



Continuous sunflower oil methanolysis over quicklime in a packed-bed tubular reactor



Marija R. Miladinović^a, Olivera S. Stamenković^a, Vlada B. Veljković^{a,*}, Dejan U. Skala^b

^a University of Niš, Faculty of Technology, Bulevar oslobođenja 124, 16000 Leskovac, Serbia

^b University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, 11000 Belgrade, Serbia

HIGHLIGHTS

- Packed-bed tubular reactor is used for continuous methanolysis reaction.
- Low cost quicklime is used as catalyst.
- Effects of process variables on the methyl esters synthesis was evaluated.
- Kinetic model was validated through simulating the axial ester concentration change.
- Operational stability and leaching of the catalyst was determined.

ARTICLE INFO

Article history:

Received 20 January 2015

Received in revised form 18 March 2015

Accepted 24 March 2015

Available online 1 April 2015

Keywords:

Biodiesel

Calcium oxide

Methanolysis

Optimization

Packed-bed reactor

Quicklime

ABSTRACT

The continuous sunflower oil methanolysis catalyzed by quicklime in a packed-bed tubular reactor of 60 cm height was studied at 60 °C using methanol-to-oil molar ratios from 6:1 to 18:1 and weight hourly space velocities from 0.188 to 0.376 (kg/kg_{cat} h). The main goal was to establish the effect of the process variables on the fatty acid methyl esters (FAME) synthesis. A full factorial design was used to evaluate the significance of the three process factors (methanol-to-oil molar ratio, flow rate of the reactants and bed height) statistically. Moreover, the recently reported kinetic model of methanolysis was used to describe variations of FAME and triacylglycerols (TAG) concentrations along the reactor length. The kinetic model predicted the axial concentration profiles of TAG and FAME in the reactor with acceptable accuracy. A high FAME content (98.5%) could be achieved at the two thirds of the bed of quicklime bits without loss of catalytic activity within 30 h of continuous operation.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Biodiesel has become the dominant alternative to fossil diesel because of a number of its positive characteristics. It is a biodegradable and safe to handle fuel that requires a small modification of the currently used engines to be applied. Although biodiesel is more costly than petroleum diesel fuel, the economic disadvantage would be resolved by using non-edible oils as the feedstock. Similarly, the use of heterogeneous catalysts offers many benefits that affect the overall biodiesel production cost positively. They are easier for separation from the reaction mixture, less corrosive and environmentally friendly. Also, they can be reused with or without appropriate regeneration. Moreover, some of inexpensive solid catalysts, efficient under mild reaction conditions, are obtained from natural or waste materials. Finally,

solid catalyst can be used in continuous large-scale production processes that reduce the price of biodiesel. Therefore, the researchers have attempted to develop technologies that will be based not only on the use of inexpensive feedstocks but also on heterogeneous catalysts and continuous operation.

CaO-based catalysts have several advantages over other solid catalysts. They can be obtained from various calcium-containing minerals and waste materials having low or no price and their catalytic performance can be improved by calcination. Depending on the resource type, CaO can be reused with [1] or without [2] regeneration of catalytic activity. Recently, quicklime (basically CaO), which is obtained from limestone, has been shown as an efficient catalyst for the sunflower oil methanolysis after calcination [3,4].

CaO-based catalysts are usually employed in the powder form in batch reactors under intensive agitation. However, fine CaO powder causes the problem in separation from the final product [5]. When larger CaO particles are applied, then intensive agitation results in

* Corresponding author. Tel.: +381 16 247203; fax: +381 16 242859.

E-mail address: veljkovicvb@yahoo.com (V.B. Veljković).

Nomenclature

C_A	Concentration of TAG (mol/dm ³)	$(-r_A)$	TAG reaction rate (mol/(dm ³ h))
C_{A0}	Initial concentration of TAG (mol/dm ³)	TAG	TAG content in the FAME/oil fraction of the reaction mixture (%)
C_{B0}	Initial concentration of methanol (mol/dm ³)	x_A	TAG conversion degree, 1
C_{cat}	Catalyst concentration (mol/dm ³)	z	Height along the catalyst bed (cm)
C_R	Concentration of FAME (mol/dm ³)	z_0	Catalyst bed height (=60 cm) (cm)
C_{R0}	Parameter of Eq. (3) (mol/dm ³)	<i>Greek symbols</i>	
k_m	Apparent reaction rate constant (h ⁻¹)	τ	Residence time (h)
k	Reaction rate constant, Eq. (6) (dm ⁶ /(mol ² h))		
K	Parameter of Eq. (3) (mol/dm ³)		
K'	Parameter of Eq. (7) (dm ³ /mol)		

their breaking up into finer particles because of deficient mechanical properties. Hence, the use of larger CaO-particles in packed-bed tubular reactors (PBTRs) could be more convenient. Because of its low cost and simple construction, this type of reactor is most commonly employed for investigating continuous methanolysis of various vegetable oils [6–12]. To the authors' best knowledge, the methanolysis of vegetable oils over quicklime has not been studied in continuous PBTRs yet. Only Kouzu et al. [3] investigated the rapeseed oil methanolysis over limestone-derived CaO in a PBTR through which the reaction mixture was recirculated.

In this study, the sunflower oil methanolysis was conducted in a continuous PBTR filled with quicklime bits based on a full factorial design. Initially, quicklime bits used as a catalyst were characterized and external liquid–solid mass transfer limitation in the PBTR was studied. Also, the operational stability and leaching of quicklime were examined. The study was aimed at establishing the effects of the process variables (methanol-to-oil molar ratio, weight hourly space velocity, WHSV, and bed height) on the fatty acid methyl ester (FAME) formation using a statistical tool. In addition, the reaction kinetics was validated under isothermal, steady-state plug flow.

2. Materials and methods

2.1. Materials

Refined sunflower seed oil (Sunce, Sombor, Serbia) was chosen for experimental test because sunflower is the most common oil-plant for the Serbian region. The acid, iodine and saponification numbers of the oil were 0.24 mg KOH/g, 129 g I₂/100 g and 190 mg KOH/g, respectively. Quicklime was bought on the local market. Methanol (99.5%) used in the methanolysis reaction was purchased from Zorka Pharma (Šabac, Serbia). Methanol (used in the HPLC analysis), *n*-hexane and isopropanol, all of HPLC grade, were obtained from LGC Promochem (Wesel, Germany).

2.2. Catalyst preparation

Quicklime was crushed and classified using standard sieves. The largest fraction with particle size of 2–3.15 mm was used in the experiments. The catalyst was calcined at 550 °C for 4 h, cooled down in a desiccator and stored in a dark, well closed glass bottle in a desiccator containing calcium chloride and potassium hydroxide pellets. Before charging into the PBTR, the activated catalyst particles were washed with methanol to remove CaO dust from their surface. The XRD diffractograms and basicity of both raw and calcined quicklime can be found elsewhere [4]. The textural properties were determined by N₂ physisorption at 77 K as described by Miladinović et al. [4].

2.3. Experimental setup

The PBTR was composed of six tubular reaction stages (internal diameter: 3 cm, bed height per stage: 10 cm and total packed-bed volume: 420 cm³) and five connectors with a sampling valve (Fig. 1), thus allowing sampling along the reactor height. Both tubular reaction stages and connectors were made of glass. Each stage contained a packed-bed of quicklime bits (82 g per stage). The total mass of quicklime in the reactor was 492 g and the total length of the catalyst bed was 60 cm. Each tubular reaction stage was enclosed within a glass jacket. The reactants were stored in the reservoirs placed on digital scales. Sunflower oil and methanol were transported by the calibrated peristaltic (12000 Varioperex, LKB, Bromma, Sweden) and piston (HPLC Pump 2248, Pharmacia LKB, Uppsala, Sweden) pumps, respectively. Prior to entering into the reactor, methanol was introduced in the oil stream, and the mixture of the reactants was heated in a preheater at 60 °C, fed to the bottom of the first stage and flew upward through the

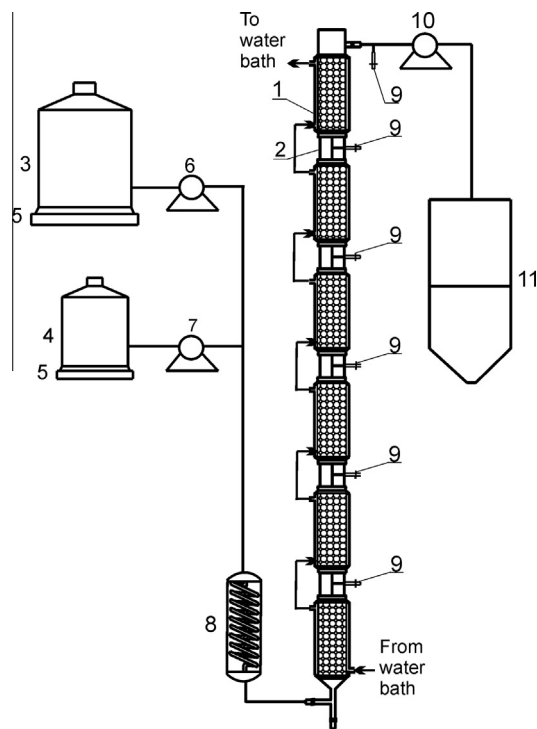


Fig. 1. Schematic drawing of the experimental set-up with the multi-stage PBTR: tubular reaction element (1), connector (2), sunflower oil reservoir (3), methanol reservoir (4), digital scales (5), peristaltic pump (6), plunger pump (7), preheater (8), sampling valves (9) peristaltic pump for the reaction mixture (10) and gravitational separator (11).

Download English Version:

<https://daneshyari.com/en/article/6635506>

Download Persian Version:

<https://daneshyari.com/article/6635506>

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