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Biodiesel: The influence of dealcoholization on reaction mixture composition after neutralization of catalyst by carbon dioxide

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ABSTRACT

Biodiesel is commonly produced by catalytic transesterification (reversible reaction) of oil/fat with excess alcohol. In the case of the basic catalyst, strong acid is usually used for catalyst neutralization; however acid converts soap to fatty acids (increases the acid number). In this paper, the utilization of carbon dioxide for catalyst neutralization is described. The advantage is that, the carbon dioxide does not transform soaps to fatty acids, but only neutralizes the catalyst (acid number is always less than 0.2 mg KOH/g). The neutralization takes place due to by an excess of CO_2, which transforms the catalyst to hydrogencarbonate. However during the alcohol removal by distillation from the whole reaction mixture, hydrogencarbonate is transformed to carbonate (catalytic properties). But the alcohol removal is fast enough that the reverse reaction to glycerides does not occur. The catalyst neutralization by CO_2 is environmentally friendly (consumed CO_2) and it can be used for all types of raw materials, alkali hydroxides and alcohols.

1. Introduction

Recently, the world importance of biodiesel production has significantly increased. The decrease of carbon dioxide emissions, the independence on imported crude oil and better sales opportunities for farmers are some of the reasons of biodiesel importance. Nowadays the mixing of fatty acid methyl esters (biodiesel) into fossil diesel fuel is requested by law in many countries [1].

Biodiesel is produced by the transesterification of edible or non-edible vegetable oils [2,3], animal fats or waste oils [4,5] and low-molecular alcohol. Transesterification is a reversible reaction. In the reaction, glycerol in the oil molecule is substituted by alcohol such as methanol and ethanol. To enhance the reaction rate, a catalyst or extra energy (high temperature and pressure – super critical state) are needed [6]. The most popular catalysis is basically catalyzed by potassium, sodium hydroxide or potassium carbonate because they are cheap and the catalysis is fast; their disadvantage is a side reaction – saponification (irreversible reaction). Acid homogeneous, heterogeneous – acid [7] or basic [8,9] and enzymatic catalyzes [10] are also possible. The catalyst accelerates the reaction in both directions (1), i.e. towards esters (E) and also to glycerides (MG, DG, and TG). The reaction is carried out with the excess of alcohol (A) because of a shifting of the reaction equilibrium towards esters. The whole reaction scheme including saponification (S – soap):

$$\begin{array}{ll} TG + A \rightleftharpoons DG + E & TG + OH^- \rightarrow DG + S \\ DG + A \rightleftharpoons MG + E & DG + OH^- \rightarrow MG + S \\ MG + A \rightleftharpoons G + E & MG + OH^- \rightarrow G + S \end{array} \tag{1}$$

The content of low-boiling material (most often alcohols) determined by flash point and methanol itself are limited by the EN 14214 to ensure the safety of biodiesel (especially during transport). The flash point (FP) decreases with increasing amounts of residual alcohol and other low-boiling solvents [11,12]. The exact correlation of methanol content in biodiesel with FP was not measured. For these reasons, the excess alcohol has to be removed after transesterification. But the reverse reaction to glycerides may occur during alcohol removal in the presence of the catalyst; therefore the catalyst is neutralized prior to alcohol removing [13] or the reaction mixture is separated to the light ester phase (EP) and heavier glycerol phase (GP) prior to alcohol removing [14].

An alkaline catalyst is usually neutralized by inorganic acids such as phosphoric acid [15]. The disadvantage of these acids is that they transform soap to fatty acid (increases acid number of biodiesel) and form insoluble potassium phosphate in methanol, which is necessary to be filtered off.

Our technology is unique in the removal of alcohol, because it is removed from the whole reaction mixture. The step has several advantages: biodiesel production take place in one single step without demanding equipment; the separation of the EP from the GP is faster because of higher differences in their densities (they are not diluted by methanol); a lower solubility of glycerol in the EP and the production of the GP with relatively high glycerol content. This technology was patented and practically used [16].

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This paper describes the usage of carbon dioxide as weak acid for the neutralization of the catalyst. Attention is also paid to other processes during methanol removal from the whole reaction mixture, e.g.: the correlation between the methanol content in the GP and methanol content in the EP.

2. Methods

2.1. Chemicals

Chemicals used for biodiesel preparation: Cold-pressed, filtered rapeseed oil, free of erucic acid (acid number 1.2 mg KOH g^{-1}, water content 610 mg kg^{-1}, density 920 kg m^{-3} at 25 °C, kinematic viscosity 35.0 mm^2/s at 40 °C, produced by the company RPN Slatiňany, Czech Republic). Potassium hydroxide pure (solid 90 wt.%). Methanol (technical). all Lach-Ner, Czech Republic. Demineralized water. Carbon dioxide (for food processing industry, Linde Gas a.s.).

2.2. Experimental procedure

The transesterification was carried out by methanol (the molar ratio of 1:6 rapeseed oil to methanol) under catalysis of 0.7 wt.% potassium hydroxide to oil in the batch reactor. The reaction took 90 min at a temperature of 60 °C and atmospheric pressure. Then the gaseous carbon dioxide was dosed into a reaction mixture (under atmospheric pressure) until the pH fell to a minimum value of 8.5 (after approximately 5 min), which was monitored by a glass electrode. After transesterification and neutralization, the whole reaction mixture (the EP and the GP together) was evaporated at a temperature of 60 °C and at the pressure of approximately 3 kPa (water pump); thereby the excess alcohol was removed (demethanolization). During the demethanolization, reaction mixture was sampled for further analysis. The concentration of various potassium salts (soaps, hydrogen carbonate and carbonate) and the concentration of mono-, di- and triglycerides were determined in the whole sample (without separation). The remaining part of the sample was after separation divided to the heavier glycerol phase and lighter ester phase. The methanol content was determined in both phases and the flash point was determined in the EP.

In order to compare the results with and without catalyst neutralization, the demethanolization of the reaction mixture without catalyst neutralization was also tested.

All regressions with data were made by the program Origin® 7.0.

2.3. Analytical methods

The contents of monoglycerides, diglycerides and triglycerides were determined by the GC method according to the EN 14105 (instrument: Shimadzu GC-2010 with a flame ionization detector).

The contents of potassium hydrogen carbonate, potassium carbonate and soaps were determined by acidimetric titration (HCl). The volume of escaped carbon dioxide from the GP was necessary to determine for the calculation of the amount of soaps and potassium hydrogen carbonate. The detailed description of determination is in [17].

The flash point was measured by the Pensky–Martens closed-cup method (EN ISO 2719) with instrument OB-305 (MIM Fabri, Hungary).

Methanol in both phases was determined by GC with TCD detection (Shimadzu GC-9AM). The metal column 1200 × 3 mm packed with Porapak Q (Waters Ass., USA), column temperature 115 °C and injection port temperature 130 °C with carrier gas He (36 cm^3/min) was used. The injected volume of the sample was 1 µl. Methanol was eluted in 1.2–1.3 min [18].

The carbon residue (CCR) of biodiesel was determined by the Conradson closed-cup method without preceding distillation. Thus, the measured values correspond directly with the US biodiesel norm (ASTM D6751) and with the EU norm (EN 14214, maximal permitted value 0.30 wt.% of 10% residue after distillation) after a multiplication by 10.

3. Results and discussion

3.1. Principle of treatment

The carbon dioxide and water form a weak carbonic acid, which cannot transform soaps (formed by side reaction – saponification) to fatty acids but neutralizes only the alkaline catalyst $-OH^-$ (2). This ensures that the acid number of formed biodiesel fills the norm (always less than 0.2 mg KOH/g) and the CO_2 cannot be overdosed.

$$2OH^- + CO_2 \rightarrow CO_3^{-2} + H_2O \tag{2}$$

The formed potassium carbonate (CO_3^{-2}) is also a catalyst of transesterification [19,20]. Therefore it can reverse the transesterification to raw materials (oil and alcohol) during the alcohol removal. Since neutralization proceeds with the excess of carbon dioxide, it was found that a reversible reaction takes place (3). Reaction is shifted towards HCO_3^-, because of excess carbon dioxide in the reaction mixture. Formed HCO_3^- is not a transesterification catalyst.

$$CO_3^{-2} + CO_2 + H_2O \rightleftharpoons 2HCO_3^- \tag{3}$$

During the distillation of excess alcohol, carbon dioxide and water are also escaping. Thus the equilibrium of the reaction (3) shifts to CO_3^{-2}, which can catalyze the transesterification towards glycerides and moreover saponificates glycerides and esters to potassium soaps. The saponification causes the formation of additional HCO_3^- (4).

$$\text{Glycerides, esters} + CO_3^{-2} \rightarrow HCO_3^- + \text{Soap} + CH_3OH \tag{4}$$

The precipitate was not formed in the reaction mixture, because the potassium (hydrogen) carbonates are dissolved in the GP.

The reactions among carbonate, hydrogencarbonate and carbon dioxide in water are known [21]. The same reactions proceed when sodium hydroxide is used as the catalyst for transesterification.

The neutralization consumes CO_2 as greenhouse gas. The potassium carbonates and hydrocarbonates, which are presented in the GP after separation, are possible to transform by phosphoric acid to potassium phosphate and CO_2 during purification of the GP [22]. The escaped carbon dioxide may be recovered and reused at the neutralization step. Therefore the neutralization does not consume any carbon dioxide (total balance of CO_2 is zero).

3.2. Correlation of methanol content with flash point

In the case of this paper, only residual methanol as a low-boiling point substance can be present in biodiesel. Therefore, the flash point was presupposed to depend only on the methanol content. The dependence of the FP on the methanol content was measured and data was curve fitted by a logarithmic function (Fig. 1). The same type of function was applied for the dependence of FP on ethanol content [23]. As one can see, the maximal value for methanol content according to EN 14214 (0.2 wt.%) corresponds with the minimal value of flash point (101 °C).

This correlation enables the determination of only methanol content and to calculate FP and vice-versa.