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Biodiesel production from Waste Frying Oil and Palm Oil Mixtures

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Biodiesel is a renewable fuel obtained from biological raw materials as vegetable oils, sugars, micro algae and bacteria among them. Particularly, biodiesel based in virgin materials, such as palm oil and produced via alkali transterification, have become an industrial standard for large scale facilities. However, the cost associated to virgin raw materials constitutes a huge percentage of production costs, and in addition to low petroleum prices, there is a need to reduce production cost without need to make important modifications in both, the plant infrastructure and processing parameters. Therefore, this work is focused in the evaluation of quality of biodiesel obtained from mixtures of palm oil and Waste Frying Oil (WFO) at low proportions. The conditions employed for the synthesis were: alkali transterification (1% w/w KOH) catalyst, molar ratio methanol/mixed oil 6:1 at 65 °C was developed. The best obtained yield was 98.69% and conversion of 95.53% for 5% WFO and 95% palm oil. Results reveal that a high amount of methyl esters and physicochemical properties evaluated under ASTM, NTC and EN standards, are comparable with Biodiesel from virgin palm oil. Also, the study demonstrates that it is possible to use WFO at low proportions with palm oil without an appreciable change in this properties compared with biodiesel from pure virgin oil. As a general estimation, potential savings could be of 3.2% in production cost.

1. Introduction

Renewable fuels have emerged as an environmental friendly alternative against to conventional fossil fuels. The last have been generating environmental damages along the twentieth century. In contrast biofuels, which are obtained from biological renewable resources such as vegetable oils, sugars, biomass (Sawangkeaw et al. 2013), micro algae, and bacteria, have had vast development at industrial scale during the first decade of 21st century.

Particularly biodiesel is obtained from virgin vegetable oil such as sunflower, soy, corn, palm and others (Borugadda et al. 2012). However, and due to cost associated to virgin raw material (Talebian-Kiakalaieh et al. 2013), and also ethical concerns (Araujo et al. 2010), other emerging resources have been gaining attention for biodiesel production: algae, microalgae, recycled materials like waste vegetable oil (Talebian-Kiakalaieh et al. 2013) and animal fats (Banković-Ilić et al. 2014). The advantage of these raw materials is the lower cost compared with virgin oils, and is an important factor considering that feedstock is the largest contributing factor in production cost (Skarlis et al. 2012) and it can fluctuate in order of 70-80% of total cost.

Important attention has the waste frying oil (WFO), a promising biodiesel feedstock. However, is has several drawbacks such as collecting logistics (Sánchez & Huertas 2012) and most important the pretreatment required due to large exposition of oil to severe conditions (Banković-Ilić et al. 2014) generating undesired compounds like high amounts of free fatty acids (Martínez-Pineda et al. 2011). The high amount of FFA affects the performance of alkali transterification (López et al. 2015) (Ordoñez et al. 2013). But, despite of that drawback of using WFO as raw material, its main advantage is the low cost, as low as 70-80% of typical virgin oil price (Balat & Balat 2010; Rincón et al. 2014). Also, from a technical point of view, if WFO is collected from facilities with standardized processes, pretreatment can be obviated (Araujo et al. 2010), making WFO an attractive alternative for process savings in well established facilities and in addition to the fact that from a

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logistic and scale point of view, a Biodiesel plant for WFO or other recicled oils at large scale is not suitable on most cases mainly due to the constant availability of raw materials. Makin, again the mixing an interesting possibility.
In the field of biodiesel characterization of raw material blends, several papers have been reported. Martínez et al. (2014) develop a deep study of a wide range of virgin oil mixings with rapeseed as base oil. De Almeida et al. (2015) analyze ternary mixings of palm oil. Jurac and Zlater (2013) study the impact of several mixtures from 10% to 50% w.t. of rapeseed oil and two samples of WFO. All mentioned papers are performed under high proportion mixings. However, at the authors knowledge studies related with low proportion mixings of WFO with virgin oil, with base transterification have not been reported.
Therefore, this article is focused in the characterization and process evaluation of biodiesel produced from palm oil – WFO at low proportion mixtures. The interest behind this, in contrast to the literature, is to evaluate the performance of biodiesel production for the mixings but under standardized conditions of alkali transterification, commonly used in majority of large scale facilities which use palm oil. The study has the aim to analyze the potential use of WFO, mixed with palm oil in standardized alkali process.

2. Materials and methods

2.1 Reagents

Virgin palm oil was bought from local distributors in Villavicencio (Colombia); WFO was gathered from restaurants in Bogotá (Colombia). Additionally, reagents were used such as: Methanol (99,8%, Panreac, Barcelona, Spain) and Potassium Hydroxide (99.9%, Merck, Darmstadt, Germany)

2.2 Treatment of the gathered WFO

20 Liters of WFO were filtered in an industrial filter frame, with filter paper plates to separate suspended solids. Once the oil was filtered, it was stored in 20-liters plastic containers at room temperature.

2.3 Characterization of the raw material

Characterization of filtered WFO and palm oil was performed. The following parameters were determined: density (ISO 6883-2000), acid number (ISO 660-2009), saponification number (ISO 3657-2002), Iodine number (ISO 3961-2009) and peroxide number (ISO 3960-2010) (Alptekin & Canakci 2009). Also, kinematic viscosity was determined with electronic viscometer (Brookfield Engineering Laboratories LV).

2.4 Experimental design for evaluation of oil mixings

An experimental design was made varying the percentage of WFO mixed with palm oil. Six different percentages were used of WFO: 0%, 5%, 10%, 15%, 20% and 100%; the rest was virgin palm oil.

2.5 Transterification

Conditions for biodiesel production from WFO were previously standardized (López et al.2015): Potassium hydroxide 1% p/p with respect to the oil mass, molar alcohol/oil ratio 6:1, temperature 60°C and 2 hours for reaction time. The reaction volume was 60 ml, in a 100ml glass reactor. A thermostat bath was used to keep the reacting mixture at 60°C. Stirring was made with a magnetic stirring plate. After reaction time, two immiscible phases were obtained and separated by funnel decantation. Washing was performed with distilled water until neutrality in waste water was obtained. Subsequently, the remaining water in the biodiesel was removed by 24 h heating at 110°C. Finally, the mass of the obtained biodiesel was measured to determine the yield of the reaction. Also, biodiesel samples for gas chromatography and cetane index were taken.

2.6 Physiochemical characterization of the obtained biodiesel

2.6.1 Cetane Index

The cetane index was determined according to the norm ASTM D-4737. The distillation curve was made using the equipment Precision PS Scientific series (Chicago, USA), series 10Z9, a thermometer PG ERTCO ASTM 400 C (Vermont Hill, USA) and a chronometer OAKTON (Ontario, Canada).

2.6.2 Calorific power

Calorific power was tested under standard ASTM D240. An analytic balance Mettler-Toledo AB 204 (Switzerland) and a calorimeter IKA C 2000 Basic S1 operated in isoperibolic mode were used. Extra-dry industrial oxygen grade 2.7 at 30 bar pressure was also used. The temperature of the calorimeter's jacket was controlled with a thermostat bath Julabo F12 at 25°C. The sulfur content was determined to make corrections as established in the norm ASTM D 240 with a spectrophotometer Spectronic Genesys 5 (Thermo Scientific, Massachusetts, USA).

2.6.3 Gases Chromatography.

The chromatography trials were carried out with Agilent 6820 (Agilent Technologies, Germany). The chromatograph was equipped with a flame ionization detector (FID) and a capillary column SGE 12 m X 0.53 mm X 0.15 μm. 1.0 μl were injected manually. The oven temperature was 120°C for 1 minute, after that temperature raised at rate of 2.25 °C/min up to 380 °C. Temperature at the injection port and the detector was 259 °C. The drag gas was nitrogen with a flow rate of 6.00 ml/s, with undivided flow. The acquisition and data processing were made with Agilent Cerity QA/QC (Agilent Technologies, Germany) software.

3. Results and discussion

3.1 Characterization of raw materials

The use of WFO biodiesel production implies adaptation and cleaning processes. Hence, a filtration stage removes particulate material in the WFO oil. Therefore, dehydration is required to remove moisture, and absorption to remove chromogens that may interfere with the reaction and biodiesel quality. Also, particulate material is removed using a filtration system. Moisture were no evaluated due to its very low content (1.34%, data not shown).

Table 1 Characterization of palm oil

Property	Present study	Literature	Standard employed	Source
Density [g/ml]	0.8703 ±0.011	0.869 – 0.879	ISO 6883-2000	NTC 431
Acid number	0.328 ± 0.013	0.589	ISO 660-2009	(LAL 1992)
Saponification number [mgKOH/g sample]	195.592 ± 1.985	195 - 205	ISO 3657-2002	(Indupalma 2012)
Iodine number [g/100g sample]	57.918 ± 0.212	50 – 58	NTC 283	NTC 431; (Indupalma 2012)
Kinematic viscosity [mm^2/s]	115.929 ± 1.02		---	

The density obtained for virgin palm oil is presented in Table 1 and for WFO is presented in Table 2. As can be seen, for density, there are no significant differences between them. In contrast, the viscosity of the WFO is higher than the virgin oil (approximately 13% higher). This result is relevant when dimensioning the industrial facility, mainly in pumping equipment in continuous processes, but it is possible to use WFO in an established plant without any change.

Table 2 Characterization of Waste Frying Oil

Property	Present study	Literature	Standard employed	Source
Density [g/ml]	0.9102 ±0.019	0.9115-0.9156	ISO 6883-2000; NTC 336	(López et al. 2015)
Acid number	2.182 ± 0.015	0.2-0.824	ISO 660-2009; NTC 219	(López et al. 2015), (Restrepo 2008)
Saponification number [mgKOH/g sample]	197.169 ± 0.934	196.98	ISO 3657-2002; NTC 335	(López et al. 2015)
Iodine number [g/100g sample]	70.254 ± 0.285	60-70	NTC 283	(López et al. 2015)
Kinematic viscosity [mm^2/s]	132.150 ± 1.66	133.33	---	(López et al. 2015)

WFO characterized presents an acid number over six times higher than the virgin oil, which represents a high content of free fatty acids (FFA) and it is an indicative of the degree of re-use of the collected oil. In fact, most of restaurants, the oil is exposed to high temperatures, humidity and oxygen for long periods (Martínez-Pineda et al. 2011). When the WFO is used to fry foods, reactions such as oxidation, polymerization, hydrolysis, cyclization and isomerization take place (Martínez-Pineda et al. 2011). The hydrolysis results in the release of free fatty acids, which limits the use of WFO biodiesel production when alkaline catalysts is used (López et al. 2015).

Also, the high content of free fatty acids causes saponification in the presence of a base catalyst (Talebian -kiakalaieh et al. 2013). Moreover, acid values for WFO reported in the literature are order of 0.2 to 0.824 (Restrepo 2008), (López et al. 2015) indicating that WFO used in this study was highly re-used oil with a high content of free fatty acids and with an acid number almost three times greater than reported in literature.

An alternative is the neutralization of fatty acids in the WFO, particularly for its use in the case of 100% WFO raw material. Therefore, determination of percentage of free fatty acids turns an important factor when defining

whether is necessary to perform the process of biodiesel: two stage esterification (conversion of fatty acids to methyl esters) or single (or multi stage) transterification (Mohammadshirazi et al. 2014).
Generally, the esterification is made in acid conditions, as long as the transterification is in alkaline conditions (Helwani et al. 2009). The criteria to perform the reaction in two stages is the percentage of free fatty acids which must be higher than 1% (Helwani et al. 2009). However, an advantage of using mixtures with low content of WFO is that after making the mixture, the content of fatty acids would be sufficiently low. Thanks to the mixture of WFO and virgin oil, stage of neutralization is not required and the technology developed in alkaline catalysts can be used.
On the other hand, WFO presents a lodine number greater than palm oil. This indicates a large content of carbon-carbon double bonds, points in the molecule where can have a large reactivity. Also, Chhetri, et al. 2008 report that about 60% of the acids present in WFO, correspond to insaturated acids, which would contribute to a higher lodine number in the WFO than in the virgin oil.
For saponification number, the oils do not exhibit large differences, which results in the widely use of WFO as raw material for soap production.

3.2 Biodiesel production

Biodiesel production was performed according to the experimental design presented previously. The objective of this paper is to determine the effect of the mixtures of WFO and virgin palm oil in the quality of biodiesel obtained. The two parameters which measures the production performance are the yield and the conversion obtained in the reaction. Yield is 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). Table 3 presents the yield of the reaction and the conversion of biodiesel for every evaluated mixture. The experimental conditions evaluated were: alkali transterification with 1% w/w KOH catalyst, molar ratio 6:1 of oil mixing to methanol at 60 °C. For all assays, the reaction yield was upper at 90%, the best yield was 98.69% for the mixture of 5% WFO and 95% palm oil. In contrast, Chen et al. 2014 report values for the palm oil with yields over 90%, using ultrasound. In the case of WFO, in our research group, López et al (2015) reported yields between 80% to 94%, which is a wide range. The obtained value in this study is similar to the one reported by Refaat et al. (2007) who reports values of 98.16% for the reaction of WFO using 1 % w/w de KOH as catalyzer, with a molar ratio methanol/oil of 6:1 at 65°C. In general, obtained results allow concluding that there is no significant change in yield when using mixtures of WFO and palm oil up to 20% of WFO.
Similarly, conversion is large when the mixture has 5% of WFO (Table 3). For Yusup and Khan (Yusup et al. 2010) conversion was about 96% for WFO with KOH as catalyst (2 %) and molar relation of 8:1 (methanol:oil, during 3 hours of reaction at 55°C, which is virtually the same obtained in this study with 59.53%.

Table 3 Performance of biodiesel obtained as a function of the percentage of used oil in the mixture

Percentage of WFO	Yield [%]	Conversion [%]
0%	92.25	92.06
5%	98.69	95.53
10%	93.79	91.1
15%	94.86	87.9
20%	94.7	88.76
100%	94.92	90.69

According to the literature, the cost of the oil is between 70 to 90% the total cost of biodiesel and can be reduced about 50% if virgin oil is completely replaced with WFO (Mohammadshirazi et al. 2014) or inclusive as long as 60 to 90% (Talebian-Kiakalaieh et al. 2013), but at the cost of modifying the process parameters and an important investment associated to esterification stage. In fact, according to Rincon et al. (2014) price of palm oil is about USD $0.46 per liter compared with WFO is about USD $0.146 per liter, so this is an advantage for the production costs. For a typical biodiesel plant of 100,000 tons/year, production savings, when replacing 5% of palm oil with WFO, could be about 3.2% without any modification in the process parameters and investment in additional equipment .

3.3 Characterization of Biodiesel obtained

The physiochemical characterization of biodiesel was performed. the density, the calorific power, cetane index and the chemical composition (gas chromatography) and are shown in **Errore. L'origine riferimento non è stata trovata.**.

Table 4 Composition of biodiesel obtained.

% of WFO	Density [g/ml]	Cetane index	Calorific Value [MJ/kg]	Methylesters [ME]	Monoglycerides [MG]	Diglycerides [DG]
0%	0.8770	56.8	39.84	99.2	0.8	0
5%	0.8772	56.6	39.80	99.2	0.8	0
10%	0.8778	55.7	39.83	98.4	1.6	0
15%	0.8773	56.3	39.83	98.7	1.3	0
20%	0.8786	56.5	39.79	99	1	0
100%	0.8895	53.3	39.68	98.5	1.5	0

For density, obtained values for different mixtures are between 0.877 g/ml and 0.889 g/l for mixtures of 0% and 100% of WFO used oil. Values are according to ASTM D-6751. For the cetane index, in each mixture, values over 52 were obtained. The ASTM D-6751 establishes that this parameter must have a value equal or greater than 40, therefore, the requirement is fulfilled. In a similar manner, the standard EN14214 is also fulfilled as it establishes that the parameter must be equal or greater than 51. The trend shows that there is a larger cetane index for biodiesel from 100% palm oil 100%, and no considerable differences have been found for mixtures with respect to this reference value. For cetane index was about 98% of the obtained value with palm oil only. The latter is important since the percentages of used oil as high as 20% do not generate a significant change in the cetane index. For case of calorific value, the addition of WFO to palm oil does not cause a significant change in this parameter. In fact, obtained values are similar indicating that the use of biodiesel in combustion would not present a reduction in the resulting power in comparison the reference case of palm oil. The biodiesel calorific value is usually in the range of 39-40 MJ/kg (Talebian-Kiakalaieh et al. 2013).

Finally, the results of the gas chromatography shows that the resulting biodiesel composition of about 8% of methyl esters. In contrast to the values presented by the literature, which reports the content of methyl esters from 100% palm oil and 100%WFO with values of 97.69 and 98.38, respectively (Ordoñez et al. 2013). Therefore, the obtained values in this study are higher and promising. In a similar manner, and according to the Colombian regulation, the content of mono-, di-, triglycerides must be maximum 0.8, 0.2 and 0.2, respectively. The test performed show values of mono and diglycerides below to the ones specified by the norm. The latter represents an important advance because it demonstrates that it is possible to use the mixture of WFO and palm oil for biodiesel production, which could translated in potential savings in raw material and production cost.

4. Conclusions

By using mixtures of used oil and palm oil up to 20% of WFO oil it is possible to obtain biodiesel. Although the content of free fatty acids in WFO is high (greater than 1%), when mixing with virgin palm oil is achieved, the final mixture does not exceed 1%; thus, the oil mixture used and virgin oil do not require prior esterification stage of free fatty acids. The best yield was obtained for a used oil concentration of 5% (yield: 98.69%; conversion 95.53%). Biodiesel obtained with mixtures up to 20% of WFO does not diminish the cetane number and the calorific value, so it would be expected that there is no change in the behavior during combustion. These results contribute to the establishment of a production process in which the WFO be employed as raw material for the production of biodiesel, which can be integrated into production plants established with alkaline catalysts, without any important modifications in process at industrial scale.

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