

Pre-treatment of Waste Cooking Oils for Biodiesel Production

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Production of waste cooking oil in big cities is a problem for public health in different countries around the world. A feasible solution is employing as raw material for biodiesel production. However, the problem is the high content of free fatty acids, moisture and solid particles presented in the oil. Therefore, this article analyses a process to treat Colombian waste cooking oils, by filtrating with a cellulose filter, drying with silica gel, and esterifying with methanol. For removing of particles it was standardized a process of filtration employing paper filter. With this process the solids remotion was 78.63%. After filtration oil was submitted to adsorption with silica gel. The experimental design was two concentration of adsorbent (0.025 g silica gel/ml oil and 0.11 g silica gel /ml oil) and two temperatures (15° C – 60°C). The best condition was temperature of 15 °C and a relation of 0.11 g silica gel /ml oil. The last step evaluated was esterification which to transform free fatty acid in methyl esters. In this reaction were evaluated two temperatures (40 °C and 60 °C), two concentration of sulfuric acid (1% w/w and 3% w/w) and two alcohol:oil molar relations (4:1 and 6:1). According to experimental results the best conditions were 60°C, 1% w/w sulfuric acid with 4:1 alcohol:oil molar relation during 2 hours. Finally oil obtained had less of 1% of moisture, 0.25% of solids suspended and 1.38 mg KOH/g oil of acid value. These attributes satisfactorily meet with ASTM and ISO standards, so it will be possible to use as raw material for biodiesel production.

1. Introduction

Fossil oil depletion and environmental concerns have given rise to investigations in processes to generate novel fuels (Naylor and Higgins, 2017). The production of biodiesel by oil transesterification is the foremost employed process today, generating a fuel with a high heating value and cetane number, which also mitigates unwanted emissions such as particulate matter, carbon monoxide, sulfur oxides and aromatic hydrocarbons. Nevertheless, the costs of the process are higher than the fossil fuel refining, mainly because of the cost of the crops (Apostolakou et al., 2009). Additionally, there is a controversy regarding the competition in the purpose of vegetables oils for food or fuel.

In order to decrease the biofuel feedstock cost, and to give a solution for the food-fuel controversy, investigations have focused in the use of the waste cooking oil (WCO) (López et al., 2015), (Alarcón et al., 2017), (Rodríguez et al., 2017) which is worldwide generated with a rate of around 15 million tons per year (Colgan 2014), leading to a considerable environmental impact (Kalam et al., 2011). According to studies carried out by World Health Organization (Martínez et al., 2013), 1 liter of WCO contaminates 1000 liters of water. Besides, there is a decrease in drainage performance and an increment in energy consumption (estimated at 25%) in the wastewater treatment stations.

Nevertheless, despite the advantages of using WCO, its previous exposure to high temperatures, and food contact, increases the moisture, free fatty acids (FFA), and particulate material contents. The main drawback of having a high FFAs content, expressed by the acid value, is that they reduce the conversion (Chhetri et al., 2008), since these FFAs react with the catalyst in the transesterification reaction and generate surfactants. Besides, the particulate material in the WCO persists through the biodiesel generation, and would cause some common problems such as carbon deposits, plugging of the fuel lines, gelling of lubricating oils, fouled piston heads and ring sticking. Moisture decreases the performance of the transesterification reaction, since water

reacts with alkaline catalysts to generate emulsions (Carlini et al., 2014), and displaces the equilibrium of the transesterification reaction toward the reactants, causing hydrolysis of the oil. Additionally, WCOs lead to the formation of polymerization reactions that increase the molecular weight, therefore also the viscosity, of the oil (Ordoñez et al., 2013; Encinar et al., 2005). Accordingly, the WCO may be submitted to some pretreatments which let the oil to reach some properties values that meet some specifications established by the standard ASTM D975.

Thus, the aim of this paper focus on studying some processes in order to treat some Colombian WCOs for producing biodiesel, evaluating the evolution of the properties in the process, to finally choice the best conditions.

2. Feedstock

60 L of WCOs were collected in different restaurants, chicken rotisseries, and bakeries located in Bogotá, Colombia. Then, WCOs were blended and disposed in an opaque plastic recipient until it was employed in the experiments. The WCO was characterized by ISO and ASTM standards as presented in Table 1. Additionally, it is presented some references previously evaluated for other WCOs.

Table 1: Characterization of waste cooking oil

Assay	Test Method	Value	Reference value
Density g/mL	ISO 6883-2000 / ASTM D1298	0.93	0.91
Acid value mg KOH/g WCO	ISO 660-2009	5.78 ± 0.11	2.47-3.6
Saponification value	ISO 3657-2002 / ASTM D558	172.65 ± 0.31	199.7-207
Iodine value	ISO 3961-2009	95.85 ± 0.55	83- 101.1
Sediments content	Gravimetry	1.17 ± 0.01	0.05
Humidity	Gravimetry	1.34 ± 0.03	1.25-1.9
Dynamic Viscosity	ASTM-D445	4.49 ± 0.02	3.82-4.18

Data for the reference value was taken from: Encinar et al. (2005), Encinar et al.(2007), Enweremadu and Mbarawa (2009), Leung and Guo (2006), Predojević and Škrbić(2009), Bouaid et al. (2007).

Density does not present a considerable change for a particular oil when it is pure and fresh, but it is affected by age, rancidity and by any special treatment that is made to the WCO. The density of the analyzed WCO is similar to that reported in the literature (Yaakob et al., 2013; Herrera and Vélez, 2008). However, it is higher than that established in NTC 431, which should be in the range 0.869 - 0.879 g / ml.

Due to the heating and cooling processes to which the oil is subjected, the FFAs content usually increases as the WCO is used. The acid value of the WCO was 5.78 mg KOH / g Oil, which has a higher value than the virgin palm oil 0.328 mg KOH / g Oil (De Almeida et al., 2015). The maximum limit established for the acidity index is 1.5 mg KOH / g oil to be accepted as an acceptable feedstock for biodiesel production (Chai et al., 2014). One way to decrease the acid value is by esterification, which transforms the FFAs to methyl or ethyl esters.

As the saponification value for the analyzed WCO was lower than the values reported in the literature, a lower molecular weight biofuel is produced, compared with the oils reported in the literature. If an oil presents iodine values lower than 60, the oil has a low degree of unsaturation which can generate unwanted reactions due to the chemical instability that triglycerides present (Chhetri et al., 2008). The results obtained for the WCO evidences a high content of unsaturations of the fatty acid chains present.

Carlini et al. (2014) establish that solids content should be lower than 0.5 %. The solids content of the WCO is 1.17%. So, it is imperative a filtration or centrifugation operation for the separation of the solids present in the oil. And, it has been established (Yaakob et al., 2013) that the oil must have a humidity percentage lower than 0.5% for the production of biodiesel, for which it is necessary to dehydrate the WCO. Finally, the viscosity of some WCOs can be so high that the behavior of the oil is similar to that of a solid (Enweremadu and Mbarawa, 2009), as presented in the analyzed WCO of this work.

3. Methodology

WCO was treated for biodiesel production by filtration, drying, esterification, and decantation as depicted in Figure 1. Samples of WCO were submitted to two different filters: a Taylor Mesh Size number 12, and a Whatman Cellulose filter paper (grade 1). Sediment content was determined by weighting the dry filters before and after the WCO percolations.

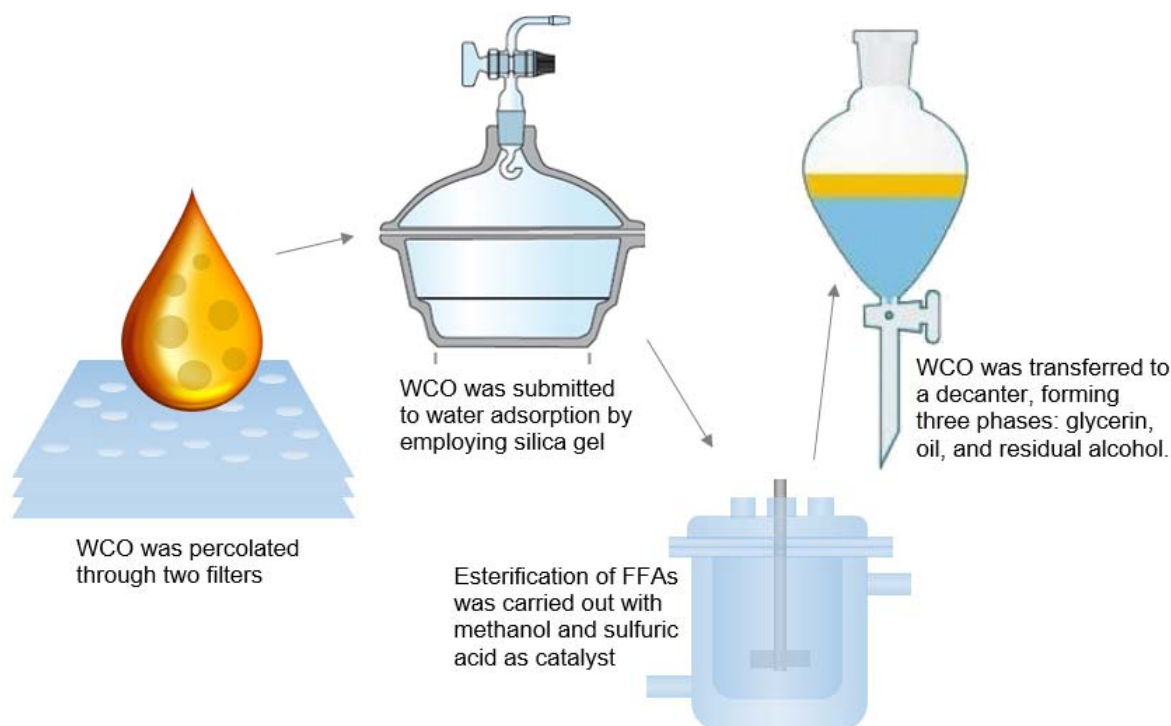


Figure 1: Methodological diagram of the WCO pretreatment for biodiesel synthesis.

Water presents in the oil was removed by adsorption. 100 mL of WCO were disposed into a glass reactor equipped with a heating jacket connect to a heated thermostatic bath. Silica gel (Merck, high purity grade) was employed as adsorbent. WCO in the reactor was stirred at 120 rpm for 2 h. It was evaluated two concentrations of adsorbent (0.025 and 0.11 g/mL of oil) and two temperatures (15 and 60 °C), according to the work of Medina *et al.* (2015). Residual humidity was evaluated every 20 minutes in samples of 2 mL (Predojević, 2008; Enweremadu and Mbarawa, 2009).

FFAs decrement was developed by the esterification reaction of short chain alcohol (Boffito *et al.*, 2013) and FFAs presents in the WCO, by employing an acid catalyst. This research works with sulfuric acid at 98% (Merck), and the reaction was carried out at 60 °C into a glass reactor of 200 mL with a heating system. It was evaluated 2 catalyst concentrations 1 and 3 % (w/w), 2 temperatures 40 and 60 °C and two molar ratios of oil to alcohol 1:4 and 1:6. Table 2 shows the experimental design for the esterification assays. Every 20 minutes, samples were taken, and content of FFA (Encinar *et al.*, 2005; Enweremadu and Mbarawa, 2009) was determined. Once esterification finished, oil was transferred to a decanter where three phases took form: glycerin (bottom), oil (intermediate), and residual alcohol (top).

Table 2: Experimental design for esterification assays.

Experiments	Temperature °C	Catalyst concentration	Molar relation oil/alcohol
1	40	1	1:4
2	40	1	1:6
3	40	3	1:4
4	40	3	1:6
5	60	1	1:4
6	60	1	1:6
7	60	3	1:4
8	60	3	1:6

4. Results and Discussion

Through the filtration process, the percentage of total solids was reduced from 1.15 to 0.25 %. According to the consulted literature (Leung and Guo, 2006; Enweremadu and Mbarawa, 2009), the oil to be used in the Biodiesel production must have a content lower than 0.5% solids, which agrees with the obtained results. In

the scaling of the production process, two sieves should be used, one for the separation of material with a size of the order of 1 mm, and another for the separation of particles of the order of 10 μm .

The tests carried out for the adsorption were denominated A (0.025 g of adsorbent / mL oil at 15 °C), B (0.11 g of adsorbent / mL oil at 15 °C), C (0.025 g of adsorbent / mL oil at 60 °C) and D (0.11 g of adsorbent / mL oil at 60 °C). Figure 2 evidences that the greatest adsorption happens when the highest level of adsorbent was used (0.11 g of adsorbent / ml of oil), corresponding to tests B and D. Meantime, regarding the temperature effect, it can be observed that the best temperature to carry out the adsorption of water is 15 °C, which is an advantage for the process because heating of the oil is not required (Encinar *et al.*, 2005; De Almeida *et al.*, 2015). According to Figure 2, through tests B and D, the oil has a moisture percentage lower than 0.2%, complying with ASTM D975, which establishes a percentage lower than 0.5 %. Of these two tests, B is preferred because it implies that the adsorption is done at room temperature (15 °C). This result is important for using waste cooking oil as raw material for biodiesel production. Different articles have been published in the way of production of biodiesel from waste cooking oil, but this article propose a previous process for adjustment this raw material.

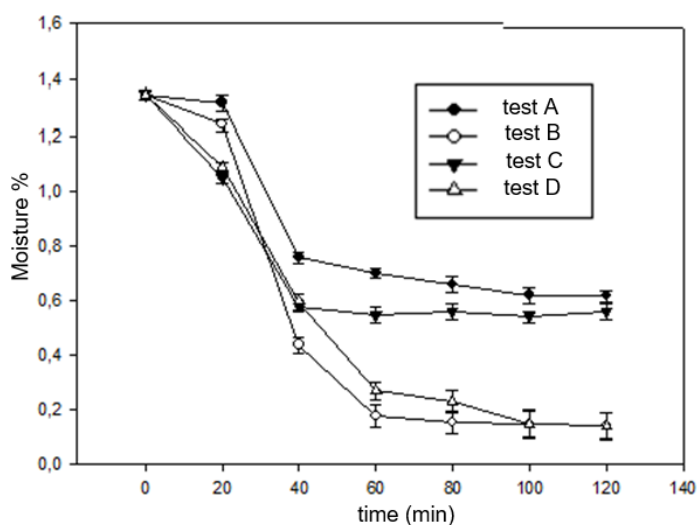


Figure 2: Moisture evolution for the experimental conditions evaluated.

Figures 3a and 3b depict the kinetics of the esterification tests, which were carried out at a temperature of 40 and 60 °C, respectively. From the aforementioned, it can be highlighted that the acid value decreases over time for all the tests. This implies that the esterification reaction progresses and neutralizes the free fatty acids that are present in the WCO. This process is recommended in the consulted literature for decreasing the FFA presents in the oil (Jagadale and Jugulkar, 2012), however it is not reported the conditions for esterification step.

In the present work, 3 variables were evaluated: temperature, catalyst percentage, and molar ratio (WCO/methanol). It can be appreciated that the temperature has a marked effect on the results obtained, since all the tests carried out at 60 °C present a greater neutralization than the tests carried out at 40 °C. As the temperature of the reactive system increases, the reactivity improves mainly because at 60 °C, the boiling point of methanol is reached, and would lead to an increase in molecular collisions that favor the reaction.

Regarding the effect of the catalyst, it is found that it is better to use a percentage of 1 % for all tests, except for tests 1 and 3 where this result is inverted. The addition of the catalyst does not cause an increase in the acid number, its contribution would be 0.014 g KOH / g oil and 0.0343 g KOH / g oil for 1 % and 3 % catalyst, respectively. On the other hand, the increase in the percentage of catalyst does not contribute to an improvement during the esterification process, as the results show when going from a percentage of 1 % to 3 %. For this reason, it is preferred to use a percentage of 1 %.

Finally, the result that has the least effect on the neutralization of free fatty acids is the oil/methanol molar ratio. The results obtained show that there is no significant difference in the molar ratio used. This implies that it is preferred to use the molar ratio 1:4 of used cooking oil to methanol, since it implies a lower amount of alcohol to recover at the end of the process. Additionally, it can be observed in Figures 3a and 3b that the time required for the advance of the reaction must be 2 h.

Accordingly, conditions which present the best esterification are: temperature 60 °C, percentage of catalyst 1% and molar ratio 1: 4 of used cooking oil to methanol and a reaction time of 2 h, which correspond to test 5

presented in Figure 3b. Under these conditions the acidity of the used cooking oil was decreased from 5.78 mg KOH / g oil to 1.38 mg KOH / g oil. The previous result allows to conclude that the content of free fatty acids is reduced and it is adjusted to Colombian normativity. In the consulted literature, it is preferred to use directly the waste cooking oil without a diminishing in the moisture content (Jagadale and Jugulkar, 2012), (López et al., 2015), (Carlini et al., 2014), however this alternative affect the conversion due to soap formation (Jagadale and Jugulkar, 2012), (Gashaw and Teshita, 2014). Other authors have preferred to heat the oil for evaporating the water present in the oil, but this process is not recommended because may be to increase the hydrolysis and FFA formation reaction (Encinar, 2005).

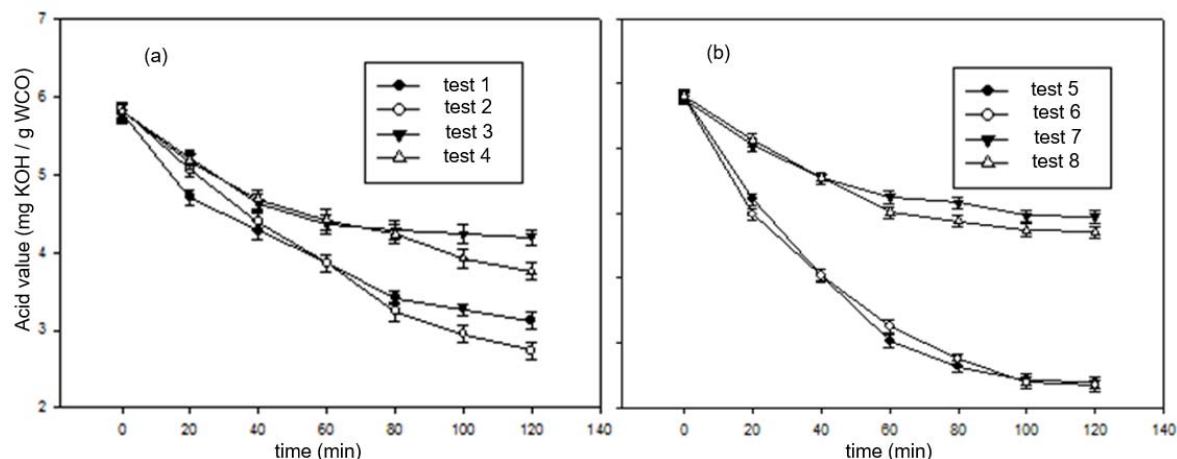


Figure 3: Evolution of the acid value in the system.

Once the test 5 was selected as the one that delivered the best results of the esterification, it was subjected to decanting. In the decantation 3 phases are formed: superior (rich in alcohol), intermediate (rich in WCO) and inferior (rich in glycerin). For test 5 the formation of glycerin is not reported, the percentage in mass of recovered oil corresponds to 86.3% and that of alcohol to 13.7%. The biodiesel formed is in liquid phase. The excess of catalyst can remain in the oil phase. However, its presence does not increase the acid value of the WCO, which would not present any inconveniences. In addition, said acid would be neutralized during the trans-esterification and would not present a problem because it would be separated during the washes, to which the biodiesel is subjected.

5. Conclusions

Through different operations a laboratory scale it is possible to adequate WCO as raw material for biodiesel production. In this way, three unit operations have been established: filtration, moisture adsorption and esterification. This process would be implemented independent of the biodiesel plant, because the objective is to commercialize oil with low moisture content, low FFA percentage and without materials suspended. At industrial level, in this plant would be incorporated the collecting of raw material and distribution to biodiesel plants. The economic analysis will determine the profitability of using this process in industrial scale.

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