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A Comparative Study of Biodiesel Production from Beef Bone Marrow

Z. Didar*

Assistant Professor, Neyshabur Branch, Islamic Azad University, Neyshabur, Iran.

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ABSTRACT: This study is concerned with the viability of producing biodiesel from waste beef bone fat and evaluate this product according to the quality requirements defined by ASTM D- 6751. Accordingly, beef bone fat was heated to remove the moisture under vacuum at 60 ℃. Alkaline Catalysed Transesterfication was carried out by using 6:1 molar ratio of ethanol to fat in the presence of 1% w/w sodium hydroxide, at 78℃ for 2h. Acid-Catalysed Transesterfication reaction of beef bone fat was carried out using 30:1 molar of ethanol to fat in the presence of 1% sulfuric acid at 78℃, for 69h. Two- stage acid base transesterification is also carried out for biodiesel production. The resulted biodiesel from alkaline reaction meet the quality requirement better than the acid reaction but both biodiesel did not comply with the European Standard parameters namely kinematic viscosity, specific gravity, density, and cloud point.

Keywords: *Beef Bone Fat, Biodiesel, Transesterification.*

Introduction

New source of energy has attracted the attention of researchers in this field recently. Biodiesel has been recognized as an interesting fuel that might substitute the diesel oil produced from petroleum. The use of biodiesel has two advantages; it could reduce the dependency on petroleum oil that leads to an increased oil prices and it also reduces the environmental pollutants (Al-Widyan & Al-Shyoukh, 2002). Huge quantities of waste cooking oils and animal fats are available throughout the world, especially in the developed countries. Management of such oils and fats pose a significant challenge due to their disposal problems and possible contamination of the water and land resources. Biodiesel is produced mostly from vegetable oils particularly palm, sunflower, soybean oils via transesterification process using sodium hydroxide as a catalyst.

Although, the commercialization production of biodiesel from these vegetable oils still has drawbacks due to the high cost of the vegetable oils and their purification for biodiesel products therefore, it is necessary to develop a process in order to produce more efficient and economical products. In fact, currently biodiesel is mainly produced from a wide range of edible vegetable oils, namely rapeseed, soybean, sunflower or palm oils however, since these feed stocks are used in the food market and their prices are expected to increase even more in the future (USDA, 2007), biodiesel from these feed stocks will be less competitive than fossil fuels that will be the main hurdle to its commercialization. For this reason, in the last few months, most of the Portuguese biodiesel plants had to stop their production. This matter encouraged the use of low-price waste sources for biodiesel production that cannot be used for human consumption, such as the waste animal fats from the meat and/or fish

*Corresponding Author: z_didar57@yahoo.com

processing industries. Biodiesel produced from animal fats represents an environmental friendly and low cost alternative. Beef bone fat is one of the major waste from gelatin production industry. Therefore this work aims to study the viability of producing biodiesel from waste animal fats of beef bone and to evaluate the product according to the quality required and defined by ASTM D- 6751(ASTM D6751).

Materials and Methods

- *Raw Materials Preparation*

Beef bones were collected from slaughterhouses and meat processing companies. The collected samples were melted and filtered in order to obtain the fat and remove gums, protein residues, and suspended particles.

- *Fatty Acid Composition Determination*

Fatty acid compositions of the raw beef bone fat was determined by gas chromatography. Raw beef bone fat was esterified using the method described by Morrison and Smith (2005). Samples of 0.0625 to 0.25 g were placed into a 5 ml reaction bottles and 1 ml of Boron fluoride-methanol reagent was added. N_2 was used to purge the air from the bottles. The bottles were tightly covered and heated at 100 ℃ for 30 min for the reaction to take place.

After 30 min the mixtures were cooled and 1 ml of hexane was added to each bottle to extract the methyl esters and 1 ml of distilled water was added to stop the esterification reaction and to allow phase separation. The mixture was then stirred well and centrifuged to separate the hexane and aqueous phases. The top portion was collected and used for GC analysis. A Young Lin Acme 6000 Gas Chromatograph equipped with a 100m long cpsill 88 capillary column and flame ionization detector was used to analyse the esterified samples. The HP 3396A integrator automatically gave individual peak retention time, peak area and area percentage of each peak.

- *Biodiesel Synthesis*

Beef bone fat was heated to remove the moisture under vacuum at 60℃.

- *Alkaline treatment*

Alkaline catalysed transesterfication of beef bone fat was conducted by 6:1 molar ratio of ethanol to fat using 1% sodium hydroxide, at 78℃ for 2h.

- *Acid treatment*

Acid catalysed transesterification of beef bone fat was carried out by 30:1 molar ratio of ethanol to fat using 1% sulfuric acid as catalyst at 78℃ for 69h. After the transesterification reaction, unreacted alcohol is removed by distillation and the rest of the mixture is cooled to room temperature and washed by water in a simple gravity settler. Further water washing is applied to separate the biodiesel from the glycerol, catalyst and alcohol.

- *Two stage acid base trasesterfication*

During the acid-catalysed stage, the amount of methanol used is 20% of the volume of the oil plus 60% excess methanol. One liter of crude beef bone marrow and 40% of the required volume of methanol was measured and added to the heated beef bone marrow at 55°C. The mixture was stirred gently for 5 min using a magnetic stirrer until it became murky. 1 ml of 95% sulfuric acid was added to the mixture. Holding the temperature at 55°C, the mixture was stirred gently for 1 h at 500 to 600 rpm. The heat was removed and stirring continued for another hour after which the mixture was allowed to settle for 2 h. To the remaining 60% of the methanol 4.9 g potassium hydroxide was added to form potassium methoxide solution. 50% of this solution was added to the acid treated mixture and stirred gently for 5 min and allowed to settle

for 6 to 12 h after which the glycerin was drained off. During the alkali-catalysed stage, the mixture was heated to 55°C and the second half of the methoxide solution was slowly stirred in, mixing at the same speed for 1 h. On completion of the reaction, the product was poured into a separating funnel and allowed to settle for 18 to 24 h. After separation of the biodiesel and glycerol, the fatty acid methyl ester was washed with 2 ml of 10% phosphoric acid added to the warm distilled water and dried with anhydrous sodium sulphate (Enweremadu & Alamu, 2010).

- *Raw material and biodiesel characterization*

Raw beef bone fat, biodiesel quality parameters and their corresponding blends with diesel were tested according to the quality requirements of ASTM D- 6751. Therefore the following parameters were evaluated;

- Kinematic viscosity was determined at 40°C using Cannon-Fenske viscometers according to the standard ASTM D445 (ASTM D445-11).
- Density was determined at 15ºC using a hydrometer according to the standard ASTM D1298-99(ASTM, 2005).
- Cloud Point was determined according to ASTM D2500-11 Standard Test Method for of Petroleum Products (ASTM D2500-11).

- *Statistical analysis*

In order to assess the significant differences among the samples, a completely randomized design was performed using the MSTATC program (version 1.41). Duncan's new multiple range test was used to describe the means with 99% confidence.

Results and Discussion

Figure 1 and Table 1 show the fatty acid profile and composition of beef bone fat. The analysis indicates that oleic acid (41.32%) followed by palmitic acid (21.68%) and stearic acid (13.21%) were the predominant fatty acids present in the beef bone fat.

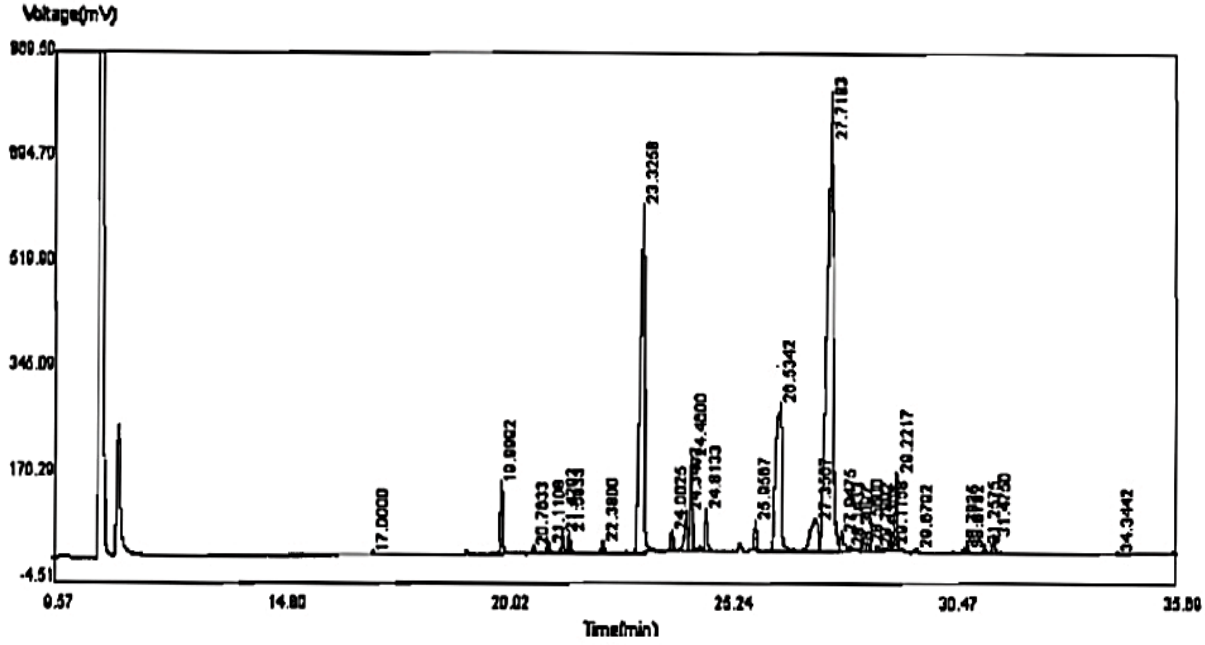

Fig. 1. Fatty acid analysis of beef bone fat

Table 1. Fatty acid composition (%) of beef bone fat

Fatty acid	%weight
C12:0	0.12
C14:0	2.38
C16:0	21.68
C16:1	0.77
C17:0	1.43
C18:0	13.21
C18:1	41.32
C18:1(tr)	3.72
C18:2	2.80
C18:2(tr)	0.58
C18:3(ω6)	0.25
C18:3(ω3)	0.39
C20:0	0.18
C20:1	0.24
C20:2	0.12
C21:0	0.72

The various fatty acid composition of different oil and fat feed stocks with different chain length, degree of unsaturation and chain branching influences the properties of the biodiesel such as cold flow, viscosity and lubricity (Knothe, 2005).

Viscosity, density, cloud point and specific gravity are the major or some characteristics of produced biodiesel to be evaluated.

High viscosity is the major problem preventing the use of vegetable oils and animal fats directly in diesel engines. The viscosity of the waste cooking oil was determined by using a Cannon-Fenske viscometer. Triplicate samples were used for the experiments. It was observed that the measured average viscosity of the beef bone fat sample was 44.28 mm^2/sec at 40°C. The viscosities of biodiesel ethyl esters for alkaline and acid catalyzed transesterification were 7.73 and 19.35 mm^2/sec at 40℃ respectively. The two-stage biodiesel transesterification has a viscosity about 4.9 (Figure 2). The obtained figures for the alkaline catalyzed and the two stage biodiesels processes were in the range recommended by ASTM. The ASTM standard for biodiesel viscosity is 1.9-6.0 mm^2/sec at 40°C.

Biodiesel production has decreased the density of beef bone marrow and the lowest density was relayed to the alkali- catalyzed biodiesel (Figure 3).

The cloud and pour point are also important properties of biodiesel fuel. Cloud point is the temperature at which a cloud of wax crystals first appear in the oil when it is cooled. These properties are related to the use of biodiesel in the cold temperature. The cloud point of ethyl ester produced from beef bone fat was found to be high as shown in Figure 4.

The specific gravity data are presented in Figure 5. It was observed that the specific gravities of raw beef tallow were decreased by the application of alkaline, acid catalysed and two-stage esterification.

Conclusion

Beef bone fat has been selected as a feedstock for biodiesel production due to its high wastage from the meat and gelatin production factories. Studies concerned with biodiesel production from beef bone fat by alkaline and acid catalyzed transesterification have been carried out to evaluate the resulted product. The produced alkaline- catalyzed biodiesel in term of kinematic viscosity at 40℃ was in agreement with those of petroleum diesel and with the international standards of biodiesel, however further research works such as fractionation of the fat section might be studied in order to improve the final product that corresponds to the international standards of biodiesel.

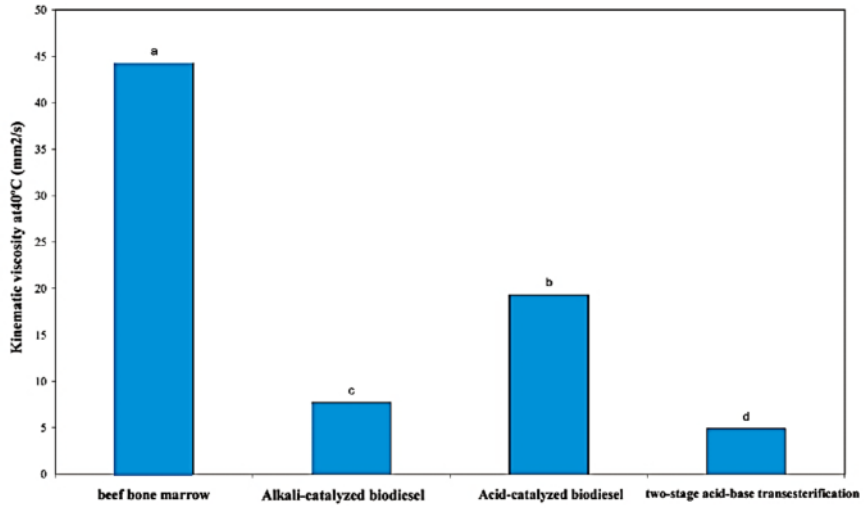

Fig. 2. Comparative kinematic viscosities among beef bone marro and biodiesels

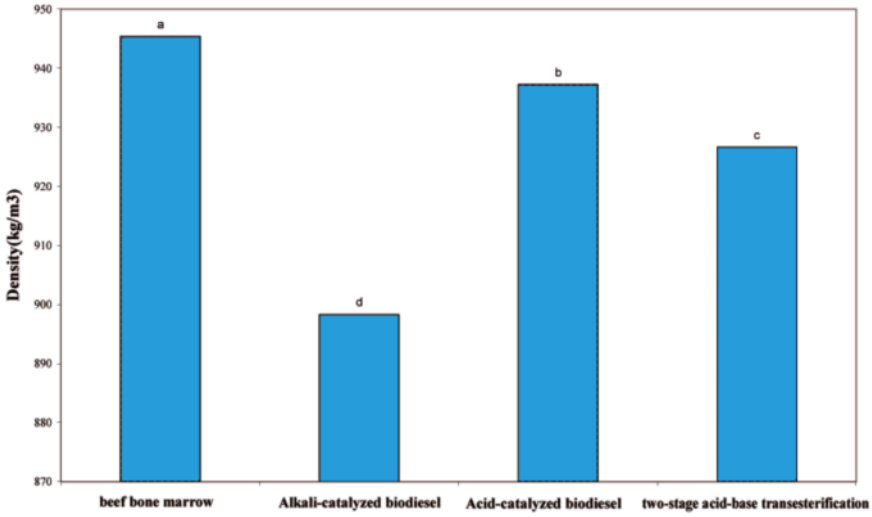

Fig. 3. Comparative densities among beef bone marrow and biodiesels

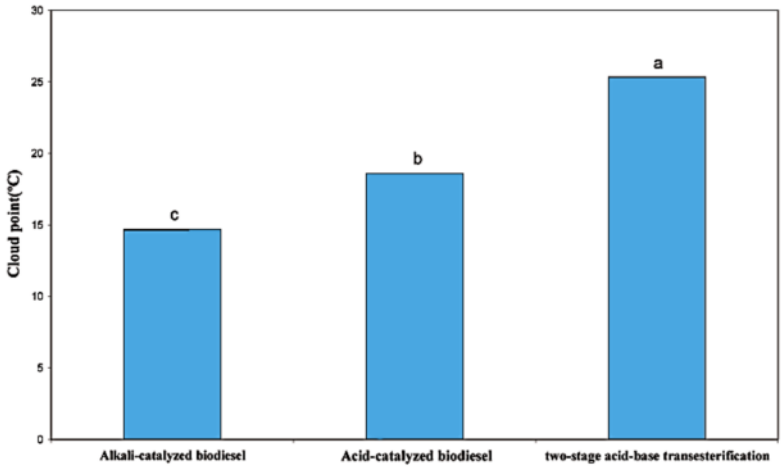

Fig. 4. Comparative cloud points among biodiesels

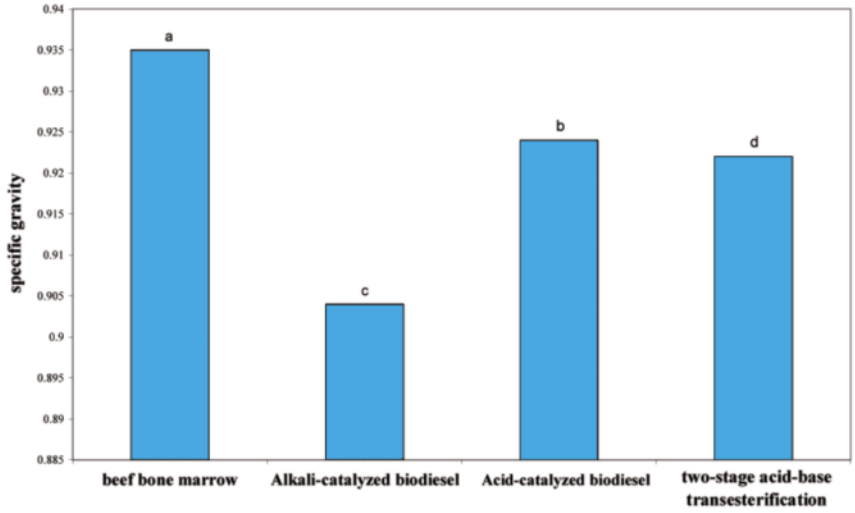

Fig. 5. Comparative specific gravities among beef bone marro and biodiesels

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