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Application of the full factorial design to optimization of base-catalyzed sunflower oil ethanolysis

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HIGHLIGHTS

- ▶ Optimization of NaOH-catalyzed ethanolysis by full factorial design with replication.
- ▶ Evaluation of the impact of three important operational factors on FAEE yield by RSM.
- ▶ RSM is a powerful tool for modeling and optimizing of biodiesel production.
- ▶ RSM helps one to understand how the process factors influence the FAEE yield.
- ▶ Interrelationships among the process factors are determined and statistically evaluated.

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ABSTRACT

In the present work, the sodium hydroxide-catalyzed synthesis of fatty acid ethyl esters (FAEE) from sunflower oil and ethanol was optimized using a 3^3 full factorial design of experiments with two replications and the response surface methodology (RSM). The effects of temperature, ethanol-to-oil molar ratio and catalyst loading on the FAEE were studied. The ANOVA results shows that at the 95% confidence level all three factors and the 2-way interactions of reaction temperature with ethanol-to-oil molar ratio and catalyst loading significantly affect the FAEE formation. A second-order polynomial equation is developed to relate the FAEE purity and the operational variables (temperature, ethanol-to-oil molar ratio and catalyst loading). The fitted model shows a good agreement between predicted and actual FAEE purities ($R^2 = 0.937$; mean relative percentage deviation ±1%), demonstrating the validity of the regression analysis in the process optimization. The optimal process conditions were: ethanol-to-oil molar ratio of 12:1, reaction temperature of 75 °C and catalysts loading of 1.25%. The RSM is proved to be suitable method for optimizing the operating conditions in order to maximize the FAEE purity.

1. Introduction

Rapid growth of population with industrial and technological developments led to the increased consumption of fossil fuels thus reducing their reserves. A way to solve this problem is the development and exploration of alternative renewable fuels, which must be technically feasible, economically competitive and environmentally acceptable such as bioethanol and biodiesel. The latter fuel is promising non-toxic, safe to handle and biodegradable fuel [1], which offer few benefits, including reduction of greenhouse gases emissions as well as regional and social development [2].

The most-used process for the biodiesel production is the alcoholysis reaction between triacylglycerols (TAGs) from vegetable oils and animal fats and alcohol in the presence of a catalyst (base, acid or enzymes). Generally, the alcohols employed in the biodiesel production are methanol and ethanol, although other short-chain alcohols can be also used [3]. The use of different alcohols has some impact on the reaction kinetics, but the final yield of esters remains more or less the same [4]. Therefore, the selection of an alcohol is based on its cost and properties. Methanol is highly toxic, so any kind of spill presents a serious problem [5]. Ethanol is preferable to methanol because of its much higher dissolving power of TAG, lower toxicity [6] and safer handling [7,8]. The further advantage of ethanol is the possibility of its production from agricultural renewable resources through fermentation. Thus, the biodiesel based on ethyl esters is a complete natural (agricultural) biofuel. Ethyl esters are more interesting as fuel than methyl esters because they have an extra carbon atom (from ethanol molecule) which slightly increases the heat content and the cetane number [9]. Another good side of ethanol is that the ethyl esters have lower cloud and pour points than methyl esters, improving the cold start [4]. Also, ethyl esters have a less negative effect on the

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environment compared to methyl ester due to low emissions of nitrogen oxides (NO_x), carbon monoxide (CO) and smoke density [10].

The alcoholysis of TAG using homogeneous catalysts has been widely studied [3,11–14]. Homogeneous base catalysts are mainly applied in industrial biodiesel production. Alkoxides of alkali metals are the most efficient, but alkali hydroxides, being cheaper and easier to handle, are most frequently used [15]. Base catalysts achieve high conversions in less than an hour of reaction at temperatures from 40 to 65 °C [3,16,17], which is their important advantage over acid catalysts (sulfuric acid) that require higher temperature (100 °C) and the longer time of the reaction (3–4 h) [4].

The influence of individual factors on the fatty acid ethyl ester (FAEE) yield and the reaction rate cannot be generalized since it depends on the reactor type, the reaction conditions, the characteristics of catalyst and the nature of TAG source. Determination of the optimal operating and reaction conditions in a reactor for a selected TAG source, alcohol and catalyst system is especially important in order to increase the process efficiency and to reduce the cost of the process. A factorial design of experiments has been used extensively for the purpose of biodiesel production process development and optimization because it allows the simultaneous analysis of the effects of many process variables at different levels as well as their interactions [18]. The RSM is usually applied in order to define optimal conditions for achieving the maximum FAEE yield.

A literature survey on optimization of base-catalyzed ethanolysis of both edible and non-edible vegetable oils is presented in Table 1. These studies were related to the ethanolysis of sunflower [8], soybean [3,19], rapeseed [20], castor [21–23], *Brassica carinata* [8], cottonseed [24] and *Raphanus sativus* [25,26] oils catalyzed with potassium and sodium hydroxides or ethoxides in different and wide ranges of ethanol-to-oil molar ratio and reaction temperature. The influence of ethanol-to-oil molar ratio, catalyst loading, reaction temperature, mixing intensity and reaction time were the most frequently examined factors affecting the FAEE yield. Catalyst loading and ethanol-to-oil molar ratio were analyzed in all reported studies, reaction temperature was not included in a study where it was replaced by reaction time, which was involved in a few researches. Stirrer speed was considered as an operational factor only in a study. The 2^3 full factorial design (three factors at two levels) in combination to the response surface methodology (RSM) has been mainly employed. Only Silva et al. [3] used a 2^4 central composite design with four factors (temperature, reaction time, alcohol-to-oil molar ratio and catalyst loading), while Valle et al. [26] applied a $2^{(5-1)}$ fractional factorial design which included five factors (agitation speed being the fifth variable). No research has been performed with four factors at three levels despite several studies have shown the existence of a significant curvature in the case of some vegetable oils [3,8,19,21–24]. There is no example in the literature involving the 3^3 full factorial design and the RSM for base-catalyzed ethanolysis of vegetable oils. Recently, such a model has been reported for optimization of base-catalyzed methanolysis of sunflower oil under ultrasound irradiation [27]. Fitting a full quadratic model, the three-level designs are useful for modeling possible curvature in the response function, although they are more expensive in experimental cost and time for conducting experiments than simpler models. The third level for factors facilitates fitting quadratic regression relationships between the response and factors [28]. Besides, data analysis is easier if the factorial design is run with replication because an average value for each run and information on the dispersion (variability) of the response are obtained.

According to the most researches, catalyst loading and ethanol-to-oil molar ratio have the greatest effect on the FAEE yield, although there are a couple of studies pointing out ignorable impacts of the latter factor [8,20,26]. Catalysts are normally expected to have a positive effect on the FAEE formation, although the negative effect was found in the ethanolysis of rapeseed [20] and cottonseed [24] oils. KOH has a positive catalytic impact on FAEE yield, independently of the type of oil [8]. In the case of castor oil, however, with increasing the amount of catalyst, the FAEE yield decreases, while the ethanol-to-oil molar ratio has a positive effect [21]. Several research groups have reported that reaction temperature has no statistically significant impact [22–25]. The influence of reaction temperature on the FAEE yield might be dependent on the type of vegetable oil. The reaction temperature is the significant variable, having a positive influence on the FAEE yield during the sunflower oil ethanolysis, but in the case of the *B. carinata* [8] and rapeseed [20] oil ethanolysis the reaction temperature manifests a negative effect (influence). According to Valle et al. [26], the agitation intensity had the negative influence on the FAEE yield from *R. sativus* L. oil in the presence of sodium ethoxide as a catalyst.

In the present work, the effects of the three, most important operational factors in different ranges on the ethanolysis of sunflower oil catalyzed by NaOH were studied. The main objective was to evaluate the effect of the catalyst loading (0.75–1.25% based on the oil weight), the reaction temperature (25–75 °C) and the ethanol-to-oil molar ratio (6:1–12:1) on the FAEE purity using the RSM. The experimental data were generated by a 3^3 full factorial design of experiments with two replications. For the first time, the impact of three most important operational variables, namely catalyst loading, ethanol-oil-molar ratio and reaction temperature was evaluated by a 3^3 full factorial design of experiments with two replications in order to optimize FAEE production by base-catalyzed ethanolysis reaction.

The ranges of process factors were chosen by considering the literature data on the properties of the ethanolysis reaction. The upper temperature level (75 °C) is close to ethanol boiling temperature (78 °C), and the lower level (25 °C) is, in fact, the room temperature. So far, the base-catalyzed ethanolysis of vegetable oils has been studied in the ranges of ethanol-to-oil molar ratio and catalyst loading of 3:1–15:1 and 0.25–1.5% (based on the oil weight), respectively. The optimal ethanol-to-oil molar ratio appears to depend on the type of TAG source, being 12:1 for soybean [29], and used frying [4] oil, 9:1 for *Cynara cardinculus* oil [6] and 5:1 for sunflower oil [8]. The ethanol-to-oil molar ratio of 6:1, which is most usually employed, was chosen as the minimum ratio in our study while the optimum ratio of 12:1 was selected as the highest one. According to the most reported studies, optimal NaOH loading is 1% [4,6,30], although much lower values of 0.3% and 0.4% have been also reported by Kucek et al. [29] and Domingos et al. [25], respectively. The catalyst loading applied in the present study was varied around the most often reported optimum value (1%). Sunflower oil has been used as a TAG source in a few studies of the kinetics [16,17] and optimization [8] of the ethanolysis reaction. The time period of 5 min was chosen based on a previous study of the base-catalyzed sunflower oil ethanolysis [31], where it was shown that the reaction reached or was close to the equilibrium in the 5 min reaction time in the ranges of the applied operational variables.

2. Experimental

2.1. Materials

Refined, edible 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 J2/100 g, respectively, determined according to the AOCS official methods [32]. The density and viscosity of the oil at 20 °C were 918.4 g/L and 92.0 mPa s, respectively. Absolute ethanol and sodium hydroxide pellets of min 98%