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Transesterification of rapeseed and palm oils in supercritical methanol and ethanol

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ABSTRACT

The results of the rapeseed and palm oils transesterification with supercritical methanol and ethanol were presented. The studies were performed using the experimental setups which are working in batch and continuous regimes. The effect of reaction conditions (temperature, pressure, oil to alcohol ratio, reaction time) on the biodiesel production (conversion yield) was studied. Also the effect of preliminary ultrasonic treatment (ultrasonic irradiation, emulsification of immiscible oil and alcohol mixture) of the initial reagents (emulsion preparation) on the stage before transesterification reaction conduction on the conversion yield was studied. We found that the preliminary ultrasonic treatment of the initial reagents increases considerably the conversion yield. Optimal technological conditions were determined to be as follows: pressure within 20–30 MPa, temperature within 573–623 K. The optimal values of the oil to alcohol ratio strongly depend on preliminary treatment of the reaction mixture. The study showed that the conversion yield at the same temperature with 96 wt.% of ethanol is higher than with 100 wt.% of methanol.

1. Introduction

Depletion of world petroleum reserves and the impact of environmental pollution of increasing exhaust emissions have lead to the search for suitable alternative fuels for diesel engines. The substitution of conventional fuels (gasoline, diesel) by renewable biofuels is considered a potential way to reduce pollution and to support the sustainable development of a country. Direct use of vegetable oil and animal fat is a promising alternative to solve these problems. Biodiesel (or fatty acid methyl esters, FAMEs) is an alternative fuel for diesel engines that is produced by chemical reaction of a vegetable oil or animal fat with an alcohol such as methanol or ethanol. Biodiesel has some environmental advantages and can be a substitute for fossil fuels. Biodiesel as renewable energy is an alternative that can reduce energy dependence on petroleum as well as air pollution (biodegradable nontoxic fuel, no aromatics, no sulfur, reduction in air pollution from particulates, CO_2, SO_x emissions, recycling CO_2 in short period, and contains 11% oxygen by weight [1]). Biodiesel is derived from regenerable sources of feedstock such as vegetable oil and animal fat by transesterification with alcohol [2].

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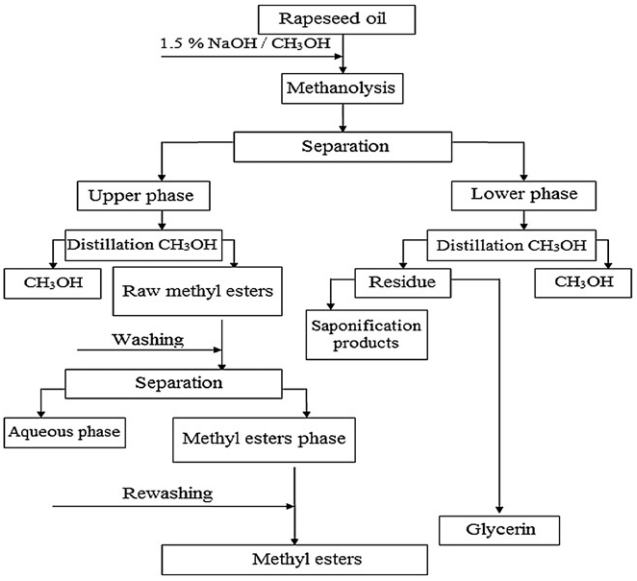

Fig. 1 – Flow diagram of the process for biodiesel fuel production using conventional (alkali-catalytic) technique.

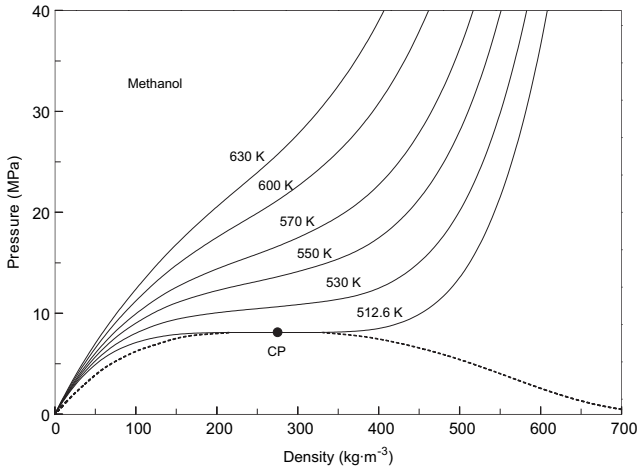

Fig. 3 – P–ρ–T diagram of the near and supercritical methanol calculated with crossover equation of state [46,47]. CP-critical point; dashed line is liquid–gas coexistence curve.

At the present time, the majority of biodiesel in the world is produced by catalytic transesterification. Most of the methods for biodiesel production use an alkaline catalyst in a batch-type process, followed by additional effort to remove the catalyst and saponified products from free fatty acid (FFA) *i.e.* separate the biodiesel product from the reaction mixture. This causes the production process to be longer and reduces the conversion yield. Several processes for the production of biodiesel have been developed by acid-, alkali-, and enzyme-catalyzed transesterification (or alcoholysis) reactions [3–11]. The conventional process has some disadvantages such as use and then extract of the catalyst, slow reaction rate [12–15] and difficult separating (need in multistep clean) of the reaction products (see Fig. 1). It is well known that the vegetable oil as a raw material for the transesterification should be water-free since the presence of water has negative effects on the reaction [16].

Water is consuming the catalyst and reduces catalyst efficiency. The water content should be below 0.06% [17]. Stavarache et al. [9] proposed a method of reagent mixing in the process of catalytic transesterification using ultrasonic cleaner (WS 1200-28), which reduces the reaction time to 10–40 min (usually this takes a few hours) [16,18]. There are commercial equipments for emulsification of reagents mixture of the transesterification process [19]. This has considerably reduced the required amount of excess methanol (almost by 50%) and increased the conversion efficiency. One of the alternatives to these methods is the process of transesterification of vegetable oils with supercritical alcohols (Fig. 2).

This method has several advantages over that of catalytic process, including high production efficiency and environmentally friendliness. Supercritical fluid transesterification

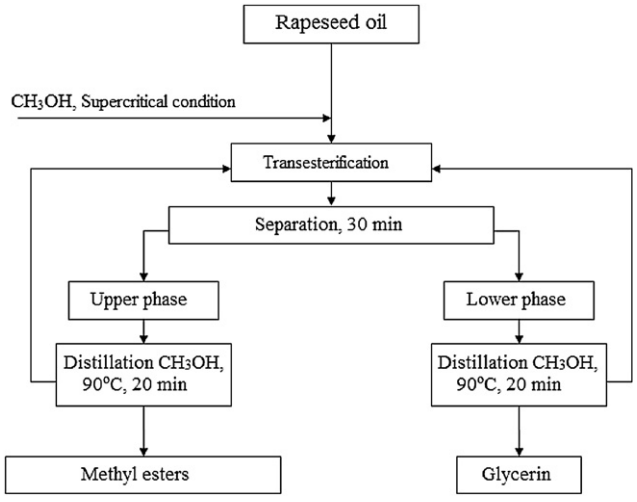

Fig. 2 – Process flow diagram for biodiesel fuel production using supercritical methanol.

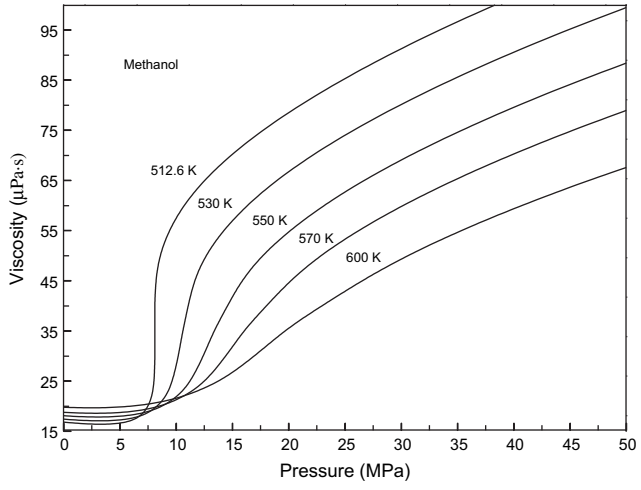

Fig. 4 – Viscosity of supercritical methanol calculated with the correlation by Xiang et al. [55].