ABSTRACT

In this paper we have chosen the methodology for optimisation of the most important variables (temperature conditions, reactants proportion and methods of purification), with the purpose of obtaining a high quality biodiesel that fulfils the European pre-legislation with the maximum process yield. Finally, sunflower methyl esters were characterised to test their properties as fuels in diesel engines, such as viscosity, ash point, cold filter plugging point and acid value. Results showed that biodiesel obtained under the optimum conditions is an excellent substitute for fossil fuels.

Keywords: alternative fuel, sunflower oil, biodiesel, transesterification.

AIMS AND BACKGROUND

The high energy demand in the industrialised world, as much in the domestic sector, as in transport and industry, its increase, and the derived problems of the widespread use of fossil fuels, make increasingly necessary the development of renewable energy sources of limitless duration and smaller environmental impact than the traditional ones.

Biodiesel obtained from energy crops produces favourable effects on the environment, such as a decrease in acid rain and in the greenhouse effect caused by combustion. Due to these factors and to its biodegradability, the production of biodiesel is considered an advantage to that of fossil fuels. In addition to this, it also shows a decrease in the emission of CO₂, SO₂ and unburned hydrocarbons during the combustion process. The supply of part of the demand with biodiesel would contribute to decreasing this dependency.

On the other point of view, energy crops have been considered as one of the best alternatives in the agricultural sector, whose production for food purposes has been limited, thus allowing the development of new industries such as agro-energy industry with employment creation and regional development. The production and yield forecast...
of energy crop as well as the possibilities of substituting diesel fuel by biodiesel, have
been studied establishing that it is possible to substitute approximately 5% of diesel fuel consumed in the region by biodiesel obtained from sunflower oil.\textsuperscript{13}

The economic aspect of biodiesel production is like a barrier for its development, due mainly to the lower price of fossil fuels. This work hoped to prove the feasibility of biodiesel production, from the point of view of the process technology and the use in diesel engines as well as the raw material availability, thus contributing to the development of this renewable energy source.\textsuperscript{3}

\textbf{EXPERIMENTAL}

Although vegetable oils may be used directly as fuels in diesel engines without refining, they present several problems mainly related to viscosity. This is the reason why different processes have been investigated in order to obtain a biodiesel with similar characteristics to those of fossil fuels.

The fatty acid composition of the sunflower oil as determined by gas chromatography analysis was: myristic acid – 0.1%; palmitic acid – 5.5%; palmitoleic acid – 0.2%; stearic acid – 5.0%; oleic acid – 48.0% and linoleic acid – 41.2%. This sunflower oil was produced in the region of South Bulgaria.

We have studied the following variables:

1. Catalyst amount. The experiments were carried out with 9% (v/v) of sodium-metoxide related to the quantity of oil that had to be transesterified.

2. Methanol amount. The quantity of methanol that we used was 15% (v/v) related to the quantity of oil that had to be transesterified.

3. Reaction temperature. The chosen levels were 55, 60 and 65°C.

4. Washing. We used washing with pure water.

The catalyst was dissolved into methanol by vigorous stirring in a small reactor. The sunflower oil was transferred into the biodiesel reactor and then, the catalyst/alcohol mixtures were pumped into the oil. The final mixtures were stirred vigorously for 1 h at 55, 60 and 65°C at ambient pressure.

The successful transesterification process produced two liquid phases: ester and crude glycerin. Crude glycerin, the heavier liquid, was collected at the bottom after several hours of precipitation. Phase separation can be observed within 10 min and can be completed within 2 h of precipitation. Complete precipitation can take as long as 18 h.

After precipitation was complete, water was added at a rate of 10% by volume of the methyl esters of oil and then stirred for 5 min, and the glycerin was allowed to settle again. Washing the esters is a two-step process, which is accomplished with extreme care.

A water wash solution at the rate of 30% by volume of oil was added to the ester and gently agitated. This process was carried out until the ester layer becomes clear.
After settling, the aqueous solution was drained, and water alone was added at 30% by volume of oil for the final washing.

In the end of the process water was removed from solution by vacuum distillation.

Afterwards, samples were analysed using chromatographic techniques to determine mono-, di-, and triglycerides, methanol and free glycerol contents. In addition, the acid value was measured as well as the total yield of the process.

RESULTS AND DISCUSSION

Statistical methods were used on the results obtained in laboratory experiments. In Table 1 the best combination of variables are presented. Table 2 shows results obtained in the laboratory on glycerides, methanol and free glycerol contents of the best sample, in which a yield superior to 95% was reached.

Table 1. Best combination of variables

<table>
<thead>
<tr>
<th>Variables</th>
<th>Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst quantity</td>
<td>9% (v/v) related to the quantity of oil</td>
</tr>
<tr>
<td>Methanol quantity</td>
<td>15% (v/v) related to the quantity of oil</td>
</tr>
<tr>
<td>Reaction temperature</td>
<td>65°C</td>
</tr>
<tr>
<td>Washing</td>
<td>yes</td>
</tr>
</tbody>
</table>

Table 2. Composition of the best sample

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Contents % (w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoglycerides</td>
<td>0.08</td>
</tr>
<tr>
<td>Diglycerides</td>
<td>0.05</td>
</tr>
<tr>
<td>Triglycerides</td>
<td>0.06</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.22</td>
</tr>
<tr>
<td>Free glycerol</td>
<td>0.03</td>
</tr>
</tbody>
</table>

The material balance for our best sample is: the yield of the methyl ester is 96.5%, glycerol content – 0.2%, Na soaps and other products – 2.3%.

The sample with best results was also analysed taking into consideration specifications for biodiesel as fuel in diesel engines. These results are shown in Table 3. Most of the parameters comply with the limits established by the European pre-legislation related to biodiesel quality and duty fulfils the characteristics that define a good quality fuel for engine purposes.
Table 3. Biodiesel characteristics as fuel

<table>
<thead>
<tr>
<th>Properties</th>
<th>Units</th>
<th>Value</th>
<th>Standards</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 15°C</td>
<td>kg/m³</td>
<td>884.4</td>
<td>EN ISO 3675</td>
</tr>
<tr>
<td>Kinematic viscosity at 40°C</td>
<td>mm²/s</td>
<td>4.21</td>
<td>EN ISO 3104+AC</td>
</tr>
<tr>
<td>Flash point</td>
<td>ºC</td>
<td>&gt;120</td>
<td>ISO 2719</td>
</tr>
<tr>
<td>Cold filter plugging point</td>
<td>ºC</td>
<td>-4</td>
<td>EN 116</td>
</tr>
<tr>
<td>Cetane index</td>
<td></td>
<td>46.5</td>
<td>EN ISO 4264</td>
</tr>
<tr>
<td>Acid value</td>
<td>mgKOH/g</td>
<td>0.4</td>
<td>ISO 6618</td>
</tr>
<tr>
<td>Higher caloric value</td>
<td>MJ/kg</td>
<td>40.1</td>
<td>ISO 8217</td>
</tr>
<tr>
<td>Water content</td>
<td>ppm</td>
<td>450</td>
<td>ISO 3733</td>
</tr>
<tr>
<td>Ash content</td>
<td>% (w/w)</td>
<td>0.006</td>
<td>ISO 6245</td>
</tr>
<tr>
<td>Sulphur content</td>
<td>% (w/w)</td>
<td>0.01</td>
<td>EN ISO 8754</td>
</tr>
<tr>
<td>Copper corrosion, 3 h at 50°C</td>
<td></td>
<td>1A</td>
<td>ISO 2160</td>
</tr>
<tr>
<td>Oxidation stability</td>
<td>g/cm³</td>
<td>19</td>
<td>EN ISO 12205</td>
</tr>
<tr>
<td>Iodine number</td>
<td></td>
<td>95</td>
<td>EN 14111</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>mg/kg</td>
<td>3</td>
<td>EN 14107</td>
</tr>
<tr>
<td>Na + K</td>
<td>mg/kg</td>
<td>2</td>
<td>EN 14108</td>
</tr>
</tbody>
</table>

A condition for the short and half-term success of biofuels is that they can be used with current engines without having to make any expensive modifications.

Emissions, duration, operation, and engine tests were carried out on a test bench with three types of fuels: 100% biodiesel, 100% diesel fuel, and blend of 10% biodiesel – 90% diesel.

Curves of power, consumption and emissions were traced considering the speed regime at full engine load, thus determining the variations that take place in each case (Figs 1–3).

During the performance of each curve, engine power, fuel specific consumption, and carbon monoxide were determined.

![Engine power at full load](image)

Fig. 1. Engine power at full load
The dependence of engine power (kW) for these three types of fuel from the different speed regime (rpm) is shown in Fig. 1. Fuel with a higher cetane index (100% diesel fuel) has a superior compression-ignition quality in diesel engines and thus better combustion characteristics. Hence, 100% biodiesel with significantly lower cetane index appeared to have the lowest engine power between the other two fuels.

Specific fuel consumption of 100% biodiesel is slightly higher that the diesel fuel as shown in Fig. 2. The lower mass based heating values of methyl ester required larger mass fuel flows to maintain constant energy input to the engine. Also at given injection pump settings, higher densities of methyl ester caused the increase in the observed mass flow.

The variation of CO emissions in relation to the diesel fuel is shown in Fig. 3. The CO emissions increase with the increase of the load. The higher the load, the richer fuel mixture is burned and thus more carbon is produced. The minimum CO emissions were determined with 100% biodiesel.
CONCLUSIONS

This research development has enabled us to confirm that sunflower oil may be used as raw material to obtain biodiesel, which can be used as fuel in diesel engines. The main conclusions are:

1. To obtain biodiesel, two stages in the sunflower oil transesterification process have been studied: the comprised reaction and purification. Transesterification controls the yield of the process, while purification is fundamental in order to fulfill the characteristics of methyl esters as fuel in diesel engines. In the reaction stage, the factors, which presented a greater influence, were methanol and catalyst quantity.

2. The best combination of factors is the following: 15% (v/v) of methanol related to the quantity of oil that had to be transesterified; 9% (v/v) of sodium-met oxide related to the quantity of starting oil; 65°C temperature and washing with pure water.

3. Biodiesel, whose characteristics as fuel in diesel engines are within the specifications of the current European standard, has been obtained, duly fulfilling the main demanded parameters. These parameters are: density, viscosity, and flash point, sulphur, which also present good values of calorific power and cetane index.

4. Methyl esters have a positive energy balance; that is, the total consumed energy in the production process is lower than the energy that they can provide as fuels.

5. The calorific value of biodiesel is 14% lower than that of diesel fuels, however, this is partially compensated by higher density, leaving the total loss of energy less than 8%.

6. CO emissions are very similar to or less than those of diesel fuel and biodiesel obtained by means of this process is of good quantity and is suitable for using in diesel engines.

REFERENCES


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