Biodiesel production from waste frying oil and determination of fuel properties

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Abstract - The depletion of crude oil resources and the awareness of the negative environmental impact of greenhouse emissions have led to find alternative energy sources to traditional resources. Thereby, recently, we witness to the development of several sectors of energy production. The new generation biofuels which add a value to the non-food parts of plant products such as waste vegetable oil which contribute to an interesting alternative energy for a sustainable development. The objective of our work is to produce biodiesel from a renewable and sustainable energy resource which is waste sunflower frying oil through transesterification process using alkaline catalyst and ethanol, to optimize some parameters with the aim of obtaining the best reaction yield and to study some biodiesel’s properties such as kinematic viscosity, density, cloud and flash points, the biodiesel was analyzed by Infra-Red spectroscopy and Gas Chromatography-Mass Spectrometry. The results of the analysis confirm that the synthesized biodiesel is a mixture of fatty acid ethyl esters, a comparative study of biodiesel has been conducted versus standard biodiesel ASTM D6751, and the results obtained show good properties when compared to those of biodiesel’s standard.

Keywords: Biodiesel - Fatty Acids Ethyl Esters - FT-IR - Fuel properties - GC-MS – Transesterification - Waste Sunflower frying oil.

1. INTRODUCTION

The diminishing resources of fossil fuels due to unbridled consumption by humans and taking into account the recent impact of the environment of the massive use of fossil fuels [1, 2], led to search alternative sources of energy that can preserve ecosystems and public health. Among the alternative possible sources, biodiesel (fatty acid alkyl esters) is a good candidate to replace diesel fuels in diesel engines. Biodiesel is a renewable fuel that can be produced from a range of organic feedstock including fresh or waste vegetable oils, animal fats, and oilseed plants. It is also non-toxic, biodegradable and so more compatible with the environment [3-5].

At present, the major obstacle to the commercialization of biodiesel is its high cost due to the high price of virgin vegetable oils [6]. On the other hand, the agri food industries and the restaurants generate large quantities of waste frying oil, which are poured in an anarchic way and may lead to environmental and health problems if they are not properly managed [7, 8]. In this sense, methods that permit to minimize the costs of the raw material are of special interest and can be reached by the use of waste frying oil to produce biodiesel [9, 10]. The use of waste frying oils seems to be the way that allows reducing the production cost of biodiesel, recycling the waste frying oils and could help to solve the problem of waste disposal.

Transesterification reaction takes place between triglycerides and an alcohol in the presence of a catalyst as shown in figure 1, to produce a mixture of fatty acid alkyl esters and a by-product, glycerol [11].

Fig. 1: Overall reaction of the transesterification of vegetable oils

Several parameters affect the transesterification reaction, such as the type and the amount of the catalyst, the alcohol to oil ratio, the reaction time, the reaction temperature and the amount of the free fatty acids [12, 13].

The transesterification reaction may be catalysed by an alkali, acid catalysed or enzyme catalysed, base catalysis leads to high yields, and it can occur at short reaction times, for these reasons, sodium hydroxide is widely used [14-17].

In general, a large excess of alcohol is used to shift the equilibrium to the right [18]. The selection of the alcohol used is based on the cost, the availability and the performance consideration. Thus, short-chain alcohols are generally used for the transesterification reaction such as methanol and ethanol [19]. Ethanol is used due to the several advantages that it presents: the most important one is the fact that it can be produced from

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agricultural resources, also the use of ethanol in the production of biodiesel improves the cold properties (such as cloud point, cold filter plugging point, or pour point) [20].

In this work, the synthesis of fatty acid ethyl esters from waste sunflower frying oil was studied using basic catalyst (sodium hydroxide). The optimization of biodiesel production was investigated with different reaction temperatures and reaction times, the obtained biodiesel was analysed using Fourier Transform Infra-Red and gas chromatography mass spectroscopy and the fuel properties of the biodiesel have been determined and discussed.

2. EXPERIMENTAL PART

In the first step, a solution of sodium ethoxide was prepared from a required amount of ethanol and sodium hydroxide. This solution was introduced into a dropping funnel and immediately added to the waste sunflower frying oil preheated to the desired temperature; vigorous stirring and a constant temperature were maintained throughout the duration of the experiment. When the reaction reached the preset reaction time, the reaction mixture was transferred into a separating funnel. The upper layer contains fatty acids ethyl esters, residual alcohol and catalyst, where as the lower layer contains a mixture of glycerol, excess of alcohol and catalyst. The bottom glycercal phase was removed and the fatty acids ethyl esters layer was then purified.

The study was carried out at two different temperatures using ethanol at various reaction times ranging from 30 to 240 min. The other factors such as molar ratio, type and amount of catalyst were fixed as common parameters in all experiments.

3. RESULTS AND DISCUSSION

3.1 Effect of reaction temperature

The reaction of transesterification can be carried out at different temperatures; it can occur at room temperature [21] or at a temperature close to the boiling point of the alcohol [22]. Figure 2 shows the effect of temperature on the yield of the reaction at different times of reaction.

![Fig. 2: Effect of reaction temperature on the yield of FAEE](image)

We note a slight reduction in the yield of the reaction when the reaction temperature increases from 25 °C to 50 °C, this is probably due to the saponification reaction which is accelerated at elevated temperatures [25].

3.2 Effect of reaction time

Transesterification reactions were carried out at various periods of time between 30 min and 240 min at the optimal reaction temperature (25 °C). Figure 3 shows the effect of this factor on the faee yield.

![Fig. 3: Effect of time reaction on the yield of FAEE](image)

Figure 3 reveals that fatty acid ethyl esters yield is low at the beginning of the reaction and increases to achieve the maximum yield at 45 min. Then the yield decreases slightly with increasing reaction time. This is in agreement with literature data which show that longer reaction time will lead to a reduction in the yield product due to the backward reaction of transesterification (hydrolysis), which tends to produce more fatty acids to form soap [21, 24].
3.3 IR analysis

Infra-Red Fourier transform analysis of the principal product was performed. Spectrum on figure 4 shows that the bands of C=O and -C-O (ester function) appear at 1737 cm$^{-1}$ and 1245 cm$^{-1}$; those results are in agreement with literature [25, 26].

![Fig. 4: FT-IR spectrum of FAEE](image)

3.4 GC-MS analysis

Analysis by mass spectroscopy reveals the presence of the molecular ion peaks of all compounds. For example, the peak at m/z 284 present in the mass spectra (Fig. 5) correspond to [C$_{18}$H$_{36}$O$_2$]$^+$. Fragment. The characteristic fragment of ethyl esters appears at m/z 239 ([M-45]$^+$) which represent the loss of ethoxy group.

The peak at m/z 88 is probably due to Mac Lafferty rearrangement. The homologous series of ions at m/z 269, 255, 241, 227, 213, 199, 185, ... of general formula [CH$_3$CH$_2$OCO(CH$_2$)$_n$]$^+$ reveals the presence of the linear hydrocarbon chain.

![Fig. 5: Mass spectrum of ethyl hexadecanoate](image)

3.5 Biodiesel properties

Fuel properties of the biodiesel produced under optimum conditions including density, kinematic viscosity, flash point and cloud point are studied and compared with the ASTM D6751 standard of biodiesel, this comparison is summarized in Table 1.

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>FAEE</th>
<th>ASTM D6751 biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 15°C</td>
<td>g/cm$^3$</td>
<td>0.889</td>
<td>0.870 – 0.900</td>
</tr>
<tr>
<td>Kinematic viscosity at 40°C</td>
<td>mm$^2$/s</td>
<td>4.79</td>
<td>1.9 – 6.0</td>
</tr>
<tr>
<td>Flash point</td>
<td>°C</td>
<td>&gt;190</td>
<td>&gt;130</td>
</tr>
<tr>
<td>Cloud point</td>
<td>°C</td>
<td>4</td>
<td>Not specified</td>
</tr>
</tbody>
</table>

The kinematic viscosity is an important property regarding the fuel injection in diesel engine, which was within the range of standards. Density is another important property characterizing fuels and affects the performance of diesel engines, because it affects the amount of fuel injected [27]. According to the standard of biodiesel the values are in the range.

Biodiesel standards specify that the flash point must be greater than 130 °C. The value of our biodiesel is high representing a benefit during storage and transport [28]. Biodiesel standards have not set precise values of cloud point due to climatic variations depending on the location of each country [20]. The value of the cloud point is slightly high compared to standards of biodiesel; this makes the produced biodiesel less suitable in cold weather.

4. CONCLUSION

This work shows that biodiesel can be produced successfully from waste sunflower frying oil using NaOH as a catalysis and ethanol; the experimental study reveals that one hour of reaction and a temperature of 25°C
represent the optimal reaction conditions and the results of the analysis (IR and GC-MS) confirm the structure of the produced biodiesel. Globally, the fuel properties of the produced biodiesel had a reasonable agreement with those of biodiesel standards ASTM D6751. The use of frying oils is an interesting alternative for the production of biodiesel because it is a cheaper raw material and also contributes to the valorization of a potentially polluting waste.

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REFERENCES


