



Biodiesel production using supercritical alcohols with a non-edible vegetable oil in a batch reactor

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ABSTRACT

In the present work, the transesterification of non-edible oil with methanol and ethanol is studied. The reactor phase transition are directly observed in a double windowed cylindrical reactor and the conversions to fatty esters is measured. The optimization of the process conditions was carried out based on a statistical design of experiments where the key process variables were studied over different ranges to obtain a reliable model for the efficiency of the reaction as a function of reaction time, temperature, pressure and alcohol to oil molar ratio. From direct observations and the modeling of the phase behavior, a better understanding of the supercritical alcohol transesterification process is obtained as well as the confirmation of the phase equilibrium predictions based on the CCA-005 model.

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1. Introduction

The production of fatty acid methyl and ethylesters is of great industrial interest because of their direct use as biodiesel. Most of the biodiesel currently produced uses rapeseed or soybean oil, methanol and an alkaline catalyst. The main products of the reaction are fatty esters and glycerin. The high value of vegetable oils as food products makes production of a cost-effective fuel very challenging [1]. However, crude oils, animal fats and waste cooking oils can also be converted into biodiesel. Some problems with processing these low cost oils are related to the presence of water and free fatty acids [2]. The transesterification of vegetable oils using supercritical alcohols is an alternative for biodiesel industrial production. Recent experimental studies of non-catalytic transesterification by Saka and Kundiana [3,4] have shown that the process is not sensitive to both free fatty acids and water contents, and high reaction rates are observed at conditions close to the critical properties of methanol.

Non-edible vegetable oils constitute another attractive option for biodiesel production. In the present work, the transesterification of fodder radish—*Raphanus sativus* L. var. *oleiferus* Stokes oil (a non-edible vegetable oil) in supercritical alcohols is studied in order to find optimum operating conditions. Fodder radish oil

has been regarded as an interesting option to produce biodiesel in Brazil, since the seeds have high oil content and the oil can be easily recovered by pressing. The plant has rapid development and has been used for green fertilization [5]. The study of the supercritical transesterification with ethanol, besides like that of methanol, is justified considering the large production of ethanol from renewable resources in South America.

In the present work, a phase equilibrium engineering analysis is applied to the transesterification of fodder radish oil in supercritical ethanol and methanol to study the influence of the pressure and a single phase condition in the transesterification reaction. Phase equilibrium engineering is the design of the phase condition required for a given process. This design is made on the basis of modeling of phase equilibria, knowledge of the phenomenological behavior or experimental information. Examples of phase equilibrium engineering applied to reaction and separation process can be seen elsewhere [6,7]. In this study, direct observations and modeling of the phase behavior is carried out in order to find feasible homogeneous operating conditions at moderated pressures. Then, the different variables affecting the non-catalytic transesterification reaction are evaluated to set the operating conditions and to demonstrate the feasibility of the operating conditions proposed previously. The best values of the variables in the experimental range studied are determined by applying a Doehlert design of experiments [8] and response surface methodology to determine how these variables influence the reaction. The results obtained are also interesting from the point of view of the continuous process

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