a. (purity 90%) were obtained from Lach:Ner, s.r.o. and carbon dioxide (for the food processing industry) was obtained from Linde gas, a.s.

2.2. Equipment

A double-walled laboratory reactor IKA® LR 2000 (volume 2 l) with a toothed disc stirrer was used. A high-performance disperser T-25 digital ULTRA-TURRAX® (IKA®, Germany) was installed in the reactor. The reactor was joined to a water pump and thermostat. A detailed description can be found in Cernoch et al. (2010c).

* Corresponding author. Tel.: +420 466 037 055.
E-mail address: martin.hajek2@upce.cz (M. Hájek).

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2.3. Procedure

Transesterification was performed as described (Cernoch et al., 2010c). Rapeseed oil (900 g) was place into the reaction vessel. NaOH or KOH were dissolved in ethanol (molar ratio to oil 7.5:1) and temperature of both liquids was controlled by separate thermostats at 25 °C. The amount of KOH was 1.22 wt.% to oil and the same molar amount of NaOH was employed (0.87 wt.% NaOH to oil). The disperser (10,000 rpm) was switched on, the catalyst solution was quickly added into the reaction vessel. This point was considered as the start of the reaction. The main stirrer was set to 200 rpm during the reaction because of satisfactory heat transfer. After 1.5 h of trans-esterification, the reaction was stopped by the neutralization of the catalyst with gaseous CO_2 dosed into the reaction mixture until the pH fell to the minimum value (approximately 5 min). Potassium or sodium carbonate and bicarbonate were formed from the catalysts (Hájek et al., 2012). The reaction mixture was evaporated for 40 min at 90 °C at the pressure of approximately 3 kPa (water pump) and the excess ethanol was removed (de-ethanolization).

After de-ethanolization, the reaction mixture was divided (without separation) into four parts and every part was thermostated to the chosen separation temperature (5, 25, 60 and 90 °C) under stirring. The stirrer was switched off and the phases were allowed to separate for 4 h (significant amount of the glycerol phase had been separated). Since separation at room temperature was not complete, the separation process was allowed to continue for an additional 20 h. After this separation (“first separation”), the mixture was divided into the upper ester phase and the heavier glycerol phase and both phases were analyzed. The glycerol phase was heated to 90 °C and, after switching off the stirrer, the next separation of this phase at room temperature took place at room temperature (“second separation”). After 24 h, the second ester phase (EP2) and second glycerol phase (GP2) were divided and analyzed.

The divided glycerol phase was heated to 90 °C and after switching off the stirrer, the next separation of this phase at room temperature took place at room temperature (“second separation”). After 24 h, the formed second ester phase (EP2) and second glycerol phase (GP2) were divided and analyzed.

To analyze chemical changes after separation, the de-ethanolized reaction mixture was stirred at the constant temperature (25 or 90 °C) for 4 h and the glyceride content was determined in whole reaction mixture after 1 h interval.

2.4. Analytical methods

The yield of the ester phase (biodiesel) was calculated as the ratio of measured weight to theoretical weight of ethyl ester (EE) multiplied by 100. The theoretical weight of EE formed from 1 g of rapeseed oil is 1.051 g.

The content of glycerides (MG, monoglycerides; DG, diglycerides; TG, triglycerides) and free glycerol (w_{FG}) were determined by the GC method according to EN 14105 by a Shimadzu GC-2010 with the help of linear calibration curves (monoolein, diolein and triolein were used as standards). The contents of esters and glycerides in the glycerol phase were determined by the same GC method, but the GP had to be treated by acidification prior to its determination by GC (Hajek et al., 2010).

The content of metals (Na and K) in the EP was determined by flame photometry (Flame 410, Sherwood Scientific Ltd.) with the help of linear calibration curves (Cernoch et al., 2010b).

3. Results and discussion

3.1. Separation – NaOH catalysis

The dependence of ester losses (measured as the content of ethyl esters in the glycerol phase-w_{EE}^{GP}) on the separation temperature is depicted in Fig. 1 (EE after the first separation). The temperature dependence of glycerides for both phases, free glycerol (w_{FG}) and sodium content (w_{Na}) of the ester phase is shown in Table 1. Ester losses in the GP decreased with an increase in separation temperature and therefore, the yield of the ester phase increased and free glycerol and sodium in the EP and glycerides in both phases also increased. Therefore, increasing separation temperatures increased the yield of the EP, but decreased its quality (more impurities).

After transesterification and de-ethanolization, the glycerol phase was liquid, but became solid after approximately 24 h (“first separation”) regardless of the prior separation temperature, because sodium soaps are solid at room temperature (Ophardt, 2003). After heating the separated GP to 90 °C, it changed to liquid and two new phases were observed. This process was fully reversible and a solid phase formed again after cooling the warm GP to a lower temperature (25 °C) during mixing. The “second” ester and glycerol phases (EP2 and GP2) were formed when the warm GP was separated at a temperature of 90 °C (“second separation”).

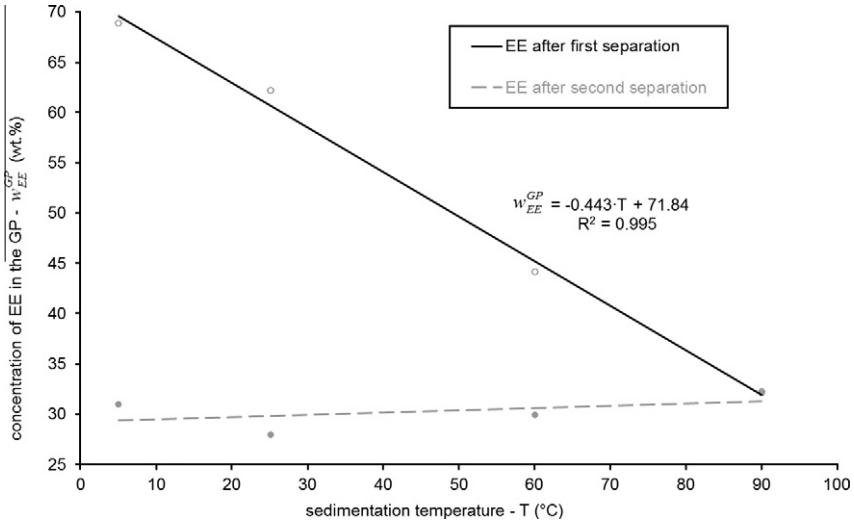

Fig. 1. Dependence of ethyl ester (EE) concentration in the GP on separation temperature (NaOH catalyst).