



Full Length Article

Experimental and kinetic modeling of acid oil (trans)esterification in supercritical ethanol

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ABSTRACT

This work reports experimental and kinetic modeling of the coupled esterification and transesterification reactions ((trans)esterification) of a model acid oil (a mixture of soybean oil and oleic acid) using ethanol at sub and supercritical conditions in a continuous tubular reactor. Process variables, namely temperature (220–350 °C), pressure (100–200 bar) and ethanol to acid oil molar ratio (2:1–20:1) as well as the effect of the initial amount of free fatty acids in the raw material were studied. The best condition for the ethylic supercritical (trans)esterification of soybean oil with 20 wt% of oleic acid was 280 °C, 100 bar, and ethanol to acid oil molar ratio of 4:1, where 80% of ester yield was reached in 60 min. It was observed that increasing the free fatty acid content increased the reaction rate and reaction yield. The proposed autocatalytic kinetic model presented a good fit in relation to the experimental data.

1. Introduction

Biodiesel is considered as one of the main energy source substitutes for the fossil fuels. In addition to the environmental benefits, one of the main advantages of biodiesel is the similarity of its properties to the petrodiesel, so few modifications are required in the current engine systems [1]. The conventional method for biodiesel production is the transesterification of triacylglycerols with a short chain alcohol, for example, methanol and ethanol, in the presence of alkali catalyst (KOH and NaOH) generating glycerol as a by-product [2–4]. However, alkaline transesterification is only suitable for raw materials containing low free fatty acids (FFA) content (lower than 1 wt%), such as refined vegetable oils [1,5]. This specificity of the raw material makes the biodiesel production not economically competitive with the petroleum-based fuel.

An alternative to overcome this disadvantage is the use of cheaper and low-quality raw materials, such as residual oils, non-edible vegetable oils and animal fats [6]. The use of these oils also can reduce the wastes with a potential hazard to the environment [7]. These acid oils normally present FFA content above the limit allowed for the transesterification, what leads to undesirable reactions decreasing the yields of the desired product [8].

The residual raw material can be processed in a two steps process (acid esterification as a pretreatment followed by alkaline transesterification), in a single reaction in the presence of heterogeneous acid catalysts or performing the reaction at supercritical conditions. When

the reaction is carried out in two steps, ester yields around 90% are obtained in about 60 min of reaction using homogeneous catalysts for both reactions (esterification as pre-treatment and transesterification) [1,9–12]. The disadvantages of a homogeneous catalysis process applied to biodiesel from acid raw material are the large volumes of neutralization residues, additional products purification steps. The use of a heterogeneous catalyst can overcome these disadvantages, but it needs catalysts capable to deal with such raw materials. The heterogeneous catalysts are less corrosive, easy to separate and reusable [13]. Many acid catalysts can catalyze simultaneous the reactions involved in acid oils [6,13,14]. From the results presented by Konwar et al. [6], Zhang et al. [13] and Boz et al. [14] for example, those authors observed the versatility of this process, since raw materials with a free fatty acid content within 5–40% were tested. However, a common feature regarding these heterogeneous catalysts is the long reaction times required to obtain high conversions (higher than 8 h).

Transesterification and esterification (biodiesel production) at supercritical conditions have been proposed as a potential technology to biodiesel production, in which it is possible to produce alkyl esters with high yields in short reaction times. This technology is more tolerant to water (moisture) and free fatty acids contents present in the raw material than other reaction systems [8]. In addition, either transesterification or esterification at supercritical non-catalyzed reaction systems eliminates the need for a catalyst simplifying the purification steps [6,15–17].

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1.1. Transesterification reaction at supercritical conditions

Saka and Kusdiana [18] were the pioneers of the supercritical method aiming the alkyl esters production. They showed that this technology has a reaction rate up to 15 times faster than the alkaline transesterification, proving the efficiency of this new technology for producing biodiesel. Supercritical technology is a non-catalytic route, which occurs at high temperatures and pressures (above the critical point of the solvent). Under these conditions, the thermophysical properties of the alcohol, such as dielectric constant, viscosity and polarity are significantly changed and can be tuned by manipulating the pressure and temperature of the system [17,19]. However, a major concern is the thermal degradation of the alkyl esters at high temperature, mainly polyunsaturated fatty acids.

Silva et al. [20] studied the thermal degradation of biodiesel produced from soybean oil and ethanol. Using thermogravimetric analysis, they proved that soybean oil biodiesel is unstable and decompose at temperatures above 300 °C. As mentioned by Liu et al. [21] and Lin et al. [22], main decomposition reactions consist of isomerization, polymerization, and pyrolysis. Ethyl fatty acid esters are relatively stable up to 275 °C, with the pyrolysis effect being pronounced between 300 and 325 °C [21,23]. Other researchers have shown that even more parallel reactions are involved at supercritical conditions, such as glycerol dehydration and other less favorable reactions (decarboxylation, methoxylation, and reformation) [24,25] that generates isomers, polymers, short chain ester, light hydrocarbons and gases, carboxylic acids, long chain alkenes, acrolein, acetol and other compounds. Palacios-Nereo et al. [26] proposed to proceed the reaction using a heating rate for preventing the thermal decomposition of the reactants and products. In their study, those authors performed three types of reactor heating: constant temperature reaction (CTR), gradual heating reaction (GHR), both with a reaction time of 75 min, and hybrid reaction (HR) combining gradual heating and a phase at constant temperature totalizing reaction time between 65 and 345 min. At CTR they observed a decrease in the ester yield in reactions above 320 °C. With GHR, degradation was not observed, but low yields were obtained. With the HR method, the authors obtained yields of 99.9% in 345 min at high temperatures. They evaluated that a heating ramp can minimize the decomposition of esters.

The supercritical transesterification reaction for different oils, such as sunflower, palm, and soybean oil has been reported by different authors [17,26–28]. Optimum conditions have been normally reported to be within 325–350 °C, 160–350 bar and alcohol to oil molar ratio 33:1–43:1, and the ester yields reached were around 80–90%. Tan et al. [29] evaluated the transesterification reaction of palm oil in supercritical methanol (SCM) and supercritical ethanol (SCE). In their study, they observed that for the same yield, SCE needs more time than SCM, but the reaction conditions (temperature, pressure and molar ratio) are milder. In relation to the kinetics of the supercritical transesterification reaction, some authors considered the overall reaction and others have used all the three reactions, either reversible or irreversible [22,28,30–32]. According to these authors, all these kinetic modeling approaches present good fit to the experimental data.

1.2. Esterification reaction at supercritical conditions

The optimal conditions of the supercritical esterification reaction are milder than the supercritical transesterification. As presented in the literature, supercritical esterification normally requires molar ration of alcohol to acid around 6:1, temperatures below 300 °C and pressures around 100 bar. Under such conditions, free fatty acid conversions of 90% can be obtained in short times (30–50 min) [33,34]. This occurs because esterification has higher reaction rates compared to transesterification [35]. Moreover, these results can be enhanced by the use of catalysts, as shown by Lokman et al. [36]. These authors used carbohydrate derived solid acid catalyst in the supercritical methyl

esterification of a palm fatty acid distillate. They obtained ester yields above 95% in only 5 min of reaction with 1 wt% of the catalyst. Santos et al. [34] evaluated the experimental and kinetic modeling of supercritical ethyl esterification of fatty acids with different chain lengths. They considered that the reaction is self-catalyzed by the free fatty acids themselves, and this consideration presented a good prediction of the model in relation to the experimental data.

Some studies show the efficiency of supercritical technology to simultaneously convert the triglycerides and fatty acids to ester, *i.e.*, in the same reactor and condition it is possible to perform the transesterification and esterification reaction simultaneously, allowing the use of residual raw materials [7,19]. Tsai et al. [22] processed waste cooking oil in a supercritical reactor and concluded that the presence of free fatty acid in the raw material contributed positively to enhance the ester yield. In that case, the fatty acid has a dual function: reactant of the esterification reaction and the catalyst of the transesterification reaction. However, the literature is scarce regarding the kinetic modeling involving reactions of acid oils with different free fatty acid contents, which is very important in the process modeling, analysis, design and optimization.

In the biodiesel production, short chain alcohols such as methanol and ethanol are generally used. Most of the works have used methanol due to its low cost and higher reactivity [35,37]. However, methanol is derived from fossil fuels and its use contradicts the main objective of biodiesel production, which is to produce a sustainable fuel. For biodiesel to be considered a fully renewable fuel it is necessary to use a bio-alcohol, such as ethanol. Other advantages of ethanol are its higher miscibility with the oil and the ethyl esters present improved cold flow properties, lower greenhouse gases emission, they are more biodegradable and present higher lubricity. The disadvantage of the ethyl ester compared to the methyl ester is the higher acid values. [21,38–40].

Glisic and Orlović [16] presented a review considering the costs involved in the biodiesel production and for its reduction two factors must be taken into account, reduction in raw material cost and energy consumption. The raw material accounts for about 60–80% of the total biodiesel production cost. The supercritical process presents the capability to process low added value raw materials with different content of free fatty acids and water. According to Glisic and Orlović [16], the economy in the raw material compensates the energy costs to set the system under the supercritical conditions of the alcohol. The energy of the system can be optimized from the integration and optimization involving cold and hot streams and energy supply to the reboiler in distillation columns. Glisic and Orlović [16] found that the biodiesel production under supercritical conditions with high molar ratio (42:1) requires the same amount of energy as a conventional alkaline transesterification process.

In general, it can be observed that the literature has pointed out the need for high ethanol to oil molar ratios (normally ranged from 25:1 to 42:1) to obtain high ester yields [22,24,28,35]. The main reason presented is generally the low solubility of triacylglycerols in short chain alcohols. In the case of acid raw materials (acid oils), the free fatty acids (FFA) can act as a co-solvent promoting miscibility between the alcohol and oil. In this case, the FFA might present a similar role of alkyl ester in the ternary system short chain alcohol + oil + solute (alkyl ester/FFA) presented by Dagostin et al. [41], favoring the miscibility of the mixture under ambient conditions and reducing the need for the use of high molar ratios.

Aiming to understand and improve the biodiesel production from low-cost raw material and using optimized amounts of ethanol, this study is focused on the coupled esterification and transesterification reactions of a model acid oil (soybean oil doped with oleic acid) in a continuous tubular reactor at low ethanol to acid oil molar ratio. The influence of different reaction parameters, such as temperature, pressure, initial free fatty acid content in the oil (AcO) and ethanol to acid oil molar ratio (Et:AO) on biodiesel yield were studied. A kinetic

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