



The effects of cosolvents on homogeneously and heterogeneously base-catalyzed methanolysis of sunflower oil

Zoran B. Todorović, Olivera S. Stamenković, Ivica S. Stamenković, Jelena M. Avramović, Ana V. Veličković, Ivana B. Banković-Ilić, Vlada B. Veljković*

Faculty of Technology, University of Niš, Bulevar Oslobođenja 124, 16000 Leskovac, Serbia

HIGHLIGHTS

- ▶ KOH and CaO catalyze the sunflower oil methanolysis in the presence of cosolvents.
- ▶ Tetrahydrofuran favors the triacylglycerol mass transfer by reducing drop size.
- ▶ The CaO-catalyzed methanolysis is not speeded up with the use of cosolvents.

ARTICLE INFO

Article history:

Received 21 August 2012
 Received in revised form 6 November 2012
 Accepted 12 November 2012
 Available online 26 November 2012

Keywords:

Calcium oxide
 Cosolvent
 Drop size
 Methanolysis
 Potassium hydroxide

ABSTRACT

Homogeneously and heterogeneously base-catalyzed sunflower oil methanolysis was investigated with and with the presence of the cosolvents. In the former case, KOH and tetrahydrofuran (THF) were used as a catalyst and a cosolvent, respectively, and the reaction was performed at the reaction temperature of 10 °C and the methanol-to-oil molar ratio of 6:1. In the latter case, CaO and various organic solvents such as THF, *n*-hexane, dioxane, diethyl ether, triethanolamine, ethyl acetate and methyl ethyl ketone were employed as a solid catalyst and a cosolvent, respectively, and the reaction was carried out at the reaction temperature of 60 °C and the methanol-to-oil molar ratio of 6:1. The rate of KOH-catalyzed sunflower oil methanolysis increased with increasing the THF concentration up to 50% of the oil mass, which was due to the self-enhancement of the interfacial area as the result of decreasing the mean drop size. No effect of THF present at the concentration of 20% on the rate of CaO-catalyzed methanolysis was observed, but at higher THF concentrations, the reaction was delayed and the final fatty acid methyl esters (FAME) yield was decreased. Of all tested cosolvents, only *n*-hexane and THF slightly improved the methanolysis reaction in its initial period, triethanolamine and ethyl acetate had no effect, while diethyl ether, dioxane and methyl ethyl ketone negatively influenced the reaction rate and the FAME yield.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

The existing commercial biodiesel production processes mainly involve the homogeneously base-catalyzed methanolysis of edible oils. This reaction system is a two phase one, where mass transfer limitations due to immiscibility of the reactants determines the overall reaction rate at the beginning of the reaction. This problem can be overcome by using vigorous mechanical agitation, enhanced reaction temperature or cosolvents. The breakage of alcoholic reactant into a fine drop emulsion in the vegetable oil by intensive mixing increases the interfacial area and the triacylglycerol mass transfer rate [1]. The enhanced reaction temperature increases both miscibility of the reactants [2] and the reaction rate constants [3]. An organic solvent added as a cosolvent reduces immiscibility

of the reactants and produces a homogeneous solution, increasing the transesterification reaction rate [4]. However, it should not be forgotten that the cosolvent addition will incur additional costs and will require an additional step for its removal from the final reaction mixture. Guan et al. [5] warned that “excessive addition of cosolvent into the reaction system could reduce the transesterification rate and increase the operating cost”.

Since the work of Boocock et al. [4], many studies have been performed on the use of various cosolvents in transesterification reactions. Most of the previous works have been related to homogeneously catalyzed methanolysis [4–19]. Tetrahydrofuran (THF) has been mainly used as cosolvent [4–7,9–11,14,16,17], probably because of its low price, non-reactivity and easy separation from the reaction mixture after completion of the reaction, since methanol and THF have close boiling temperatures (65 °C and 67 °C, respectively). Some other solvents have been also investigated as cosolvents in transesterification reactions. Boocock et al. [7]

* Corresponding author. Tel.: +381 16 247 203; fax: +381 16 242 859.
 E-mail address: veljkovicvb@yahoo.com (V.B. Veljković).

recommended the use of THF as the best cosolvent. According to Guan et al. [12], dimethyl ether as an environmentally friendly solvent could replace THF as a cosolvent for the transesterification process. The same research team [5] used several cosolvents (THF, dimethyl ether, diethyl ether and methyl tertiary butyl ether) and found that dimethyl ether was the best one. Park et al. [18] have suggested the use of methyl esters as a cosolvent. Delgado [9] used methyl tertiary butyl ether and THF in the transesterification and interesterification of triacylglycerols with a mixture of methanol and methyl acetate, to enhance the reaction rate and to obtain methyl esters and triacetin. Encinar et al. [10] tested various cosolvents: diethyl ether, diisopropyl ether, dibutyl ether, methyl tertiary butyl ether, THF and acetone, among which methyl tertiary butyl ether and diethyl ether showing the best results. Pena et al. [19] studied the effect of three alkaline catalysts (CH_3ONa , NaOH , and KOH) and hexane as a cosolvent on the transesterification of castor oil. Hancsók et al. [14] employed THF and dioxane as cosolvents in a combined acid/base-catalyzed transesterification for the production of fatty acid methyl esters (FAME) from used frying oil having a high free fatty acids amount. Hernando et al. [15] studied the transesterification of rapeseed and soybean oils combining the use of tert-butyl methyl ether and microwave irradiation to reduce the mass transfer limitation in the first reaction stage. However, no study on the use of any of above-mentioned cosolvents in transesterification reactions has included the drop size measurement to visualize their effect on the overall reaction rate.

The increasing demand for biodiesel requires improvement of its manufacturing process, which means the use of large production capacities, new catalytic systems, non-edible vegetable oils and simplified operations ensuring a high biodiesel yield and smaller amounts of wastes. For instance, the use of heterogeneous (solid) catalysts in biodiesel production bears a number of benefits, compared to that of homogeneous catalysts. The processes of separation and purification of solid catalyst and products is greatly simpler and cheaper than those related with the use of a homogeneous catalyst. Also, the solid catalyst can be used repeatedly, reducing the operating costs. Despite the above benefits, the use of cosolvents in heterogeneously catalyzed methanolysis has been described only in a few papers [20–23]. A disagreement between different researchers on the importance of cosolvents, such as THF and *n*-hexane, for the performance of heterogeneously catalyzed methanolysis reactions is present in the available literature. The positive action of THF was reported by Gryglewicz [20] and Yang and Xie [23], while Ilgen et al. [21] and Kim et al. [22] observed an inhibitory effect of THF. Kim et al. [22] found that methanolysis reaction was improved in the presence of *n*-hexane, while Ilgen et al. [21] and Yang and Xie [23] reported a negative effect of this cosolvent. The observed disagreement on the effect of cosolvents on heterogeneously catalyzed transesterifications should be investigated in order to be clarified.

The present paper deals with homogeneously and heterogeneously base-catalyzed sunflower oil methanolysis with the presence of some cosolvents at the 6:1 methanol-to-oil molar ratio. In the former case, KOH and THF were used as a catalyst and a cosolvent, respectively. The reaction was conducted at 10 °C to lower the reaction rate and to facilitate the observation of mass transfer limitation in the beginning of the reaction. The goal was to show variations in the Sauter mean drop size and the drop size distribution during the reaction carried out in the presence of various concentrations of THF (from 0% to 100% of the oil mass). In the latter case, CaO and various organic solvents such as THF, *n*-hexane, dioxane, diethyl ether, triethanolamine, ethyl acetate and methyl ethyl ketone were employed as a heterogeneous catalyst and a cosolvent, respectively. The initial amount of catalyst was 5% (based on the oil mass), as it was used in a previous study [24], and the amount of THF was from 0% to 100% of the oil mass. The reaction was con-

ducted at 60 °C. The main aim was to reflect the effect of THF and some other cosolvents having different hydrophobicity and polarity on the CaO -catalyzed sunflower oil methanolysis.

2. Experimental

2.1. Materials

Commercial sunflower oil (Sunce, Serbia) was used. Methanol (99.8%) and KOH (85%) were purchased from Lachema (Czech Republic) and Merck-Alkaloid (FYR of Macedonia), respectively. CaO (extra pure) was from Centrohem (Serbia). Immediately before use CaO was activated by calcination at 550 °C for 2 h, as recommended elsewhere [24]. To avoid adsorption of water and carbon dioxide from the air on catalytic active sites on the catalyst surface, the activated CaO was cooled and then stored in a well closed, glass bottles in a desiccator containing CaCl_2 and KOH . Also, the following solvents were used: diethyl ether (Lachner), *n*-hexane (99%, Promochem, Germany), ethylacetate (99.5%, Merck), *n*-butylacetate (99%, Zorka-Šabac, Serbia), dioxane (p.a., Merck-Alkaloid), methyl ethyl ketone (HPLC grade 99.5%, JT Baker), propylene carbonate, triethanolamine (99%, Aldrich-chemic), *n*-hexane and 2-propanol (HPLC grade, JT Baker). The properties of the employed cosolvents and methanol, as well as minimum molar ratios required for achieving a complete dissolution of methanol and sunflower oil, are presented in Table 1. Standards of triolein, diolein, monoolein and a mixture of methyl esters of palmitic, stearic, oleic, linolenic and linoleic acids (20% of each ester) were purchased from Sigma Co.

2.2. Catalyst characterization

Morphological and textural properties of commercial (raw) CaO and calcined CaO were characterized by the nitrogen physisorption method. The morphology of samples was examined using a JEOL JSM 530 scanning electron microscope. High-resolution adsorption nitrogen adsorption-desorption isotherms were determined using a Sorptomatic 1990 Thermo Finnigan at –196 °C. Typically, 4 g of samples was used in analysis after outgassed under at 110 °C during 18 h. Data space volume was determined using helium. The textural parameters were calculated according to common methods using software package Advanced Data Processing Ver. 5.17.

Using the part of the adsorption isotherm which includes best linear fit for relative pressure up to 0.2, the specific surface area was calculated using the Brunauer, Emmett and Teller method [32]. Total pore volume was calculated at maximal adsorption pressure. Mesopore volume and pore size distribution were obtained according to the Barrett, Joyner and Halenda method [33] from desorption branch of isotherm, using standard isotherm Lecloux and Pirard [34]. The Dubinin–Radushkevich method was used for the calculation of micropore volume [35].

The basic strength of the catalyst was determined by the Hammett indicators method and expressed by an acidity function [36]. The following Hammett indicators were used: phenolphthalein ($H_- = 9.3$), thymolphthalein ($H_- = 10.0$), thymol violet ($H_- = 11.0$), 2,4-dinitroaniline ($H_- = 15.0$) and 4-nitroaniline ($H_- = 18.4$). The catalyst basic strengths were quoted as being stronger than the weakest indicator that exhibited a color change, but weaker than the strongest indicator that produces no color change.

2.3. Methanolysis

2.3.1. Homogeneously base-catalyzed methanolysis

The homogeneously base-catalyzed methanolysis without and with adding THF as a cosolvent was performed in a 1 L glass

Download English Version:

<https://daneshyari.com/en/article/6641883>

Download Persian Version:

<https://daneshyari.com/article/6641883>

[Daneshyari.com](https://daneshyari.com)