

Use of supercritical methanol/carbon dioxide mixtures for biodiesel production

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Abstract—The use of supercritical conditions for the production of biodiesel from both vegetables oils and waste-oils may be of great industrial interest because it can be carried out without those catalysts necessary in the conventional transesterification process, therefore avoiding a complex separation between the product and the catalyst. However, the use of supercritical alcohol requires higher operating temperatures and pressures. In this work, CO₂ was added to the reaction mixture in order to reduce the operating conditions (temperature, pressure and molar ratio of alcohol to vegetable oil). The novelty of using CO₂ may have two advantages: a possible combination of supercritical CO₂ extraction of the oil and its subsequent transesterification reaction without CO₂ depressurization, and a reduction of the supercritical temperature and pressure of the mixture. The effects of temperature (280-350 °C), pressure (140-280 bar), methanol-to-oil molar ratio (20-30), CO₂-to-methanol molar ratio (0.05-0.2) and residence time (0-45 minutes) on the yield of methyl esters (biodiesel) were studied in a batch reactor, obtaining in all cases a relatively low increase in the yield when CO₂ was present in the medium. The yields of biodiesel were tested with three vegetable oils used as model compounds (palm, sunflower and borage), obtaining similar results.

Keywords: Biodiesel, Transesterification, Supercritical Methanol, Vegetable Oils, Co-solvent

INTRODUCTION

Biodiesel can be produced from green resources and it has important environmental benefits [1]. The use of biodiesel in comparison with conventional diesel can decrease CO₂ emissions by 78% [2]. Indeed, biodiesel has less of both sulfur and aromatics content, so it is safer and more biodegradable than normal diesel. Furthermore, many studies are focused on producing alternative renewable fuels to solve the problems caused for dependency on fossil fuels as the main energy sources. In addition, biodiesel can be used in existing engine models without any modification required and mixtures with conventional diesel have been commercialized as transportation fuel.

Many studies based on conventional transesterification for producing biodiesel have been carried out with different vegetable oils and alcohol precursors at different reaction conditions. The transesterification reaction takes place in some consecutive and reversible steps where esters and glycerol are formed from oil and an alcohol using either acid or basic catalysts [3]. However, these processes need both high energy consumption and production costs due to long reaction times and a complex separation process between the product and the catalyst. Moreover, feedstock pretreatment is necessary to remove moisture and free fatty acids. To overcome those problems, the transesterification reaction of the triglycerides of a vegetable oil using an alcohol (methanol or ethanol) in supercritical state has been carried out in different studies.

It is expected that this innovation would increase the conversion rate of the process, reduce the reaction time and allow feedstock flexibility, as the moisture and the initial free fatty acids content does not significantly affect biodiesel production in the supercritical technology. Furthermore, this process does not need any catalyst or auxiliary chemicals. Therefore, it presents environmental advantages as a large amount of wastes is not generated as well as a simple separation of the products (biodiesel and glycerol byproduct) is possible [4-6].

Many studies have focused on the effect of operating conditions of different plant oils on the transesterification reaction under supercritical state. Temperature, reaction time and methanol/oil molar ratio are the most influential parameters in batch reactors as well as pressure (directly related to the reaction temperature and the filling volume of the reactor) and the stirring rate. Pinnarat et al. [7] identified the best conditions for each feedstock studied. In general, high temperature, pressure and alcohol/oil ratio are needed to produce high conversions. Moreover, these conversions and properties of biodiesel obtained depend on the oil used.

Nevertheless, several authors have presented different reaction conditions to obtain the maximum biodiesel yield when the process is carried out in batch reactors and supercritical methanol conditions are employed. Many authors obtained as the optimal methanol/oil molar ratio in the range 40 : 1-45 : 1. However, a wide range of temperature between 280 and 400 °C and a reaction time between 4 and 30 minutes are presented as the optimum values depending on the type of oils and batch reactor used. In general, a high fatty acid methyl ester (FAME) content (90-95%) has been achieved under optimal conditions, but this result can vary between 70 and 95% [2,8].

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On the other hand, biodiesel production under supercritical conditions has the disadvantage of high equipment cost. So, this approach can be less viable on an industrial scale. Moreover, an excess of alcohol is needed to enhance the forward reaction. Although these costs can be comparable to those of the pretreatment and separation process in the conventional approach, the high alcohol/oil molar ratio needed (greater than 40:1) would create difficulties for recovery and reuse the excess methanol at industrial scale [9]. Hence, if methanol used was reduced, the process would be economically feasible [10]. As a consequence, many studies have focused on how to work under supercritical conditions but reducing the temperature and the pressure required. Some of them have added carbon dioxide [11], hexane [2], propane [12] or calcium oxide [13] as co-solvents, therefore decreasing the temperature, the pressure and the amount of alcohol required.

Among the different types of co-solvents that can be used, gaseous co-solvents, such as CO₂ or propane, have some advantages in comparison with liquid co-solvents. In terms of product purification, only a small amount of co-solvent (0.1 mole per mole of methanol) is necessary to reduce operating conditions, and co-solvent recycling because gaseous co-solvents can be easily separated by depressurization. Moreover, liquid co-solvents and methanol have similar boiling points; thus they can be simultaneously recovered by distillation, but this step would require an additional energy input [2].

Economic studies showed that the conventional method with alkali and acid catalysts needs higher total investment and operation costs in comparison with the process carried out under supercritical conditions [14,15]. In those studies, biodiesel is produced from waste cooking oil in presence or not of a catalyst. In absence of catalyst, propane was used as a co-solvent reducing energy requirements and operating costs.

Different types of vegetable oils have been used for the production of biodiesel, being the most widely studied soybean, rapeseed, sunflower and palm oils [3,4,6,10-13,16-24]. However, it is possible to use other types of oils. In the case of the type of alcohol used, methanol is advantageous as it allows the separation of glycerol in the same step. Biodiesel is mostly produced from soybean oil, methanol, and an alkaline catalyst. However, soybean oil has a high value as a food product so it is a challenge to produce a cost-effective fuel. Therefore, some studies analyze the production of biodiesel using the large amounts of low-cost oils and fats, such as restaurant waste and animal fats that are available [1].

In the work presented here the transesterification reaction of borage oil using methanol under supercritical conditions was studied. The raw material, borage (*Borago officinalis*), is a plant that belongs to the Boraginaceae family, which comprises some 1550 tubiflora species from temperate and warm countries, almost all of which are herbaceous or woody shrubs. Borage is grown in plantations on fallow or uncultivated land that is not too dry and steep, particularly on low-lying land. These plants generally flower in early spring, but they can flower sooner when they are in very sheltered and warm places or later on high ground in the interior. The use of borage oil as a raw material for supercritical production of biodiesel has not been studied before, being of great interest given that the plant is extremely easy to cultivate.

Moreover, in the present study experiments were carried out in a batch reactor with CO₂ as co-solvent to obtain information to be used in the optimization of the process. The effects of temperature (280-350 °C), pressure (140-280 bar), methanol-to-oil ratio (20-30), CO₂-to-methanol ratio (0.05-0.2) and residence time (0-45 minutes) on the yield of methyl esters (biodiesel) were studied. Furthermore, the yields of biodiesel obtained from borage oil were compared with other vegetable oils (palm and sunflower). The study of the effect of CO₂ can be of great interest for the integration of the supercritical CO₂ extraction of oils from plants or oil wastes, and the subsequent direct supercritical transesterification reaction, without depressurization and without CO₂ separation between the two processes. Besides, since CO₂ has a moderate critical point (31 °C and 73.8 bar), the presence of CO₂ may produce a reduction in the critical properties of the mixture with the alcohol, being possible to carry out the supercritical reaction under milder conditions. What is more, the presence of CO₂ increases the solubility between methanol and oils, so the yield of the reaction may increase.

Therefore, the object of the present research is the analysis of production of biodiesel from borage oil as a new raw material, verifying the possible improvement related to the use of CO₂ as co-solvent and comparing those results with the ones obtained from conventional oils.

EXPERIMENTAL

1. Equipment

Supercritical methanol transesterification reactions on vegetable oils were carried out in a 1 L batch reactor made from 316 stainless steel by Parr Instrument Company. The vessel was fitted with an electric furnace. A constant temperature was maintained from the set point at ± 2 K by means of an electronic controller (PID). A rupture disk with a burst pressure of 350 bar was incorporated as a safety device in case of pressure build-up in the reactor during an experiment. The gas inlet, K thermocouple, pressure gauge, safety rupture disc and pressure transducer were situated on the top head. The pressure and temperature were measured inside the reactor and were controlled in real time up to maximum values of 345 bar and 500 °C, respectively. The operating procedure was as follows: initially, oil and methanol with different ratios were charged in the reaction vessel. The system was pressurized with carbon dioxide (as co-solvent) and nitrogen (to reach desired initial pressure) and it was then heated to the desired temperature for each experiment. When the desired temperature was reached, this time was taken as the zero time for the reaction and these conditions were maintained for a specific reaction time. After this time, the vessel was placed in a water bath in order to quench the reaction. When the mixture reached room temperature the gas was vented. The vessel was then opened and the contents of the autoclave were collected. The remaining contents of the autoclave were also collected by washing with methanol. The liquid product was then allowed to settle in order to separate into two phases. The upper phase was glycerin and excess methanol, whereas the lower phase contained the methyl esters produced in the reaction and unreacted oil. A schematic diagram of the equipment used in this work is shown in Fig. 1.

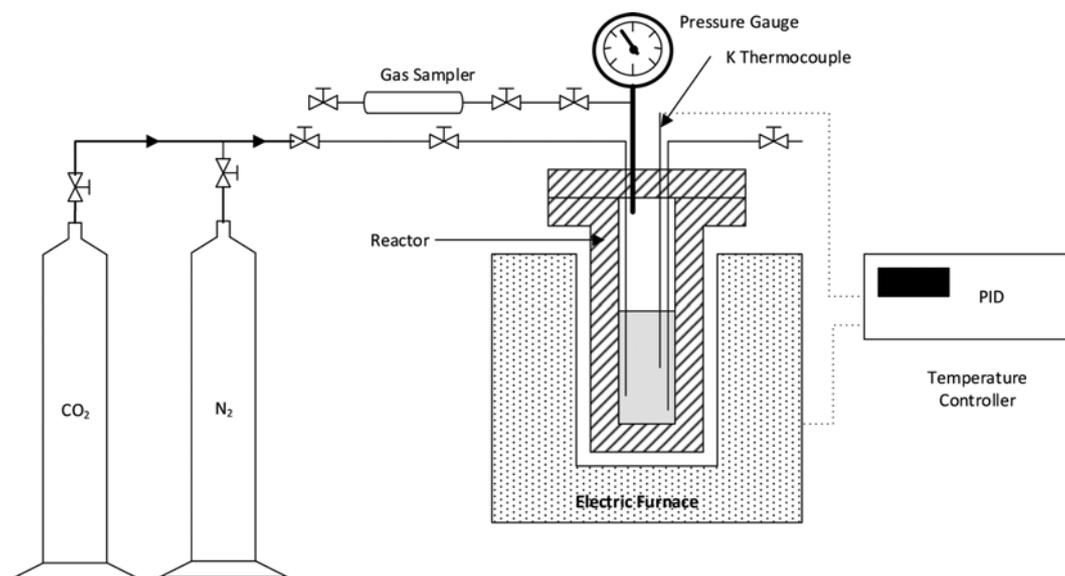


Fig. 1. Schematic drawing of the batch reactor.

Table 1. Fatty acid composition of the borage oil (%)

	Result	Range
C16:0 palmitic acid	9.5	5.0-15.0
C18:0 stearic acid	4.3	1.0-6.0
C18:1 oleic acid	18.8	14-22
C18:2 linoleic acid	36.9	30-45
C18:3 gamma linolenic acid	20.1	18-28
C20:1 eicoseanoic acid	4.3	2-6

2. Materials and Analytical Methods

Borage oil was provided by Plantis Magister S.L. (Barcelona, Spain). The composition in fatty acids of the borage oil is shown in Table 1. Refined palm oil which was supplied by Bio-Oils Huelva, S.L. and a refined edible sunflower oil were used. Methanol (99.9%) was obtained from Panreac.

The conversion of the reaction was determined by chromatographic analysis of the fatty acid methyl esters (FAME). The determination was carried out on a gas chromatograph from Agilent

Table 2. Operation conditions tested and yield obtained

Type of oil	Temperature (°C)	Pressure (bar)	Reaction time (min)	Methanol/oil molar ratio	CO ₂ /Methanol molar ratio	Biodiesel yield (%)
Palm	300	280	20	25	0	49.3
Sunflower	300	280	20	25	0	75.3
Borage	300	280	20	25	0	68.6
Palm	300	280	20	25	0.1	52.7
Sunflower	300	280	20	25	0.1	78.2
Borage	300	280	20	25	0.1	73.7
Borage	280	147	10	25	0.1	67.2
Borage	300	147	10	25	0.1	64.1
Borage	320	147	10	25	0.1	68.1
Borage	350	147	10	25	0.1	35.6
Borage	280	147	10	20	0.1	66.2
Borage	280	147	10	30	0.1	66.1
Borage	280	147	10	25	0.05	64.1
Borage	280	147	10	25	0.2	58.8
Borage	280	147	5	25	0.1	53.7
Borage	280	147	30	25	0.1	73.4
Borage	280	147	45	25	0.1	74.4
Borage	300	140	10	25	0.1	64.1
Borage	300	180	10	25	0.1	68
Borage	300	280	10	25	0.1	74.3

Technologies (model 6890N) with a capillary column (model TR-CN100, 60 m length \times 0.25 mm of internal diameter \times 0.20 mm diameter) and a flame ionization detector. The oven temperature was 185 °C and the flow rate was 38.02 cm/s. The carrier gas was hydrogen and the auxiliary gases were air and hydrogen.

RESULTS AND DISCUSSION

According to the optimal conditions found in Han et al. [11], in which soybean oil was used, initial conditions were selected as temperature of 280 °C, pressure of 147 bar, methanol/oil ratio of 25 and a reaction time of 10 minutes. From those initial conditions, several experiments were carried out to improve the yield obtained. Table 2 shows the operation conditions tested and the yield obtained. To establish the reproducibility of the results some selected experiments were replicated five times. The variation in the biodiesel yield was less than $\pm 2\%$.

1. Effect of CO₂/Methanol Molar Ratio

Since CO₂ has a moderate critical point (31 °C and 73.8 bar), the presence of CO₂ may produce a reduction in the critical properties of the mixture with the alcohol. However, the critical temperature and pressure of the mixtures are not a linear mole fraction average of the pure component critical conditions. As can be seen in Fig. 2, the critical pressure of the mixtures is always higher than those presented by the pure components. On the other hand, critical temperatures of the mixtures methanol/CO₂ are always lower than that for pure methanol. In this way, the presence of carbon dioxide in the reaction medium may lead to two different effects, the need of lower temperature and higher pressure to reach the critical point.

The effect of CO₂/methanol molar ratio in the range 0.05-0.2 on the transesterification of borage oil was studied. Since borage oil has not been studied before, the increase in the yield of transesterification due to the presence of carbon dioxide has been also proved with two other oils previously studied: palm oil and sunflower oil. The use of three different oil in this first test makes possible to generalize the results, since the composition and characteristics of the obtained biodiesel vary as a function of the initial feedstock used, which has a specific chemical composition depending on the plant species from which the oil was obtained, where it was

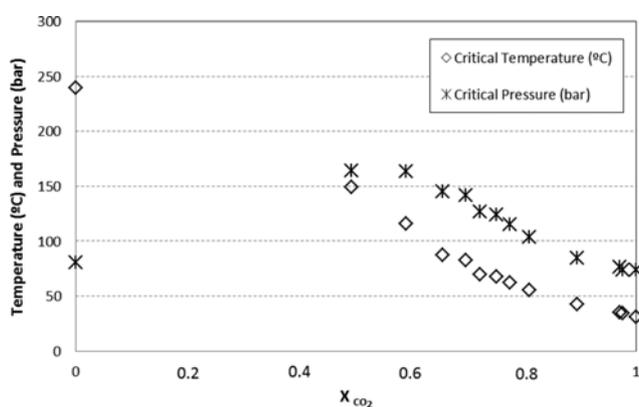


Fig. 2. Critical temperatures and pressures for CO₂/Methanol mixtures. Plotted from data appearing in study of Yeo et al. [25].

Table 3. Critical temperatures and pressures for CO₂/Methanol mixtures for different molar fractions of carbon dioxide (calculated based on the work of Reid et al. [26])

CO ₂ /MeOH	X _{CO₂}	Critical temperature (°C)	Critical pressure (bar)
∞	1	31	73.8
0.2	0.167	210.9	91.4
0.1	0.091	224.2	87.0
0.05	0.048	231.6	84.2
0	0	239.6	80.9

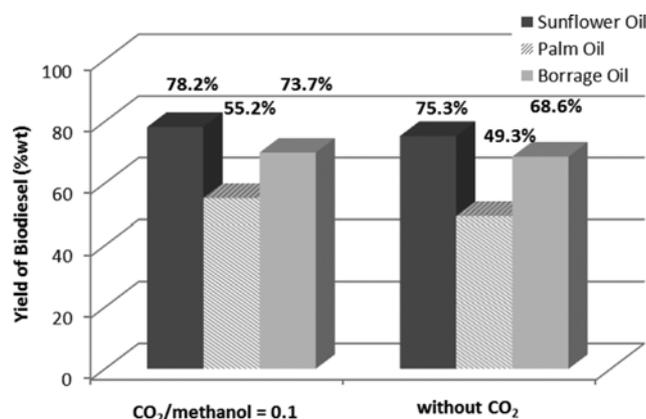


Fig. 3. Comparison of the experiments at 300 °C with and without added CO₂ as co-solvent on the yield of FAME from different vegetable oils (pressure=280 bar; reaction time=20 min; methanol/oil molar ratio=25 and CO₂/methanol molar ratio=0.1).

cropped and in what conditions.

As mole fractions used in this study did not appear in the work of Yeo et al. [25], critical points of the mixtures were calculated based on equations shown by Reid et al. [26] and they are presented in Table 3.

Experiments were carried out at 300 °C, 280 bar, methanol/oil molar ratio=25, CO₂/methanol molar ratio=0.1 and a reaction time of 20 minutes with three different oils (borage, sunflower and palm). The results are represented in Fig. 3.

As can be seen, an improvement in the FAME yield was obtained in all experiments in which CO₂ was added. As several authors claimed [10-12], CO₂ as co-solvent is added to the reaction system in order to increase the mutual solubility between methanol and vegetable oil under supercritical conditions. It is well known that supercritical carbon dioxide is a good solvent for non-polar compounds such as oils, and the presence of supercritical CO₂ in the reaction medium may foster the reaction between methanol and triglycerides, therefore improving the yields of reaction. The improvements obtained are only in the range from 3% to 6%, but they are statistically significant because they are higher than the experimental error, being 1.34% the confidence level of 95% of results from experiments replicated five times.

The best result was obtained with sunflower oil, which gave a yield of 78% of methyl esters. One possible reason for this result may be based in the composition of the vegetable oil, since the yield of

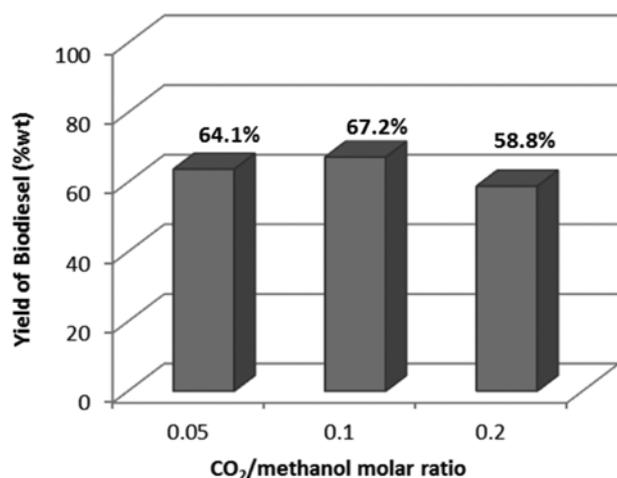


Fig. 4. Effect of CO₂/methanol molar ratio on biodiesel yield at 280 °C, 147 bar, 10 minutes and methanol/oil molar ratio=25 in the batch reactor.

fatty acid methyl esters may be different between saturated and unsaturated FAMES. As reported by Demirbas [13] sunflower oil contains a high percentage of poly-unsaturated fatty acids. Warabi et al. [27] obtained reactivity for unsaturated fatty acids slightly higher than for saturated fatty acids, in accordance with the results obtained in the present study. However, some studies [18,22,28] have reported that unsaturated FAMES yield decreases with longer reaction times because of side reactions. These different effects suggest that there is a non-linear behavior of the effect of fatty acids composition, which depends on the experimental range adopted and the system used.

Once the positive effect of CO₂ had been demonstrated in the reaction medium with different oils, the rest of the experiments were carried out with borage oil. Three different CO₂/Methanol molar ratios were tested and the results are presented in Fig. 4. According to the methyl esters content obtained with a constant methanol-to-oil molar ratio of 25, at 280 °C the highest yield was achieved with a CO₂/methanol molar ratio of 0.1 (fatty acid methyl ester, 67.2 wt% yield). The addition of more CO₂, however, produced a decrease in the yield. Therefore, an increase in the amount of the co-solvent can cause dilution and this decreases the probability of reaction, thus leading to a slight reduction in the FAMES content. As can be seen in a previous study [11] when CO₂/methanol molar ratio is very low, the optimal reaction temperature drops sharply with increasing amount of CO₂. Nevertheless, this optimal temperature keeps constant from a certain point of the ratio. This fact indicates that a high-energy barrier exists for the transesterification reaction so either a high reaction temperature or the presence of a catalyst is required to achieve good biodiesel yield. If X_{CO_2} is up to 0.2, critical temperature could be reduced to 210 °C but the biodiesel yield would be very low (<10%). The results obtained in the present work are similar to those obtained by other authors when CO₂ was used as the co-solvent [20] for the supercritical methanol transesterification of rapeseed. In that study an optimum yield of 51.9 wt% of biodiesel was obtained at 270 °C with a methanol/oil molar ratio of 42.

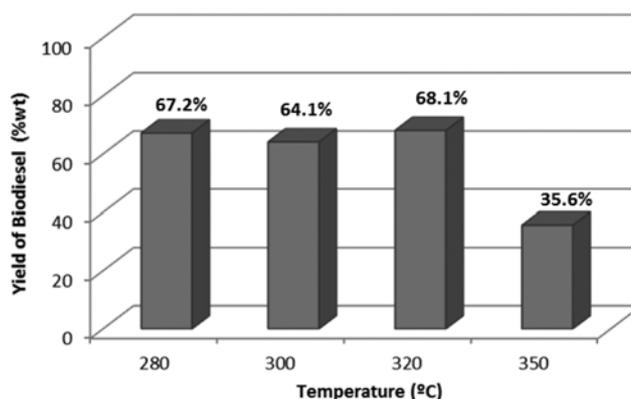


Fig. 5. Yields of FAME at various temperatures in the batch reactor (pressure=147 bar; reaction time=10 min; methanol to borage oil molar ratio=25 and CO₂ to methanol molar ratio=0.1).

The relatively low improvement found does not justify the addition of CO₂ to the reaction medium, but it fosters the design of an integrated process of supercritical CO₂ extraction of oils (from plants or oil wastes) and the subsequent direct supercritical transesterification.

The influence of the rest of important process variables (temperature, pressure, reaction time, methanol/oil molar ratio) was examined in order to identify the best conditions.

2. Effect of Temperature

The effect of temperature on the formation of biodiesel was investigated in the range 280–350 °C. The experiments on borage oil were carried out maintaining a methanol/oil molar ratio of 25, a CO₂/methanol ratio of 0.1, a pressure of 147 bar and a reaction time of 10 minutes. In batch-type reactors the reaction pressure usually increases on increasing the temperature, and thus the effect of pressure is never studied apart from temperature on the transesterification. In this study, the effect of temperature has been separated from the pressure effect by introducing initially a calculated amount of nitrogen to obtain the same final pressure in the system for all temperatures tested. The obtained data are shown in Fig. 5. It can be seen that only a small difference in the yields of methyl esters is observed at temperatures between 280 and 320 °C. The highest FAME yield was obtained at 320 °C with borage oil.

The effect of reaction temperature is produced as the properties of the alcohol change with temperature and chemical kinetics is accelerated. When CO₂ is present, it is possible to work with a supercritical mixture at lower temperature, but the reaction rates obviously decrease as temperature decreases. Furthermore, thermal degradation can occur at a lower temperature when CO₂ is used. This result could be due to an enhancement in the yield of thermolabile intermediates at lower temperatures in the presence of CO₂. A lower FAME content was obtained at a temperature of 350 °C, due to the thermal decomposition of unsaturated fatty acids at temperatures above 300 °C. It can be seen in Fig. 6, where chromatograms for products obtained at 300 °C and 350 °C are compared.

3. Effect of Methanol/Borage Oil Molar Ratio

The effects of varying the methanol/oil molar ratio on the formation of methyl esters were evaluated by carrying out transesterification reactions on borage oil in the batch reactor at 280 °C and

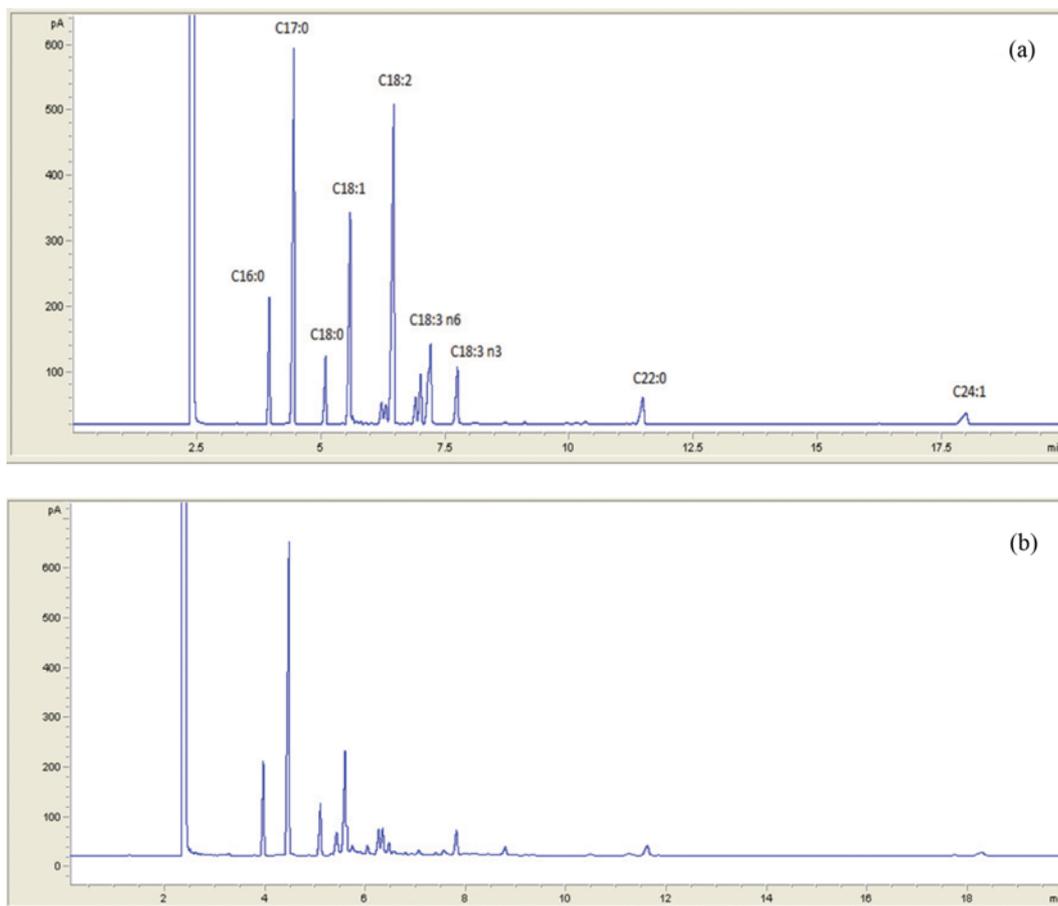


Fig. 6. Chromatograms for products obtained in the transesterifications carried out with thermal degradation (b) and without thermal degradation (a). FAME composition: palmitic acid (C16:0), stearic acid (C18:0), oleic acid (C18:1), linoleic acid (C18:2), linolenic acid (C18:3 n6), gamma linolenic acid (C18:3 n3), erucic acid (C22:0), nervonic acid (C24:1). And Heptadecenoic acid (C17:1) internal standard.

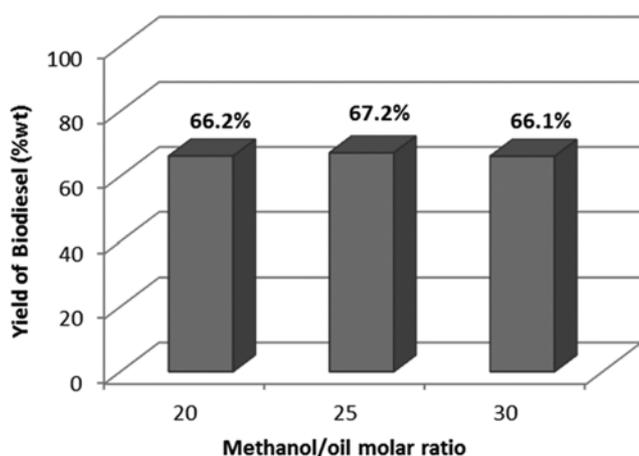


Fig. 7. Yields of methyl esters as a function of methanol/oil at 280 °C, 147 bar, 10 minutes and $\text{CO}_2/\text{methanol}=0.1$ in the transesterification of borage oil in the batch reactor.

a $\text{CO}_2/\text{methanol}$ ratio of 0.1. It can be seen from Fig. 7 that the results are very similar in the range of molar ratios from 20 to 30. There is only a slight improvement on using a methanol/oil ratio

of 25. However, a higher biodiesel yield was obtained in comparison to the results presented by Rathore and Madras [22], where similar conditions of temperature and methanol/oil molar ratio were used but a co-solvent was not employed in that case. In that study a biodiesel yield of around 60% was obtained in 40 minutes on using palm oil. In the present study a conversion of 67% was achieved in only 10 minutes.

4. Effect of Reaction Time

Biodiesel yield can be significantly modified by the reaction time. Experimental data from experiments of the borage oil transesterification carried out with different reaction times in the batch reactor are shown in Fig. 8. The extent of the transesterification reaction increases with longer reaction times so FAMEs yield is increased. However, unsaturated FAMEs can be lost because the side degradation reactions are more important, and thus, a reduction in the biodiesel yield is obtained [29]. Similar results were described in a previous paper, where longer reaction time increased biodiesel yield but the yield remained almost constant at reaction times in the range 30–40 minutes [22]. In another study, He et al. [18] carried out experiments at 320 bar and a 40 : 1 molar ratio of methanol/soybean oil. The FAME yield increased on increasing the residence time with temperature lower than 280 °C. However, the

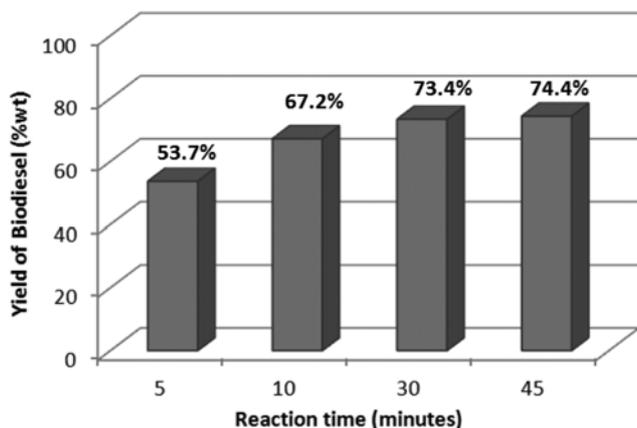


Fig. 8. Effect of reaction time on the reaction of borage oil at 280 °C, 147 bar, methanol/oil molar ratio=25 and CO₂/methanol molar ratio=0.1 in the batch reactor.

yield obtained was never higher than 72% at 280 °C even on using a residence time of 50 minutes. Therefore, similar results were obtained in the present study with a lower pressure and molar ratio. In this study, the highest FAME yield was obtained at 45 minutes. However, this reaction time is considered to be too long for a continuous process.

5. Effect of Pressure

Pressure is another operating variable that can have an important effect on the biodiesel yield. Hence, experiments with borage oil were carried out in the batch reactor at a fixed temperature of 300 °C, a methanol/oil molar ratio of 25, a CO₂/methanol molar ratio of 0.1 and a reaction time of 10 minutes to determine the effect of pressure. The obtained data are shown in Fig. 9. The yield increased on increasing the pressure because higher density is presented when pressure is increasing, which produces an improvement in the reaction rate. The yield of FAME was 64.1% at 140 bar. When the pressure reached 280 bar, the yield of borage oil methyl ester increased to 74.3%. Hence, a change from 140 to 280 bar led to an increase in the yield of around 8%. This result shows that an increase of pressure above 140 bar would not be justified

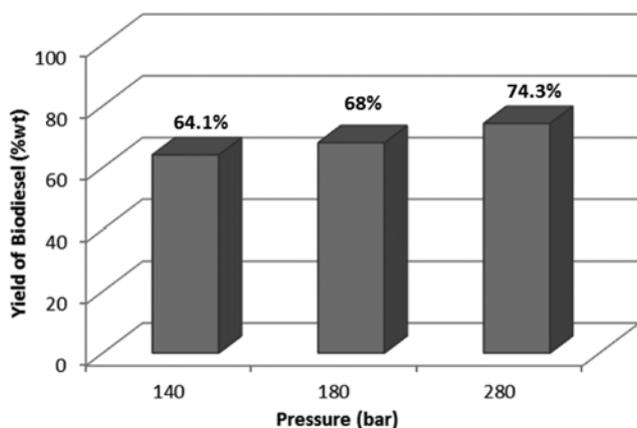


Fig. 9. Effect of pressure on yield of FAME from borage oil at 300 °C, 10 min, methanol/oil molar ratio=25 and CO₂/methanol molar ratio=0.1 in the batch reactor.

in a real application, since the technical and economic resources needed to duplicate the pressure are not compensated with an 8% of yield improvement.

6. Selected Conditions and Maximum Yield

Different conditions may be selected if the criterion is only the maximum yield or if a good relationship between yield and practical conditions (less severe, less expensive) is the aim. Regarding the maximum yield, the highest conditions the best yield. Although, temperatures ≥ 350 °C must be avoided due to thermal degradation of FAMES. Therefore, the best conditions for borage oil would be a temperature of 320 °C, pressure of 280 bar, CO₂/methanol molar ratio=0.1, methanol/oil ratio of 25 and a reaction time of 45 minutes. However, the reduction of 40 °C of temperature, 140 bar of pressure and 35 minutes of reaction time, produces only a slight decrease in the yield (<15%) but makes the process more suitable from a commercial point of view.

The highest methyl esters content obtained in this study was below 75%, being similar to that reported by He et al. [18], where the authors obtained 72% conversion at 280 °C and 50 minutes of reaction time with soybean oil. This conversion was increased to 82% when temperatures were above 300 °C and a reaction time of 25-30 minutes. However, higher yields (around 95%) were reported in other works when co-solvents were employed [11,12,29]. For those studies obtaining lower yields, Sawangkeaw et al. [30] (who obtained a methyl esters content of less than 88%) established some hypotheses for these slightly lower methyl esters contents when compared with other papers. One hypothesis is related to the difference of temperature gradient presented in batch reactors with different volume between the reactor wall and the fluid in the reactor center. This hypothesis was verified with some experiments carried out in both 5.5 and 250 mL reactors at 350 and 400 °C and 30 minutes of reaction time. The 250 mL reactor had a stirrer and it was heated externally. In this reactor the temperature near to the wall of the vessel was always slightly higher than that in the center so thermal cracking reaction may be produced in the wall surroundings, therefore explaining the slightly lower methyl esters content obtained. In the case of the 5.5 mL reactor, the FAME content obtained is higher for the same operation conditions, so it can be established that there was no temperature gradient. If experiments carried out at 350 °C, 10 minutes, a methanol/oil molar ratio of 42 and a co-solvent/oil molar ratio of 0-5 in both reactors were compared, a slightly higher FAME content was obtained in the 5.5 mL reactor. Therefore, the hypothesis that thermal cracking reaction was presented in the 250 mL reactor may be plausible. This effect could be even more marked in the 1 L reactor vessel used in the present study, thus giving lower yields.

CONCLUSIONS

Biodiesel synthesized in supercritical methanol was investigated using three different feedstocks (borage, palm and sunflower). The results of this study highlight the interesting possibility of using borage as a raw material, being extremely easy to cultivate and providing good yields in the transesterification process. The yield of borage oil methyl ester was 74.3% at 300 °C, 280 bar, 10 minutes, methanol/oil molar ratio=25 and CO₂/methanol molar ratio=0.1.

Comparison of the three different oils showed that, in general, the best result is obtained with sunflower oil, which produces a yield of 78.2% of methyl esters at 300 °C, 280 bar, methanol/oil molar ratio=25, CO₂/methanol molar ratio=0.1 and 20 min. When CO₂ was used as a co-solvent, a slight improvement was obtained in the yield for the three oils studied at temperatures of 300 °C, but was found that higher temperatures produce a marked thermal degradation. Only small differences were observed between the oils studied, so the effect of CO₂ may be similar for supercritical methanol transesterification of other oils. The relatively low improvement found (<6%) does not justify the addition of CO₂ to the reaction medium, but it fosters the design of an integrated process of supercritical CO₂ extraction of oils (from plants or oil wastes) and the subsequent direct supercritical transesterification.

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