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Modeling and optimization of sunflower oil methanolysis over quicklime bits in a packed bed tubular reactor using the response surface methodology

Marija R. Miladinović [a], Olivera S. Stamenković [a], Predrag T. Banković [b], Aleksandra D. Milutinović-Nikolić [b], Dušan M. Jovanović [b], Vlada B. Veljković [a,*]

[a] University of Niš, Faculty of Technology, Bulevar oslobođenja 124, 16000 Leskovac, Serbia
[b] University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Department of Catalysis and Chemical Engineering, Njegoševa 12, 11000 Belgrade, Serbia

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ABSTRACT

The effect of the residence time (i.e. liquid flow rate through the reactor), methanol-to-oil molar ratio and reaction temperature on the fatty acid methyl esters (FAMEs) content at the output of a continuous packed bed tubular reactor was modeled by the response surface methodology (RSM) combined with the 3^3 full factorial design (FFD) with replication or the Box-Behnken design (BBD) with five center points. The methanolysis of sunflower oil was carried out at the residence time of 1.0, 1.5 and 2.0 h, the methanol-to-oil molar ratios of 6:1, 12:1 and 18:1 and the reaction temperature of 40, 50 and 60 °C under the atmospheric pressure. Based on the used experimental designs, the model equations containing only linear and two-factor interaction terms were developed for predicting the FAME content, which were validated through the use of the unseen data. Applying the analysis of variance (ANOVA), all three factors were shown to have a significant influence on the FAME content. Acceptable statistical predictability and accuracy resulted from both designs since the values of the coefficient of determination were close to unity while the values of the mean relative percentage deviation were relatively low (<±10%). In addition, both designs predicted the maximum FAME content of above 99%, which agreed closely with the actual FAME content (98.8%). The same optimal reaction temperature (60 °C) and residence time (2.0 h) were determined by both designs while the BBD model suggested a slightly lower methanol-to-oil molar ratio (12.2:1) than the 3^3 FFD model (12.8:1). Since the BBD realization involved three times smaller number of experimental runs, thus requiring lower costs, less labor and shorter time than the 3^3 FFD, it could be recommended for the optimization of biodiesel production processes.

1. Introduction

The most widely studied process for biodiesel synthesis is the base-catalyzed methanolysis of vegetable oils. The researchers have commonly aimed at the optimization of the process variables (i.e. reaction conditions) in order to maximize the FAME yield. When many variables affect the biodiesel synthesis, the application of a statistical experimental design is preferable in comparison with the traditional "one-factor-at-a-time" optimization method. This approach allows studying and analyzing the influence of the process variables on the selected response with a smaller number of experiments, which considerably reduces laboratory work and reagent consumption required to get objective conclusions.

Although the application of mechanistic models, such as those applied to the flow reactors [1,2], is a preferable option, as they allow for a better extrapolation, the statistical models are widely used for modeling and optimization of biodiesel production processes, as well as the evaluation of the statistical significance of the process factors' effects on the desired response. The response surface methodology (RSM) is most frequently applied in combination with the full factorial design (FFD) [3–7], central composite design (CCD) [8–11] or Box-Behnken design (BBD) [12,13]. Both the 2^4 FFD and BBD have quite recently been applied for the optimization of biodiesel production from sunn-hemp oil catalyzed by KOH and CaO [14] and para rubber seed oil catalyzed by SO_3H-MCM-41 [15] in a batch stirred reactor, but the two designs were not compared. The second order polynomial equation is commonly used as an approximation of FAME content or yield in the ranges of the investigated process variables such as the methanol-to-oil

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

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molar ratio, reaction temperature, reaction time or residence time, and catalyst amount or height of catalyst bed [3,6–8,11,12,16–21]. This approach permits assessment of the statistical significance of the process factors and their interactions using the analysis of variance (ANOVA). Finally, knowing the relationship between the response of interest (FAME content, yield or productivity) and the process factors, the optimal levels of the factors can be determined.

In the case of the continuous biodiesel synthesis, the CCD is the most commonly applied experimental design combined with the RSM. Baroutin et al. [9] employed the face-CCD consisting of 20 runs and six replicates of the center point, which was coupled with the RSM to estimate the effect of reaction temperature, catalyst amount and cross flow circulation velocity of the reactants on the biodiesel production in a packed bed membrane reactor. Hu et al. [17] optimized the gas-liquid countercurrent integrated process for biodiesel production using the orthogonal plan of CCD with 12 runs followed by the RSM to determine the optimal values of the factors. A couple of optimization studies of the reaction conditions in packed-bed tubular reactors (PBTRs) refer to the lipase-catalyzed alcoholysis of vegetable oils [22,23].

The present work is focused on the optimization of the biodiesel synthesis in a PBTR filled with quicklime bits. The optimization method is based on the BBD and the 3^3 FFD coupled with the RSM. The main goals were to evaluate the effects of the residence time (i.e. liquid flow rate through the reactor), methanol-to-oil molar ratio and reaction temperature on FAME content at the reactor output by the ANOVA and to correlate the FAME content with these process factors. The two experimental designs of different structure and complexity were compared with respect to the estimated errors in order to check if the simpler BBD can adequately replace the more tedious, more time consuming and more expensive FFD. So far, the BBD has not been compared with other experimental designs when applied to the optimization of a continuous heterogeneously catalyzed biodiesel synthesis.

2. Materials and methods

2.1. Materials

Refined sunflower oil (Sunce, Sombor, Serbia) was used. The acid, saponification and iodine values of the oil were 0.24 mg KOH/g, 190 mg KOH/g and 129 g I_2/100 g, respectively, determined according to the AOCS official methods. The oil consisted of the following fatty acids: palmitic acid 7.3%, stearic acid 3.4%, oleic acid 34.4% and linoleic acid 54.9%. Certified methanol of 99.8% purity and quicklime stones were purchased from Lachema (Neratovice, Czech Republic) and at the local market, respectively. The HPLC grade methanol, 2-propanol and *n*-hexane were obtained from LAB-SCAN (Dublin, Ireland).

2.2. Catalyst preparation

Quicklime bits were used as a solid catalyst in the experiments. The catalyst preparation included quicklime stones' crushing, classifying of quicklime bits using standard sieves as well as calcining, storing and washing the 2–3.15 mm bits fraction, as described elsewhere [2]. Textural properties of both raw and calcined quicklime have already been reported by Miladinović et al. [2,24], such as its specific surface area (2.0 m^2/g), specific total pore volume (7.2 mm^3/g) and the most abundant pore diameter (3.7 nm). The calcined quicklime contained mainly CaO (>99%) with negligible amount of $CaCO_3$ while other metal oxides were not detected by the XRD analysis [24]. The quicklime bits could be used within 30 h of continuous operation without loss of catalytic activity [2].

2.3. Equipment

The experimental set-up consisting of a packed bed tubular reactor and auxiliary equipment is schematically presented in Fig. 1. The tubular reactor was a glass column (internal diameter: 3.5 cm) with a glass jacket. The column was first packed with a glass Raschig rings layer (5 mm; about 2 cm high), and two glass beads layers (2 and 3 mm; each about 1 cm high), forming a pre-bed, in order to promote better distribution of the reactants. When calculating the flow rate through the packed bed, the bed porosity of 0.45 was adopted. Washed quicklime bits were then added to the column (bed height: 44 cm) while water, thermostated at 60 °C, was pumped through the jacket from a heating circulator bath. The reservoirs for sunflower oil and methanol were placed on digital scales and their weights were monitored with time. Sunflower oil and methanol were transported by calibrated peristaltic (12000 Varioperpex, LKB, Bromma, Sweden) and piston (HPLC Pump 2248, Pharmacia LKB, Uppsala, Sweden) pumps, respectively. Methanol was introduced into the sunflower oil stream before the reactor, the mixture of the reactants was fed to the bottom of the reactor through a centrally placed glass tube (internal diameter: 6 mm) and flew upward through the reactor. Passing from the top to the bottom of the reactor, the mixture of the reactants was preheated to the desired temperature. Samples of the outlet reaction mixture were taken by means of a sampling valve during at least three residence times. The constant composition of the outlet reaction mixture during this period of time proved the steady-state operation of the reactor. For instance, at the methanol-to-oil molar ratio of 12:1, the temperature of 60 °C and the residence time of 2 h, the values of FAME content determined

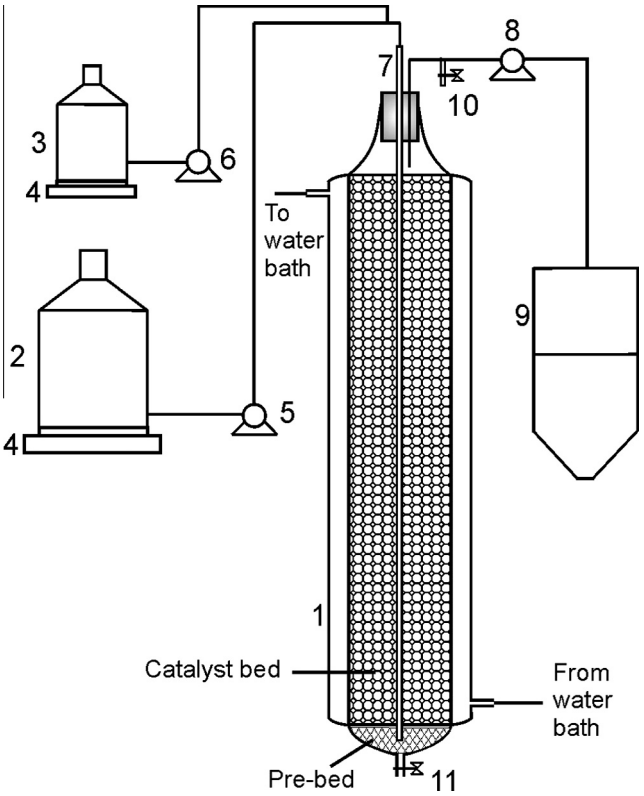

Fig. 1. Schematic drawing of the experimental set-up containing a PBTR: reactor column with a jacket (1), sunflower oil reservoir (2), methanol reservoir (3), digital scales (4), peristaltic pump (5), plunger pump (6), glass tube for reactants supplying (7), peristaltic pump for the reaction mixture (8), gravitational separator (9), sampling valve (10) and draining valve (11).