Optimization and kinetics of sunflower oil methanolysis catalyzed by calcium oxide-based catalyst derived from palm kernel shell biochar

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HIGHLIGHTS

- CaO-rich catalyst obtained from palm kernel shell biochar (PKSB) has promising potential for biodiesel production.
- Sunflower oil methanolysis catalyzed by PKSB-based catalyst is optimized.
- Optimum reaction conditions ensure the best FAME content of 99%.
- Reaction rate law is changing- and first-order with respect to TAG and FAME.
- PKSB catalyst can be reused without any treatment in three consecutive cycles.

ARTICLE INFO

ABSTRACT

Sunflower oil methanolysis over CaO-based palm kernel shell biochar (PKSB) catalyst was assessed by coupling full factorial design with modeling, optimization and kinetic studies. According to the analysis of variance, the effect of reaction temperature and methanol-to-oil molar ratio on the fatty acid methyl ester (FAME) synthesis is significant, while the effect of catalyst loading is statistically negligible. The optimum reaction conditions are found to be catalyst loading of 3 wt%, temperature of 65 °C and methanol-to-oil molar ratio of 9:1, ensuring the best FAME content of 99%. The kinetic model of the methanolysis of sunflower oil, catalyzed by PKSB-based catalyst, combines the changing- and first-order reaction rate laws with respect to triacylglycerols and FAMEs, respectively. The high activation energy (108.8 kJ/mol) indicates the temperature sensitivity of the reaction. The CaO-based PKSB catalyst can be reused without any treatment in three consecutive cycles with no significant drop in activity. Since the calcium content in the biodiesel product is higher than the standard limit, the overall process should include a purification stage.

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1. Introduction

Biodiesel is an alternative fuel that is technically applicable, economically competitive and environmentally beneficial. Conventionally, biodiesel production is performed by homogeneous base-catalyzed transesterification (most frequently methanolysis) of plant oils and animal fats because of moderate reaction conditions and a short reaction time. However, these processes have several drawbacks such as the impossibility of catalyst reuse, difficulty of operation, energy demand for the separation and purification of biodiesel, and the production of a large amount of wastewater in the purification stage [1]. These problems can be overcome using heterogeneous (solid) catalysts that offer many benefits such as easy separation from the reaction mixture, less risk of corrosion, less environmental hazard and possibility of reuse.

Among the solid catalysts, calcium compounds in the form of neat, loaded, mixed or supported CaO, are very often used as catalysts for transesterification of oily feedstocks. The CaO-based catalysts possess high basicity, require mild reaction conditions, produce high biodiesel yield, have low or no cost and are easy to prepare from widely-available materials of natural origin or waste precursors. In the past few years, ashes of different origins have been tested as catalysts for biodiesel production [2–4]. Recently, Bazargan et al. [5] have shown that calcium carbonate contained in palm kernel shell biochar (PKSB) is a promising source material for producing a CaO-based catalyst with activity for the

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transesterification of sunflower oil. CaO-based catalysts are usually employed in powder form in batch reactors, although they are also used in packed-bed reactors [6,7].

For increasing the process efficiency, knowledge of the effect of reaction conditions on biodiesel yield and transesterification reaction rate are of great importance. Statistical [8–14] and experimental [15–18] optimizations have been used to evaluate the effect of reaction conditions on CaO-catalyzed transesterification reactions and to determine the optimal reaction conditions ensuring the highest biodiesel yield. Since the experimental approach is time consuming and cost-excessive, statistical methods are more powerful. So far, response surface methodology (RSM) combined with the central composite [8–10,14], Box–Behnken factorial [11,12] or factorial [13] design has been used. Various kinetic models supposing zero [19,20] or first order [21–28] reactions with respect to triacylglycerols (TAGs) have been used for methanolysis reactions over calcium-based catalysts. In fact, the reaction order varies during the transesterification reaction from the zeroth order to the first order [24,29]. More complex models [7,26] involve the liquid–liquid mass transfer limitation to predict the reaction rate during the whole course of sunflower oil methanolysis. These kinetic models have been recently verified for calcium-based catalysts including CaO [30,31].

In the present work, the CaO-rich PKSB catalyst was used in sunflower oil methanolysis under moderate reaction conditions and atmospheric pressure. The influence of the most important operational factors, namely reaction temperature, methanol-to-oil molar ratio and catalyst loading, on the sunflower oil methanolysis over the PKSB catalyst were studied in the following ranges: 45–65 °C, 9:1–15:1 and 3–7% (based on the oil weight). The experimental data were generated by a 3^3 full factorial design of experiment (DOE) with five central points. This study included both the optimization and kinetics of the methanolysis reaction over the PKSB catalyst aimed at developing the statistical and kinetic models describing the relationship between fatty acid methyl ester (FAME) content, and the operating variables and the time variation of the TAG conversion degree, respectively. In addition, leaching of calcium and reusability of the PKSB catalyst was evaluated in order to estimate its potentials for biodiesel production at a commercial scale. Finally, the biodiesel product was characterized in accordance with biodiesel standard requirements.

2. Materials and methods

2.1. Materials

The PKSB is in the form of a fine black powder (particle size ranged from about 1 μm to more than 100 μm). Obtained from a gasifier for electricity production, it was calcined at 800 °C for 2 h under atmospheric pressure immediately before use as a catalyst [5]. The catalyst has been thoroughly characterized elsewhere, showing that after calcination, the catalyst is predominantly composed of calcium oxide. In fact, the calcination process breaks down the calcium carbonate content of the kernel shell biochar into gaseous carbon dioxide which leaves the system, and calcium oxide which remains. Also, the basic strength of the catalyst is in the range 11.0–15.0, with a total basicity of 0.516 mmol/g [5].

Edible sunflower oil (Dijamant, Zrenjanin, Serbia) was purchased in a local shopping store. The acid value of the oil was 0.2 mg KOH/g. Certified methanol of 99.5% purity was purchased from Zorka Pharma (Šabac, Serbia). Methanol, 2-propanol and n-hexane, all of HPLC grade, were purchased from LAB-SCAN (Dublin, Ireland). Hydrochloric acid (36 wt%), was purchased from Centrohem (Belgrade, Serbia). Anhydrous sodium carbonate and sodium sulfate were obtained from Sigma Aldrich (Saint Louis, USA).

2.2. Equipment and reaction conditions

The methanolysis reaction of sunflower oil over the PKSB catalyst was performed at atmospheric pressure in a 250 mL three-neck glass flask, equipped with a reflux condenser and a magnetic stirrer. The flask was placed in a water tank keeping the temperature constant at the desired level by circulating water from a thermostated bath. A 3^3 full factorial design with five central points was used to optimize the reaction at methanol-to-oil molar ratios of 9:1, 12:1 and 15:1, PKSB catalyst amounts of 3%, 5% and 7% (based on the oil weight) and temperatures of 45, 55 and 65 °C. These reaction conditions were chosen by considering the literature data on the methanolysis reaction catalyzed by CaO [32–37]. So far, the CaO-catalyzed methanolysis of sunflower has been studied in the ranges of methanol-to-oil molar ratio and catalyst loading of 6:1 to 18:1 and 1% to 10% (based on the oil weight), respectively. Hence, we narrowed ranges of both methanol-to-oil molar ratio and catalyst loading to 9:1 to 15:1 and 3–7%, respectively. The upper temperature level (65 °C) is actually methanol's boiling temperature, and the lower level (45 °C) ensures an acceptable reaction rate. The catalyst loading was varied around the reported optimum value for CaO-based catalysts (5%) [5]. Sunflower oil has been used as a TAG source in a few studies of the kinetics [28,29] and optimization [38] of the methanolysis reaction catalyzed by neat CaO and quicklime. The methanolysis reaction was also performed under the optimal reaction conditions determined by the applied design of experiments and RSM. The final reaction mixture was used to obtain biodiesel for characterization and to evaluate calcium leaching.