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Production of Aviation Biofuel from Palm Kernel Oil

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In order to partially replace the use of fossil fuels in the aeronautical sector, it is proposed to produce FAME-type biofuels from palm kernel oil. Short chain methyl esters can be used so that the FAME biodiesel have no significant effects on the cold properties of the Jet Fuels when these are mixtures. In this sense, a study of the production of biodiesel FAME from palm kernel by transesterification oil at bench scale was carried out using a batch reactor with the optimal value of the process conditions that were obtained in a previous work but at laboratory level. In that research, the input variables were the methanol-oil ratio, the temperature and the amount of catalyst (% KOH). In this work, the response variable was on the production yield of methyl esters, which were analysed by GC. Physicochemical characterization of the generated biodiesel and an economic analysis of the bank-scale process was carried out to envision a future implementation in the Colombian Air force. Using additives, the improvement of the cold flow properties (such as freezing point and cloud point) of mixtures of FAME of Palm Kernel Oil with Jet Fuel A1 can be contemplated.

1. Introduction

Air transport worldwide has had a vertiginous growth in recent years. In fact, an annual increase close to 5% in demand is estimated until 2036 (Gutiérrez-Antonio et al., 2018). Although the aerial modality is relatively smaller compared to the terrestrial one, it is responsible for almost 12% of the global emissions of the entire transport sector (Chuck, 2016). Within a crucial panorama of climate change in the world, the above proposes challenges for the air transport industry that cannot be addressed only by improving efficiency. Therefore, it is necessary to take other measures such as considering the use of biofuels, which play a critical role in reducing CO_2 emissions (Schäfer, 2016).

The alternative to the use of biofuels at the air level has not had the same level of development as at the ground level, mainly due to the need for technical validation of the fuel with certification for purposes of flight safety. However, some developments of research and pilot tests have proposed different technologies to produce "Biojet Fuels", mainly of four types. First, there are HEFA, Hydro-processed Esters and Fatty Acids of vegetable oils, in future of algae oils. The second alternative is F-T, Fischer-Tropsch kerosene (BTL: Biomass to Liquid) from lignocellulosics. Third, there is DSCH/SIP, Direct Sugar to Hydrocarbon / Synthesized Iso-Paraffinic fuel (sugar to farnesene from, e.g., sugar cane). Finally, there are other alternatives that have no ASTM certification yet (the previous three already have it), such as Bio-GTL (Biogas to Liquid via biomethane and a wide range of biomass feedstock), ATJ (Alcohol to Jet), HDCJ (Hydrotreated depolymerized cellulosic jet) and PTL (Power-to-Liquid; electrolysis and subsequent synthesis either via FT or methanol) (Thrän & Ponitka, 2016).

The technology that uses the hydroprocessing of vegetable oils is what generates a biofuel that is physically-chemically similar to Jet Fuel, which is known as biokerosene (Mayorga, Cadavid, et al., 2019). Although it generates a high quality product using a wide range of raw materials, this technology requires high investment costs for the industrial production plant (Aatola et al., 2008). For a couple of decades, in many countries they have implemented the fossil diesel substitution policy with FAME-type biodiesel resulting from the transesterification of vegetable oils, a technology that has become highly available due to its moderate

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temperature and pressure conditions, and the use of homogeneous catalysts. In some parts of the world, there has been an overproduction of vegetable oils and a potential oversupply of FAME, which in the Colombian case generates only 75% of the installed capacity (Federación Nacional de Biocombustibles, 2016). Consequently, the market could offer the possibility of using FAME biodiesel as a partial substitute of Jet Fuel for the aeronautical sector.

Previously, some authors have addressed the replacement of kerosene with FAME-type biofuels through the prediction of the properties of the fuel mixture (Llamas, Lapuerta, Al-Lal, & Canoira, 2013). Mixtures until 20% volume of FAME of palm kernel with fossil jet fuel were evaluated showing that it is possible to substitute until 10%, if the IATA relaxes a few of its standards. The use of FAME as aviation fuel has been studied by several researchers who achieved favourable results with mixtures of up to 20% replacement of Jet Fuel, since with higher values, deviations of cold flow properties are outside of the acceptance interval of the standards used (Lapuerta & Canoira, 2016). The cold properties, such as freezing and cloud point of the mixtures between FAME and Jet Fuel, can be improved with the use of conventional biodiesel containing methyl esters of shorter chain fatty acids, in addition to the optional additive handling (Mayorga, Cadavid Estrada, et al., 2019).

In this way, this work investigates the production of FAME biodiesel obtained from palm kernel oil, since this oil contains approximately 48% of lauric acid (C12:0) and 16% of myristic acid (C14:0) (Ahmad et al., 2009). The stearic and linoleic acids reach no more than 2% of the total, since in the rest of the mass acids with longer chains of 16 and 18 carbons predominate as palmitic and oleic acids (See Table 1). Considering a future escalation of palm kernel oil biodiesel production at the industrial level to incorporate into the Colombian aviation fuel market, several tests were carried out at the bench level of this process based on previous results obtained for the optimization of the biodiesel yield obtained. In that previous work at laboratory level, the factors in the experimental design were methanol-oil ratio, temperature and amount of catalyst (% KOH). In both studies, the response variable is the production yield of methyl esters, which were analysed by GC. Physicochemical characterization of the generated biodiesel and an economic analysis of the bank-scale process are carried out.

2. Experimental

2.1 Materials

Methanol for analysis (>99.9%) and potassium hydroxide (ACS grade) were purchased from Merck (Darmstadt, Germany). Refined palm kernel oil was obtained from Integrasas S.A.S (Bogotá D.C., Colombia) with a saponification index of 230-254 mg KOH/g, an iodine index of 17-19 and an acid value of 0.1% as lauric acid. The fatty acid profile of the acquired palm kernel oil is presented in Table 1.

Table 1: Fatty acid profile of palm kernel oil

Lauric C12:0	Miristic C14:0	Palmitic C16:0	Stearic C18:0	Oleic C18:1	Linoleic C18:2	Others
47.8	16.3	8.5	2	15.4	2.4	<1

Chromatographic grade standards for methyl esters of fatty acids (FAME: laurate, myristate, palmitate and oleate) were provided by Sigma Aldrich-Merck (St. Louis, United States). For chromatographic analysis, tricaprin was used as internal standard (Fluka, Buchs, Switzerland).

2.2 Equipment

As shown in Figure 1, in general terms the reactor batch at bench scale consists of two cylindrical tanks with conical ending: (1) the methoxide tank and (2) the reactor tank, each with agitators and motor; (3) a control panel; and (4) a product deposit. The equipment for the production of biodiesel is made of 304 stainless steel. Each batch can generate about 20 gallons of biodiesel.

Figure 1: Batch reactor at bench scale.

2.3 Analysis

With the FAME, once separated from glycerine, and washed with water, several characterization tests were performed in the current study based on the characterization of the fuel. The tests used were: ASTM D7777-13, ASTM D4052-11, ASTM D92-12, ASTM D93-15, ASTM D88-07, ASTM D445, ASTM D482-13, ASTM D874-13ª, ASTM D1796-11e1, ASTM D4377 -00, ASTM D95, ASTM D86-12, ASTM D1218-12, FTIR, ASTM D-2500, ASTM D2270-10e1, and ASTM D240-14.
For chromatographic analysis by gas, the samples were prepared taking 20 mg of the product with 5 mg of the internal standard and completing until 1.5 ml with hexane. Then, 1 µl of this sample was manually injected into the Agilent 6820 GC equipment (Agilent Technologies Co. Ltd., Shanghai, China), which has a flame ionization detector (FID), a fused silica precolumn (0.3 m x 0.53 mm) and a fused silica capillary column Supelco SGE HT-5 (12 m x 0.53 mm x 0.15 µm) (SGE International Pty. Ltd., Victoria, Australia). The oven temperature was stabilized at 140 °C during 1 minute; then, it was increased from 140 °C to 380°C in 12 minutes (at 20 °C/min), and it remained in the latter for 10 min. The temperature of the injector and detector are 350 °C and 390 °C, respectively. The flows used were 6 ml/min of nitrogen as carrier, 40 ml/min of hydrogen gas and of H_2 and dry air were 40 and 360 ml/min of dry air for the FID. Data were acquired and processed with the Cerity software (Agilent Technologies Co. Ltd., Shanghai, China). Finally, the economic analysis was made considering a simple structure of costs.

3. Results and Analysis

For bench scale fuel generation, the main operating conditions, together with the required quantities of reagents, are summarized and presented in Table 2.

Table 2: Test in bench reactor

Assay	Molar relation	%[KOH]*	Temperature [°C]	Oil [kg]	Methanol [l]	KOH [g]
1	4.5	0.5	55	38	9.78	190
2	6	0.5	47	36	12.36	180
3	4.5	0.5	47	38	9.78	190
4	6	0.5	55	36	12.36	180
5	4,5	1	55	38	9,78	380
		Amount total required		186	54	1120

In the previous tests, the highest yield for biodiesel was achieved in assay No.1 with a biodiesel yield of 94.9% as a result of the GC analysis for a sample of this assay. On the one hand, Figure 2(a) shows a chromatogram of the occurrence of palm kernel oil, first its fatty acids peaks, next the appearance of the tricaprine peak at 13 minutes of retention, then diglycerides peaks and finally triglycerides peaks. On the other hand, in Figure 2(b), the chromatogram shows the appearance of methyl laurate, methyl myristate, methyl palmitate and methyl oleate, around 5.6, 6.7, 7.7 and 8.6 minutes, respectively. This indicates that the transesterification reaction was carried out with high conversion. In contrast, the peak of tricaprine marks the difference between the presence of glycerides in the sample and methyl esters. The quality of the obtained biodiesel is very good.

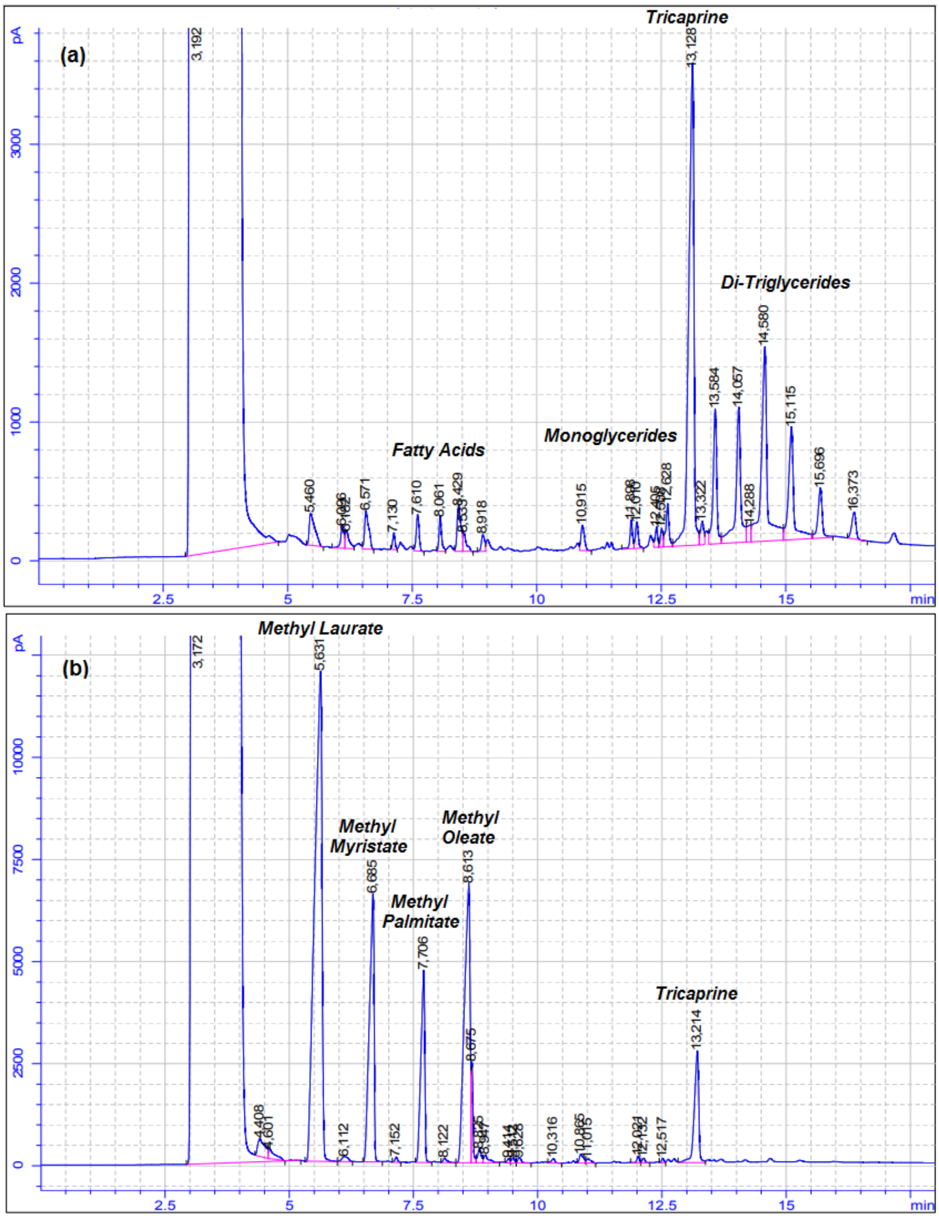

Figure 2: Chromatograms of (a) kernel palm oil and (b) biodiesel obtained.

The characterization was performed on the sample after the transesterification under the initial conditions of the process. These features correspond to some of the ones mentioned in the standard ASTM D 6751. However, it is important to keep in mind that as not all the tests established in that norm were executed, it is not possible to ensure that the obtained biodiesel achieves all the specifications. Table 3 presents the results of the characterization.

Table 3: Characterization of Palm Kernel Biodiesel FAME.

Parameter		Unit	ASTM	Value	Range ASTM D6751
Density (15°C)		g/cm^3	D7777-13	0.888	0.860 – 0.900
Cinematic viscosity (40°C)		cSt	D445	4.22	1.9 – 6.0
Flash point	Open cup-Cleveland	°C	D92-12	119	93 min.
	Closed cup-Pensky Martens	°C	D93-15	107	100 min.
Heat Value		MJ/kg	D240-14	37.4	Not contained
Cloud point		ºC	D-2500	7	Report
Water and sediments		% volume	D1796-11e1	0.00	0.05% max.
Ash		% mass	D482-13	0.07	0.18 max.*
Sulphated ash		% mass	D874-13a	0.01	0.02 max.*
Distillation Temperature		ºC	D1160	140	360 max.
Refraction Index		-	D1218-12	1.4340	Not contained

All specifications comply with ASTM D6751, which is for B100. However, in future work it is necessary to compare the values of the requirements of the regulations for aviation fuels such as ASTM D1655-19, IATA, Def Stan 91-91 and ASTM D7566 in the mixtures between this biodiesel and Jet Fuel A1. With respect to the standard of aviation fuels, the critical specifications would correspond to the heat value and the freezing point, which must be of 42.8 kJ/kg and -40°C, respectively. These values will tend to get worse (the first to be reduced and the second to increase) as the proportion of FAME increases in the mixture with fossil fuel. The specification with respect to the freezing point can be improved with additives, so that the mixture meets the restriction. This can be performed in the next work.
According to the analysis of fixed, variable, personal and input costs for the production of biodiesel from palm kernel oil, the respective litre value of biodiesel produced in a small-scale reactor is established. Table 4 establishes the value of the biofuel for each batch made.

Table 4: Associated costs in the production of fuel per run.

Item	Quantity	Unit	Unit Cost USD	Total Cost USD
Kernel palm oil	20	kg	2.45	48.96
Methanol	5	l	12.04	60.18
Potassium hydroxide	174.7	g	0.05	8.67
Electric energy	2.4	kWh	0.14	0.33
Technical staff	12	h	2.42	28.92
Total USD				147.06

Thus, using the amounts listed in Table 4 and making the respective separation of biodiesel from glycerin, 28.14 l of biodiesel are obtained, therefore, its unit value is 5.22 USD. In Colombia, the cost of Jet Fuel A1 is less than 1 USD, thus the mixing in the current condition would not be profitable, unless environmental costs are considered and the production volume of palm kernel FAME is increased.

4. Conclusions

The increase in the amount of methanol favours the yield when the amount of catalyst does not exceed 1% of the weight of oil. However, it is necessary to ensure an effective separation process of sodium methoxide from biodiesel for refining. Based on the characterization tests developed, biodiesel produced from palm kernel oil at laboratory scale is within the parameters established under the American and European standards. According to the cloud point results, it is recommended to deepen the research on the addition of additives that reduce the temperature of crystal formation in biodiesel.
The economic analysis demonstrates that considering only the costs of the inputs, the value of the litre of biodiesel is above the commercial value of fuel, since at an international level the value is 0.79 USD/l. Nevertheless, it must be considered that when increasing the capacity in production the value tends to

decrease. Besides, this was a bank-scale test, which is actually an intermediate between the laboratory scale and the pilot scale, which means this is a process still under research and development.

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