Biodiesel as Renewable Energy Sources-Production via Transesterification of Waste Frying Oil

Amel Asselah and Abir Ben Amra

***Abstract*—** The biofuel has attracting increasing attention worldwide as a clean energy for the future to substitute fuel, which their production derives from conventional ways that are so expensive and polluant using fossil fuels. The aim of the present study is to valorize a potential agro-food waste namely fried oil (80% soybean oil and 20% sunflower oil) whose use is very frequent by it transformation into biofuel, which represents a renewable and non-polluting source of energy. Two stakes emerge from this study, the economic stake : production of biofuel (renewable energy) at low cost, good efficiency and good quality and the environmental stake: conversion and recovery of used vegetable oil waste. The process allowing this transformation is based on the transesterification reaction of the oil using alcohol in basic homogeneous catalysis, which is very efficient and cost. Based on literature, many catalysts like acids, alkalis and enzymes (Lipase) are used for this process. This reaction is an imperative process for biodiesel production, as it can reduce the viscosity of the feedstock/vegetable oils to a level closer to the conventional fossil-based diesel oil. It has been widely used for the conversion of triglycerides into esters. Parametric study relating to temperature, time, stirring speed, type of catalyst and solvent influencing transesterification reaction was studied. To confirm that the biodisel obtained is a good quality, this latter was analyzed by gas chromatography to determine its composition and their physico-chemical properties were studied. The results of the esterification of this oil show that the quality of the produced biodiesel is directly related to the temperature. The physicochemical characteristics in terms to density, viscosity, higher calorific value, pour point, cloud point, freezing point and acid number were determined and indicating that the physico-chemical properties for the produced biodiesel are comparable to those of commercial diesel according to EN14214 and ASTM D6751 international standards..

***Keywords*—** Biodiesel, Biomass, Renewable Energy, Transesterification.

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I. Introduction

The industrialization requires more and more fuel, causing the increase in atmospheric pollution and concentrations of greenhouse gases. Faced with this problem, the use of biofuels is a cleaner alternative to oil. These biofuels produced from renewables have the advantage of reducing oil consumption and reducing greenhouse gas emissions [1]. Biodiesel production has attracted considerable attention in the recent past as a biofuel. It is a biodegradable biofuel and an ecological alternative to diesel, produced by transforming oils of vegetable, animal or used origin into alkyl esters [2], [3]. It has the advantages of renewability, non-toxic, high flash point and less pollution [4]. From an environmental point of view, used edible oils presenting a serious ecological problem and can be recovered and recovered into fuels, due to the fact that they are very rich in triglycerides and free fatty acids. Transesterification is one of the most important methods used for transforming vegetable oils into diesel fuel. This is a process in which vegetable oils, animal fats or microalgae-based oils are mixed with an alcohol in the presence of a catalyst [5]. This study aims to produce biodiesel meeting the international quality standards, from used vegetable oil: frying oil by the transesterification reaction and compare them to commercial diesel or petrodiesel.

II. Experimental section

A. Reagents

The raw material used to carry out this work is used vegetable oil, from frying, composed of 80% soybean oil and 20% sunflower oil, with a frequency of 4 times.

The different reagents used are: potassium hydroxide (>85%, Sigma-Aldrich), sulfiric acid (95-98%, Merck), methanol (99,7%, Honeywell), ethanol (99,9%, Scharlau), isopropanol (99,8%, Scharlau) and toluene (99,8%, Sigma-Aldrich).

B. Production of Biodiesel

The synthesis of biodiesel was carried out by transesterification of waste vegetable oil (200 g) with alcohol (methanol, ethanol, isopropanol). The transesterification is carried out with methanol in the presence of catalyst 1% (KOH, H_2SO_4) at different temperatures (30 to 70 °C). The reaction time varies from 30 up to 150 minutes and the synthesis is maintained at stirring speeds ranging from

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250rpm up to 1500rmp. The influence of reaction temperature, time, stirring speed, type of catalyst and solvent on the yield and quality of biodiesel was studied. The molar ratio of base oil and base alcohol is (1:3). Different steps following transesterification have been performed to purified the biodiesel obtained. The reaction yield is calculated according to the following formula:

$$R\ (\%) = \frac{m_B}{m_O} \times 100 \qquad (1)$$

With m_b : mass of biodiesel, m_o : mass of frying oil.

C. Gas Chromatography Analysis (GC)

Four samples were analyzed by gas chromatography: sample 1 and 2 produced by the reaction with methanol in a basic medium and an acidic medium respectively; sample 3 and 4 produced by the reaction with ethanol and isopropanol respectively in a basic medium. GC analysis was carried using Supelcowax capillary column of 60m x 0,25 mm ID., 0,25 µm film thickness, with Perkin Elmer Clarus 500, France, coupled with flame ionization *detection (*FID).

D. Physico-Chemical Characteristics of used Frying Oil

The physicochemical characteristics of the produced biodiesel were determined according to the standard methods: ASTM D445 for the viscosity, *NFT 60-201* for water content, *ASTM7467* for the higher calorific value, ASTD97 for the pour point, ASTM D2500 for the cloud point, the D2386 for freezing point, ASTM D1298 for the density and ASTM D664 for total acid number [6], [7]; and were compared to those obtained for commercial diesel.

III. Results and Discussion

A. Effect of temperature and reaction time on the yield of biodiesel

These experiments were carried out by varying the reaction times from 30 to 150 minutes, and the temperatures from 30°C to 70°C. Figure 1 shows the reaction yield values according to the time and temperature.

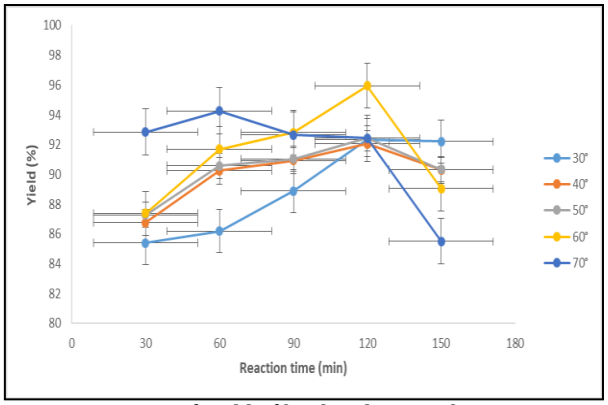

Fig. 1 Variation of yield of biodiesel versus the temperature and reaction time

Figure 1 shows that the temperature of 60°C for a duration of two hours gives the best synthesis yield, which is consistent with the work of Patel et al. [8].

B. Influence of stirring speed

A series of experiments was carried out at a temperature of 60°C for two hours by increasing the speed from 250 rpm to 1500 rpm. The Figure 2 shows the change in yield with increasing stirring speed.

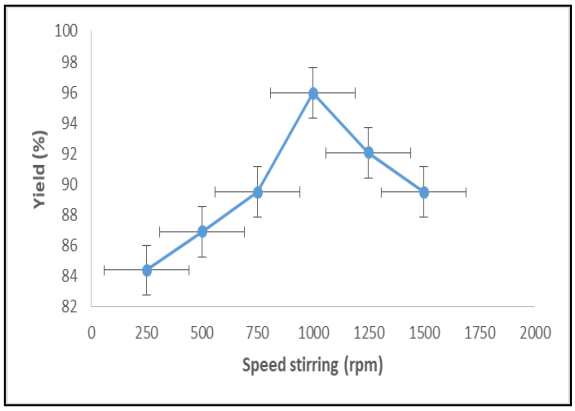

Fig.2 Effect of stirring speed on yield

Figure 2 shows the presence of the ascending phase with a peak at 1000 rpm reaching of 95,96% of yield and a second phase decreasing to 1500 rpm.

C. Influence of the free fatty acid content (FFA)

Two experiments were carried out using frying oil with an FFA rate of 0.83% and new oil with an FFA rate of 4.63%. In Table 1, the obtained yields are given:

TABLE I
EFFECT OF FREE FATTY ACIDS ON YIELD

Type of oil	UFO (used frying oil)	OO (old oil)
Yield (%)	95,96	84,75

The rich oil in FFA gave a lower yield compared to that which is has a lower percentage of FFA. That means that free fatty acids negatively influence the yield of the transesterification reaction.

D. Effect of the type of catalyst

Two experiments were carried out, one with a basic catalyst (KOH) and other with an acid catalyst (H_2SO_4) under optimal conditions. The yields obtained are 95,96% and 10% for the basic and acid catalyst respectively.

E. Influence of the type of Alcohol

In this work, the transesterification reaction was carried out by substituting methanol with ethanol and isopropanol. Several tests are carried out by changing the molar ratio as well as increasing the temperature. The poor separation of the two phases is thanks to the miscibility of these alcohols with the oils. The effect of the type of alcohol will be confirmed by gas chromatography analysis.

F. Gas Chromatography Analysis

The GC-FID chromatogram of sample 1 in Figure 3 reveals the presence of several peaks. These peaks were identified as fatty acid methyl esters.

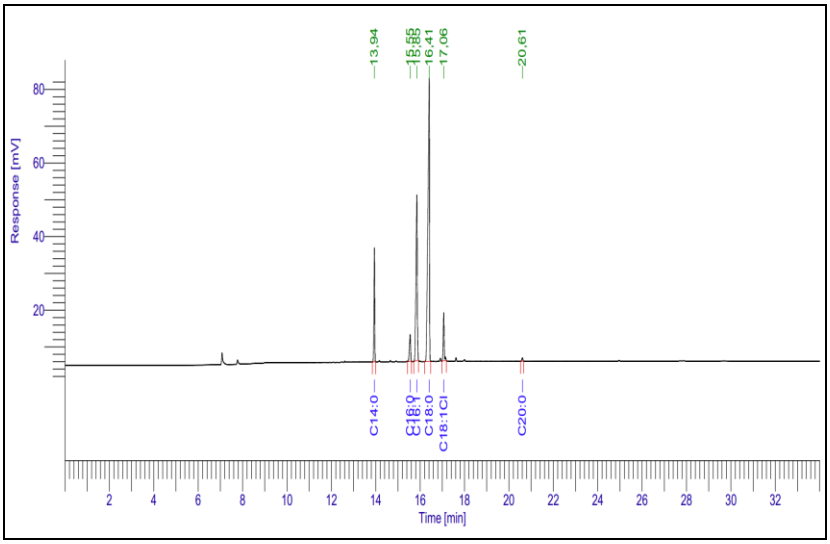

Fig.3 Chromatogram of biodiesel produced by methanol in basic medium

The data of GC for sample1 shows that biodiesel is mainly composed of methyl octadecanoate (C18:0), methyl hexadecanoate (C16:1) with 53,35% and 25,81% respectively and a small quantity of methyl tetradecanoate and methyl tetradecanoate; and the traces of methyl tetradecanoate and methyl eicosanoate. The total surface area of the biodiesel obtained is 732906,29 µV*sec.

The data of sample 2 reveal that the produced biodiesel from transesterification by methanol in an acidic medium has a similar composition to that of biodiesel produced by methanol in basic medium except that it is mainly composed of methyl hexadecenoate, methyl tetradecanoate and methyl octadecanoate [9-11].

In Figure 4, the chromatogram of sample 3 resulting from the transesterification reaction with ethanol in a basic medium is given.

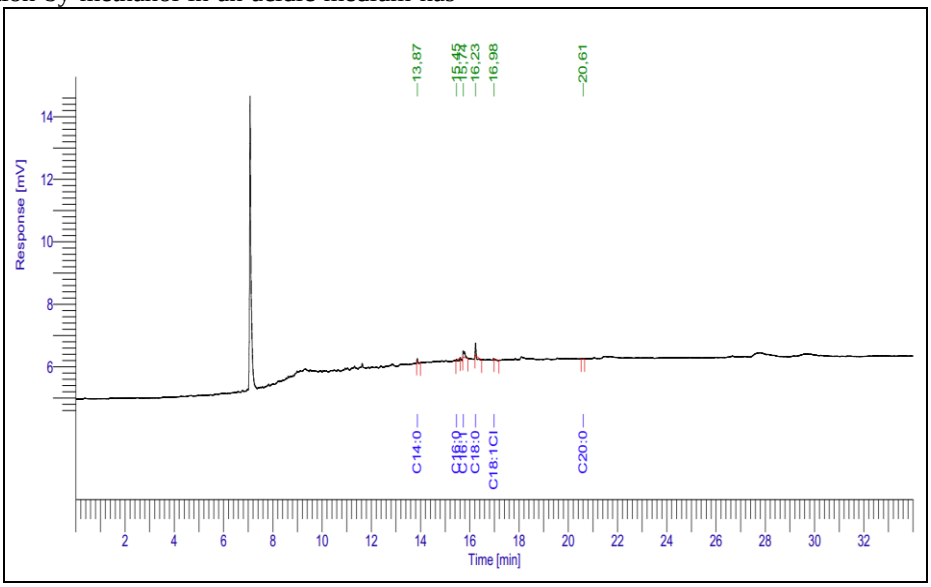

Fig.4 chromatogram of biodiesel produced by trans-esterification with ethanol in basic medium

The chromatogram in Figure 4 of sample 3 displayed a conformal distribution associated with biodiesel but in very small quantities with the presence of the solvent peak, which means that the trans-esterification reaction is not complete.

The surface area of biodiesel obtained from this reaction is 2246,31 µV*sec.

The data of sample 4 shows that the biodiesel resulting from transesterification by isopropanol has the same composition as that obtained by methanol but with a low

biodiesel, which represents 24 times less than that of the biodiesel obtained by methanol.

G.Physico-chemical characteristics of biodiesel

The physicochemical characteristics of produced biodiesel and commercial diesel, namely: water content, total acid number, viscosity, density, HCV, pour point, freezing point and cloud point are summarized in Table 2. The results are compared to the European standard EN 14214 and the ASTM D6751 standard.

TABLE II
PHYSICO-CHEMICAL CHARACTERISTICS OF THE PRODUCED BIODIESEL AND COMMERCIAL DIESEL.

Samples / **Parameter**	**Biodiesel**	**Commercial Diesel**	**EN14214**		**ASTM D6751**	
			min	***max***	***min***	***max***
Water content (ppm)	324,7	43,0	-	500	-	-
TAN (mg KOH/g)	0,11	0,02	-	0,5	-	0,8
Viscosity (mm^2/s)	5,32	2,69	3,5	5	1,9	6
Density at 15°C	0,886	0,8220	0,86	0,9	0,81	0,86
HCV	39,737	45,845	-	-	-	-
Pour point	-6	-18	-	-	-15	10
Freezing point	-9	-21	-	-	-18	7
Cloud point	-2	-4	-	-	-	-

The values obtained in Table 1 indicate that the value of water content for biodiesel, is compliant with EN14214 international standard, as of commercial diesel which has a content of 43ppm.

Table 1 demonstrates that the acid numbers of produced biodiesel and commercial diesel are 0,11 mgKOH/g and 0,02 mgKOH/g respectively and comply with ASTM D6751 and EN 14214 standards. This confirms that the transesterification reaction refines the oils of these free fatty acids.

In our case and with regard to the viscosity results, we can clearly observe that the produced biodiesel and commercial diesel have viscosities of 5,32 and 2,69 mm^2/s respectively. That of produced biodiesel is well above the values specified by European standard EN14214, unlike that of commercial diesel. However, the viscosity values are within the range required by ASTM D6751. According these values, the produced biodiesel can be used directly as biofuel.

The produced biodiesel and commercial diesel display density values of 0,886 and 0,822 respectively, which complies with the values required by the EN14214 standard, except that that of biodiesel is slightly higher than the requirements of the ASTM D6751 standard.

The HCVs given in Table 1 show that the produced biodiesel as well as commercial diesel yielded acceptable values by both standards.

The pour point obtained by biodiesel complies with the ASTM D6751 standard, unlike commercial diesel whose value is lower than that required by the standards.

We note that the freezing point of produced biodiesel complies with standards of ASTM D6751. However, commercial diesel produced a freezing point that did not meet the requirements of the standard.

By comparing the cloud point value obtained for biodiesel which is -2°C to that obtained for commercial diesel, which is -4°C, we note that that of biodiesel is close to that of commercial diesel.

IV. Conclusion

The results of this study revealed that the best yield was obtained with an optimal temperature of 60°C for a period of two hours with stirring at 1000rpm using a basic catalyst. Furthermore, the experiments carried out demonstrate that methanol is the best solvent for the transesterification reaction of used vegetable oil. This study showed that the esterification of frying oil presents physico-chemical characteristics comparable to those of petrodiesel or commercial diesel, according to international standards EN14214 and ASTM D6751. We can suggest that synthesized biodiesel is a fuel very close to diesel, both in terms of characteristics and the energy released and it can be used as an alternative of petrodiesel. It would be interesting to apply the synthesized biodiesel in diesel engines and resume the transesterification reaction without the use of a catalyst.

Acknowledgment

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