



Acceleration and simplification of separation by addition of inorganic acid in biodiesel production

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ABSTRACT

This paper describes a new approach to transesterification stopping and separation improving by the addition of inorganic acid, hydrochloric and phosphoric, to the whole reaction mixture after the reaction. The transesterification of oil was carried out by methanol and potassium hydroxide as the catalyst. The inorganic acid neutralises methoxide ions (formed from methanol and potassium hydroxide) and transforms soaps (formed by oil saponification) to fatty acids, which increases the acid number. The principle of stopping is the neutralization of the methoxide ions only. Best results are achieved by concentrated phosphoric acid with a ratio of 0.25 wt% to oil. The advantage is that separation is relatively fast (5 h) and the biodiesel conforms to EN 14214 without any other purification processes such as centrifugation, wet and dry washing and drying of the ester phase. Moreover, the content of glycerol in the formed glycerol phase is approximately 75%. This method of biodiesel production, which uses neutralization of methoxide ions after the transesterification followed by separation, saves energy because no purification processes are needed and no waste is formed. The biodiesel is more environmentally friendly because less energy is consumed.

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1. Introduction

Biodiesel, which is usually produced by the transesterification of triacylglycerides with low molecular alcohols, can be considered as one of the solution to fuel with similar combustion properties to petroleum diesel (Kapilan and Reddy, 2012). The triacylglycerides are contained in the vegetable oils, animal fats, microalgae or used frying oil.

The catalyst is necessary at mild reaction conditions (Marulanda, 2012). A homogenous alkali catalyst (KOH, NaOH and CH₃ONa) is the most often used in industry (Leung et al., 2010), (Cvengros and Cvengrosova, 2004). However, these catalysts cannot be reused because they are consumed by (i) the neutralization of the free fatty acids (FFAs), which are contained in oil or (ii) a side saponification reaction (Witoon et al., 2014). Moreover, the formed soaps make separation difficult (Wang et al., 2010). If the content of water and free fatty acids in oil is high, then the strong acids are more suitable as a catalyst (Su, 2013). The enzymatic or heterogeneous catalysts are also studied (Ferrero et al., 2016).

The stop of transesterification as a reversible reaction is one of the steps of biodiesel preparation (Reshad et al., 2017). In the case of homogenous alkali catalysts (KOH, NaOH), one method is the separation of the ester from the glycerol phase (GP), where the catalyst remains. Another method of stopping is to neutralise the catalyst by acid addition into the reaction mixture. It is possible to use weak acid such as gas carbon dioxide (Hajek et al., 2008) or strong inorganic acids. However, the use of inorganic acid is primarily applied for the kinetics studies (not for biodiesel production): the Shahidul and Bundy (2012) used concentrated phosphoric acid and Darnoko and Cheryan (2000) used concentrated hydrochloric acid.

In the case of stopping by separation, the ester phase (EP), which is usually known as crude biodiesel, contains impurities such as the unreacted glycerides, glycerol, FFAs, methanol, salts, soaps and vegetable dyes. Soaps, water, remaining catalyst and other impurities are usually present in the GP. Both phases have to be purified, i.e. further technological steps are necessary, which increases energy consumption of biodiesel production (Chuah et al., 2017). The crude biodiesel has to be purified by one of the following methods or their combination: wet or dry washing (traditional purification methods), membrane extraction or purification with the aid of ion liquids. Before the water washing, the alcohol excess is sometimes removed by distillation or evaporation; the neutralization of the

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Nomenclature

<i>an</i>	acid number of the EP, mg KOH g ⁻¹
<i>K</i>	potassium content in the ester phase, mg kg ⁻¹
<i>water</i>	water content in the EP, ppm
<i>w_G</i>	glycerol content in the EP, wt%
<i>w_{GF}</i>	free glycerol content in the EP, wt%
<i>w_{H₂O}</i>	water content in the GP, wt%
<i>w_{MG}, w_{DG}, w_{TG}</i>	weight ratio of MG, DG and TG in the whole reaction mixture to the initial weight of oil (key component), wt%
<i>w_{Salts}</i>	salts content in the GP, wt%
<i>w_{Soaps}</i>	soaps content in the GP, wt%
<i>Y</i>	yield of esters, wt%

Abbreviations

<i>EP, GP</i>	the ester phase, the glycerol phase
<i>FFAs</i>	free fatty acids
<i>TG, DG, MG</i>	triacylglycerides, diacylglycerides, monoacylglycerides; together these substances are referred to as glycerides

remaining catalyst is a part of the washing process and slightly reduces the water consumption. The water washing can be carried out by using hot deionized water (50–60 °C), acidified water, organic solvents and water or by using membrane to prevent formation of emulsions from water. Then washed biodiesel is dried over sodium sulphate or molecular sieves followed by filtration or by stripping with hot gas. The main drawback is the formation of wastewater during the process, which must be adequately treated before reusing or disposal, which is energy consuming (Stojkovic et al., 2014). Berrios and Skelton (2008) have found that adding of acid to the wash water helps with removing soaps. In this study, the authors concentrated on effective parameters of wet washing, they used three types of water (tap water, distilled water and water with 3 wt% of phosphoric acid) and three volume rates of water to biodiesel: 0.5:1, 1:1 and 1.5:1. The quality of water washing was monitored by the decrease of water content, soaps amount in the EP and the remaining catalyst. The best results for soaps and catalyst were achieved with acidified water at 60 °C with volume rate of water to biodiesel 1.5:1. In the case of water amount, the best results were achieved with tap water at 60 °C and volume rate of water to biodiesel 0.5:1 (Abbaszadeh et al., 2014). Pinheiro et al. (2014) performed a single washing-step of biodiesel purification, they used methanol as extractor agent, which could play an important role in the industrial process, due to less use of water for biodiesel purification. Usually, the water to biodiesel volume rate of 3:1 is used, in their proposition it was approximately 1:1. However, the used methanol had to be purified, which increased the energy consumption (Pinheiro et al., 2014) (Berrios and Skelton, 2008)

A more modern way of purification of crude biodiesel is dry washing, which removes impurities by adsorption or passing biodiesel through a bed of ion-exchange resins. Several sorbents are used for cleaning such as magnesium silicate (magnesol), calcium magnesium silicate and cheap biosorbents. A different type of ion-exchange resins can be also used for the purification of crude biodiesel instead of purification by water (Atadashi et al., 2011), one million litres of biodiesel are needed to replace about one thousand kilograms of ion-exchange resins (Brown et al., 2008). The disadvantage is reusing of resins, which is not recommended by the producers. The resins can be regenerated from free glycerol (from the crude biodiesel), but they cannot be regenerated from soaps or

metals (Munson et al., 2010). The main disadvantages of dry washing are (i) the purified biodiesel does not conform to standard EN 14214 and (ii) there is no utilization of solid waste after washing (Berrios and Skelton, 2008). The novel methods for purification of crude biodiesel are membrane extractions (Amelio et al., 2016) or usage of ion liquids and deep eutectic solvents, but these methods are not used on a commercial scale (Zhao and Baker, 2013). The main drawback is the high price of membranes and ion liquids, but their main advantage is that they are ecologically friendly (Troter et al., 2016).

This paper describes the neutralization of methoxide ions after transesterification (formed from potassium hydroxide and methanol) by inorganic acids (phosphoric and hydrochloric acid). The method of catalyst neutralization is used for production of biodiesel by transesterification, not only for stopping the reaction in the case of kinetics studies. The acid has to be added precisely, so that only methoxide ions remainder after the transesterification is neutralised. During the subsequent neutralization, the remaining methanol is removed by distillation and the reaction is separated in the separator funnel. The advantage is that the biodiesel conforms to EN 14214 after separation by gravitational field, i.e. this method replaces all purification processes. Therefore, the whole process of biodiesel production is less energy consuming and accordingly more environmentally friendly. This method has potential to be widely used in the industrial scale (Shahidul and Bundy, 2012) (Darnoko and Cheryan, 2000)

2. Materials and methods

In this section, (i) the chemical substances, which were used for experiments, (ii) the detailed description of transesterification process and (iii) analytical method determining important properties of the EP and the GP were introduced.

2.1. Material

Oil: the cold-pressed filtrated rapeseed oil without erucic acid, acid number 0.37 mg kg⁻¹, density 920 kg m⁻³ and water content 260 ppm (produced by the company Usti Oils s.r.o., Czech Republic)
 Methanol: 99.8% purity (Penta, Czech Republic)
 Catalyst: KOH, 85% purity (Lach-Ner Neratovice, Czech Republic)
 Phosphoric acid H₃PO₄, concentration 85 wt% (Penta, Czech Republic)
 Hydrochloric acid HCl, concentration 35 wt% (Penta, Czech Republic)

2.2. Transesterification of rapeseed oil and neutralization of the catalyst

Approximately 420 g (0.477 mol) of rapeseed oil was put into the reaction vessel and heated to the reaction temperature. It was approximately used 0.8 wt% of catalyst (KOH) to oil, the exact amount was calculated according to Hajek et al., (2009). The reaction conditions were the following: the molar ratio of methanol to oil 6:1, the reaction temperature 60 °C, the reaction time 90 min and the 400 rpm. The catalyst was dissolved in methanol and mixture was also heated to the temperature 60 °C and then put into the reaction vessel. Immediately after 90 min of transesterification, the remaining methoxide ions were neutralised by inorganic acid (H₃PO₄ or HCl) at the same conditions, i.e. the same temperature and type of reactor. The neutralization process was controlled by the pH and was finished, when the pH of reaction mixture stabilized (approximately after 2 min). The pH was also monitored within the whole transesterification process including neutralization, which was measured by electrode for pH measurement in

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