

CONTINUOUS PRODUCTION OF BIODIESEL FROM VEGETABLE OIL USING SUPERCRITICAL ETHANOL/CARBON DIOXIDE MIXTURES

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Abstract. Biodiesel production is worthy of continued study and optimization of production procedures because of its environmentally beneficial attributes and its renewable nature. Transesterification of triglycerides using supercritical ethanol on ion-exchange resin catalyst was investigated to study the ethyl ester conversion process. The reaction parameters investigated were the reaction time, pressure and temperature at a constant molar ratio (alcohol to triglycerides), and their effect on the biodiesel formation. Addition of a co-solvent, supercritical CO₂ (critical point at 31 °C and 7.3 MPa), increased the rate of the supercritical ethanol transesterification reaction, making it possible to obtain high biodiesel yields at less harsh temperature conditions. The experiments were conducted at temperatures of 150 – 200 °C, pressure from 150 to 250 bar and reaction times from 2 to 10 min, and molar ratios of ethanol to vegetable oil from 20 to 45. The evolution of the process was followed by gas chromatography, determining the concentration of the ethyl esters at different reaction times. Results showed that ethyl esters obtained in the continuous fixed bed reactor under supercritical conditions can achieve 80% yield of biodiesel at reaction time of 4 minutes

Keywords: Biodiesel; Transesterification; Supercritical fluids; Ethyl ester; carbon dioxide.

INTRODUCTION

Biodiesel is receiving increasing attention as an alternative, non-toxic, biodegradable, and renewable diesel fuel. Biodiesel is an alternative diesel fuel defined as the mono alkyl esters of long chain fatty acids derived from vegetable oils or animal fat. With the continuous uncertainty and increasing environmental impact associated with the utilization of petroleum-based diesel fuel, the demands for biodiesel had increased significantly in recent years. The environmental, operational and economic benefits associated with the utilization of biodiesel as an alternative fuel for diesel engines have been demonstrated by numerous independent studies and have been well accepted [1,2]. Biodiesel synthesis is chemically described as the transesterification of triglycerides (oil sources) into alkyl esters using alcohol, typically progressed under an acid, base or enzyme catalyst. The overall process is a sequence of three consecutive and reversible reactions, in which di- and monoglycerides are formed as intermediates [3]. The stoichiometric reaction requires 1 mol of a triglyceride and 3 mol of the alcohol. 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. Several aspects, including the type of catalyst (alkaline or acid), alcohol/vegetable oil molar ratio, temperature, purity of

the reactants (mainly water content) and free fatty acid content have an influence on the course of the transesterification.

Heterogeneous catalyst posed several advantages over homogeneous catalyst such as easy separation of catalyst from product, can be easily recuperated into pack bed reactor (continuous process), and can be regenerated and reused. Several researchers have reported the potential economic advantages of the heterogeneous catalytic process over the alternative homogeneous one [4,5].

Supercritical fluid (SCF) has received a special attention as a new reaction field due to its unique properties [6-8]. 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 (CO₂) as cosolvent [9]. The addition of cosolvent in combination with supercritical conditions seems to be an efficient means to reduce significantly the operating temperature. Just a few works are available in the open literature regarding the use of cosolvents in the supercritical transesterification, such as the use CO₂ [9-12].

Methyl and ethyl ester of fatty acids are the most popular ester used as biodiesel. The methods of preparation of methyl and ethyl esters have their own advantages and disadvantages. The formation of ethyl esters is environmentally attractive because unlike methanol, ethanol is produced from renewable resources. Also ethanol has better solvent properties than methanol for solubility of oil. On the other hand, methanol makes higher equilibrium conversion due to higher reactive intermediate methoxide. Kulkarni et al. [13] reported the advantage of using mixture of methanol and ethanol with KOH as catalyst. Vieitez et al. [14] have performed the continuous transesterification of vegetable oils under ethanol supercritical using different molar ratio and temperatures with a ester content of 75%.

The aim of the present work is to investigate the effect of operating conditions in the transesterification of vegetable oil using supercritical ethanol/CO₂ with solid acid catalyst. For this purpose the experiments were carried out in a continuous reactor, in the temperature range of 150°C to 200°C, pressure from 150 to 250 bar, oil to ethanol molar ratio from 1:20 to 1:45 and varying the residence time. This study showed that SCM has higher optimum yield of 88.2% compared to 80 % of supercritical ethanol (SCE) reaction.

MATERIALS AND METHODS

Materials

The vegetable-sunflower-based oil (S5007) used in the experiments was from Sigma Aldrich (Barcelona, Spain). The mixture ethanol /CO₂ 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.

High-pressure apparatus

The experimental reaction system used in this work is shown in Figure 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. [9].

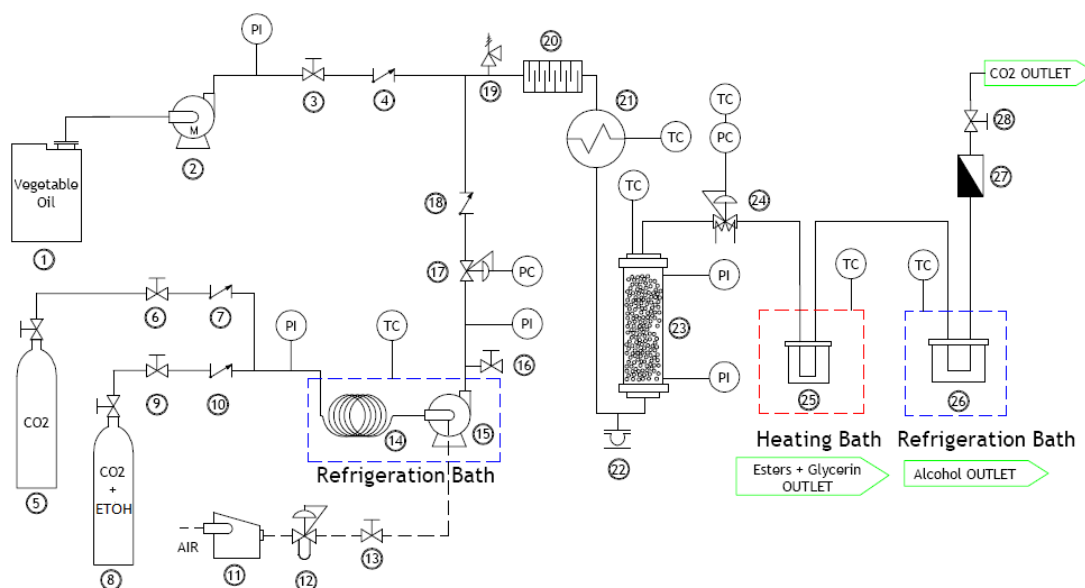


Figure 1: Scheme of the experimental Installation for the continuous production of Biodiesel: 1-Synthetic oil; 2-Oil piston pump; 3-Line valve; 4-Check valve; 5-CO₂ Bottle; 6-Line valve; 7-Check valve; 8-CO₂/Methanol mixture bottle; 9-mixture line valve; 10-mixture check valve; 11-Compressor; 12-Pressure 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.

Analysis of fatty acid ethyl ester (FAEE)

The reaction samples were analyzed by gas chromatography (Shimadzu 2010). The gas chromatograph (GC) was equipped with a FID detector and a capillary column (Teknokroma SupraWax-280 with dimensions 30 m x 0.32 mm x 0.25 μm). Helium was used as carrier gas with the initial oven temperature at 120 °C held for 1 min and increased to 250°C, hold 11 min at 10°C/min. The injection and detector temperatures were 250 °C with a split ratio of 1:10. Methyl heptadecanoate was used as internal standard. Compounds were quantified upon analysis following the standard UNE-EN 14103 [15].

Analysis of mono-, di-, triglycerides and glycerol

The concentrations of free and total glycerol and mono-, di- and triglycerides were analyzed by gas chromatography based on European standard EN 14105 [16]. Compounds were quantified by capillary column gas chromatography (Shimadzu 2010) equipped with a cold on-column injection. The capillary column used was a Teknokroma TRB-Biodiesel fused silica column with an internal diameter of 0.32 mm and 10 m of length.

RESULTS

The operating conditions were chosen considering the optimal conditions determined from a previous work on vegetable-sunflower-base oil [9]. The critical properties and other parameters of the pure components are listed in Table 1. Several experiments were conducted in a temperature range between 150°C and 200°C, pressure range from 150 to 250 bar, oil-to-vegetable oil molar ratio from 1:20 to 1:45, reaction time of 2 to 10 min and the catalyst mass and the mixture of methanol/carbon dioxide were kept constant at 9 g and 25/75 wt%, respectively.

Table 1: Critical data for pure components.

Components	Molecular weight (kg.kmol ⁻¹)	Critical Temperature, Tc (°C)	Critical Pressure, Pc (bar)	Acentric factor, ω	Reference
Ethanol	46	241	61	0.644	17,18
CO ₂	44	31	74	0.239	17,19
Triolein	884	705	3.3	1.978	20,21
Ethanol/CO ₂ ^a	90	120	126	0.321	9,23

^aEstimation Chuev Prausnitz [22]: Molar composition of ethanol/CO₂ = 0.25 (fraction molar);

Effect of pressure

In order to determine the effect of pressure on the supercritical ethanolysis reaction using carbon dioxide as cosolvent with SAC-13 as catalyst, the temperature and oil-to-ethanol were kept constant at 200 °C and 1:25, respectively.

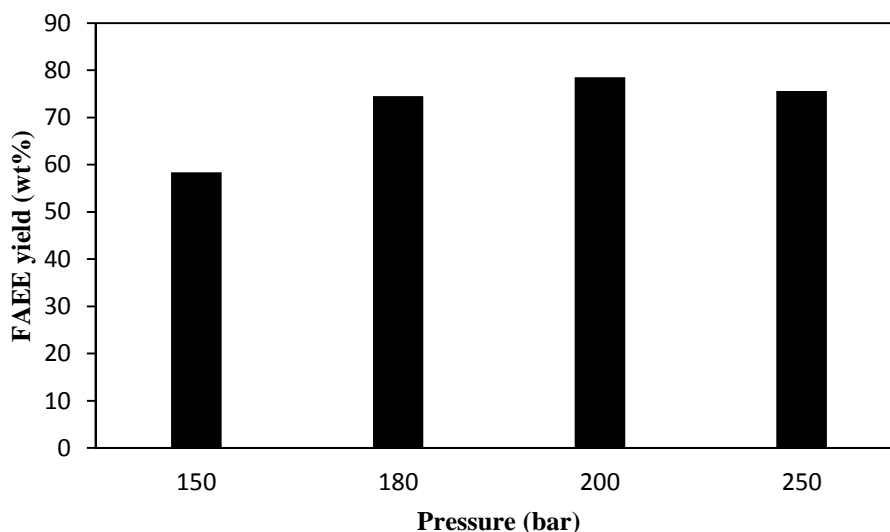


Figure 2: Effect of pressure on the FAEE yield at 200 °C, oil to ethanol molar ratio of 1:25 and reaction time of 10 min.

Our results showed that the reaction rate is linear with reaction pressure. Figure 2 presents the effect of pressure on the yield of ethyl esters for supercritical transesterification using ethanol and carbon dioxide as cosolvent at 200°C. At 150 bar, which is slightly below the critical pressure, ethyl ester formation was lowest. At 180, 200 and 250 bar, the conversion was almost constant, indicating that the reaction pressures were high enough to perform transesterifications, and the equilibrium is reached. According to Figure 2 pressure does not appear to have a pronounced effect on the reaction conversion.

Few studies related the effect of pressure on the supercritical transesterification. He et al. [24] related the effect of pressure on the continuous transesterification with methanol and observed a positive effect in the range of 100-400 bar. Silva et al. [25] and Bunyakiat et al. [26] observed that pressure did not affect the transesterification conversion with supercritical alcohols.

Effect of temperature

Transesterification of vegetable-sunflower-base oil was carried out at various temperature using SCE and CO₂ as cosolvent. The pressure and molar ratio of ethanol to oil were kept constant at 200 bar and 25, respectively. Effects of the reaction temperature on the ethyl ester yield are shown in Figure 3. At 150 °C, the reaction rate and the ethyl ester yield were relatively low. As expected, the conversion of triglycerides increased with the reaction temperature. The experiments were carried out at temperature between 200°C and 150°C due to the maximum reaction temperature of the catalyst used in this study is 210°C. After 9 min, the ethyl ester yield was around 80% at 200 °C.

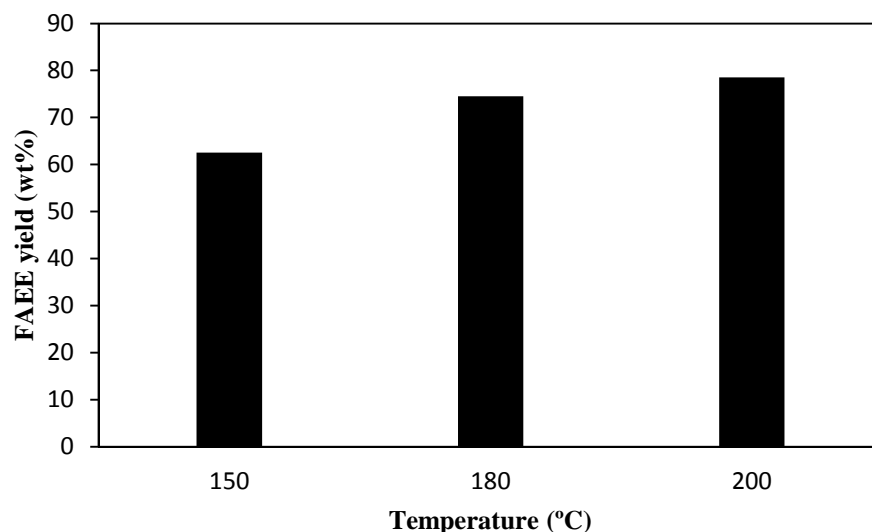


Figure 3: Effect of temperature on the FAEE yield at 200 bar, reaction time of 10 min and oil to ethanol molar ratio of 1:25.

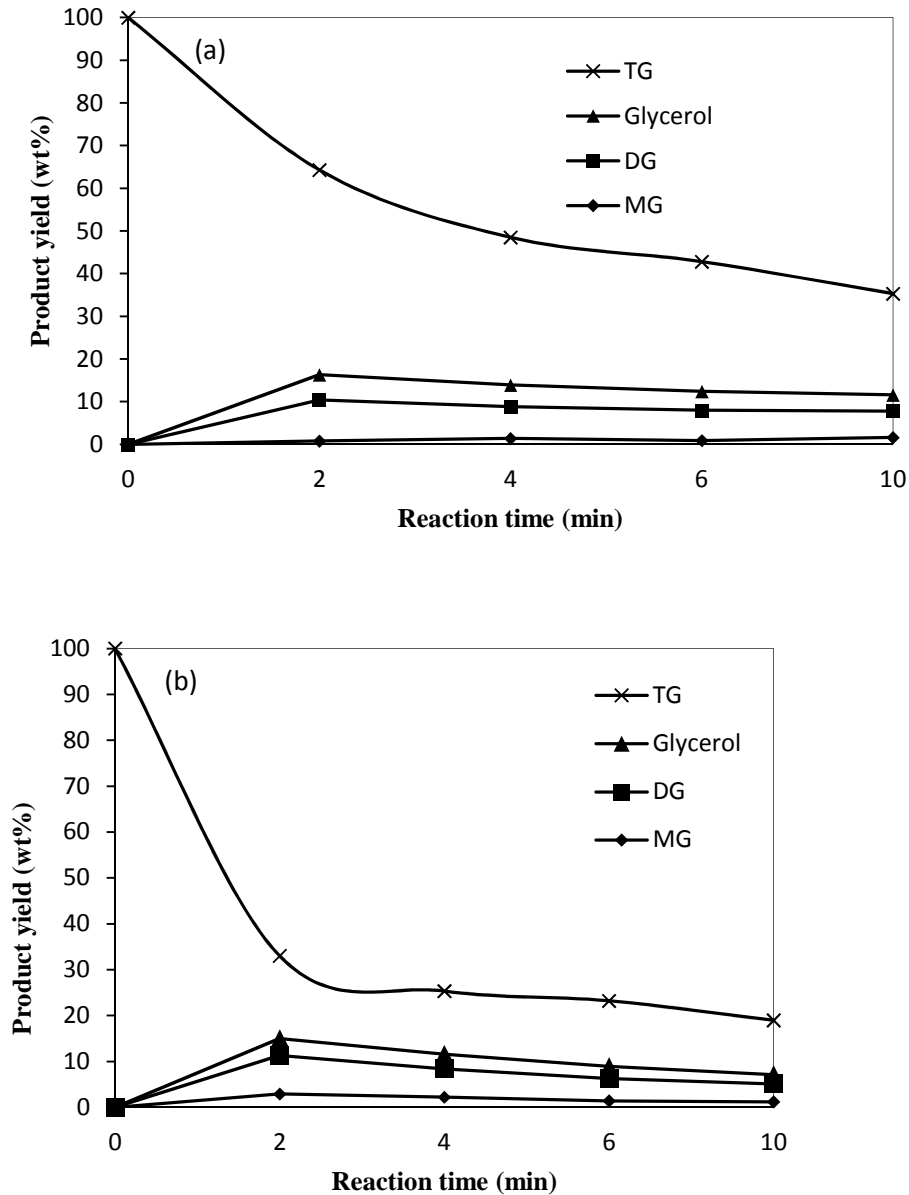


Figure 4: Profiles of the yield of monoglycerides, diglycerides, triglycerides and glycerol at a pressure 200 bar and an ethanol-to-oil molar ratio of 25:1: (a) 150°C; (b) 200°C.

The variation of triglycerides and the consequent transesterification reaction products, monoglycerides, diglycerides and glycerol with the reaction time for the temperatures of 150 °C and 200 °C, pressure of 200 bar and oil-to-ethanol molar ratio of 1:25, at different reaction times are showed in the Figure 4. Comparing the results presented in Figure 4 (a) and (b), the temperature affects the reaction rate of other components of the reaction medium of the SCE with cosolvent. Consumption of TG was favored with increasing temperature. In approximately 3 min the percentage of consummated TG is 55 wt% at 150°C and 27 wt% at 200°C and an increase in reaction time (9 min) the conversion is slightly higher, demonstrating the high conversion of TG under these conditions. Temperature has lower influence on mono- and di- than triglycerides.

The accumulation of glycerol, which is a byproduct of the transesterification reaction, is directly related to the advancement of the reaction. The supercritical system does not require the use of water. After supercritical reaction, when the processed fluid returns to atmospheric pressure and room temperature, the output stream naturally separates into ethanol and biodiesel. After post-processing the ethanol is recycled and after the lower glycerol layer is removed and the biodiesel is ready for analysis. However, traces of glycerol can remain dissolved in the FAEE phase along with small amounts of unreacted triglycerides, diglycerides and monoglycerides, while unreacted alcohol is distributed between the two layers. To determine the free glycerol content in the biodiesel samples, GC analysis was performed, by following the ENE-1405 standard [16]. Table 2 shows the concentrations of free glycerol which without any purification, with respect to glycerol, all of the experimental values is below the imposed maximum limit of 0.020 wt% for the free glycerol, all of the biodiesel samples under different reaction conditions comply with the free glycerol requirements.

Table 2: Free glycerol content of biodiesel produced at 200 bar.

Run	Temperature (°C)	Reaction time (min)	FAEE (wt%)	Free glycerol (wt%)
1	150	2.2	48.5	0.0135
2	150	4.5	55.8	0.0128
3	150	6.5	59.4	0.0129
4	150	8.8	62.5	0.0121
5	200	2.2	64.9	0.0108
6	200	4.5	68.7	0.0111
7	200	6.5	73.9	0.0107
8	200	8.8	78.5	0.0109

Effect of mole ratio of ethanol to oil

Transesterification is an equilibrium reaction (Eq. (1)). To shift the equilibrium to right, it is necessary to use a large excess of the alcohol or else to remove one of the products from the reaction mixture.

Transesterification reactions of the vegetable-sunflower-base oil under ethanol/CO₂ supercritical were carried out to verify the effect of molar ratio of ethanol to oil on the formation of ethyl ester. The range of the molar ratio used in the experiments was 20 to 45, as can be seen in the Figure 4. The temperature and pressure were fixed at 200 °C and 200 bar, respectively, the reaction time was 4 minutes and the mass of the catalyst was 9 g.

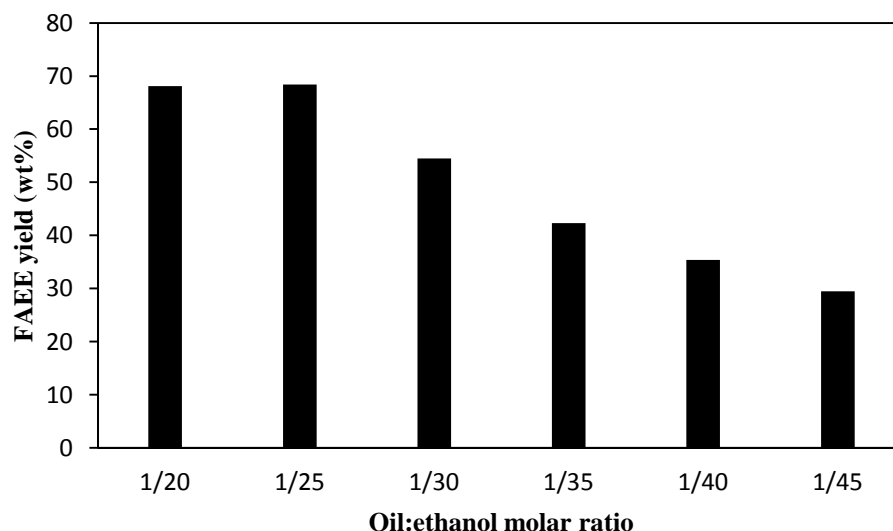


Figure 5: Effect of the oil to ethanol molar ratio on FAEE yield at 200°C, 200 bar and reaction time of 4 min.

One of the most important variables affecting the yield of ethyl ester is the molar ratio of alcohol to triglycerides. This effect has already been widely discussed [24]. In this study for the effect of molar ratio, the experimental procedure was slightly modified. The ethanol and CO₂ were pumped separated. The water content on the ethanol bottle was 0.2 %wt for these experiments. The results of this study are shown in Figure 5. It is observed that by increasing the amount of ethanol the transesterification is slower process. A possible explanation is that an excess of alcohol may be capable of suppressing the backward reaction of fatty acid ethyl esters to mono- and diglycerides, thus avoiding a conversion decrease at longer reaction time. Another explanation is that increasing the molar ratio-to-oil, the reaction has a higher water concentration in the mixture and the yield is lower. These results are in agreement with the hypothesis that the presence of water in the reaction medium decreases the rate of reaction [27]

Comparison between supercritical methanol and supercritical ethanol reactions using carbon dioxide as cosolvent

In the previous investigation of the process used for the biodiesel production by methanolysis using CO₂ as cosolvent under supercritical conditions and SAC-13 as catalyst was analyzed [9]. One of the objectives in this paper is investigate and compares the reaction performance of vegetable-sunflower-base oil transesterification under supercritical methanol and ethanol.

Methanol is the most used alcohol in the biodiesel production due to its suitable physicochemical properties, low cost and easy phase separation. Although ethanol is currently more expensive, its advantages are a much superior because its dissolving power in vegetable oils and low toxicity compared to methanol. The greatest number of vegetable oil ethanolysis researches was done in the South America countries, especially in Brazil, which is one of the greatest producers of ethanol from biomass in the world.

The transesterification using ethanol as solvent was carried out at the same operating conditions of the previous work using methanol [9] with the comparison purpose. Table 3 shows the experiments using methanol and ethanol on the supercritical transesterification. The reaction time of ethanolysis was higher to increase the yield.

Table 3: Comparison of supercritical transesterification methods.

Run	Solvent	Reaction time (min)	% Yield
1	methanol/CO ₂	0,5	73,4
2	methanol/CO ₂	1	79,7
3	methanol/CO ₂	2	88,0
4	methanol/CO ₂	4	88,2
5	ethanol/CO ₂	2	58,4
6	ethanol/CO ₂	4	68,6
7	ethanol/CO ₂	6	73,4
8	ethanol/CO ₂	10	76,4

Figure 6 shows the ester content in the products obtained by transesterification of vegetable-sunflower-base oil in supercritical methanol/CO₂ (Figure 6a) and in supercritical ethanol/CO₂ (6b), at 250 bar and 200°C, and at different reaction time.

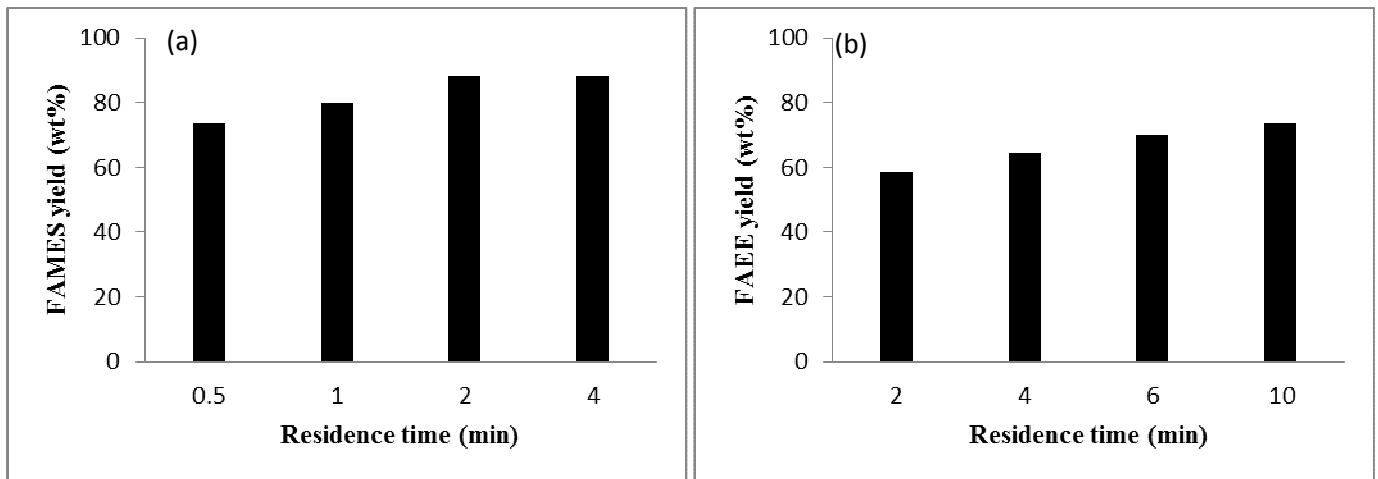


Figure 6: Effect of alcohol in supercritical transesterification reaction on the yield of biodiesel. Operating conditions: 200°C, 250 bar and oil to alcohol molar ratio of 1:25. (a) Supercritical methanol reaction; (b) Supercritical ethanol reaction.

Reaction time plays a crucial in biodiesel production as it can influence the productivity and economic consideration. Compared to conventional catalytic reactions which required hours of reaction time, supercritical alcohol reaction can be completed in lower duration of 10 min. As shown in Figure 7, the yield of biodiesel increased with the

increment of time for SCM and SCE reaction until the optimum conditions of 4 and 10 minutes, respectively. Compared to conventional catalytic methods, which required at least 1 hour reaction time to obtain similar yield, supercritical technology has been shown to be superior in terms of time and energy consumption. Apart from the shorter reaction time, it was found that separation and purification of the products were simpler. The experiments were carried out at optimum temperature for SCM and SCE respectively as discussed previously and 25 molar ratio of alcohol to oil. At optimum condition the results using methanol or ethanol in the transesterification presented good yields. The yields of biodiesel were 90% and 80% for SCM and SCE, respectively. The lower yield values in the case of FAEE can be attributed to the problems in the purification step due to the higher inter-solubility of the mixture.

The reactivity of methanol with triglycerides is higher than ethanol, hence SCE reaction required longer reaction time to achieve optimum yield compared to SCM reaction. This observation can be best explained by the reactivity of triglycerides with alcohol, which decreases with increasing alkyl chain of alcohol [8]. This might be due to the long chain alkyl group hindering the (-OH) group in alcohol from reacting with triglycerides to form fatty acid alkyl ester. SCE reaction has lower yield of biodiesel compared to SCM reaction.

CONCLUSIONS

Continuous transesterification of vegetable-sunflower-base oil under supercritical ethanol using CO₂ as cosolvent was successfully attempted. In this study the effects of the process variables were evaluated. Results showed that the best conditions are 200 °C, 200 bar, molar ratio of ethanol-to-oil of 25, at a reaction time of 4 minutes. The reaction conversions were obtained at mild temperature and pressure conditions in compare with other supercritical process. Compared to conventional catalytic methods, which required at least 1 hour reaction time to obtain similar yield, supercritical methanol technology has been shown to be superior in terms of time and energy consumption. The merit of this method is that much lower reaction temperatures and pressures are required due to add of a cosolvent, which makes the process safer and lowers production costs and the purification of products after supercritical transesterification is much simpler and more environmentally friendly.

Supercritical alcohol technology has been shown to be able to produce biodiesel by using methanol and ethanol as the source of alcohol. The study showed that both methanolysis and ethanolysis of vegetable-sunflower-base oil at different temperatures and reaction time can be conveniently performed in order to maximize the alkyl ester content in the product. Comparing the two methods (SCM and SCE) in term of optimum yield, the performance of SCM obtained higher ester contents than SCE with values of 90% and 80%, respectively, with a reaction time of 4 minutes. The reaction rate of the both methods was 20 times faster than conventional process.

Acknowledgments

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