

Comparative study of frying oil pre-treatments for biodiesel production using green chemistry metrics

I.Miroud, R.Koliai, H. Kerras, N.Outili*

Laboratory of environmental engineering processes (LIPE), Process engineering faculty,
Constantine3 University, Algeria, email: nawel.outili@univ-constantine3.dz.

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Abstract

In this work we have been interested in the pretreatment of cooking oils to reduce their free fatty acids (FFA), which have a negative effect on biodiesel production due to their saponification reaction in the presence of the basic catalyst used to activate the transesterification reaction.

The application of adequate pretreatment of waste cooking oil recovered from university restaurants would consequently increase the yield of biodiesel production.

Two pretreatment methods were performed: acid esterification (neutralization) as a chemical method and adsorption using activated carbon as a physical one.

The results showed that the two methods gave the best results in terms of FFA conversion, but the adsorption pretreatment had the most greenness character with a green chemistry balance of 83.05% compared to 78.25% for esterification method.

Keywords: frying oil; biodiesel; free fatty acids; transesterification; pretreatment; green chemistry.

I. INTRODUCTION

The depletion of fossil resources has led scientists to seek other sources of energy to heat, generate electricity or travel. Biofuels, developed for over 40 years, are considered as an alternative to petroleum fuels. Biodiesel is a renewable energy, used as an alternative to fuel for diesel engines.

One of the most widely used methods of obtaining biodiesel is the transesterification of vegetable oils using an alcohol and an acid or basic catalyst [1]. In order to make the process more profitable and more respectful of the environment, the use of waste oils is increasingly favored for so-called second generation biodiesel [2]. However, repeated use of oils, in frying for example, increases the amount of free fatty acids (FFA), which would decrease the production yield of biodiesel [3]. Thereby, several pretreatment methods had been investigated by previous work to reduce the FFA of the waste oil before its use in a transesterification reaction [4].

Alpetkin and Canakci [5] used sulfuric, hydrochloric and sulfamic acids as catalysts for a transesterification pretreatment of a high FFA content of a chicken fat. The results showed that Sulfuric acid was the best acid catalyst with a reduction of the chicken fat FFA from 15% to below 1%, which gave high ester yield after basic transesterification with KOH.

A waste frying oil collected from chicken frying restaurants was pretreated by Asri et al [6] using several types of activated adsorbents. Activated carbon, bleaching earth and coconut coir were used without chemical or physical treatment. Coconut coir adsorbent had given the best result.

Adsorption is also used by Diaz and Brito [7] as a pretreatment method for reducing FFA from oils prior to

transesterification reaction for biodiesel production using a strong anion-exchange as adsorbent. Adsorption was compared to an esterification pretreatment and was qualified as an easier and suitable method.

Therefore, two from the most used pretreatment methods were tested in this work: activated carbon adsorption and acid esterification.

On the other hand, nowadays, chemical processes and production have to be applied in the way to respect the environment and green chemistry principles must be taken into account in the conception of processes additionally to yield and productivity [8].

The twelve green chemistry principles were developed by Anastats and Wagner [9] and several green chemistry metrics were used by researchers to quantify the "greenness" of any synthesis or process [10].

First, the vegetable oils used in frying from zero to four times, were characterized measuring their viscosity, density, pH, acid value, saponification value and refractive index [11]. These properties were also measured after the application of a considered pretreatment method.

In this study, in addition to the properties and the conversion yield, green chemistry principles were considered.

Indeed, green chemistry metrics [12] were used to select the most "greenness" pretreatment to be used to reduce waste oil FFA. Nine green chemistry parameters were used to evaluate and compare the green chemistry balance according to the used pretreatment method, namely: atom economy (Eat), carbone efficiency (Ec), reaction mass efficiency (RME), environment factor (E), stoichiometry factor (Fst), Danger, toxicity, CMR (cancerigen Mutagen Reprotoxic) and the used renewable mass fraction

compared to the total mass of the method .

II. METHODOLOGY

First, frying oils (soybean oil) were collected from university restaurants, filtered and characterized by measuring their pH, humidity, density using a pycnometer, viscosity using the ball method, acidity and saponification numbers using NaOH titration method [13].

Then, pretreatment methods were applied to reduce FFA: adsorption using activated carbon and neutralization using acid esterification.

For the adsorption pretreatment method (Figure1), 10 wt% of activated carbon were mixed with filtered oil and stirred at 300 rpm for 30 min at a temperature of 55 ° C. After this time, the frying oil was filtered twice on filter paper.



Figure 1: Pretreatment using activated carbon adsorption

Secondly, a pretreatment is carried out by an esterification reaction with methanol and catalyzed by 1% sulfuric acid at a temperature of 55 ° C and for 1 hour of reaction. The oily phase of esters is recovered after decantation (Figure2).



Figure 2 : Esterification pretreatment resulting phases

The FFA conversion, energy consumption and physicochemical properties cited above were measured after each pretreatment method.

Depending on the used method (reaction or separation method) green chemistry parameters were calculated and the green chemistry balance estimated for each of them.

The used metrics in this work were: mass efficiency of the pretreatment, environmental factor, fraction of renewable mass, danger, toxicity, atomic and carbon efficiency and stoichiometric factor, for more details on these parameters,

the reader can refer to [12-14].

III. RESULTS AND DISCUSSION

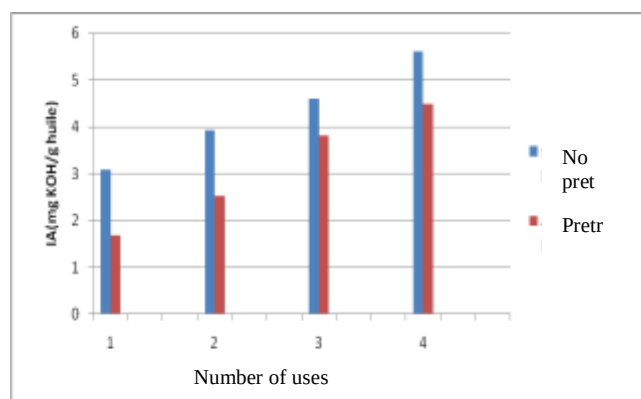
In this section, the results of the measured characteristics according to the number of uses are presented in table1.

Table 1. Vegetable oil characteristics according to the number of its use.

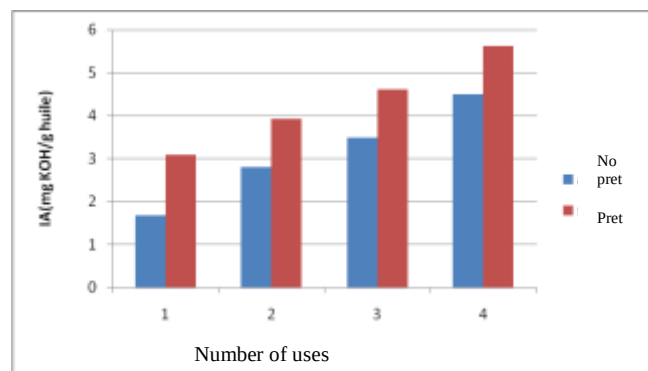
Oil	No use	1 use	2 uses	3 uses	4 uses
AV (mg KOH/g oil)	1.01	3.08	3.95	4.6	5.6
Is (mg KOH/g oil)	192.88	208.66	210.41	199.89	182.35
Ir	1.4746	1.4743	1.4741	1.4741	1.4738
pH	7	6	5	5	4
d	0.906	0.907	0.908	0.908	0.909
W (g water/g oil)	0.002	0.006	0.022	0.022	0.028

The results show that the acid value (AV) is the most affected factor by the number of use. Indeed, using the vegetable oil in frying for several times releases the free fatty acids in the oil, this decreases the pH value. Also, the humidity of the oil (W) increases according to the number of using it in frying.

After pretreatments application, the treated oil was also characterized and the results concerning the AV are presented in Figure 3 below in comparison to the no treated one and for each pretreatment method.



a) Activated carbon pretreatment.



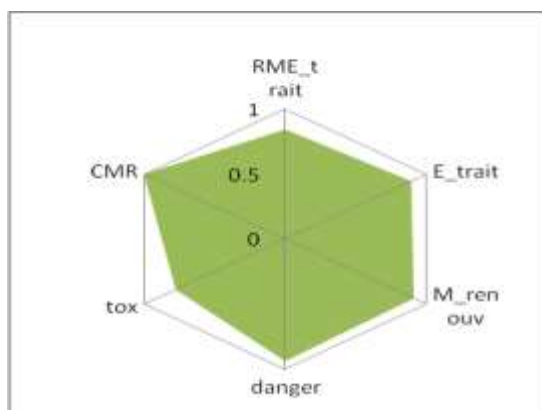
b) Esterification pretreatment

Figure 3. Effect of the two pretreatment methods on acid value according to the number of use of the oil in frying.

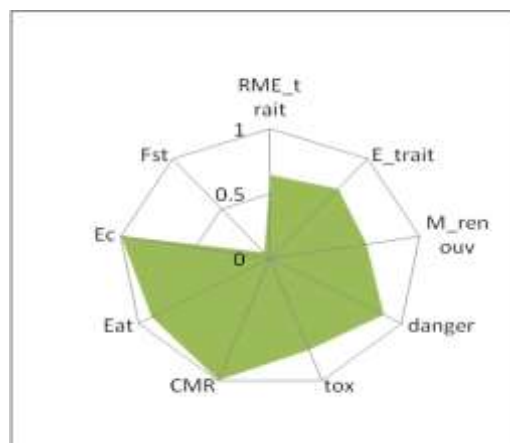
The results show a positive effect of each pretreatment method on acid value reduction and also the decrease of FFA according to the number of use of the oil in frying that show the slight reduction of the pretreatment efficiency. The comparison between the two methods clearly shows that the physical pretreatment using adsorption was comparable in efficiency to the chemical one using esterification. For the oil used, only one time, the two methods reduced the FFA to almost 50% of its value while it was reduced only 20% for the oil used four times in frying.

Since the FFA reduction efficiency of the two methods is comparable, the green chemistry parameters are used in order to be able to choose the greenest and most environmentally friendly method. So, in the second part of the work, the green chemistry parameters were estimated for each method according to the nature of the method. Indeed, adsorption is a physical separation method that used the adsorbent and the esterification is a reaction that used reactants and a catalyst.

Figure 4 shows the green chemistry balance which is represented by the green surface of the radar representing the average of the different parameters used for each case. The results show that adsorption had a good green chemistry balance comparing to esterification pretreatment with 83.05% and 78.25% respectively.



a) Activated carbon



b) Esterification

Figure 4. Comparison of green chemistry balance of the three pretreatments.

As shown in the figure 4, the very low value of the stoichiometric parameter Fst, which accounts for the use of a reactant in excess (in this case, the methanol) has a very negative effect on the green character of the oil pretreatment method by esterification, because this will generate a large amount of waste and which is more toxic. Finally, all the calculated parameters and green chemistry balance were in favor of a pretreatment of frying oils using adsorption instead of esterification.

IV. CONCLUSION

This work presented the results of a comparison study of two pretreatment methods to reduce FFA of used frying oils for an efficient use as a feedstock to produce biodiesel via transesterification reaction. Adsorption on activated carbon was used as a physical pretreatment method and acid esterification as a chemical one.

In addition to the efficiency of reducing FFA, green chemistry parameters were used in order to choose the most environmentally friendly method.

The results showed that the two methods gave comparable efficiency of FFA reduction, but the adsorption pretreatment had the most greenness character with a green chemistry balance of 83.05% compared to 78.25% for esterification method. The results will have a positive effect on the production of biodiesel, which is a next step of this present work.

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