Biodiesel Production from Castor Oil under Subcritical Methanol Conditions

Nuria Sánchez, José M. Encinar, Gloria Martínez, and Juan F. González

Abstract—**Biodiesel is a potentially sustainably renewable fuel for diesel engines; transesterification is the most used method to produce it and high quality vegetable oils are the most usual raw material. Non-edible vegetable oils such as castor oil can provide an alternative feedstock. In this work biodiesel was obtained by transesterification of castor oil with subcritical methanol; the reaction was carried out in an hermetic reactor at temperatures higher than methanol boiling point and with a small amount of potassium methoxide as catalyst. The effect of methanol:oil molar ratios were analyzed, observing that high proportion of alcohol is needed to reach high ester content, the best results were reached with 24:1 MeOH:oil molar ratio. Regarding catalyst concentration, 8.7 mM (0.12 wt%) were enough to achieve good results. A temperature of 150 °C and 1 h of reaction, at 10 bar, were the mildest conditions to reach an ester content higher than 90 wt %. The highest ester content, 94.7 wt %, was achieved at 220 °C, 36 bar and 4 h of reaction time. Hence good quality biodiesel from castor oil can be produced in subcritical methanol conditions, using a small amount of basic catalyst.**

Index Terms—**Biodiesel, methanol, subcritical, transesterification.**

I. INTRODUCTION

Biodiesel is a promising diesel fuel substitute because it is a clean renewable fuel which can be used in any direct injection engine without the need to redesign the current technology. Biodiesel is derived from renewable and domestic feedstock and shows higher biodegradability than fossil fuels excellent lubricity and negligible sulfur content [1], [2]. For biodiesel-diesel blends, comparable engine efficiency was showed. From an environmental point of view, in spite of higher emission level of NOx, the emission from biodiesel combustion contained lower amounts of CO, CO_2, HC and smoke [3].

The most common method to obtain biodiesel is the transesterification of vegetable oils or animal fats. In the reaction, triglycerides are reacted in presence of a catalyst with an alcohol with short-chain [2], [4]. Methanol is the most used alcohol because it is the least expensive alcohol and it shows chemical advantages such as its shorter chain and its polar nature [1], [5]. Conventionally, the catalysts employed for transesterification reaction are homogeneous alkaline catalysts such as NaOH, KOH, CH_3ONa and CH_3OK. The most suitable ones are methoxides due to their ability to dissociate into the methoxide and the metal ion without the production of water during transesterification reaction [6].

Biodiesel feedstock can be categorized into three groups: vegetable oils (edible or non-edible oils), animal fats and used waste cooking oil. Biodiesel has been mainly produced from edible vegetable oils all over the world. More than 95 % of global biodiesel production is made from edible vegetable oils and this fact has an influence on the global imbalance to the market demand and the food supply by their high prices and the reduction of food sources. Moreover, it will cause deforestation in some countries [5]. The price of this kind of feedstock makes 70 - 80 % of the total biodiesel cost. Non-edible oils, which are not used in human nutrition and whose plants could grow in the barren lands, should be increasingly used. Non-edible oil plants usually can be cultivated in lands unsuitable for human crops with much lower cost than the cost for edible oil plants [7].

Castor oil is one of the most often used non-edible oil in biodiesel synthesis [7]. Castor plant is originally a tree or shrub and there are different varieties that can be cultivated. Castor oil seeds usually contain 40 - 55 % oil and the average yield of castor oil seed in the world is about 1.1 t ha^{-1}, although it may be possible to obtain a maximum of 4.2 t ha^{-1}. Therefore, castor is amongst the plants with the highest oil yield potential [8].

The conventional method to produce biodiesel is basic-transesterification using a homogeneous catalyst. But this process requires steps of neutralization and washing of the catalyst which increase biodiesel cost [9]. In this process, a large volume of waste water and some saponified components that need to be treated before discharging to the environment or recycling to the process are produced. Moreover, chemicals that are used as catalyst and neutralizers are difficult to recover and the washing step that removes the saponified components in the crude biodiesel is the longest of these steps, since the saponified components interfere with a retard phase separation [10].

Some heterogeneous and lipase catalysts are being developed to fight against these drawbacks, but they have not overcome all of these problems. As much heterogeneous catalyst as lipase catalyst can be more easily separated than homogeneous catalyst but they tend to lose their catalytic activity after several reuse and they have high cost [11]-[14].

Saka and Kusdiana proposed the preparation of biodiesel via non-catalytic method with supercritical alcohol with the aim of overcome these problems [15]. Supercritical fluids are good solvents for many substances when compressed into its state of above the critical temperature and critical pressure.

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These fluids have both gaslike viscosities and liquidlike densities [15], [16]. This process does not require any catalysts or auxiliary chemicals and does not generate significant wastes [10], [15].

Supercritical methanol was used to obtain biodiesel from different oils such as rapeseed, sunflower, soybean and palm kernel [15], [17]-[19]. The highest conversion efficiency was achieved with reaction temperatures between 280 and 400 ℃ and pressures between 20 and 45 MPa. Meanwhile, methanol critical temperature is 240 ℃ and critical pressure 8.09 MPa. Under these conditions the CH_3OH:oil molar ratios more used were close to 42:1 with reaction times around 30 min.

Biodiesel synthesis from castor oil under supercritical ethanol in a catalyst-free continuous process was investigated. The effect of water concentration on the reaction medium, reaction temperature, pressure and substrates flow rate was studied. After the optimization of these variables, the maximum ester content was 74.2 % at 300 ℃, 20 MPa, with a flow rate of 0.8 mL min^{-1} and 5 wt % water concentration. A favorable effect on ester content was observed when water concentration was increased, unlike the effect of water on the conventional alkaly-catalyzed process [20].

Other authors used methanol and ethanol at subcritical and supercritical conditions to obtain biodiesel from castor oil [21]. The best results were obtained under supercritical conditions and with alcohol:oil molar ratios close to 40:1.

The use of supercritical ethanol or methanol conditions implies high energy expenses and huge cost of the equipments because they have be kept at high temperature and pressure [22]. An alternative method to obtain biodiesel could be the use of methanol at pressure higher than atmospheric but lower than supercritical. By this way, the amount of catalyst would be minimum, therefore the expense in catalyst and neutralizer would be decreased and the waste water flow would be smaller [23].

In this work, the production of biodiesel from castor oil was carried out under subcritical conditions using few amount of catalyst. CH_3OK was used as catalyst and MeOH:oil molar ratio, catalyst concentration, reaction temperature and reaction time were studied to know their effect on biodiesel quality.

II. MATERIALS AND METHODS

A. Materials

Refined castor oil, supplied by INTERFAT (Barcelona, Spain), was transesterified using methanol (99.6 %) as alcohol and potassium methoxide (90 %) as catalyst, they were purchased from Panreac and Alfa Aesar, respectively. Sulphuric acid (95-98 %) to neutralize the catalyst was also purchased from Panreac. The reagents used for oil characterization were of analytical grade. Methyl esters (employed as standards in the chromatographic determination) were purchased from Sigma-Aldrich.

B. Transesterification Reaction

The reactions were carried out in the system shown in Fig. 1. A cylindrical reactor of 350 mL made of PTFE. It is located in a vessel of stainless steel and is equipped with magnetic stirring, heating system, sampling outlet, pressure gauge and temperature controller. The reaction vessel was charged with given amounts of oil and a methanol/CH_3OK solution. Then, the reaction mixture was stirred and heated up to the reaction temperature. The time of reaction was counted when the heating system was switched on. At the end of the reaction a sample was poured out of the reactor and it was neutralized with H_2SO_4. Then it was washed with distilled water until glycerol, methanol and the salts of the neutralization were removed. The remaining water was removed by heating at 110 ℃.

C. Analitical Procedure

Castor oil was characterized by the measure of fatty acid profile, density at 15 ℃, viscosity at 40 ℃, water content and saponification, iodine and acid value. The used methods were described in previous works [24].

Biodiesel samples were analysed by gas chromatography, VARIAN 3900 gas chromatograph with flame ionization detector was used. The column was a polyethylene glycol column (Zebron ZB-WAX PLUS, Phenomenex, length: 30 m, film thickness: 0.5 μm and i.d.: 0.32 mm), the carrier gas was helium at a flow rate of 1.4 mL min^{-1}, and the analysis was carried out at 220 ℃ for 34 min and at 245 ℃ for 29 min with a ramp of 20 ℃ min^{-1}. Injector and detector temperatures were 270 and 300 ℃, respectively. The internal standard method was used with methyl heptadecanoate as standard for minority esters and methyl erucate for methyl ricinoleate. The solvent was ethyl acetate and calibration curves were carried out for all the esters.

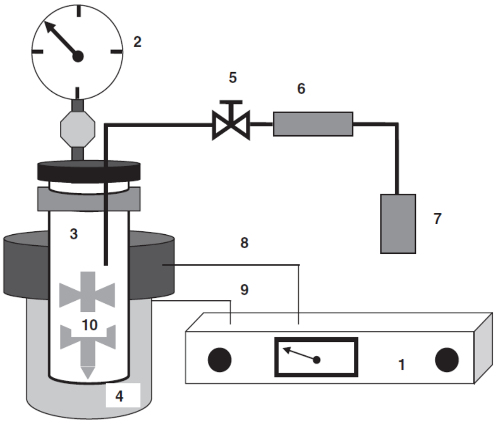

Fig. 1. Subcritical methanol transesterification system. 1: monitor control, 2: pressure monitor, 3: cylindrical vessel made of Teflon, 4:electrical furnace, 5: product exit valve, 6: condenser, 7: collecting sample, 8: agitation rate control, 9: temperature control and 10: magnetic stirrer.

III. RESULTS AND DISCUSSION

A. Raw Material

Raw material properties and its fatty acid profile were shown in Table I. The oil composition of feedstock used in this work is similar to the composition of the castor oil used by other authors [25]. Both have about 90 % ricinoleic acid, 4.5 % linoleic acid and 3.6 % oleic acid. Ricinoleic acid, in which there is a hydroxyl group, shows special chemical and physical properties such as high density and viscosity, high hygroscopicity, low iodine value and high solubility in alcohols. The latter property promotes transesterification reaction even at low temperature [8], [26].

TABLE I: CASTOR OIL FATTY ACID PROFILE AND PROPERTIES

Fatty acid profile:	
C16:0 palmitic	1.3 %
C18:0 stearic	1.2 %
C18:1 oleic	3.6 %
C18:2 linoleic	4.6 %
C18:3 linolenic	0.4 %
C18:1OH ricinoleic	88.9 %
Density at 15 ℃	961 kg m^{-3}
Viscosity at 40 ℃	262 cSt
Water content	0.31 %
Saponification value	179.3 mg_{KOH} g^{-1}
Iodine value	80.5 m_{I2} g^{-1}
Acid value	1.19 mg_{KOH} g^{-1}
Molecular weight	926 g mol^{-1}

The use of acid or basic catalysis in transesterification reaction depends on the acid value of the raw material. Generally, a value up to 2 mg_{KOH} g^{-1} is suitable to use a basic catalyst [27]. The acid value of the oil used in this work is 1.19 mg_{KOH} g^{-1}, therefore potassium methoxide was used as a catalyst in transesterification reaction; as far as basic catalysts are preferable in the case of oils with low acid value [26] and methoxides are more active than hydroxides [6].

B. Effect of MeOH:Oil Molar Ratio on Biodiesel Production

TABLE II: REACTION CONDITIONS AND RESULTS

Run	MeOH:oil molar ratio	Catalyst Concentration (mM)	Temperature (℃)	Time (min)	Ester Content (wt %)
1	42:1	8.7	220	4	69.7
2	36:1	8.7	220	4	86.9
3	24:1	8.7	220	4	94.7
4	12:1	8.7	220	4	81.8
5	6:1	8.7	220	4	60.3
6	24:1	10.0	220	4	91.2
7	24:1	5.0	220	4	90.0
8	24:1	1.0	220	4	72.6
9	24:1	8.7	190	4	93.8
10	24:1	8.7	150	4	92.9
11	24:1	8.7	170	1	92.7
12	24:1	8.7	150	1	91.9
13	24:1	8.7	100	1	63.6

In this work were studied the effects of the most important variables in the transesterification of castor oil under subcritical methanol conditions. These variables were MeOH:oil molar ratio, catalyst concentration, reaction temperature and reaction time. The conditions of the runs carried out were collected in Table II. In this table the ester content reached in each reaction was also shown.

The molar ratio of methanol to oil is a key parameter in the reaction. Biodiesel production could be improved by excess amounts of methanol because it shift the equilibrium to the right-hand side. However, high amounts of alcohol increase the cost of the process. Runs 1 - 5 were carried out to study the effect of MeOH:oil molar ratio on transesterification reaction. The ester content of the biodiesel produced in each reaction was plotted in Fig. 2.

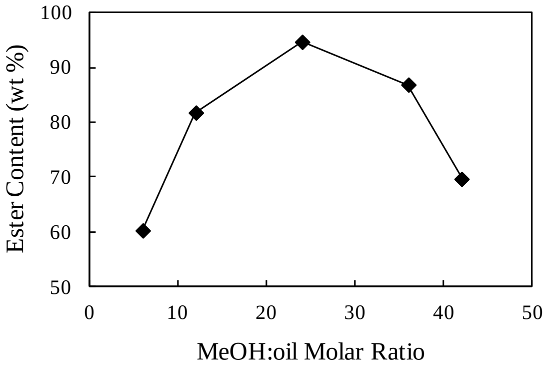

Fig. 2. Influence of MeOH:oil molar ratio in ester content. Reaction conditions: 8.7 mM CH_3OK, 220 ℃ and 4 h.

Under the used conditions, increasing the molar ratio of methanol to oil from 6:1 to 24:1, methyl ester content was increased from 60.3 % to 94.7 %. Nevertheless, higher MeOH:oil ratios led to biodiesel with lower purity. This fact was observed in previous works [28] where rapeseed oil was used.

For noncatalytic reactions in supercritical alcohol, using another type of oil, it was suggested that a higher molar ratio of alcohol is required for better transesterification as excess of alcohol increases the contact area between triglycerides and alcohol. Thus maximum conversions were obtained at molar ratios of 42:1 and 41:1 [29]-[31]. However, castor oil shows high solubility in alcohols, therefore, the contact between triglycerides an alcohol is better.

On the other hand, the presence of high amounts of alcohol complicates the separation between glycerol and biodiesel. Besides, the washing of the biodiesel is more difficult [32]. The decrease of methyl ester content with higher MeOH:oil ratios could be caused by the higher solubility of glycerol in biodiesel and the higher difficulty to wash the biodiesel, it could have some impurities.

C. Effect of Catalyst Concentration on Biodiesel Production

The use of supercritical methanol conditions was suggested to avoid the use of catalyst for the reaction of transesterification, because one of the main stages of biodiesel production is its washing [10]. However this technology shows some limitations such us the high energy consumption and the huge cost of the equipments that have to work at high temperature and pressure [22]. To decrease these costs it would be possible to work under subcritical conditions using minimum amounts of catalyst [23].

In this work, low concentrations of CH_3OK were used as catalyst. This catalyst have shown high activity in the transesterification of castor oil [33]. In Fig. 3 was shown the ester content reached when different amount of catalyst were used for the reaction. Concentrations lower than 8.7 mM resulted in an incomplete conversion of the triglycerides into fatty acid esters. These reactions were developed at 220 ℃ under methanol vapor pressure with a MeOH:oil ratio of 24:1. At atmospheric pressure was optimized the ester content and the best conditions were 45 ℃, 64 mM of CH_3OK and 18.8:1 as MeOH:oil molar ratio [33]. Hence more severe temperature and greater concentration of MeOH allowed a catalyst concentration seven times lower, from 64 mM to 8.7 mM.

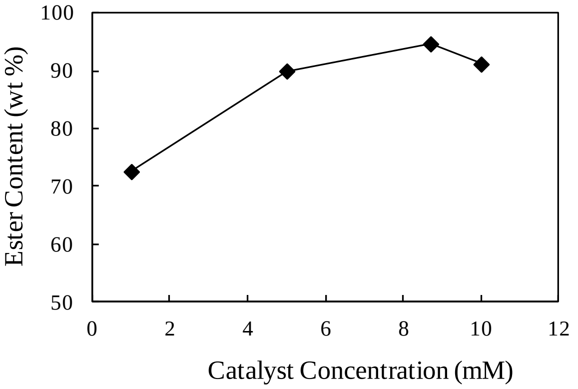

Fig. 3. Influence of catalyst concentration in ester content. Reaction conditions: 24:1 MeOH:oil molar ratio, 220 ℃ and 4 h.

Other authors also showed the benefits of working under subcritical methanol conditions such as the required catalyst amount was decreased by 90 % when comparing with the base-catalyzed system at atmospheric pressure [23].

D. *Effect of Reaction Temperature and Time on Biodiesel Production*

Runs 3, 10 and 11 show the effect of the reaction temperature on the transesterification of castor oil. The ester content reached was plotted in Fig. 4.

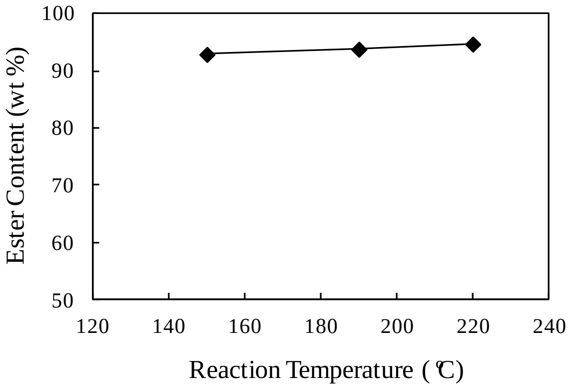

Fig. 4. Influence of reaction temperature in ester content. Reaction conditions: 8.7 mM CH_3OK, 24:1 MeOH:oil molar ratio and 4 h.

The higher temperature, the higher ester content, although there is just a small difference between the percentage of methyl ester for each biodiesel. The increase of 40 ℃ of temperature led to the increase of 1 wt % of methyl ester content.

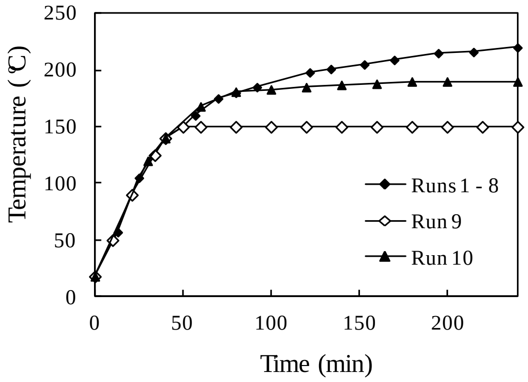

Fig. 5. Temperature profiles.

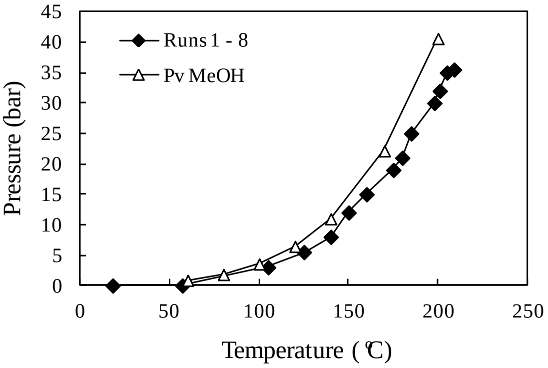

Fig. 6. Pressure vs. temperature for the different runs and vapor pressure of methanol vs. temperature.

The reactions collected in Fig. 4 had a reaction time of 4 hours, although the reaction medium were not at 220, 190 or 150 ℃ for 4 h. Firstly the reaction temperature was close to 20 ℃ because the reaction mixture was settled in the reactor at atmospheric temperature and reaction time was counted from the heating system was switched on. All the reaction followed similar temperature profile, and they are shown in Fig. 5.

As can be seen in Fig. 5, if the reaction time was decreased, 220 ℃ could not be reached. Therefore, in the reactions which were carried out with 1 hour of reaction time, 170, 150 and 100 ℃ were the programmed temperatures (Runs 11 - 13, Table II). As it could be expected, the ester content achieved in one hour, was lower than the best result of 94.7 wt %, which was achieved after 4 hours of reaction.

In Fig. 6 the pressure and temperature of the system were drawn to compare with the variation of vapor pressure of methanol when temperature changes. Methanol and castor oil will form an unique solution in the reactor, and its vapor pressure, shown in Fig. 6, was lower than methanol vapor pressure. This fact reminds of Raoult's law for ideal mixtures, because the oil vapor pressure is lower than methanol one, thus mixture vapor pressure was lower than methanol one.

IV. CONCLUSIONS

In this work the transesterification of castor oil under subcritical conditions was carried out. The effect of the main variables was evaluated and the conditions which led to the maximum ester content were 8.7 mM of CH_3OK, 24:1 MeOH:oil molar ratio, 220 ℃ and 4 h of reaction. The increase of catalyst concentration and MeOH:oil molar ratio did not improve the final result. However higher temperature could enhance the ester content, although small improvements would be expected with high expenses of energy. The mildest conditions to achieve an ester content higher than 90 wt % were 150 °C and 1 h of reaction, at 10 bar.

In summary, by coupling the base catalysis with subcritical methanol, biodiesel was synthesized from castor oil with a high yield.

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