Bioresource Technology 101 (2010) 2071–2075

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Ethanolysis of rapeseed oil – Distribution of ethyl esters, glycerides and glycerol between ester and glycerol phases

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ARTICLE INFO

Article history:
Received 2 September 2009
Received in revised form 5 November 2009
Accepted 7 November 2009
Available online 11 December 2009

Keywords:
Biodiesel
Transesterification
Ethanolysis
Separation
Distribution

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 catalyzes 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 (Stamenković 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. Methods

2.1. Apparatus

The double-walled laboratory reactor IKA® LR 2000 with volume of 2 l was used. A toothed disc stirrer served as the main stirrer. High-performance disperser T-25 digital ULTRA-TURRAX® with maximal speed of 24,000 rpm was installed into the reactor. The

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doi:10.1016/j.biortech.2009.11.035

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 g^{-1}, water content 600 ppm and density 0.920 g 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 neutralization of the catalyst by gaseous CO_2 dosed into the reaction mixture until pH fell to a minimum value (approximately after 5 min) (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 h to EP and GP by gravitation in a separatory funnel.

Twenty one 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 R_D) 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 (Isaacson, 1970), the experiments 9–17 are additional experiments and they all originate in our previous work (Černoch et al., 2010). 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.

Table 1
The experimental range of reaction conditions.

Reaction conditions	Bottom limit (−1)	Top limit (+1)
Reaction temperature: T (°C)	25	65
Reaction time: t (h)	1.5	2.0
Weight ratio of catalyst to oil: c (wt%)	0.89	1.33
Molar ratio ethanol to oil: MR (−)	6.0:1	7.5:1
Rotations of disperser: R_D (rpm)	10,000	20,000

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 Fig. 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 (Fig. 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 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 et al., 2010)). 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 et al., 2010). 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.