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Physicochemical study of used frying oil as feedstock for the production of biodiesel

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Abstract. A diagnosis was made of the availability and quality of the used frying oil of the establishments dedicated to chicken fry in the city of San José de Cúcuta, to evaluate its technical feasibility as a feedstock in the biodiesel production. A survey was applied to 21 restaurants, evidencing that they reuse the oil less times when having a high monthly consumption (*i.e.* more than 80 liters, contrary to those consuming less than 60 liters, which reuse the oil more than 3 times. As a final disposition, 86% of establishments sell the used frying oil at \$750/liter and 14% deliver it to be used by external persons. The physicochemical properties of used frying oil were analyzed as: fatty acid profile, density, moisture content, refractive index, acidity index, peroxide index and saponification index. The used frying oil presented high content of oleic acid (42.45%) and palmitic acid (33.52%), converting it into a potential feedstock by presenting fatty acids characteristics from palm oil, which is the main source for the production of biodiesel in Colombia. To improve the organoleptic characteristics of the used frying oil (dark colour, strong odour, emulsions), it was subjected to heating and filtering to remove the particles that affect the yield of biodiesel production.

1. Introduction

In 2018, considering the environmental commitments of Colombia in the Paris Agreement for the reduction of its greenhouse gas (GHG) emissions to 20% [1], the B10 biodiesel mixture was established throughout the national territory (*i.e.* 10% biodiesel, 90% diesel), with the exception of the three border departments that are under the B2 mix [2]. The production of biodiesel for the year 2018 is projected at 620 million liters [2], which is based on the use of palm oil as a feedstock in Colombia; due to this, the production is eventually affected by the climatic conditions that cause damage in the palm crops. Additionally, the implementation of biofuels is a great contribution in the reduction of carbon dioxide emissions, because the combustion of conventional diesel leads to emissions of 3.5 kg CO₂/kg Diesel [3], while using biodiesel the GHG emissions are reduced by 41% [4]. However, despite the advantages of using biofuels, these present some drawbacks related mainly to the feedstock of agricultural origin, since the high demand for biodiesel in the country leads to the expansion of palm crops, contributing to deforestation and affecting biodiversity due to the presence of crops that exceed 75% of the area that is destined by 55% for natural ecosystems [5]. Similarly, the use of these food crops for energy purposes ends up negatively impacting the country's food security. According to the above, it is essential to act quickly to work on the social and environmental aspects that are being



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directly affected by the use of palm oil as a feedstock. For this, the present study projects the utilization of used frying oil as feedstock for the biodiesel production. Therefore, a diagnosis was made to determine the amount of used frying oil (UFO) that is generated in the San José de Cúcuta city, Colombia, by fried chicken restaurants and likewise, a sample was collected to evaluate the physicochemical characteristics of the oil and analyze its technical potential as a feedstock in the biodiesel production.

2. Materials and Methods

2.1. Availability and obtaining of used frying oil

A representative sample of the population was taken, according to the establishments distributed in the 10 communes of San José de Cúcuta city, Colombia. A survey was applied to 21 establishments which consisted of a series of questions (*e.g.*, oil consumption, type of oil, degree of reuse, final disposal) to identify the availability, consumption and current use of the UFO. Additionally, aspects of general knowledge related to used oil (environmental impacts, collection, use) were consulted.

2.2. Pre-treatment and physical-chemical characterization of used frying oil

The UFO was subjected to a heating and filtration process using a cloth sieve, the sample presented a dark colour, a very strong smell and the formation of a dense and viscous phase that was found to be sedimented together with the remains of some foods that were removed. In order to evaluate the characteristics of the UFO and identify the content of fatty acids, parameters such as density, refractive index, moisture content [6], acidity index [7], peroxide index [8], saponification index [9] and fatty acid profile [10] were analyzed.

3. Results and discussion

3.1. Current situation of used frying oil

3.1.1. Average oil consumption. According to the information collected about oil consumption in each establishment, these can be classified into three groups, the large consumers occupying 57.89% of the total (*i.e.* consumption greater than 80 liters/month), 31.57% as medium consumers (*i.e.* between 60 to 80 liters/month) and 10.52% as small consumers (*i.e.* less than 60 liters/month). It was evidenced that the large consumers are located in the area identified as commune 1, which is the downtown area of Cúcuta city where most of the commercial activity takes place and where the largest number of restaurants is located (8 establishments) intended for frying chicken.

3.1.2. Reuse of oil. As shown in Figure 1, most establishments (38%) reuse oil more than three times a week without removing it from their machines, followed by 33% that reuse it three times, 19% of establishments only reuse it once, while 5% decide to reuse it twice times and another 5% does not reuse it. The number of times they reuse the oil is below than that identified in another study [11] where the surveyed establishments reuse the oil between 5 and 20 times, which depends on certain factors (*e.g.* amount of prepared food, type of food, cleaning frequency). This factor is very important to evaluate the quality of the UFO, because the reuse of vegetable oils leads to being exposed to high temperatures, long frying times and the presence of oxygen producing oxidation, lipolysis and hydrolysis reactions, generating volatile and non-volatile components [12]; its constant use also causes the rancidity of food, generating the production of free radicals and in some cases the formation of trans fatty acids, which are harmful to human health [13].

On the other side, a relation is established between the degree of reuse of oil and its consumption, where large consumers reuse oil less often as shown in Figure 2. Establishments B and F they do not reuse oil or they reuse one time maximum, consuming 300 and 360 liters/month, respectively. Contrary to those who consume lower amounts of oil, who reuse it more than 3 times to meet the

demand and the low amount of oil with which they work. This connection allows to conclude that the higher the oil consume of the establishment, the lower the degree of reuse of it.

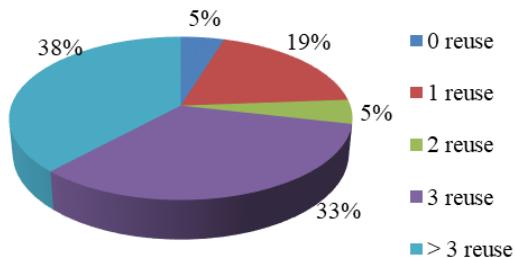


Figure 1. Degree of reuse of the UFO.

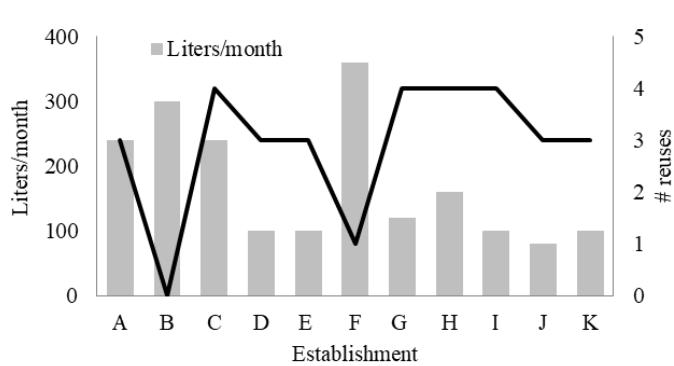


Figure 2. Relationship between oil consumption and its reuse.

3.1.3. Final disposition of the used frying oil. With the information collected it is established that 86% of establishments sell the UFO as a measure of final disposition, generating an additional income for their business of \$750 per liter of UFO sold. However, 14% of them re-pack the UFO and deliver it to an external person. In comparison with other studies carried out, it has been found that out of 49 investigated establishments, the majority recycles the waste oils, with the exception of three that discharge it to the drain [12]; unlike the study made by Solarte and Vargas [14], it is identified that 43.45% of the people consulted freeze the waste and throw it away, 20% pour it through the dishwasher, 16.55% reuse the oil and 10.34% consume the oil completely or they give away, only 9.66% re-pack the oil and take it to a storage place. On the other hand, establishments surveyed by Naranjo de Vidal [15], the 69% throw the oil in the trash and 31% re-package it to deliver it to people who use it for agricultural purposes.

The final disposition of the UFO in San José de Cúcuta city is an adequate solution to the environmental problems that cause its presence in the sewerage and water sources, because the recycling and the selling allows it to be used as feedstock for new products. However, the action of pouring it through the dishwasher is more common in domestic households as a result of the people misinformation and the lack of post-consumer programs that include them. Which shows that each of the measures that are established for final disposal depends on the management carried out by each establishment, the knowledge they have about the environmental impacts of a good disposition and the use they make of waste oil.

3.2. Physicochemical characterization of the used frying oil

The UFO presented a density of 0.962 g/cm^3 , similar to that reported in studies in which used oils had a density of 0.921 g/cm^3 [16] and 0.919 g/cm^3 [17]. However, its value is higher compared to

the required limit ($0.891 \text{ g/cm}^3 - 0.899 \text{ g/cm}^3$) for a crude palm oil [18]. On the other hand, it presented a similar refractive index to that obtained in the investigations made by Sanaguano [19] and Murcia et al. [20] with 1.461 and 1.460, respectively. According to Soto [21], this property is characteristic for each oil and indicates the purity of the oil and it is related to the degree of saturation, which is influenced by the damage suffered by the oil when exposed to oxidation. The moisture content of the UFO was very low (0.055%) compared to the 0.5% required for a crude palm oil [18]. However, it is similar to the different contents expressed by Tacias et al. [22] for the oil samples and residual cooking fats analyzed in his study, as well as those obtained by Murcia, *et al.* [20], 0.104% and 0.089% for waste oil and used oil, respectively. This characteristic has great importance in the biodiesel production since a high content of water in the feedstock affects negatively the reaction conversion inasmuch as promotes the hydrolysis of triglycerides and increases the content of free fatty acids (FFA) in the oil [23], so this parameter of the UFO is optimal for the good performance of a transesterification as it is exposed [24], who recommends working with a moisture content lower than 0.5% in the biodiesel production.

The acidity index of the UFO is 5.116 mgKOH/g, which is above the maximum allowed value (5 mgKOH/g) that must have the feedstock for the biodiesel production [16], being similar to 5.61 mgKOH/g reported by Cifuentes [17] for this type of oils; at the same time it is higher than the value reported by Zelaya [25] and Herrera and Vélez [26] which are 1.6 mgKOH/g and 0.824 mgKOH/g, respectively. This is an important factor in defining if the process of obtaining biodiesel it is carried out in two stages (*i.e.* acid esterification and alkaline transesterification), for which it is taken into account that the acid number must be less than 5 mgKOH/g; in this case the sample of UFO collected exceeds the level of the free fatty acids, which indicates that the oil has been reused several times so it is necessary to perform an acid esterification to reduce the FFA and to avoid low yield in the chemical transesterification process. However, enzymatic transesterification is not affected by the amount of FFA present in the oil.

According to the previous, this factor is essential to define the design of the production process, which tends to be an inconvenience to use the UFO as raw material at industrial level because it implies the realization of an additional stage causing the increase of production costs [27]. The peroxide index obtained for the UFO was 1.505 meqO₂/kg, which is within the acceptable values for a residual oil (less than 20 meqO₂/kg) [26], this property indicates the degree of oxidation that the UFO presents due to the conditions to which it was exposed (heat, air, light) causing its rancidity that can be evidenced when compared with the values between 0 and 5 that pure oils should have [26]; this parameter depends on the use and storage of the UFO, so there are several values as reported between 0.2 meqO₂/kg and 4 meqO₂/kg for the different cooking oil residues and animal fat collected [28]. The UFO sample obtained a saponification index of 174.68 mgKOH/g, which is below the other results reported in the investigations of Bulla [16] and Murcia et al. [20], however, it is similar to the index obtained by Casallas et al. [29] of 172.65 mgKOH/g.

3.2.1. Composition of the fatty acids profile. The fatty acid content of the sample was determined, because the frying and storage conditions can cause alterations of the saturated, monounsaturated and polyunsaturated fatty acids in the oil. The results obtained in the profile of fatty acids are listed in Table 1 as well as the values reported for crude palm oil (CPO) [18] and the characterization of palm olein (PO) [30].

The UFO collected comes from vegetable oil constituted by a mixture of palm olein and soybean oil. It can be seen that it contains a large percentage of oleic and palmitic acid, those are characteristic in the composition of palm olein, indicating that the sample contains a greater percentage of this type of oil. The results demonstrate the increase in oleic acid content in the UFO compared to pure palm olein, which is attributed to the hydration of the more unsaturated fatty acids by the presence of water and the high temperatures during frying [31,32]. Similarly, the high content of myristic acid and the decrease in the presence of oleic acid in the sample indicates the prolonged use of the oil [22]. The UFO sample is similar to the content of fatty acids present in crude palm oil, which makes it a

favorable option to replace this oil as feedstock in the biodiesel production, because palm oil is the main source in Colombia for the production of biodiesel [1].

Table 1. Fatty acid profile of UFO and vegetable oils.

Fatty acids	UFO	CPO [18]	PO [30]
Oleic acid, Methyl ester (C18:1)	42.7%	36.0 - 44.0%	42.4%
Palmitic acid, Methyl ester (C16:0)	33.5%	39.3 - 47.5%	37.1%
Stearic acid, Methyl ester (C18:0)	7.4%	3.5 - 6.0%	5.4%
Myristic acid, Methyl ester (C14:0)	3.9%	0.5 - 2.0%	1.3%
Palmitoleic acid, Methyl ester (C16:1)	2.4%	< 0.6%	-

3.3. Potential use of used frying oil for the biodiesel production

The average generation of oil in San José de Cúcuta city, Colombia, is close to 1700 liters/month, which indicates that around 40800 liters of UFO are being generated per year; taking into account that if this oil is used as feedstock in the biodiesel production process in an efficient way complying with the minimum percentage of methyl ester conversion required (96.5%) [33] and having the required equipment on an industrial scale, about 39372 liters of biodiesel will be obtained annually (247.62 barrels/year) from used frying oil. This product could be mixed with conventional diesel and comply with government guidelines and at the same time achieving the reduction in the GHG emissions.

According to the physicochemical characterization of UFO, it can be established that the sample collected is a technically suitable alternative to be used as a feedstock in the production of biodiesel from an alkaline transesterification, because its content of water is very low so it will not lead to the formation of soap in the process. However, due to the high content of FFA that it is necessary to carry out an esterification as a previous stage to avoid the formation of emulsions that affect transesterification. Studies conducted by [16,17,19,27] in which used cooking oils are employed to produce biodiesel by means of chemical transesterification obtained conversions of 96.41%, 90.28%, 85.72% and 98.4%, fulfilling the latter with the required value (96.5%) by quality standards for biodiesel (e.g. EN14214). On the other hand, enzymatic transesterification can be a favorable option for the biodiesel production from UFO because the high content of FFA and moisture does not affect the reaction, on the contrary, it transforms all the FFA of the oil, promoting better performance [34], even studies have been found in which high percentages of biodiesel conversion of 88% – 90% [35] and 97.8% [36] have been obtained from this process when using residual cooking oils and a mixture of used oil with canola oil, respectively.

Finally, in Colombia the Resolution 316 of 2018 has emerged and it regulates and promotes the recycling of residual frying oil [37], so to propound the large-scale use of this agroindustrial waste as well as being a favorable option to solve the problem of palm crops also would allow to face the negative environmental impacts caused by the incorrect disposition of oils when they are discharged to water sources and sewage, this would generate a positive environmental impact on the soil, biodiversity, sources of water and the country's air quality by significantly reducing carbon dioxide emissions, because the emission rate when using biodiesel from waste cooking oil is 2.83 KgCO₂/kgBiodiesel [38].

4. Conclusions

The frying conditions (high temperatures, water, light, air) to which the oil is exposed in the preparation of foods have a considerable influence on its organoleptic and physicochemical characteristics, which was evidenced in the increase in the UFO density (0.962 g/cm³), property related to the generation of FFA, confirmed through the high acidity index (5.116 mgKOH/g) and the low moisture content (0.055%) presented by the sample, this indicates the high temperatures and prolonged periods of time to which the oil was exposed, leading the water evaporation and UFO oxidation. Likewise, the organoleptic characteristics that were identified (dark colour, strong odour,

emulsions) show the constant reuse that the oil had, in addition to the peroxide index (12.505 meqO₂/kg) it indicates the oxidation state of the sample. When comparing the fatty acid profile of the UFO with the feedstock used in Colombia for the biodiesel production, it is established that the UFO can be a potential alternative to replace the crude palm oil in the biodiesel production.

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