

Production of Biodiesel from Waste Cooking Oil and Castor Oil Blends

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At present the production of biodiesel from castor oil (*Ricinus communis* L) has been restricted due to the high cost of vegetable oil. An alternative to reduce production costs is the blend of castor oil and waste cooking oil. This is a good alternative to improve the waste cooking oil which is a water contaminant and a health problem in many countries. Initially the two oils were characterized by density, viscosity, iodine index, saponification index and free fatty acids percentage, where the results were consistent with those reported in the literature. Subsequently the mixture between 0% and 20% of waste cooking oil with castor oil was conducted. The transesterification was performed under the conditions previously defined: temperature 60 ° C, molar ratio of 6 mol of methanol / 1mol of oil, catalyst potassium hydroxide (KOH) at 1% w/w with respect to oil. The highest yield was 99% for 85% mixture of castor oil and 15% waste cooking oil, since the results of the other mixtures used were up to 89% yield. The results obtained in gas chromatography showed an average composition of 97.6 of methyl esters. The calorific value was 36,645 J / g for the 85% blends of castor oil and 15% waste cooking oil, it was found that the above mixture was the best of all blends made. Through this work it is concluded that it is possible, from a technical point of view, to use the mixture of castor oil and waste cooking oil for biodiesel production, which can reduce costs in the production of biodiesel from castor oil.

1. Introduction

Biodiesel is an alternative diesel fuel consisting of the alkyl monoesters of fatty acids derived from vegetable oils and animal fats (Talebian-Kiakalaieh et al. 2013). Some oils employed for the production are palm oil (Wirawan et al. 2008), (Acevedo et al. 2015), castor oil (Sánchez et al. 2015), (Deshpande et al. 2012) and waste cooking oil (Talebian-kiakalaieh et al. 2013), (López et al. 2015). The most used oil around the world is the palm oil due to high productivity and low cost (Verma et al. 2016). However, it is desirable to include other oils that produce a higher calorific value similar to biodiesel, e.g. produced from castor oil, but the cost is higher than palm biodiesel (Nurdin et al. 2015), (Hailegiorgis et al. 2016).

The castor oil is a colorless or pale yellowish liquid extracted from the seeds of the castor-oil plant. Castor (*Ricinus communis* L) is cultivated around the world because of the commercial importance of its oil which is used in the manufacture of a number of industrial chemicals like surfactants, greases and lubricants (Hailegiorgis et al. 2016). Some reports presented in the literature (Sánchez, Encinar, et al. 2015), (Kilic et al. 2013), (Sánchez et al. 2015), (Dias et al. 2013) have showed conditions for biodiesel production by transesterification of castor oil with methanol. However the high cost of this oil, coupled with high viscosity, has greatly led to its industrial application (Nurdin et al. 2015), (Amin et al. 2016). Castor oil belongs to the group considered strategic raw materials for the production of biodiesel (Verma et al. 2016), especially because it has a low acid value, iodine and saponification index (Amin et al. 2016). The yield reported is near to 90% (Kilic et al. 2013), (Dias et al. 2013), so the productive process is attractive. However, biodiesel from Castor oil shows higher viscosity than the proposed specification, so it can be sometimes considered not suitable (Santana et al. 2010). Additionally, the cost of Castor oil is higher than other oils. In this way it is possible to use blends with other oils, such as waste cooking oil, to reduce the cost of production and the viscosity of the raw material.

On the other hand, waste cooking oil is a liquid residue originated from using domestic and industrial oils (Ordoñez et al. 2013). Cooking oil essentially is composed of 45% monounsaturated compounds, 12% polyunsaturated compounds and 43% saturated compounds (Yakushin et al. 2013); however, Chhetri et al (2008) reported that about 60% of the acids that constitute used cooking oil are unsaturated acids. This oil can be collected and re-used primarily to produce biodiesel (Talebian-kiakalaieh et al. 2013). Waste cooking oil is produced principally in household, hotels and restaurants. In general, oil is normally exposed to high temperature, humidity and oxygen for long periods of time (Martínez-Pineda et al. 2011), in the range of 150°C to 180°C (Chhetri et al. 2008). When oil is used for frying, reactions such as oxidation, polymerization, hydrolysis, cyclization and isomerization typically occur (Martínez-Pineda et al. 2011). Hydrolysis results in the release of free fatty acids, which limit the potential use in the production of biodiesel when alkaline catalysts are used (Ordoñez et al. 2013). The fatty acid profile changes during frying, the levels of palmitic acid increased while those of linoleic acid decreased, and high correlations were found between palmitic, oleic and linoleic acid in all oils (Martínez-Pineda et al. 2011). The use of waste cooking oil as biodiesel feedstock reduces the cost of biodiesel production since the feedstock costs constitute approximately 70-95% of the overall cost of biodiesel production (Apostolakou et al. 2009). Hence, the use of waste cooking oils and non-edible oils should be given higher priority over the edible oils as biodiesel feedstock. Meng et al (2008) have reported a conversion of 89.8%; Phan and Phan (2008) have reported a conversion of 88-90% for production of biodiesel from waste cooking oil. Previously in our researching group (López et al. 2015), we have obtained biodiesel from waste cooking oil with a 98% of yield and methyl-esters percentage of 99.1%. Therefore waste cooking oil is a good alternative for the biodiesel production (Apostolakou et al. 2009).

The aim of this paper is proving the use of blends of waste cooking oil and castor oil for biodiesel production, which is expected to reduce production costs of biodiesel. In other way, the blend is an advantage because it reduces the free fatty acid of the blend compared to waste cooking oil. Since the price of waste cooking oil is about 2-3 times cheaper than virgin oils, it is an attractive option for biodiesel production when it is mixed with castor oil.

2. Materials and methods

2.1 Materials

Castor oil was purchased from Incorp S.A.S. (INCORP S.A.S, Medellin, Colombia) and used cooking oil was collected in Bogota restaurants. On the other hand, methanol of 98% purity was purchased from Panreac (Barcelona, Spain); potassium hydroxide purity 85%, sodium hydroxide and 98% pure ethanol 95% purity were purchased from Merck (Darmstadt, Germany). Phenolphthalein solution in 95% ethanol, potassium iodide, chloroform, Wijs reagent, sodium thiosulfate, hydrochloric acid and soluble starch were acquired at J.T. Baker (Center Valley, United States).

2.2 Methodology

2.2.1 Filtration of waste cooking oil

Remove impurities in the waste cooking oil, which would interfere during the reaction and become particulate matter for the obtained biodiesel. Waste cooking oil was filtered using filter paper (Whatman 1). The filtered oil was stored in plastic containers at room temperature, until use according to the experimental design.

2.2.2 Characterization of the raw material

2.2.2.1 Density: It was determined by using a 10 ml pycnometer at room temperature, according to Standard ASTM D-5.

2.2.2.2 Viscosity: Cannon viscometer LV Model 2020 is used at a temperature of 40 °C, according to Standard ASTM D-445.

2.2.2.3 Acidity Index: The determination of the acid number was performed according to the ASTM D-1980. The test was developed by taking a sample of the oil which is dissolved in a solution of diethyl ether and 95% ethanol, the free acid presented in the sample is titrated with a methanol potassium hydroxide solution 0.1M.

2.2.2.4 Iodine Index: it was determined following the standard ASTM D-5554. The test consisted of diluting 0.2 grams of assay in a solvent and Wijs reagent addition, after potassium iodide and water were added and the release of iodide was titrated with a sodium thiosulfate solution.

2.2.2.5 Saponification Index: According to the ASTM standard D-5558. The test consisted in fully saponifying 2 grams of the oil by an excess alcoholic solution of potassium hydroxide, then titrating said excess alkaline solution with 0.5N hydrochloric acid.

2.3 Reaction transesterification

The biodiesel was conducted in conditions previously established (López et al. 2015): molar ratio methanol to oil 6: 1, percentage of catalyst (potassium hydroxide) 1%, reaction time 2 hours. The reaction was conducted

in a glass reactor of 100 ml capacity with a volume of 60 ml, where the temperature was maintained at 60 ° C with a thermostat bath. At the end of the reaction time two phases were obtained: biodiesel and glycerol, whereby the reaction mixture was placed in a decanter funnel. Separating the two phases by decanting, allowed that the upper phase (rich in biodiesel) was collected. Water was added for phases separation. The procedure was repeated to ensure that the water pH was neutral. Biodiesel was heated on a heating plate to a temperature of 110 ° C for 30 minutes to dry and remove water that could have been penetrated.

2.4 Experimental design

Blends containing 0%, 5%, 10%, 15%, 20% and 100% of waste cooking oil in castor oil were trans-esterified to obtain biodiesel. The reactions were performed in duplicate.

2.5 Characterization of biodiesel

2.5.1 Calorific Value

A calorific pump IKA C 2000 (IKA, Ireland) was used for this test. Close to 1 gram samples were weighed and placed in the glass of the pump where combustion takes place. Oxygen is used at a pressure of 350 psi.

2.5.2 Gas chromatography

Triglyceride content was determined by using a gas chromatograph Varian 450 -GC (Agilent Technologies, China) equipped with a DB-1403 column (Agilent Technologies, China) 30 m x 0.320 µm x 0.25µm. The initial temperature in the nozzle was 60 ° C for 3 seconds, which increased with a ramp 200 ° C / min to 380 ° C and was maintained for 22 min. Column initial temperature was 50 ° C for 1 minute and then increased with a ramp of 15 ° C / min to 180 ° C, followed by a second ramp 7 ° C / min to 230 ° C and finally he employed a third ramp 30 ° C / min to 380 ° C where it was maintained for 10 min. The detector used was FID (flame index detector), which was maintained at 380 ° C; the carrier gas used was hydrogen at a flow rate of 3 ml / min.

Additionally the content of methyl esters was determined. For this purpose, similar conditions to triglyceride determination were employed except that the third ramp on the chromatography column was not employed. The injected sample volume for the two methods was 1 µL.

3. Results

3.1 Characterization of oils

The characterization of the oils is presented in Table 1. The density of castor oil obtained experimentally in this work is 0.9707 g / ml, which is within the range reported in the literature (0.9625 g / ml and 0.9772 g / ml)(Sánchez et al. 2015). The waste cooking oil has reported density of 0.9115 g / ml and 0.9156 g / ml(López et al. 2015), comparing these with the density values obtained in this work, we concluded that there is not a considerable difference with values reported in the literature. Regarding the absolute viscosity, it was determined at a temperature of 40 ° C for the two oils. Sanchez et al (2015a) reported a value of 174.71 cP viscosity for castor oil, but the author establishes that this value may vary depending on the source of oil extraction. As waste cooking oil, Lopez (2015) reported for the wasted cooking oil a value of 40 cP, close to the value obtained in this work.

The acid value determines the free fatty acids contained in each oil (Kapilan et al, 2009). Studies like Amin (2016)reported an acid value for the castor oil of 0.2399. The waste cooking oil has acid values in the range of 0.2 to 0.824 (Meher et al. 2004). It is possible to conclude that the oil used in this work (1.0268±0.016) presents a very high level and it is inferred that it has been over-used. For this reason we propose the blend of two oils to obtain a mixture with low level of free fatty acids. The iodine value indicates the amount of this compound which can absorb the vegetable oil in unsaturated bonds, that is, that the larger the index value is greater adsorption on the double bonds present in the oil (Alam et al. 2014). The literature has values in the range from 82 to 90 for the castor oil (Amin et al. 2016) and the waste cooking oil in the range 60 - 70 (López et al. 2015), so the experimental values obtained in this work are above the reported rank indicating presence of a greater number of double bonds oils reported.

Table 1. Characterization of the castor and waste cooking oils.

Property	Density [g/ml]	Viscosity [cP]	Acid Value	Iodine [g/100 g of substance]	Saponification [mg of KOH/g]
Castor	0.9707 ±0.009	215±1.13	0.5601±0.020	92.01±0.01	181.678±1.985
Waste cooking	0.9119±0.013	42.2±1.01	1.0268±0.016	72.22±0.05	196.238±0.845

The saponification number indicates the amount of potassium hydroxide (KOH) needed to saponify (converted to soap) one gram of oil. The number reported in the literature for castor oil range varies from 176 to 187 mg

KOH / g oil (López et al. 2015), where it is evident that the value obtained in this work is within the reported. On the other hand, the value for waste cooking oil was 196.98 mg KOH / g oil (Sánchez et al. 2015a), comparing the experimental value obtained in this work is similar to that reported in the literature, which was 185.6 mg KOH / g oil.

3.2 Biodiesel production

The results obtained for biodiesel production are presented in Table 2. Yield is defined as the ratio of produced methyl esters to initial oil weight and conversion is the ratio of converted oil weight to initial oil weight (Al-Hamamre and Yamin 2014). According to this Table, in all trials yields above 85% were obtained. Lopez et al (2015) reported a yield of 80%, Chuah et al(2016) reported a yield of 97% and Phan and Phan(2008) reported a yield of 88-90%for waste cooking oil. For castor oil, Kilic et al (2013) have reported a yield upper of 90% and Dias et al(2013) a yield of 92%. These results show that the addition of waste cooking oil to the oil mixture does not affect yield, so castor oil may be partially replaced by waste cooking oil until 20%. Conversion is upper of 90% for all trials and it is similar to other reports presented in the consulted literature(Meng et al. 2008), (López et al. 2015).

Table 2. Performance results and calorific value of the Biodiesel obtained

Percentage of Waste cooking oil	Yield [%]	Conversion [%]	Calorific Value [J/g]
0%	91.250 ± 0.010	90.07 ± 0.002	35672 ± 0.006
5%	92.660 ± 0.008	94.75 ± 0.001	36312 ± 0.002
10%	97.880 ± 0.002	91.25 ± 0.005	36198± 0.005
15%	99.890 ± 0.001	97.25 ± 0.002	36645 ± 0.001
20%	95.450 ± 0.007	94.22 ± 0.005	36150 ± 0.008
100%	85.430 ± 0.011	90.25 ± 0.004	37255 ± 0.005

Mixture of castor and waste cooking oil is useful to decrease the production costs, because the waste cooking oil is lower than the castor oil. According to literature, there is a decrease up to 70% for production costs of biodiesel when using waste cooking oil (Chen et al, 2017). In this way the mixture of oils for biodiesel production is an alternative that it is possible to integrate to any established process. Additionally, conversion of waste cooking into biodiesel has a benefit for health and environmental impacts in anyplace.

3.3 Calorific Value

The calorific value obtained for all samples of biodiesel are in the range of 35,000 J / g to 38,000 J / g as shown in Table 2. In this table it is seen that the presence of the waste cooking oil in the oil mixture makes the calorific value increases. Biodiesel has a higher calorific power produced only from used cooking oil, followed by 85% mixture of castor oil and 15% waste cooking oil. As presented in the literature, the calorific value of biodiesel from castor oil is at 36,947.4 J / g (Nurdin et al. 2015),(Amin et al. 2016) and waste cooking oils in 37,520 J / g (Kathirvel et al. 2016). These results confirm that the biodiesel obtained complies with the reports and that there is a considerable change in the calorific value by adding waste cooking oil to castor oil.

Table 3. Results of Gas chromatography of biodiesel obtained

Percentage of waste cooking oil	Methylesters [ME]	Monoglycerides [MG]	Diglycerides [DG]	Triglycerides [TG]
0%	97.4	0.4	0	0
5%	97.6	0.59	0	0
10%	97.8	0.66	0	0
15%	97.8	0.70	0	0
20%	97.9	0.69	0	0
100%	98.2	0.8	0	0

3.4 Chromatography analysis

Table 3 shows that the methyl esters content are in the range between 97.4 and 98.2. In the literature, values upper than 84.8 % for castor oil (Sánchez et al. 2015) and 99.1% for waste cooking oil (López et al. 2015) are reported. On the other hand, according to the norm ASTM D-1945 the content of the monoglycerides and diglycerides should be 0.8 and 0.2 at the most, respectively. The content of methyl esters obtained in the gas

chromatography for both oils and their mixtures are in the ranges established in the literature. The above ratifies that the addition of waste cooking oil to the castor oil does not affect the production of biodiesel, since it is noticeable in the composition of the obtained biodiesel, the yield of the reaction and in the calorific power.

4. Conclusions

Biodiesel was obtained from blends of castor oil and waste cooking oil by transesterification. The results obtained in this work showed that the yield, for blends of castor oil with waste cooking oil, were up to 92.66%, being the mixture of 85% castor oil and 15% waste cooking oil that obtained the greater yield (99.89%). In addition the calorific value obtained for this mixture is 36645 J/g being the highest with respect to the other mixtures evaluated and there is no greater difference with respect to the biodiesel obtained entirely from waste cooking oil. In terms of costs it can be said that the castor oil is above the waste cooking oil 70%, and with the blends it reduces the cost of the biodiesel to 30% less compared to if only castor oil were used. With this work, it can be concluded that it is possible to integrate the waste cooking oil into productive processes to obtain biodiesel from castor oil, and reduce the costs of the biodiesel generated. In addition, it will be possible to integrate used cooking oil into a production process without continuing to generate impacts on the environment.

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