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Advances on kinetics and thermodynamics of non-catalytic supercritical methanol transesterification of some vegetable oils to biodiesel

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ABSTRACT

Kinetic and thermodynamic parameters of the non-catalytic supercritical methanol transesterification reaction of castor, jatropha, pongamia, tobacco, soybean and jojoba oils to biodiesel production were evaluated in the present study. The experiments were conducted in an 83 ml closed batch reactor at different temperatures (250–350 °C) and reaction times (15–90 min), and at optimal methanol-to-oil molar ratios (15:1 in the case of jojoba wax-oil and 43:1 for the rest of the oils). The pressure reached in the reactor ranged from 10 to 43 MPa. Integral method was used to determine appropriated reaction orders by an adjustment of experimental data to pseudo-zero, pseudo-first and pseudo-second order kinetic equations using Levenberg-Marquardt algorithm. Pseudo-first-order kinetic equation was found to be the most appropriate to describe the supercritical transesterification reaction of the vegetable oils studied. Rate constants and Arrhenius parameters were calculated, the activation energy followed the sequence: castor oil < jatropha oil < tobacco oil < pongamia oil < soybean oil < jojoba wax-oil. It is difficult to explain the behavior of jojoba and castor oils in relation to that of the rest of vegetable oils because they have a very different structure and fatty acid composition, respectively. However, the aforementioned sequence observed for the rest of vegetable oils (jatropha, tobacco, pongamia and soybean oils), which have a similar structure and fatty acid composition, can be attributed to the content of linolenic acid in the oil: the higher the content of linolenic acid, the higher the activation energy and the lower the reaction rate. Finally, thermodynamic study showed that the non-catalytic supercritical methanol transesterification reaction is non-spontaneous (endergonic) and endothermic in nature.

1. Introduction

It is widely known that the reserves of fossil fuels are running out and the concern over environmental degradation and over-exploitation of natural resources has driven the search for alternative renewable energies to fossil fuels for the future [1,2]. In addition, mitigating anthropogenic changes due to Global Warming will require “abatement” technologies or renewable energies in order to reduce greenhouse gasses emissions [3]. Biodiesel can be one of these renewable energies due to it has been reported that around 50–80% of CO_2 emissions can be saved by using biodiesel compared to petroleum diesel [4]. Biodiesel is defined as a mixture of long chain fatty acid methyl esters (FAMEs) derived from renewable lipid feedstocks, such as vegetable oils or animal fats, which are formed mainly by triglycerides (TGs). Biodiesel is composed by FAMEs with fatty acid chain lengths of C14:0-C24:3 [1] for its use in compression ignition engines, among others. Biodiesel offers several advantages compared to diesel fuel, such as no sulfur emissions, less CO production and significant reduction in smoke [5].

Several methods for the transesterification of vegetable oils and animal fats to biodiesel production have been reported to date, such as homogeneous and heterogeneous acid- and alkali-catalyzed, enzyme-catalyzed, microwave- and ultrasound-assisted, and non-catalytic supercritical processes [6]. Among all the aforementioned methods, the supercritical process has undergone vigorous development as the technology offers several advantages over other methods, including the fact that it does not require either the use of catalysts, or the pretreatment of feedstocks, and can be applied to a wide variety of feedstocks with a high reaction rate and short residence times [2,7]. Moreover, the purification of the products is much simpler and more environmentally-friendly compared to conventional catalytic processes

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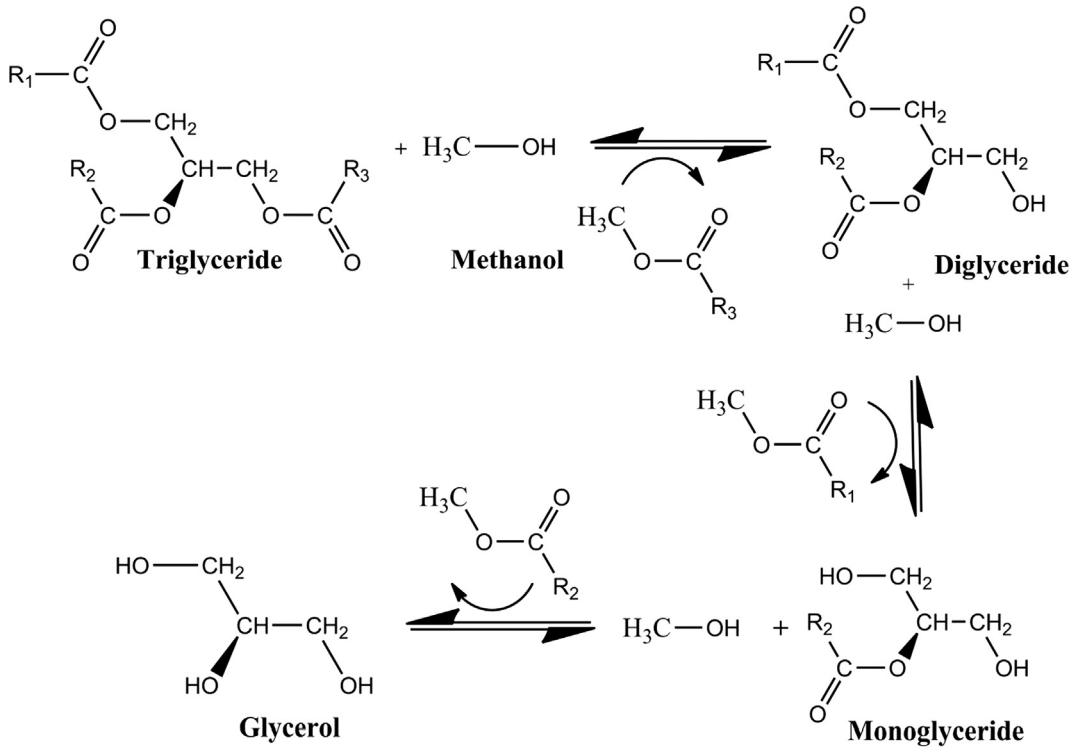

Fig. 1. General scheme of transesterification reaction of triglycerides using methanol.

in which saponification products and catalyst have to be removed from the biodiesel fuel [2,7,8].

There are two fundamental aspects to consider while studying chemical reactions, one dynamic (kinetics) and one static (thermodynamics). Chemical kinetics deals with the speed with which a reaction occurs, the variables that affect it (generally, reactant nature, concentration, temperature, pressure, phase or phases in which the reaction occurs and catalyst presence) and the mechanism through which takes place the reaction. Therefore, kinetics informs of the time necessary for equilibrium to be reached. In the case of thermodynamics, only the initial and final states of the system are of interest. Thus, thermodynamics deals with the systems in equilibrium, studies the direction and extent of the reaction, and report whether a reaction is possible or not. Hence, from the kinetic and the thermodynamic study it can be known the path through which the reaction takes place (*i.e.*, the mechanism of the reaction) [9].

The typical transesterification reaction of TGs in the presence of methanol for producing both FAMEs and glycerol occurs in three consecutive and reversible steps (see Fig. 1). In the first one, 1 mol of methyl ester and 1 mol of diglyceride (DG) are obtained from the one initial mol of TG. In the second stage, 1 mol of monoglyceride (MG) and a new mol of methyl ester are produced from the mol of DG formed in the first stage. In the last step, the mol of MG from the second stage produces a new mol of methyl ester and 1 mol of glycerol [2].

The alcohol-to-oil molar ratio for the supercritical alcohol transesterification of vegetable oils has been widely studied in the literature and there is a clear consensus that the optimal alcohol-to-oil molar ratio ranged from 40:1 to 45:1, regardless the type of oil used [2,5,7,10–19]. In the case of jojoba wax-oil, which is composed of complex esters (each one containing only an ester bond) of monounsaturated fatty alcohols and acids instead of TGs, the optimal alcohol-to-oil molar ratio for its supercritical transesterification (occurring in only one reversible step) ranged from 13:1 to 15:1 [7]. Therefore, optimal methanol-to-oil molar ratios of 15:1 and 43:1 were used in the present study for the supercritical transesterification of jojoba and the rest of vegetable oils, respectively.

The kinetic study of the transesterification reaction is usually carried out by both integral and differential methods. The complexity of this type of reactions makes it necessary to use approximations in order to simplify the calculations, such as to consider alcohol in excess, which obliges to ignore the inverse reactions, and the transesterification global reaction without intermediate steps [20–24]. Conversely, some authors take into account the reaction intermediates to calculate the kinetic parameters [25,26]. In the case of non-catalytic supercritical transesterification and esterification, some different kinetic models for single-step global reactions have been reported in the literature, such as first-order and irreversible transesterification solved by the integral method [20,21,27]; first-order and irreversible transesterification solved by the differential method [28]; first-order and reversible esterification solved by the differential method using non-linear optimization [29]; first-order and irreversible esterification solved by the integral method [30]; pseudo-first-order and irreversible transesterification solved by the integral method using non-linear regression fitting [31]; and second-order and irreversible microwave-assisted esterification solved by the differential method using non-linear regression fitting [32].

As can be appreciated, a wide variety of ways to calculate the kinetic parameters of non-catalytic supercritical transesterification of vegetable oils has been used. However, to the best authors' knowledge, in order to establish the best reaction order, no study has yet been carried out on the fitting of the experimental data to integrated kinetic equations for different reaction orders. Therefore, the aim of the present study is to provide the best fit functions and kinetic parameters for the kinetic modeling of non-catalytic supercritical methanol transesterification of castor, jatropha, pongamia, tobacco, soybean and jojoba oils by testing different reaction orders. In addition, the values of some