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Production and Characterization of Biodiesel from Waste and Vegetable Oils

M. N. Younis, M. S. Saeed, S. Khan, M. U. Furqan , R.U. Khan & M. Saleem
*The Institute of Chemical Engineering and Technology,
University of the Punjab, Pakistan*

Abstract

Biodiesel production was carried out by using vegetable oil (Mustard, Soybean, Canola, Waste vegetable oil). To characterize the biodiesel produced, different ASTM standard tests were carried out. Besides standard tests, FTIR (Fourier Transform Infra Red) spectrophotometry of biodiesel was also performed. Results reveal that characteristics of biodiesel depend on the feed stock. The best combination of properties is obtained from Canola oil based Biodiesel. Biodiesel produced from waste vegetable oil was also found very convenient to be used and properties were comparable to an ordinary diesel fuel (mineral diesel).

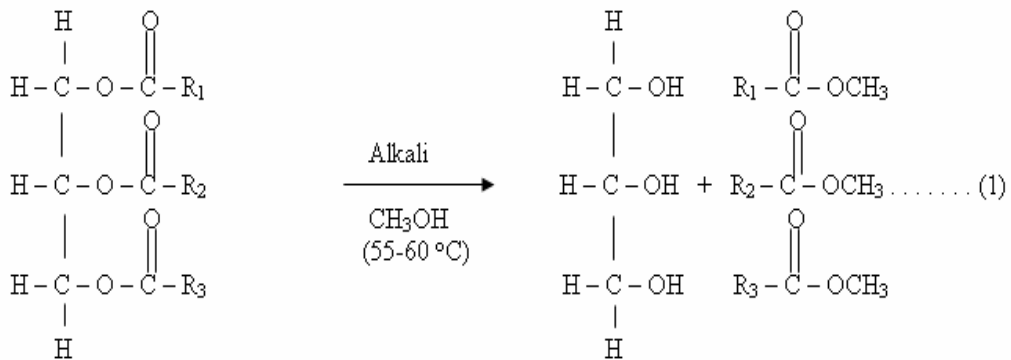
Key Word: *Transesterification, Biodiesel, Characterization, Waste Oil*

Introduction

Biodiesel falls in the category of the biofuels. Biofuels were introduced decades ago to overcome the environmental pollution caused by the use of ordinary fuels i.e. sulphur and heavy metals oxide. Ordinary fuels are fossil ones. Biodiesel is free of lead, contains almost no sulfur or aromatics (toxic compounds such as benzene, toluene and xylene), and substantially reduces emissions of unburned hydrocarbons, carbon monoxide and particulate matter (soot), which have been linked to respiratory disease, cancer and other adverse health conditions. It has been found that NO_x in exhaust is very high if biodiesel is used. However it can be controlled and reduced by adjusting the engine timing. Some types of catalyst exhaust tips are also developed to capture the NO_x in the exhaust system, while CO_x production rate is very low as compared to ordinary diesel fuel. Also there are no emissions of the sulfur compounds. Sulfur compounds cause acid rain which is the main cause of soil erosion.

Another reason for the research on biofuels is to meet the world's requirement of fuel. Fossil fuel reserves are decreasing due to increase in fuel demands. The basic idea of researches is to go for alternative which yields as good efficiency as fossil fuels and economical as well. Many kinds of biofuels are used these days, among them ethanol based fuel is used as an alternative of gasoline and biodiesel is used as an alternative of diesel fuels. Biodiesel is the cleaner fuel and it requires no engine modification. It can directly be used in diesel engines. It has also been reported that diesel engines run longer with biodiesel. 75% less pollution is caused by biodiesel compared to ordinary diesel (Canakc et

al.,2006). The most important is that biodiesel can be produced from any vegetable oil including waste vegetable oil (Zhang et al.,2003). Biodiesel can be blended with ordinary diesel with no additive required for making them miscible. Better lubrication is achieved by using biodiesel in the engine (Schumacher et al., 2001). As far as fuel economy is concerned, biodiesel's fuel economy is same as conventional diesel. Biodiesel is environmental friendly and is biodegradable. Chemical reaction for the manufacturing of biodiesel using vegetable oil is as follows:



This is a Transesterification reaction (Fukuda et al.,2001). Fatty acid reacts with methanol in the presence of alkali (Catalyst). Fatty acid methyl ester (FAME) and Glycerol are the products. Side reaction (i.e. saponification) can occur in the presence of moisture and excess amount of alkali. In saponification reaction the methyl group of FAME is replaced by metal ion of alkali.

Materials and Methods

Raw Materials

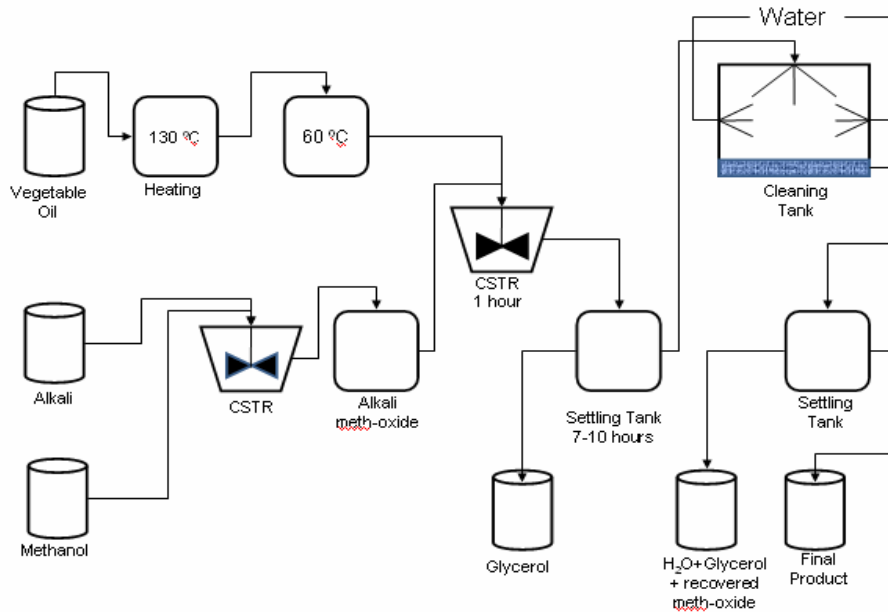
The raw materials used for the production of biodiesel are vegetable oils, methanol, Sodium hydroxide (NaOH) / Potassium hydroxide (KOH). Vegetable oils (Mustard oil, Soybean oil, Canola oil) are purchased from local market and waste vegetable (Al-Widyan et al.,2002) oil was obtained from KFC restaurant.

Procedure

Methanol and alkali were mixed in a closed CSTR. Waste vegetable oil was filtered to remove inorganic residues and added into a CSTR. The mixture was heated up to 60-70 °C to remove the water contents present in the oil. The temperature was maintained below the boiling temperature of methanol for 40-60 min. After completion of the reaction, binary mixture (Biodiesel and Glycerol) was produced. Biodiesel and glycerol have different specific gravities and separated using gravity decanter. The biodiesel was washed with hot water

till no more alkali was found. Recovered alkali could be recycled while glycerol was the byproduct of the process. A block diagram is shown in figure 1.

Figure 1: Block diagram of Biodiesel production process from edible oil waste



Characterization of Biodiesel

Characterization of biodiesel was done through different experiments, using ASTM standards. ASTM standard adopted for pour point was D97, for carbon residue was D189 and for flash point was D93. These standards were used to compare the properties.

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Table 1: Test results of biodiesel fuel samples

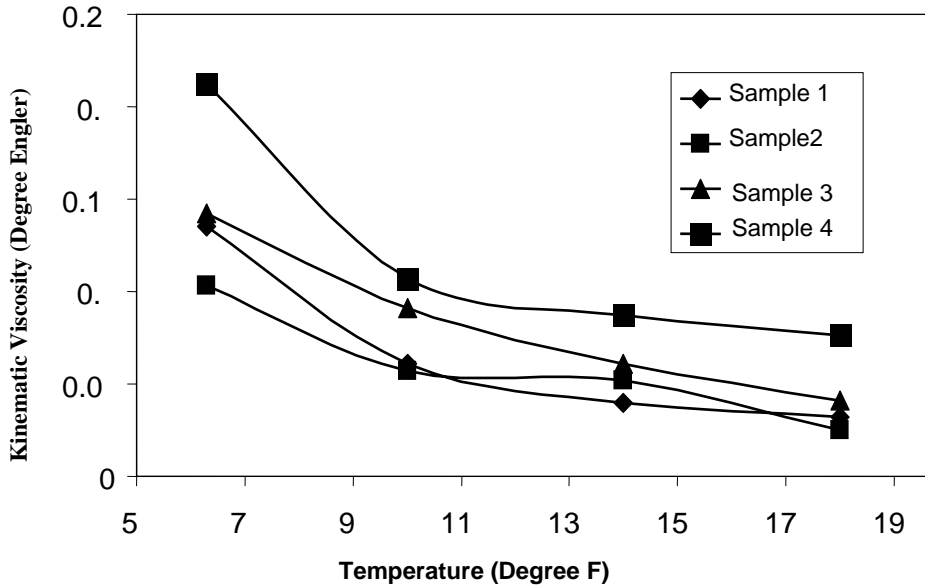
| Properties | Sample 1 | Sample 2 | Sample 3 | Sample 4 |
|------------------------------|----------|----------|----------|----------|
| Density (g/cm ³) | 0.888 | 0.895 | 0.896 | 0.903 |
| Specific gravity | 0.890 | 0.896 | 0.897 | 0.904 |
| Cloud point (°C) | 4 | -2 | -3 | -2 |
| Pour point (°C) | 2 | -5 | -9 | -9 |
| Carbon residue (%) | 0.14 | 0.14 | 0.20 | 0.19 |
| Flash point (°C) | 78 | 104 | 62 | 80 |

The density of sample 4 was the highest among all the samples. Sample 4 was prepared from waste vegetable oil. Specific gravity of the samples was obtained at 15 °C and density of water was taken from literature. Cloud point is the lowest temperature at which the first cloudy layer appears on the surface of fuel. From the cloud points of the four samples, sample 1 was found not appropriate to be used as fuel in colder regions because it could freeze at low temperatures (Imahara et al., 2006). The sample 2 ,3 and 4 were more appropriate to be used as a fuel. Sample 1's cloud point was higher because of the presence of associated water which has been reported later in the FTIR test. Pour point is the lowest possible temperature at which the fluid does not flow for 5 to 10 seconds. Pour point of sample 3 and sample 4 was very low and therefore they could be used as fuel in colder regions. However sample 1 was not found good as its pour point was 2 °C. Carbon residue test was carried out in Conradson apparatus. Sample 1 and sample 2 generated less carbon as compared to the sample 3 and sample 4. Flash point calculation were also done, and were used as selection criteria in compression ignition engines.

Viscosity

ASTM standard D2161 was followed to measure Kinematic Viscosity in stokes.

Figure 2: Effect of Temperature on Kinematic Viscosity (Degree Engler) of product samples.



Kinematic viscosity was found and graphically reported as degree Engler. A graph of degree Engler and temperature is shown in Figure 2. The term ‘Degree Engler’ is used when viscosity is measured with the Engler Viscometer. A sudden fall in viscosity was observed when temperature was 180°F for sample 2. In sample 3 a smooth viscosity curve is shown, that reports a decrease in viscosity with increase in temperature. In sample 4 a sudden decrease in viscosity was obtained, when temperature was increased from room temperature to 100°F.

FTIR (Fourier Transform Infrared Spectrophotometry)

For FTIR the IR light goes from the glowing source to a beam splitter, usually made of polished KBr, placed at a 45° angle. The reflected beam strikes a stationary mirror, while the transmitted light beam strikes a mirror that moves at a constant speed. The beams return from the mirror to recombine at the beam splitter. The beam from the moving mirror has traveled with different distance than the beam from the fixed mirror and the two beams combine to create interference. The interferogram which simultaneously contains all frequencies passes through the sample compartment to reach the detector (Wade, 2004). The interferogram is said to be in the time domain, corresponding to the energy seen by the detector as the mirror moves through the signal, a standard computer algorithm called a Fourier transform, converts the time domain to the frequency domain spectrum that allows us to see the strength of absorption as a function of the frequency. IR is the phenomenon in which vibration of the bonds are

observed instead of electron excitation IR spectroscopy observes the vibrations of bond and provides evidence of the functional group. When IR radiation is passed through the organic compounds, some of the frequencies are absorbed and appear as absorption bands, while other frequencies do not interact with the compound and are transmitted without being absorbed. Only those frequencies are absorbed which match with the vibration frequencies of the bonds. IR spectroscopy is therefore basically called vibrational spectroscopy. Vibrational motion is that type of motion in which the bonded atom moves to and fro. There are two types of vibrational motions.

- Stretching vibrations is the vibrational motion in which internuclear distance between the bonded atom increases and decreases along the bond axis.
- Bending vibrations is the type of vibrational motion in which position of bonded molecule change with respect to the bonded atom; the inter-atomic distance remain unchanged.

IR spectrum is the plot between vibrational frequency and transmittance. IR spectrum is the ECG of the organic compound.

Fundamental band occurs due to the vibrational transition from ground state to the first excited state. Weak bands are other than fundamental bands, like overtones. Overtones are not actual bands, they are weak bands. It is the additional frequency of absorption which has twice the frequency of normal frequency. Transition from ground state to 2nd excited state produce overtones (Sharma, 2007).

Fourier Transform Infrared Spectrophotometry tells us about the type of functional group present in the sample of oil taken and also about the concentrations of bonds by using values of transmittance.

Figure 3 : The infrared spectrum of Biodiesel sample1

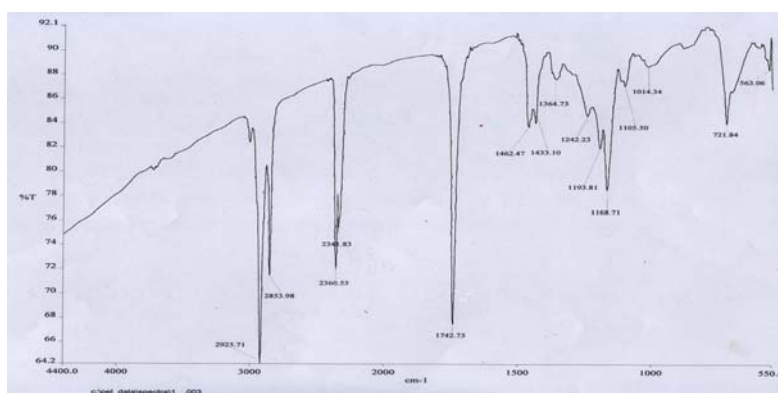
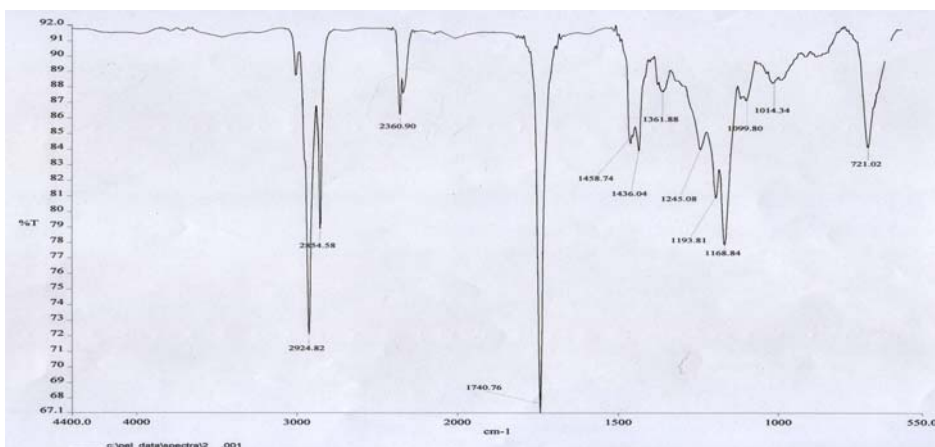


Table 2 Infrared Positions of various bond vibrations of sample 1
(Galen W et al, 1960)

| Peaks (cm ⁻¹) | Bond | Mode | Transmittance % | Concentration |
|---------------------------|---------------|---------|-----------------|---------------|
| 2925.71 | C – H | Stretch | 64.4 | Medium |
| 2853.98 | C – H | Stretch | 71.3 | Weak |
| 2360.55 | C ≡ C | Stretch | 72 | Weak |
| 2341.83 | C ≡ C | Stretch | 75 | Weak |
| 1742.73 | C = O | Stretch | 67.6 | Medium |
| 1462.47 | O – H , C – H | Bending | 83.7 | Weak |
| 1433.10 | O – H , C – H | Bending | 83.8 | Weak |
| 1364.73 | O – H , C – H | Bending | 87.8 | Weak |
| 1242.30 | O – H | Bending | 84.2 | Weak |
| 1193.81 | C – C , C – O | Bending | 81.7 | Weak |
| 1168.71 | C – C , C – O | Bending | 78.3 | Weak |
| 1105.50 | C – C , C – O | Bending | 86.2 | Weak |
| 1014.34 | C – C , C – O | Bending | 88.4 | Weak |
| 721.84 | C – H | Rocking | 84 | Weak |

The FTIR of sample 1 is as above. The type of bond found most abundantly was C-H and C=O. Modes of bonds are stretch, bending and rocking. In this FTIR C – H bond strength is ‘medium’ and properties in the table also different from other samples like cloud and pour point . The steep shown in graph of FTIR (fig 2) is because of associated water present in the sample of biodiesel prepared from ‘Mustered oil’.

Figure 4: The infrared spectrum of Biodiesel sample2

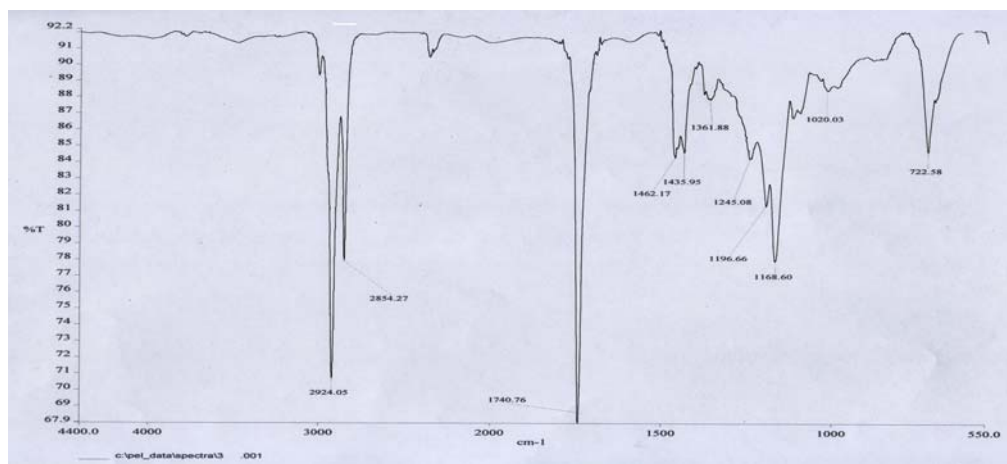


**Table 3 Infrared Positions of various bond vibrations of sample 2
(Galen W et al., 1960)**

| Peaks (cm ⁻¹) | Bond | Mode | Transmittance % | Concentration |
|---------------------------|--------------|---------|-----------------|---------------|
| 2924.82 | C – H | Stretch | 72 | Weak |
| 2854.58 | C – H | Stretch | 78.90 | Weak |
| 2360.90 | C ≡ C | Stretch | 86 | Weak |
| 1740.76 | C = O | Stretch | 67.10 | Medium |
| 1458.74 | O – H, C - H | Bending | 84.10 | Weak |
| 1436.04 | O – H, C - H | Bending | 83.50 | Weak |
| 1361.88 | O – H, C - H | Bending | 87.50 | Weak |
| 1245.08 | O – H, C – O | Bending | 83.50 | Weak |
| 1193.81 | C – C, C – O | Stretch | 80.60 | Weak |
| 1168.84 | C – C, C – O | Stretch | 77.40 | Weak |
| 1099.80 | C – C, C – O | Stretch | 87.00 | Weak |
| 1014.34 | C – C, C – O | Stretch | 88.00 | Weak |
| 721.02 | C – H | Rocking | 84.00 | Weak |

FTIR of sample 2 is shown above. C=O bonds were found abundantly in this sample. While other functional groups as shown in table above were also present. Further there was no water contamination in this sample.

Figure 5: The infrared spectrum of Biodiesel sample3

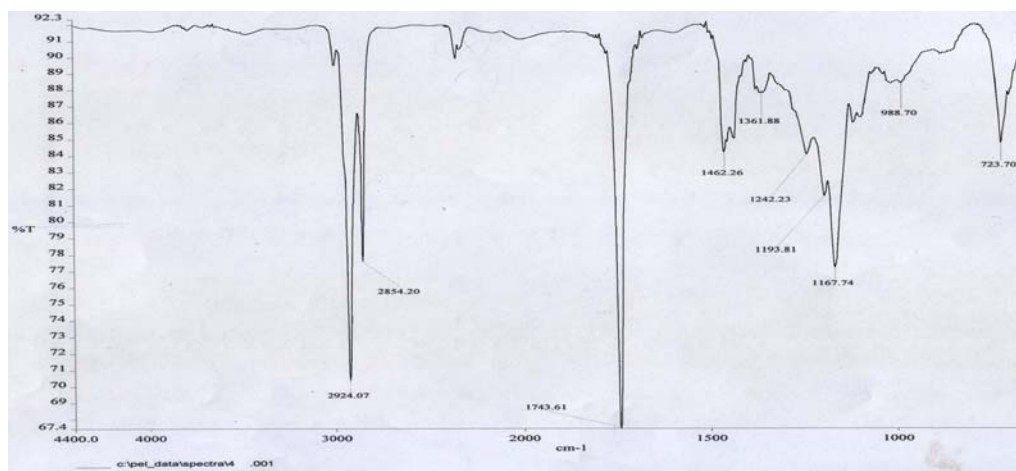


**Table 4 Infrared Positions of various bond vibrations of sample 3
(Galen W. et al., 1960).**

| Peaks (cm ⁻¹) | Bond | Mode | Transmittance % | Concentration |
|---------------------------|--------------|---------|-----------------|---------------|
| 2924.05 | C – H | Stretch | 70.60 | Weak |
| 2854.27 | C – H | Stretch | 77.78 | Weak |
| 1740.76 | C = O | Stretch | 68.10 | Medium |
| 1462.17 | O – H, C - H | Bending | 84.63 | Weak |
| 1435.95 | O – H, C - H | Bending | 84.30 | Weak |
| 1361.88 | O – H, C - H | Bending | 87.50 | Weak |
| 1245.08 | O – H, C - O | Bending | 84.00 | Weak |
| 1196.66 | C – C, C – O | Stretch | 81.00 | Weak |
| 1168.60 | C – C, C – O | Stretch | 77.80 | Weak |
| 1020.03 | C – C, C – O | Stretch | 88.10 | Weak |
| 722.58 | C – H | Rocking | 84.50 | Weak |

FTIR of sample 3 is as above. C=O are in medium range. Other functional groups concentration was found weak as compared to C=O but they were also present. There was no associated water present in this biodiesel sample.

Figure 6: The infrared spectrum of Biodiesel sample 4



**Table 5 Infrared Positions of various bond vibrations of sample 4
(Galen W. et al., 1960)**

| Peaks (cm ⁻¹) | Bond | Mode | Transmittance % | Concentration |
|---------------------------|--------------|---------|-----------------|---------------|
| 2924.07 | C – H | Stretch | 70.30 | Weak |
| 2854.20 | C – H | Stretch | 77.60 | Weak |
| 1743.61 | C = O | Stretch | 67.50 | Medium |
| 1462.26 | O – H, C - H | Bending | 83.70 | Weak |

| | | | | |
|---------|--------------|---------|-------|------|
| 1361.88 | O – H, C - H | Bending | 87.50 | Weak |
| 1242.23 | O – H | Bending | 83.50 | Weak |
| 1193.81 | C – C, C – O | Stretch | 81.30 | Weak |
| 1167.74 | C – C, C – O | Stretch | 77.00 | Weak |
| 988.70 | C – C, C – O | Stretch | 87.80 | Weak |
| 723.70 | C – H | Rocking | 84.30 | Weak |

C = O functional groups were present with medium concentration. In sample 4, associated water was not present.

Conclusion

Fatty acid methyl ester (i.e. Biodiesel) was manufactured through different vegetable oils i.e. fresh (Mustard, Canola, Soybean oil) and waste vegetable oil. Alkali was converted into alkali meth-oxide. Under similar reaction conditions different samples of biodiesel were prepared. All samples were tested in accordance with ASTM standards. The samples density, specific gravity, Engler viscosity, carbon residue, cloud point, pour point and flash point were reported. The most important test was FTIR spectrophotometry. In FTIR the bonds concentration within the samples were analyzed so that the characteristic of the sample could be easily evaluated. Through FTIR the presence of different functional groups in the samples were also inferred. Besides the biodiesel some unreacted raw material was also present in the samples. The peaks in the FTIR results clearly showed the presence of a glycerol in a very little quantity. The samples were washed before subjected to the final tests in order to remove the traces of glycerol present in the samples.

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