Optimization of the frying oil waste transesterification reaction time to biodiesel

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Abstract

The present work deals with the transesterification of a vegetable oil waste collected from the university campus Ain El Bey of Constantine3 University, restaurant kitchens. The main objective was to recycle this oil and convert it into biodiesel. Since the transesterification reaction is reversible, its yield was improved by using an excess of alcohol, such as Methanol, and Potassium Hydroxide as a basic catalyst. Also, the reaction time is a very important factor because for a short time the oil conversion will not be total whereas for a long time the energy consumption increases since the reaction requires heating, beside the risk that the reverse reaction will take place, reducing significantly the production yield.

The results show that the obtained oil was a very interesting source for the production of biodiesel, as it has been used only once in frying, the reaction time was reduced and the characteristics of the biodiesel produced were in the standards.

Keywords: *biodiesel, transesterification, valorization of biomass, waste oil.*

I. Introduction

Every year, a large amount of waste oils and fats that are unsuitable for human consumption or that cannot be processed further are produced around the world. One potential way to use this raw material available at low cost is its conversion to biodiesel [1]. Biodiesel is a biofuel produced by chemical processes from vegetable oils or animal fats and an alcohol that can be used in diesel engines, alone or mixed with diesel fuel [2].

It is produced by converting triglyceride oils with an alcohol into esters, using different methods, a transesterification reaction catalyzed by acid, base, ion exchange resins, and lipases or in supercritical medium [3]. There are several parameters that affect the biodiesel yield through the transesterification of vegetable oils, namely, the molar ratio of alcohol to oil, the catalyst concentration, the temperature [4], the reaction time and the speed of agitation.

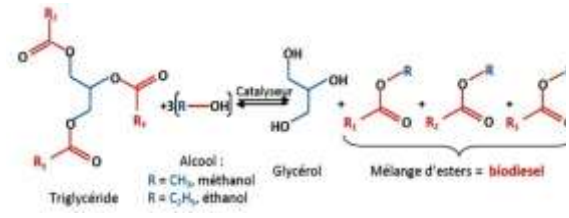
Several studies were interested at the time of the reaction: Ehren C et al [5] found that 5min was sufficient for the transesterification of cottonseed oil. Another work was carried out by MA Rahman et al [6] on the optimization of biodiesel prepared from a transesterification of microalgae for a maximum yield of biodiesel (86.1%) and optimal conditions found a time of 20 min. Maryam Ijaz et al [7] optimized a 45min time for the production of biodiesel from castor oil. Ogunsuyi H.O et al [8] worked on the production of biodiesel using African pear seed oil for optimal conditions and a time of 120 min.

The literature review shows that the reaction time depends on the process and the oil used. For our work we have chosen to study the effect of this reaction time on the transformation of our recovery oil and its effect on some key parameters of the quality of biodiesel produced, namely: density, the acidity index, the yield and especially the conversion rate.

II. Materials et methods

In this work, basic catalyzed transesterification was used with the optimal operating conditions recommended by the literature: the molar ratio

methanol / oil (6: 1), the mass concentration in catalyst (1% KOH), and the temperature of reaction T (55°C). The used device was composed of a water bath in which a reaction mixture of waste oil was introduced with the alcohol in the presence of the catalyst. Fixed agitation at 350 rpm was applied during different reaction times (5min, 10min, 15min, 20min, 45min and 120min). After the transesterification of the waste oils and the decantation of the reaction mixture, the heavy phase, which was the glycerin produced by the reaction below, was removed and the biodiesel obtained was then washed with distilled water in order to remove the excess of the reaction mixture, Methanol and catalyst (FIG. 1). At the end, sodium sulfate was added for drying. The overall reaction is shown in the following figure:



(A) (B) (C)

Figure 1. The biodiesel production procedure: (A) the reaction, (B) decantation, (C) biodiesel washing

After recovery of the biodiesel produced, several tests and measurements were carried out in order to characterize the biodiesel (according to the available products and material):

II.1. Acidity number (AN)

This is the number of milligrams of KOH required to neutralize the free fatty acids (FFA) present in 1g of oil [9]. The biodiesel was dissolved in Methanol and a titration was carried out with a KOH solution of known concentration and phenolphthalein was used as an indicator. The acid number is measured as follows:

$$AN = \frac{(56.1 \times C_{KOH} \times V_{KOH})}{m_{échantillon}} \quad (1)$$

C_{KOH}: molar concentration of KOH(mol/ml), V_{KOH} : volume of KOH in ml, 56 molecular weight of KOH (g/mol) sample mass (g).

II.2. Conversion rate

As the transesterification reaction is a reversible reaction, the conversion rate makes it possible to check whether the reaction carried out with an excess of methanol is complete, that is to say if all the oil has been transformed into biodiesel. 3 ml of each sample is dissolved in 27 ml of methanol and stirred for 10 seconds [5]. If the reaction is not complete, the unreacted oil decants at the bottom of the beaker. The conversion rate is then calculated according to the relation:

$$\text{Conversion rate} = \frac{V_C}{V_T} \times 100 \quad (2)$$

With V_C : volume converted to biodiesel (ml), V_T : total volume of the sample (ml).

(A) (B)

Figure 2. Conversion test to biodiesel : (A) Total conversion to biodiesel, (B) : Partial conversion

II.3. The yield

Biodiesel yield is defined as the ratio of the mass of biodiesel produced to the mass of oil used: [4]

$$n = \frac{m_{biodiesel}}{m_{huile}} \times 100 \quad (3)$$

II.4. Density

The density of a substance is equal to the density of the substance divided by the density of the reference body at the same temperature [10]. A 10 ml pycnometer was weighed empty (m_a) then, filled with water and weighed (m_b), after filling the pycnometer with biodiesel produced we recorded the weight (mc) [11]. The measurements were carried out at the same temperature of 20 ° C. and the density is given by the formula:

$$\rho_{20}^{20} = \frac{(m_c - m_a)}{(m_b - m_a)} \quad (4)$$

II.5. The pH

It is a measure of the acidity or basicity of a solution. We measured the pH of biodiesel produced using a pH meter [11].

II.6. Viscosity

Viscosity is another important property of biodiesel since it influences the operation of the injection system, it is defined as the resistance to flow and it strongly depends on the temperature [12] [13]. A glass pasteur pipette (with 2 lines) has been filled with a very precise volume of biodiesel and we measured with a chronometer the time required for the liquid to travel the distance between the two lines, the viscosity is then given by the formula:

$$\text{Viscosity} = \frac{V}{d \times t} \quad (5)$$

V the biodiesel volume (mm^3), d distance between the two lines (mm), t the time required by the biodiesel volume to flow between lines (s).

II.7. Saponification number

A known amount of biodiesel is mixed with an excessive amount of alcoholic KOH. After saponification, the remaining KOH is estimated by back titrating against an acid standard (blank test).

$$\text{Saponification number} = \frac{56.11 * (V' - V) * N}{m} \quad (6)$$

V' the volume in ml of acid 0.5N required for blank test, V the volume in ml of acid 0.5N required for the sample and m the weight in g of the used sample [14].

II.8. Ester number

The ester number value of the biodiesel samples was calculated as the difference between the saponification number and the acid number [4], therefore:

$$\text{Ester number} = \text{saponification number} - \text{acidity number} \quad (7)$$

II.9. Refractive index

The refractive index of oils varies according to their insaturation. The refraction measured by the prism depends on the change in the speed of propagation of the light. This change will be proportional to the saturation of the fatty acids [15]. The réfractive index was measured using a refractometer.

III. Results and discussion

Before carrying out the experiments, we first measured the acidity index of the used oil recovered from the university restaurant. This measure gives an idea of the amount of catalyst to be used.

III.1. Acidity number of the used oil

The oil studied (Safia, 100% soybean oil) was used only once in frying potatoes. In order to compare, the acid number of the same pure oil is also measured. The measurements were made three times; here we give the average value. The results are shown in Table 1.

Table1. Acidity number and KOH quantity required to neutralize FFA.

Oil	V_{KOH} (ml)	AN	V_{KOH} supp (ml)
Safia	0.4333	2.43143	0.1215
Used (1fois)	0.5667	3.1795	0.1683

The acidity number found is in accordance with Codex Alimentarius standards for vegetable oils 2.2-7.26 mg KOH / g oil [16]. The acid value of the waste oil is close to that of the pure oil since it is only used once. The volume of KOH used to catalyze the reaction will be reduced to that required to neutralize the FFAs present in the oil to be used.

3.2. The reaction yield and conversion rate

In this work, we studied the influence of various transesterification reaction time (5min, 10min, 15min, 20min, 45min and 120min) at a temperature

of 55 ° C, with a mass ratio of Methanol / Oil of 6/1 and 1% by weight of KOH increased by the amount needed to neutralize FFA.

The results obtained are given in table 2. From these results and as shown in table 2 and figure 3, the yield increases with time and it is less than 90% for a reaction time less than 15 min. For the conversion rate, the obtained biodiesel is oil-free and the reaction was total from a reaction time of 15min.

Table2. Reaction yield and conversion variation with reaction time.

Time (minutes)	Yield (%)	Conversion rate (%)
5 min	76.4	80
10 min	82.6	83.333
15 min	92.2	100
20 min	91.6	100
45 min	93.4	100
120 min	91.8	100

Figure 3 shows the difference between the conversion rate and the yield, hence the interest of their combination to calculate an effective yield.

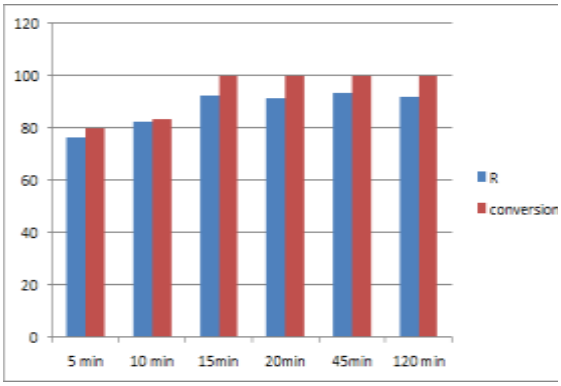


Figure 3. Reaction yield and conversion variation

Figure 4 shows the plot of the evolution of the actual biodiesel yield obtained by multiplying the yield by the conversion rate, which is more explicit. For example, a yield of 82.6% is obtained after 10 min, but the quantity obtained in the product of the reaction is not 100% biodiesel, hence an effective yield of 68.8%, calculated taking into account the conversion rate of 83.33% corresponding to this reaction time.

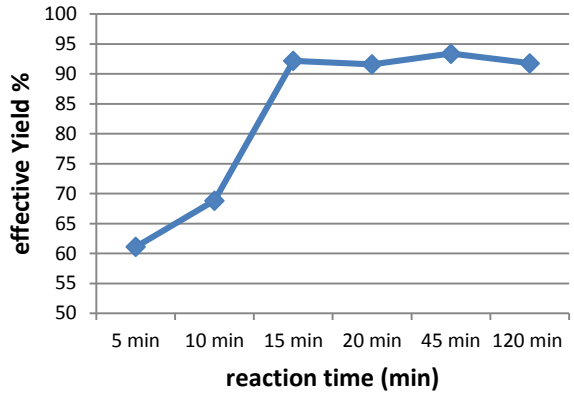


Figure 4: Effective yield versus reaction time.

From this result, it is showed that the optimal time for a biodiesel production with a real yield greater than 90% and ensuring a total conversion of the oil into biodiesel is 15 min.

III.4. Physicochemical properties of the obtained biodiesel

The physicochemical properties of biodiesel from used cooking oil, compared to those of ASTMD 6751 and EN14214 [17] [3] [18], are shown in table 3.

Table3. Physicochemical properties of the obtained biodiesel

time / property	5 min	10min	15min	20min	45min	120min	ASTM D6751	EN 14214	Used oil (once)
density	0.88775	0.88775	0.88775	0.88775	0.87755	0.87755	0.87-0.9	0.86-0.9	0.894
IA	0.89776	0.78554	0.72943	0.61721	0.61721	0.5611	< 0.8	< 0.5	3.1795
pH	10.631	10.36	8.1	8.107	8.975	8.25	7-9	9	7.12
I BRIX	1.45703	1.45560	1.45679	1.45703	1.45655	1.45655			1.47385
IS	37.40	44.88	44.88	52.369	29.925	26.932			104.73
IE	36.502	44.09446	44.150	51.75149	29.30779	26.3709		96.5min	101.44
Viscosity (mm^2/s)	5.71	6	5.23	6	6	5.42	1.9-6	3.5-5	60.05

The main characteristics (viscosity, acidity index, density and refractive index) are in good agreement with standards ASTMD6751 and EN14214, as regards the pH; the value recorded for biodiesel, it is a little further to the reference for the time 5 min and 10 min; The values obtained for the saponification index are much lower compared to those reported in the literature with a saponification index of 165.43 mg KOH/g for cottonseed oil [4] and 192 (192 mg KOH / g) in [18].

IV. Conclusion

Biodiesel is one of the most important sources of renewable energy. It is non-toxic, biodegradable, its calorific value is important and its use reduces the emission of greenhouse gases.

In this work, a valuation study of a used vegetable oil was carried out whose objective was the optimization of the transesterification reaction time. The analysis of the optimization results showed that a time of 15 min was necessary to reach an effective efficiency of the order of 92.2%. The characteristics of the obtained biodiesel were within the required standards and the results showed that the cooking oil recovered from university restaurant kitchens was a very interesting source of biomass to be enhanced by its quality due to its use in frying only once. As a result, a more detailed study to optimize the transesterification operating conditions as well as to consider a techno-economical assessment of this process.

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