



The removal of free fatty acids from methyl ester



Aleš Vávra, Martin Hájek*, Frantisek Skopal

Department of Physical Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 95, 532 10 Pardubice, Czechia

ARTICLE INFO

Article history:

Received 19 January 2016

Received in revised form

12 October 2016

Accepted 31 October 2016

Available online 4 November 2016

Keywords:

Biodiesel

Transesterification

Neutralization of acids

Acid number

Calcium hydroxide

ABSTRACT

This paper focused on the removal of free fatty acids from the ester phase. Transesterification was stopped by neutralization of the catalyst (KOH) by phosphoric acid addition to the reaction mixture. The advantages of this method are a very fast separation, an ester phase that does not contain potassium ions and free glycerol, and a relatively high purity of the glycerol phase. The disadvantage is the formation of free fatty acids, which were removed by the addition of calcium hydroxide, a reaction that formed solid calcium soaps that were removed by centrifugation. The conditions of removal (independent variables), such as the acid number of the input ester phase, molar ratio of calcium to FFAs and addition of water, were studied. The relations between independent and dependent variables (acid number, amount of calcium ions and water in the ester phase) are described. The model allowed for the calculation of conditions, so that the biodiesel fulfilled EN14214: a molar ratio of calcium to FFAs of 3.33:1, the addition of 1.45 μl water to 1 g of the ester phase and a reaction time of 3 h. This preparation of methyl ester is nearly without waste and does not use water for purification.

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1. Introduction

The world's consumption of fuels and demand for alternative fuels has increased over the past several years. One of the solutions to fuel consumption is biodiesel (alkyl esters of higher unsaturated and saturated fatty acids), which is an alternative fuel to petroleum diesel. The physico-chemical properties of biodiesel are similar to those of petroleum diesel; therefore, it can be used without modifying engines [1]. It is also biodegradable, non-toxic, sulphurless and environmentally friendly, as well as being a renewable source of energy [2–4].

Biodiesel is prepared by the transesterification of triglycerides contained in oil and low alcohols, most often methanol. Transesterification has to be catalysed under mild reaction conditions; without a catalyst, it is only possible at a high temperature and pressure – in the supercritical stage [5,6]. The homogenous alkali catalyst (NaOH, KOH, and CH_3ONa) is the most frequently used in industry because of its low cost and high efficiency [7]. Other types of homogeneous catalysts are strong acids, such as concentrated HCl and H_2SO_4 , which are usually used for the transesterification of a raw material with a higher content of free fatty acids and water [8,9]. On the other hand, the reaction has a much slower rate (i.e.,

longer reaction time), and strong acids have corrosive properties [2,10]. Other types of catalysts that are suitable for transesterification are heterogeneous or enzymatic catalysts, for which various enzymes are used [11–14]. Recently, many types of heterogeneous acids and alkali catalysts have been reported, such as ion exchange resins, heteropolyacids [15,16], supported alkali metal catalysts [17], alkali and alkaline earth oxides [18] and mixed metal oxides [19]. Heterogeneous catalysts can also be used for to prepare biodiesel from oils with a high content of FFAs [20].

The use of a homogeneous basic catalyst has several limitations: the catalyst is not reusable because it is consumed by the neutralization of the free fatty acid (contained in oil) or a side saponification reaction [21,22]. Moreover, the formed soaps cause problems during separation [23,24]. Transesterification is a reversible reaction that has to be stopped.

One possibility of how to stop transesterification is catalyst neutralization by gaseous carbon dioxide [25] or strong acid [26] addition to the reaction mixture. Another possibility is to separate the ester from the glycerol phase (while the catalyst remains in the glycerol phase). However, the glycerol phase is usually of low quality because it contains many impurities, such as water, soaps, and the remaining catalyst; therefore, it is necessary to purify this phase, i.e., further technological treatment is necessary. The ester phase also contains many impurities, such as the remainder of the glycerides, glycerol, FFAs, methanol, soaps and salts. Therefore, it is necessary to purify the ester phase, usually in a few steps:

* Corresponding author.

E-mail address: martin.hajek2@upce.cz (M. Hájek).

Nomenclature

an_{in}	acid number of the input ester phase (mg g^{-1})
an_{out}	acid number of the output ester phase (mg g^{-1})
Ca^{+2}	calcium content in the ester phase (mg kg^{-1})
EP	ester phase
f	speed of the stirrer (rpm)
FFAs	free fatty acids
MR	molar ratio of FFAs to calcium hydroxide (–)
t	time (h)
T	temperature ($^{\circ}\text{C}$)
V_w	amount of water added (μl)
water	content of water in the ester phase (ppm)

neutralization of the remaining catalyst by the addition of a mineral acid (neutralization is part of the biodiesel washing process and reduces washing water consumption) and removal of methanol (by stripping, vacuum flash vaporization or falling film evaporation). The last step is washing with hot water to remove the remaining impurities, thus forming wastewater. Consequently, wastewater, which is separated from the biodiesel phase by gravity or by a centrifuge, has to be adequately purified [27]. Moreover, the removal of the remaining water from the ester phase (EP) is also necessary [28]. The high cost of raw materials and necessity of purifying the crude biodiesel results in the high cost of biodiesel production. For large-scale production of biodiesel by homogeneous catalysts, the production requires a number of washing and purification steps so that the biodiesel meets specifications according to standards such as EN 14214 [29].

Since the higher fatty acids and their corresponding methyl esters are very similar chemical substances with similar properties, such as boiling points, melting points, and so on, it is very difficult to separate them by physical methods, such as distillation or cryoscopy. They can be separated by chromatography methods [30], but only for analytical determination [31]. Any similar procedure for removing FFAs from methyl ester has not yet been published in the literature.

In this paper, a strong acid is used to neutralize the catalyst. However, soaps are transformed to FFAs, which remain in the EP and increases the acid number (higher than specified by EN 14214). On the other hand, the water, glycerides and potassium contents are fulfilled according to EN 14214. Therefore, our attention was focused on the removal of the formed FFAs from the ester phase (biodiesel) by the addition of $\text{Ca}(\text{OH})_2$. The formed solid calcium soaps were removed by centrifugation. The conditions of removal are described and ensure that the produced biodiesel fulfils the specifications of EN 14214.

2. Materials and methods

2.1. Materials

Cold-pressed filtrated rapeseed oil without erucic acid, with an acid number of 1.6 mg g^{-1} , density of 920 kg m^{-3} , and water content of 600 ppm (produced by company RPN Slatiňany, Czech Republic), was used for transesterification with methanol (purity 99.8%, Penta, Czech Republic). Potassium hydroxide, purity 85% (Lach-Ner Neratovice, Czech Republic), was used as the catalyst. Other chemicals included: phosphoric acid, purity 85% (Penta, Czech Republic); calcium hydroxide, purity 99.9%, (Lach-Ner Neratovice, Czech Republic); and citric acid monohydrate, purity 100%, (Lach-Ner Neratovice, Czech Republic).

2.2. Research strategy

Transesterification was carried out by a homogeneous catalyst (methanol and KOH were used as catalysts, see 2.2); however, the reaction was stopped by neutralizing the catalyst with phosphoric acid, which was added to the whole reaction mixture (before separation). The advantages were a very fast and easy separation that only lasted several minutes (without centrifugation), zero potassium content and free glycerol in the ester phase, and a relatively high purity of glycerol in the glycerol phase (86–90 wt%). The side product of the neutralization was solid potassium phosphate, which was filtered from the reaction mixture and could be used as a fertilizer. Phosphoric acid was used to neutralize the catalyst (KOH); however, soaps also converted to FFAs. The FFAs increased the acid number, which could be higher than the EN14214 value; on the other hand, the absence of soap improved the separation. Therefore, calcium hydroxide was used to remove FFAs from the EP. The formed calcium soaps, which were solid, were removed from the EP by centrifugation.

Independent variables, such as the acid number of the input ester phase, molar ratio of calcium to FFAs and addition of water, were chosen because these variables influence the kinetic and thermodynamic aspects of the process. The upper and lower limits were chosen on the basis of preliminary experiments for each independent variable. The experiments were designed according to the Plackett–Burman designs. Dependent variables, which influence removal, were chosen: the acid number of the final ester phase (EP), amount of calcium ions and amount of water in the EP.

Linear models were used to describe the relation between the dependent (acid number, amount of calcium ions and water in the EP) and independent variables because the natural patterns of these dependences were unknown and because linear models are the simplest. Before statistical analysis, the independent variables were normalized in the interval from 1 to –1 (Table 1). The linear models were constructed with the help of statistical testing (significance of parameters, exclusion of outliers, regression triplet, etc.) according to [17]. The program STATISTICA 10 (StatSoft® CR) was used for statistical analysis.

2.3. Preparation of biodiesel with FFAs

Biodiesel was prepared in a batch glass reactor (1000 ml) from rapeseed oil, the molar ratio of methanol to oil was 6:1; the amount of catalyst (KOH) was calculated with respect to the acid number of oil according to [32]; the reaction temperature was $60 \text{ }^{\circ}\text{C}$, the time was 90 min; and 400 rpm was used. The catalyst was neutralized by the addition of hydro-phosphoric acid to the entire reaction mixture until the pH decreased to 2–3. Phosphoric acid neutralized the catalyst and formed free fatty acids from the soaps. The product of neutralization was solid potassium phosphate (KH_2PO_4), which was filtered from the reaction mixture. After filtration, distillation of excess methanol was carried out at a temperature $65 \text{ }^{\circ}\text{C}$ and a pressure of approximately 1 kPa. Then, the mixture was cooled to $25 \text{ }^{\circ}\text{C}$ and separated into the ester phase and glycerol phase. The ester phase, with a higher acid number, was used to remove FFAs.

The removal of FFAs was carried out in a spectrophotometer, where the addition of calcium hydroxide to the EP was monitored by transmittance at a constant wavelength, 567 nm (100% transmittance signifies pure methyl ester). An EP with a different acid number was used (Table 1). First, calcium hydroxide and water were weighed and placed into the cuvette ($50 \times 30 \times 20 \text{ mm}$), and then, 20 g of the EP was added. The amount of calcium hydroxide was calculated with respect to the amount of FFAs in the EP (1).

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