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Continuous production of biodiesel using supercritical fluids: A comparative study between methanol and ethanol

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ABSTRACT

Biodiesel was produced from vegetable oil (triglycerides) by transesterification with supercritical ethanol and carbon dioxide as cosolvent in the presence of solid acid catalyst. The objective of this work was to evaluate transesterification kinetics for biodiesel production from vegetable oil under supercritical conditions. Experimental investigation was carried out with vegetable oil and ethanol at molar ratio of 1:25, temperature between 150 and 200 °C, reaction time from 2 to 10 min and pressure around 200 bar in a continuous reactor. The biodiesel products were analyzed by gas chromatography. The effects of methanol to ethanol to temperature and reaction time towards biodiesel yield are discussed in detail. From this study, it was found than an optimum biodiesel yield of 80% can be attained at a relatively short reaction time around 6 min using supercritical condition with ethanol and carbon dioxide as cosolvent.

1. Introduction

Biodiesel is a renewable and environmentally friendly energy that can be produced from a range of organic feedstock including fresh or waste vegetable oils, animal fats, and oilseed plants. It is also an important substitute for petroleum diesel. The resulting biodiesel is quite similar to conventional diesel fuel in terms of its main characteristics, unlike petrodiesel, it is biodegradable and does not contribute to global warming due to the closed carbon cycle [1–4].

Biodiesel is produced by the transesterification of triglycerides (TG) (usually vegetable oils). TG reacts with an alcohol in the presence of a strong acid or base, producing a mixture of fatty acids alkyl esters and glycerol [5,6]. Chemically, biodiesel is called a methyl ester if the alcohol used is methanol. If ethanol is used, it is called an ethyl ester. The overall process is a sequence of three consecutive and reversible reactions, in which di- and monoglycerides (DG and MG) are formed as intermediates [6]. The stoichiometric reaction requires 1 mol of a triglyceride and 3 mol of the alcohol and glycerol (G) is the side product. The three reactions are consecutive and reversible. However, an excess of the alcohol is used to increase the yields of the alkyl esters and to allow its phase separation from the glycerol formed. The transesterification global reaction can be represented by Eq. (1).

$$Triglyceride(TG) + 3\ Alcohol \xleftrightarrow{catalyst} RCOOR'' + glycerol \quad (1)$$

Transesterification consists of a sequence of three consecutive reversible reactions. The first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides, and finally monoglycerides into glycerol, yielding one ester molecule from each glyceride at each step. The reactions are reversible, although the equilibrium lies towards the production of fatty acid esters and glycerol [7–10]. The actual mechanism of the transesterification reaction consists of sets of equilibrium reactions in series and all of the reactions are reversible [6,11,12]. Alcohol provides the alkyl group that substitutes the fatty fraction of triglyceride. Short-chain alcohols such as methanol, ethanol, and butanol are the most frequently employed. The selection of the alcohol is based on cost and performance consideration. From an environmental point of view, ethyl ester utilization is also more advantageous than the utilization of methyl esters. Ethanol can be produced from agricultural renewable resources, thereby attaining total independence from petroleum-based alcohols. Also, ethanol, as an extraction solvent, is preferable to methanol because of its much higher dissolving power for oils. For this cause, ethanol is sometimes used as a suitable alcohol for the transesterification of vegetables oils. The fuel qualities of alkyl esters have received varying evaluations in terms of alcohol used. Huber et al. [13] and Saraf and Thomas [14] commented that higher or branched alcohols can produce biodiesel with better fuel characteristics. In contrast, Tyson [15] reported that methyl ester and ethyl ester are similar in heat content, but ethyl ester formed by transesterification reaction is slightly less viscous than methyl ester. Therefore, producing ethyl esters rather than methyl esters is of considerable interest, because, in addition to the entirely agricultural nature of the

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ethanol, the extra carbon atom provided by the ethanol molecule slightly increases the heat content and the cetane number [16].

The reaction can be alkali catalyzed, acid catalyzed or enzyme catalyzed and chemically catalyzed processes have proved to be more practical because of the short reaction times and low cost compared with enzyme catalyzed [17]. Base-catalyzed transesterification involves stripping the glycerin from the fatty acids with a catalyst such as sodium or potassium hydroxide, and replacing it with an anhydrous alcohol, usually methanol. The resulting raw product is then centrifuged and washed with water to cleanse it of impurities. This yields methyl or ethyl ester (biodiesel), as well as a smaller amount of glycerol, a valuable by-product used in making soaps, cosmetics, and numerous other products [18]. An alternative method for the production of biodiesel is to use heterogeneous (solid) catalysts in the transesterification process. Heterogeneous (solid) catalysts have the general advantage of easy separation from the reaction medium and reusability. Heterogeneous catalysis is thus considered to be a green process. The process requires neither catalyst recovery nor aqueous treatment steps: the purification steps of products are then much more simplified and very high yields of methyl esters, close to the theoretical value, are obtained [19]. Glycerin is directly produced with high purity levels (at least 98%) and is exempt from any salt contaminants [20,21].

Supercritical fluid (SCF) has received a special attention as a new reaction filed due to its unique properties [22–25]. Supercritical alcohol can form a single phase in contrast to the two phase nature of oil/alcohol mixture at ambient condition. This is due to a decrease in dielectric constant of alcohol at supercritical state. Our research group has been using methanol supercritical (SCM) and carbon dioxide (CO_2) as cosolvent [26]. The addition of cosolvent in combination with supercritical conditions seems to be an efficient means to reduce significantly the operating conditions. Just a few works are available in the open literature regarding the use of cosolvents in the supercritical transesterification, such as the use CO_2 [26–30].

With these considerations, and as a continuation of previous works [26], we carried out a study on the transesterification process of vegetable–sunflower-based oil utilizing supercritical ethanol (SCE) and carbon dioxide as cosolvent with solid acid catalyst, in order to characterize the ethyl esters obtained for their applications as fuels in internal combustion engines. The aim of this work was to experimentally investigate how the temperature and reaction time affect on biodiesel yield vegetable oil supercritical methanol (SCM) and ethanol (SCE) conditions using CO_2 as cosolvent.

2. Experimental section

2.1. Material description

The vegetable–sunflower-based oil (S5007) used in the experiments was from Sigma Aldrich (Barcelona, Spain). The mixture ethanol/CO_2 1:3 molar ratio was supplied by Abello Linde S. A. (Barcelona, Spain). The solvents, standards and reagents used in the derivatization step required for the chromatography analysis were supplied by Sigma Aldrich. A commercial catalyst (Nafion® SAC-13) was purchased from Sigma Aldrich.

2.2. Supercritical ethanol transesterification method

The continuous flow experimental set up is shown in Fig. 1. The catalytic supercritical transesterification was carried out in continuous mode in a fixed bed titanium reactor (152 mm of length and internal diameter of 15.5 mm) which can sustain high temperature and pressure needed in supercritical treatment as reported by Maçaira et al. [26].

The mixture of ethanol and CO_2 is liquefied in a refrigerator containing ethylene glycol, before being pumped with a diaphragm pump (Dosapro Milton Roy, maximum flow 4.17 L/h). The oil was pumped using a HPLC pump (Gilson 305 pump). The three fluids are mixed in a static mixer (Kenics® model 37-04-065, Chemineer, U.K.; 200 mm length and 2.5 mm inner diameter). The reactant mixture was preheated to the desired operating temperature before entering the reactor. The titanium reactor was heated by an electrical heating jacket and monitored by two thermocouples directly connected at the inlet and outlet of the reactor. The reaction temperature was controlled with a precision better than 5 °C. Pressure is measured in the inlet and outlet of the reactor, to check for pressure drops in the fixed bed reactor. Samples were collected periodically in a glass vial placed in the reactor outlet after reaching the steady state condition. The stationary states of the reactor were determined after 30 min and two samples were collected for each experiment and the average error was below 1%.

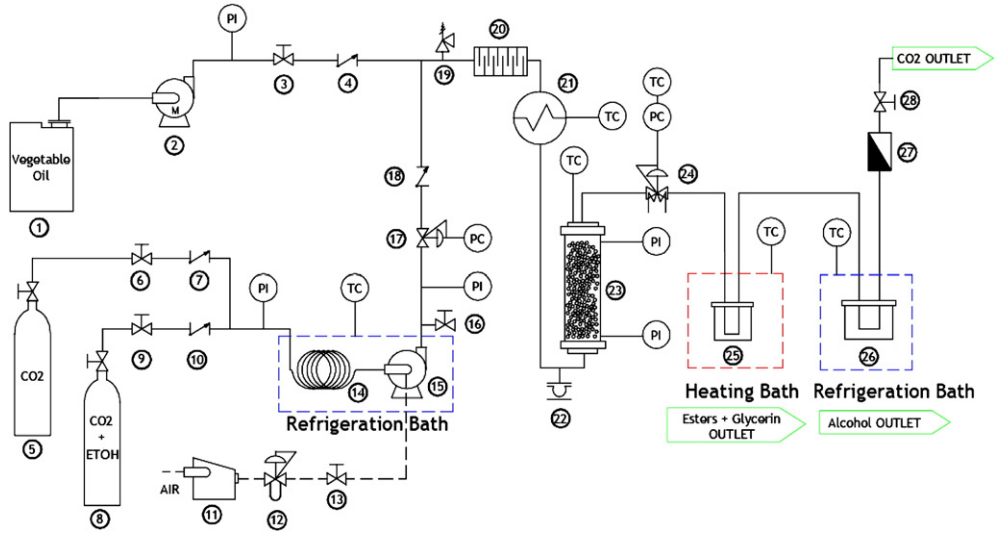

Fig. 1. Scheme of the experimental installation for the continuous production of biodiesel: 1 — synthetic oil; 2 — oil piston pump; 3 — line valve; 4 — check valve; 5 — CO2 bottle; 6 — line valve; 7 — check valve; 8 — CO2/ethanol mixture bottle; 9 — mixture line valve; 10 — mixture check valve; 11 — compressor; 12 — pressure regulator; 13 — line valve; 14 — cooling device; 15 — mixture pump; 16 — purge valve; 17 — pressure regulator; 18 — check valve; 19 — safety valve; 20 — static mixer; 21 — pre-heater; 22 — rupture disk; 23 — fixed bed reactor; 24 — expansion needle-valve; 25 — sample collector; 26 — alcohol collector; 27 — flowmeter; 28 — line valve.