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Enhancement of the jojobyl alcohols and biodiesel production using a renewable catalyst in a pressurized reactor

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ABSTRACT

In this paper, the study of the methanolysis of Jojoba oil using CaO derived from mussel shells in a Parr reactor has been conducted through the use of two different mathematical tools: Surface Response Methodology and kinetic modeling. First of all, the factorial design of experiments allowed to determine the influence of the three chosen variables in the process. The three variables studied are the reaction temperature, the methanol:Jojoba oil ratio and the catalyst percent. The variables which have the higher positive effect on the methanolysis of Jojoba oil, in a pressurized environment, are the methanol:oil ratio and the temperature whereas the catalyst percent has a slight negative impact on the process, within the experimental limits. The reaction time was reduced from 10 to 5 h and the Jojoba oil conversion reached a maximum of 96.3% when the Parr reactor reaches 10 bars approximately; which supposes a great advance regarding other studies conducted at atmospheric pressure. Finally, a kinetic model, which includes the assumption for mass transfer limitations on the process, was obtained using the same variables as the design of experiments and it fits the experiments accurately.

1. Introduction

These days, some of the most promising alternative processes for biodiesel production are still unprofitable or economically improvable because of their limitations such as long reaction time, difficulties in the separation steps, unaffordable amounts of solvents and many more. One of these cases is the Jojoba oil methanolysis and ulterior jojobyl alcohols synthesis through a two-step crystallization separation, where biodiesel is the co-product as it can be seen in Fig. 1. This entire process was designated as Jojoba oil biorefinery and it was designed and studied by Sánchez et al. [1–4] where high-added value monounsaturated alcohols were obtained as main product and biodiesel as co-product after transesterification reaction and crystallization separation.

Jojoba oil is usually obtained by cool pressing and consecutive solvent extraction of Jojoba seed [5], which can be found in a perennial shrub under extreme weather conditions [6]. The countries which have the highest production of this oil are the United States, Israel, Mexico and South Africa because of the suitable soil for the Jojoba cultivation. The whole seed is not completely extractable and only 55% of the jojoba seed can be obtained in oil form [6,7] when cool pressing and solvent extraction are combined. Regarding the oil, it is important to clarify that its composition is completely different from the rest of vegetable oils because is formed by long chains of esters instead of glycerides [6]. The peculiar molecular composition of this oil confers special properties that are valuable for the chemical and pharmaceutical industries [8]. That is the reason why Jojoba oil production will probably increase in order to satisfy the current market demand.

Jojobyl alcohols and monounsaturated alcohols represent a group of chemicals with an associated high-added value because of its numerous applications in pharmaceuticals, cosmetics or surfactants [9]. In addition, it has been proved that alcohols with a carbon-chain between 14 and 20 and a number of unsaturations between 1 and 4 are antiproliferatives and can fight against enveloped viruses [10]. Therefore, the cost of this alcohols is one of the limitations of its use because 1 g of this pure alcohols can reach 55 $ in the market nowadays (Nucheck Prep).

The co-product in the Jojoba oil methanolysis is the fatty acid methyl esters, or biodiesel, which can be used to increase the profitability of the process [2,3]. Biodiesel is defined by the ASTM as "long-chain monoalkyl esters derived from vegetable oils or animal fats" and among its many advantages are the reduction of CO_2 global emissions, it is renewable, and it reduces the dependency from

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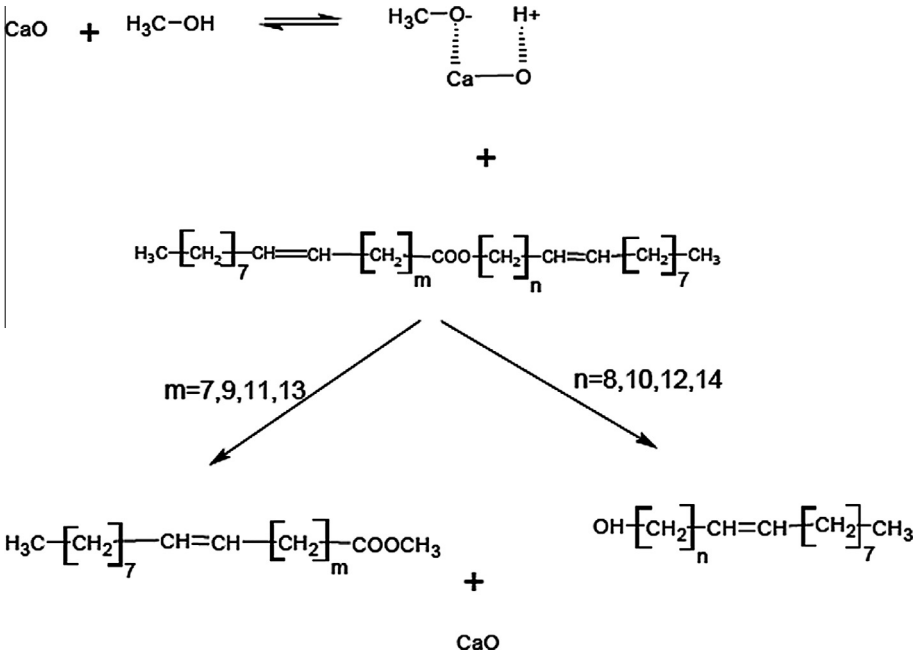

Fig. 1. Scheme of the methanolysis of Jojoba oil using CaO as catalyst.

fossil fuels [11]. This biofuel has experienced a huge controversy related to the possibility that many crops are being used for energy intentions instead of food purposes [12] and that caused the controversy named "fuel vs food" [13]. Because of this scenario, non-edible oils, such as Jojoba and Jatropha oils, and biofuels derived from algae have been investigated by many researchers in order to clear up the biodiesel situation [14,15].

Biodiesel is usually obtained through transesterification reaction using homogeneous, heterogeneous or enzymatic catalysts. In the case of Jojoba oil, the most interesting type of catalysts are heterogeneous. In the case of homogeneous catalyst, several difficulties arrived due to the washing and purifying steps required [1,2]. Among all the heterogeneous catalysts used for conducting the transesterification reaction, CaO has received many attention because its activity, it can be recycled and its low-cost [1,16–20]. Moreover, CaO can be obtained from natural sources such as mussel or egg shells through calcination process resulting in a green, renewable catalyst. The most important drawback in the use of CaO for the transesterification is its rapid poisoning by CO_2 and H_2O from the air and it must be used immediately after calcination step for avoiding the loss of catalytic activity [1].

In this paper, the main objective was to reduce the reaction time of the methanolysis of Jojoba oil using a pressurized atmosphere with a Parr reactor. In a previous study [1], the reaction time for this process was set in 10 h at atmospheric pressure with an associated oil conversion of 93.9%, which does not permit to have a biofuel which fulfill the minimum requirements marked by the European Legislation after the crystallization separation. However, the use of a pressurized atmosphere under slightly more severe reaction conditions allows to increase the Jojoba oil conversion (96.3%) and to reduce up to half the reaction time of the methanolysis. Also, the study includes the optimization of the process using a full central composite design were the maximum oil conversion is reached at 140 °C, methanol:Jojoba oil ratio of 6 and 6% of catalyst percent where the study determines that the oil conversion reaches 98% after 5 h of reaction time. Finally, the kinetic model has been determined for this process and it fits the 15 experiments adequately. It is very important to clarify that, all the equations are only valid within the range of the variables.

2. Materials and methods

2.1. Reagents and materials

Jojoba oil was purchased from Jojoba Israel (Kibbutz Hatzerim, Israel). The oil has been already characterized according to AOCS official method and UCM method as reported elsewhere [1]. Certified methanol of 99.8% purity and GC standards were supplied by Sigma Aldrich. The catalyst was obtained by the calcination of mussel shells (*Mytilus galloprovincialis* species) from local market as detailed elsewhere [1,18]. The catalyst preparation has been already detailed and published elsewhere [1].

2.2. Experimental setup

Experiments were performed in a 600 cm^3 pressurized Parr reactor, where 110 cm^3 of Jojoba oil were poured into the reacting vessel. The diameter of the blade used was 4.5 cm and the reactor was equipped with a two-blade system. The reaction temperature was achieved using an electric mantle and the reaction temperature was controlled by Haake GH Fisons (Germany) bath whereas the heat created by the agitation system was stabilized by Thermomix 1420 (B. Braun Melsungen AG, Germany) bath.

Experiments have been conducted following these steps: Jojoba oil, the methanol and the catalyst were added to the reactor and then the vessel was hermetic sealed. When the set temperature was reached a sample was taken out, and just at that moment the reaction time was considered zero. During the experiments the pressurized environment and impeller speed were maintained constant. When the reaction was finished the product went through a filtration process and the catalyst was recovered. Finally, the samples were purified using a Buchi Rota vapor R3 (Buchi Labortechnik AG, Switzerland) for eliminating the surplus of methanol and were analyzed by gas chromatography.

2.3. Product analysis

Fatty Acid Methyl Esters (FAME), Jojoba oil and jojobyl alcohols were monitored using a Bruker scion 436 chromatograph equipped