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Complete analysis of castor oil methanolysis to obtain biodiesel

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HIGHLIGHTS

- Response Surface Methodology was suitable to optimize castor oil transesterification.
- The most influential variables were methanol:oil ratio and catalyst concentration.
- High ester content could be reached in a wide range of experimental conditions.
- The optimum conditions led to biodiesel with 97 wt% ester content.

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ABSTRACT

Biodiesel production provides an alternative non-fossil fuel without the need to redesign current direct injection engine technology. In this work biodiesel production from castor oil was analyzed studying all of the main variables of the process. Experimental design was used to evaluate the influence of catalyst concentration, methanol:oil molar ratio, reaction temperature and reaction time in the methyl ester content reached by castor oil transesterification. Results were analyzed by Response Surface Methodology and a quadratic polynomial model was achieved. The model fitted properly the data, as was shown by the validation experiments. The most influential variables were catalyst concentration and methanol:oil molar ratio and the optimum conditions were 0.064 mol L^{-1} of CH_3OK, 18.8:1 as methanol:oil molar ratio, 45 °C and 10 min of reaction. In these conditions, 97 wt% methyl ester content biodiesel was achieved.

1. Introduction

Biodiesel is a promising diesel fuel substitute because it is a clean renewable fuel which can be used in any direct injection engine without the need to redesign the current technology. Biodiesel is derived from renewable and domestic feedstock and shows higher biodegradability than fossil fuels excellent lubricity and negligible sulfur content [1,2]. For biodiesel–diesel blends, comparable engine efficiency was showed. From an environmental point of view, in spite of higher emission level of NOx, the emission from biodiesel combustion contained lower amounts of CO, CO_2, HC and smoke [3].

The most common method to obtain biodiesel is the transesterification of vegetable oils or animal fats. In the reaction, triglycerides are reacted in presence of a catalyst with an alcohol with short-chain [2,4]. Methanol is the most used alcohol because it is the least expensive alcohol and it shows chemical advantages such as its shorter chain and its polar nature [1,5]. The most employed catalysts are homogeneous alkaline catalysts such as NaOH, KOH, CH_3ONa and CH_3OK and methoxides are the most suitable due to their ability to dissociate into the methoxide and the metal ion without the production of water during transesterification reaction [6].

Biodiesel feedstock can be categorized into three groups: vegetable oils (edible or non-edible oils), animal fats and used waste cooking oil. Biodiesel has been mainly produced from edible vegetable oils all over the world. More than 95% of global biodiesel production is made from edible vegetable oils and this fact has an influence on the global imbalance to the market demand and the food supply [5]. In addition, the price of this kind of feedstock makes 70–80% of the total biodiesel cost. Non-edible oils, which are not used in human nutrition and whose plants could grow in barren lands, should be increasingly used. Non-edible oil plants usually can be cultivated in lands unsuitable for human crops with much lower cost and no influence in food market [7].

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Castor oil is one of the most often used non-edible oil in biodiesel synthesis [7]. Castor plant is originally a tree or shrub and there are different varieties that can be cultivated. Castor oil seeds usually contain 40–55% oil and the average yield of castor oil seed in the world is about 1.1 t ha^{-1}, although it may be possible to obtain a maximum of 4.2 t ha^{-1}. Therefore, castor is amongst the plants with the highest oil yield potential [8]. Biodiesel from castor oil has been obtained and its properties has been studied, as well as, the properties of blends with biodiesel from different origin and diesel fuel [9,10].

The study of biodiesel production is usually carried out by the analysis of the influence of the reaction parameters in the transesterification of triglycerides. To carry out this analysis Response Surface Methodology (RSM) is one of the most suitable methodologies. This is a useful statistical technique to optimize a process because it allows the simultaneous consideration of many variables at different levels and the interactions between those variables. Moreover this methodology only requires a reduced number of experimental runs to generate statistically acceptable results [11].

There are a lot of works where ethanolysis of castor oil with basic homogeneous catalyst has been studied; the most relevant ones are listed below. De Oliveira et al. [12] assumed a Taguchi experimental design to study the influence of NaOH concentration (0.5–1.5 wt%), ethanol:oil molar ratio (3:1–9:1) and reaction temperature (30–70 °C) and time (1–3 h). All main variables of reaction were studied and 96.2% of conversion was reached under the optimal conditions (0.5 wt% catalyst, 3:1 ethanol:oil, 70 °C and 3 h). De Lima da Silva et al. [13] used RSM to optimize the transesterification reaction of castor oil using ethanol as alcohol and sodium ethoxide as catalyst. The studied parameters were reaction temperature (30–80 °C), catalyst concentration (0.5–1.5 wt%) and ethanol:oil molar ratio (12:1–20:1). The best results (93.78 wt% ester content) were reached at 30 °C with large catalyst content and lower ethanol:oil ratio or with lower catalyst content and large alcohol percentage. Cavalcante et al. [14] kept 30 °C as a constant parameter and studied the influence of ethanol:oil molar ratio, catalyst content and reaction time in the yield of biodiesel after the transesterification of castor oil with KOH as catalyst. In this work, the highest yield (close to 86%) was obtained using 11:1 as ethanol:oil molar ratio, 1.75 wt% KOH and 90 min as reaction time. Barbosa et al. [15] studied the production of biodiesel from castor oil and mixed castor and soybean oils. In the used conditions, they managed only 30% ethyl esters content after 30 h of reaction. Montoya et al. [16] used NaOH as catalyst and adopted RSM as methodology to optimize catalyst amount, ethanol:oil ratio and reaction temperature. The maximum ethyl ester content was 93.64 wt% using 1.2 wt% catalyst with respect to oil weight, 9.86:1 ethanol:oil molar ratio, 30 °C and 1 h.

On the other hand, the number of works where methanol was used is more limited. Meneguetti et al. [17] started with a comparison of ethanolysis versus methanolysis. In this work they concluded that similar yields could be obtained using both alcohols but reaction time for methanolysis was shorter. Canoira et al. [18] achieved total transesterification conversion using 1 wt% CH_3ONa, 5:1 methanol:oil molar ratio and 40 °C, although the study of variables was carried out one by one. Dias et al. [19] grew castor plants, extracted its oil and produced biodiesel. Moreover, they established models to predict biodiesel yield and methyl ester content among other properties. The models depended on reaction temperature and reaction time. The highest reached ester content was 83.41 wt%, carrying out the reaction at 65 °C for 8 h.

Considering the background, methanolysis has been less studied than ethanolysis as route to obtain biodiesel from castor oil; although this has been showed as a faster route. In addition, it is important a global study where optimal conditions were established taking into account all the main variables. In this way, the aim of this work was to achieve the optimization of the parameters which affect methanolysis of castor oil, using CH_3OK as catalyst. Catalyst concentration, methanol:oil molar ratio, reaction temperature and reaction time were studied in this work by the RSM. In addition, catalyst concentration was considered as molar concentration taking into account the total reaction medium, instead of as percentage based on the oil weight, because the effect of the alcohol:oil molar ratio could be mask by the increase or decrease of the real catalyst concentration in the medium.

2. Materials and methods

2.1. Materials

Refined castor oil, supplied by INTERFAT (Barcelona, Spain), was transesterified using methanol (99.6%) as alcohol and potassium methoxide (90%) as catalyst, both were purchased from Panreac and Alfa Aesar, respectively. Sulfuric acid (95–98%) to neutralize the catalyst was also purchased from Panreac. The reagents used for oil characterization were of analytical grade. Methyl esters (employed as standards in the chromatographic determination) were purchased from Sigma–Aldrich.

2.2. Transesterification reaction

The reactions were carried out under atmospheric pressure in a spherical glass reactor (500 mL) provided with a condensation system, sampling outlet, magnetic stirring, heating and temperature control system. A water batch was used to maintain the reaction temperature. The amount of oil and alcohol was fixed to reach 300 mL in every reaction and the catalyst concentration was measured as molar concentration. To carry out the experiments, the oil was preheated up to desired temperature, and then the alcohol-catalyst mixture was added to the reactor. Reaction time was established for every reaction and sulfuric acid was used to stop the reaction by catalyst neutralization. The final mixture was washed with distilled water until glycerol, methanol and the salts of the neutralization were removed. The remaining water was removed by heating at 110 °C.

2.3. Experimental design and statistical analysis

A central composite design (CCD) was applied to find out the influence of the operational conditions of the transesterification reaction, such as catalyst concentration, methanol:oil molar ratio, temperature and reaction time, on the methyl ester concentration. A three-level-four-factors CCD was adopted, requiring 29 experimental runs whose operational conditions are shown in Table 1. The variables were coded in the range of −1 to +1 to allow a direct comparison between variables according to Eq. (1):

$$x_i = \frac{2(X_i - X_{\min})}{(X_{\max} - X_{\min})} - 1 \quad (1)$$

where x_i is the normalized value of the variable X at condition i; X_i is the actual value; $X_{\min}$ and $X_{\max}$ are the lower and upper limit, respectively. The limits for each variable were chosen by considering preliminary tests: catalyst amount: 0.028–0.064 mol L^{-1}, methanol:oil molar ratio: 9:1–22:1, reaction temperature: 33–57 °C and reaction time: 10–30 min.

Experimental reactions were run at random to minimize errors due to possible systematic trends in the variables. Results were analyzed via RSM in order to fit a second-order polynomial model (Eq. (2)). Model fit quality was evaluated by variance analysis (ANOVA) for the model and a confidence level of $\alpha = 5\%$ was used