

Biodiesel Production from Beef Tallow –A procedural changeGanapathi Vedula¹, B V Appa Rao², Aditya Kolakoti³^{1&3}Research Scholar, Department of Marine Engineering,
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Abstract- Raw vegetable oils are comparatively lower in viscosity when compared to the animal fats. Animal fats appear in solid state and especially beef tallow is the one like that. Care is to be taken in the treatment of biodiesel in the initial stages is crucial in getting better yield of quality biodiesel. There is a change in the transesterification procedure and in the methoxide preparation also which ought to be followed to get best and fast results. The final product is subjected to chromatography testing to analyze the fatty acids in the ester prepared. This revealed the saturated fatty acid content in the Beef Tallow Methyl Ester (BTME). Finally the characterization has been done to bring out the properties of the BTME.

Keywords- Beef Tallow Methyl Ester; Gas Chromatography; Fatty Acid Composition; Elemental Analysis.

I. INTRODUCTION

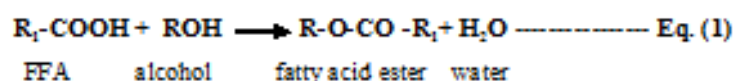
Renewable fuels are the methyl esters derived from edible and non-edible oils, these fuels are eco-friendly and emit less tail pipe emissions. As the demand for alternative renewable sources is increasing at a faster rate due to pollution and limited reserves of fossil fuel. Now the research is directed towards alternative fuels and their applications in diesel engines [1-4]. Biodiesel derived from edible oils like palm, coconut, sunflower, rice bran, rapeseed, soya bean, mustard and etc are suitable to replace the conventional petrodiesel but on the other hand edible oils create imbalance in the food chain. The substitution of conventional diesel fuels with fatty acid methyl esters already comprises a commercial activity in many countries of the world [5-6]. However, the use of biodiesel has not expanded into developing countries like India, due to the higher prices than conventional diesel fuel. The higher cost of biodiesel is due to its production mostly from expensive high-quality virgin oil. Use of low-cost feedstock such as waste frying oils and fat oils can help to make biodiesel competitive in price with petroleum diesel fuel [7-8]. The raw oils are in semi-solid state and possess high viscosity, due to high viscosity these oils are treated before their application. There are different methods to reduce the viscosity of the raw oils such as pre-heating, pyrolysis, mineralization and transesterification [9-11]. Transesterification received the greatest attention and widely accepted method. Literature on the production and characterization of different non-edible oils were reported here. Haq Nawaz Bhatti et al. [12] used waste tallow (chicken and mutton fat) as low cost sustainable potential feed stock for biodiesel production. A total of 98.29% and 97.25% fatty acids were identified in chicken and mutton fats. Both fats were found highly suitable to produce biodiesel with recommended fuel properties. Seunghun Choi and Youngtaig Oh [13] from the results of analytical experiment indicated that the animal fat biodiesel (BD) mainly consists of saturated fatty acids. High cetane number can be produced from animal fats. Compared with diesel fuel, animal fat BD has shown different spray patterns and smoke emission particle distributions. The animal fat BD properties were in reasonable agreement with the international ASTM D6751, EN 14214 and Korean national standards of BD. Teresa M. Mata et al. [14] technological point of view it is possible to use animal fats and fish oil as feedstock for biodiesel production. From the sustainability perspective, beef tallow biodiesel seems to be the most sustainable one. In this paper an attempt was made on the production and characterization of animal fat biodiesel with acid esterification process followed by transesterification.

II. MATERIALS**Materials used:**

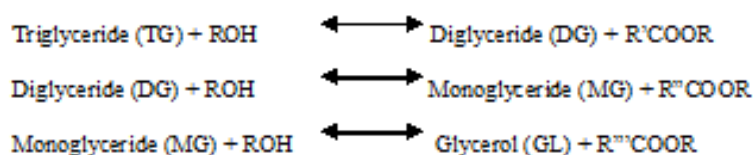
Raw beef tallow which is in semi-solid was collected from local slaughter shop. 99.9% pure methanol (CH_3OH), sulphuric acid (H_2SO_4), sodium hydroxide (NaOH) and phosphoric acid (H_3PO_4) were purchased from Sigma Chemicals Limited Visakhapatnam.

III. BIODIESEL CHARACTERIZATION

Transesterification is the general term used to describe the important class of organic reactions, where an ester is transformed into another interchange of alkyl groups so it is also termed as alcoholysis. The transesterification is an equilibrium reaction and the transformation occurs by mixing the reactants. However, the presence of a catalyst accelerates considerably the adjustment of the equilibrium. General equation for transesterification reaction is given below.



Beef Tallow comprises of larger quantities of free fatty acids (FFA), triglycerides, small amounts of mono and di-glycerides. In the transesterification of beef tallow, a triglyceride reacts with an alcohol in the presence of a strong acid or base, producing a mixture of fatty acid alkyl esters and glycerol. The overall process is a sequence of three consecutive and reversible reactions in which a triglyceride is converted stepwise to di-glycerides, then mono-glycerides and these are finally converted into fatty acid alkyl monoester (Biodiesel) and glycerol (By-product) as follows.



The stoichiometric reaction requires one mole of triglyceride and three moles of alcohol. However, an excess of the alcohol is used to increase the yield of alkyl esters and to allow the phase separation from the glycerol formed. Several aspects, including the type of catalyst (base or acid), alcohol to beef tallow oil molar ratio, temperature, purity of the reactants (mainly water content in alcohol) and free fatty acid content has an influence on the course of the transesterification. Hence in this experimentation, the reactants of high purity have been used (methyl alcohol with 99.9% purity). The mechanism of the base-catalyzed transesterification reaction of beef tallow oil is shown in the **Figure 1**. The first step (Eq.1) is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst.

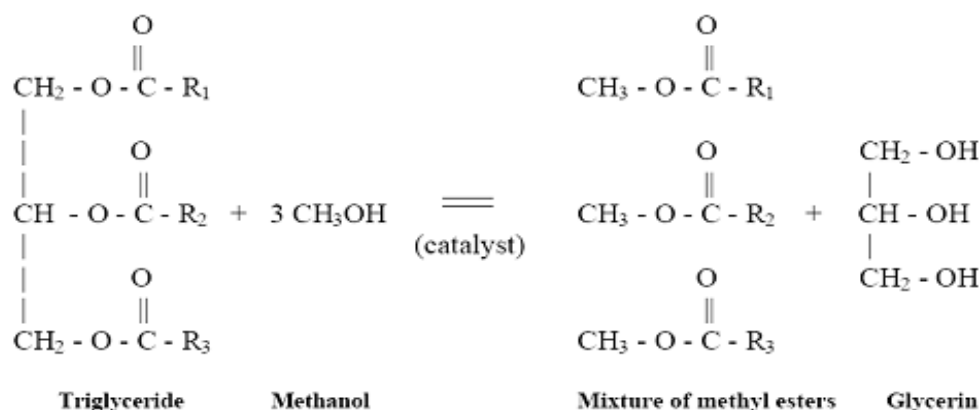


Figure 1. Mechanism of the base-catalyzed transesterification process

Most of the waste feedstock has high free fatty acid content. The free fatty acids (FFA) present in beef tallow create a major problem, if they are initially processed through base-catalyzed transesterification process. Because the FFA react with the base catalyst to form soaps, which leads to loss of catalyst and ester product. This increases production processing cost altogether. This reason necessitates an initial acid catalyst for esterification of FFA. Esterification is followed by transesterification, but under acid conditions, it is much slower than under caustic conditions and it won't do a complete oil-to-methyl ester conversion as the reaction is much more equilibrium sensitive. For the first stage, it forms a compound out of an acid and an alcohol. The alcohol is still methanol, but instead of using lye (sodium hydroxide), the catalyst in this reaction is sulfuric acid (battery acid) with a purity of 95%. The sulfate ion in the sulfuric acid combines with the sodium ion in the lye during the second stage reaction to form sodium sulfate, which is a water-soluble salt and is removed in the water wash. No sulfur remains in the biodiesel product. Transesterification does not alter the fatty acid composition of the feed stocks. The entire process of transesterification is shown in the flowchart (**Figure 2**).

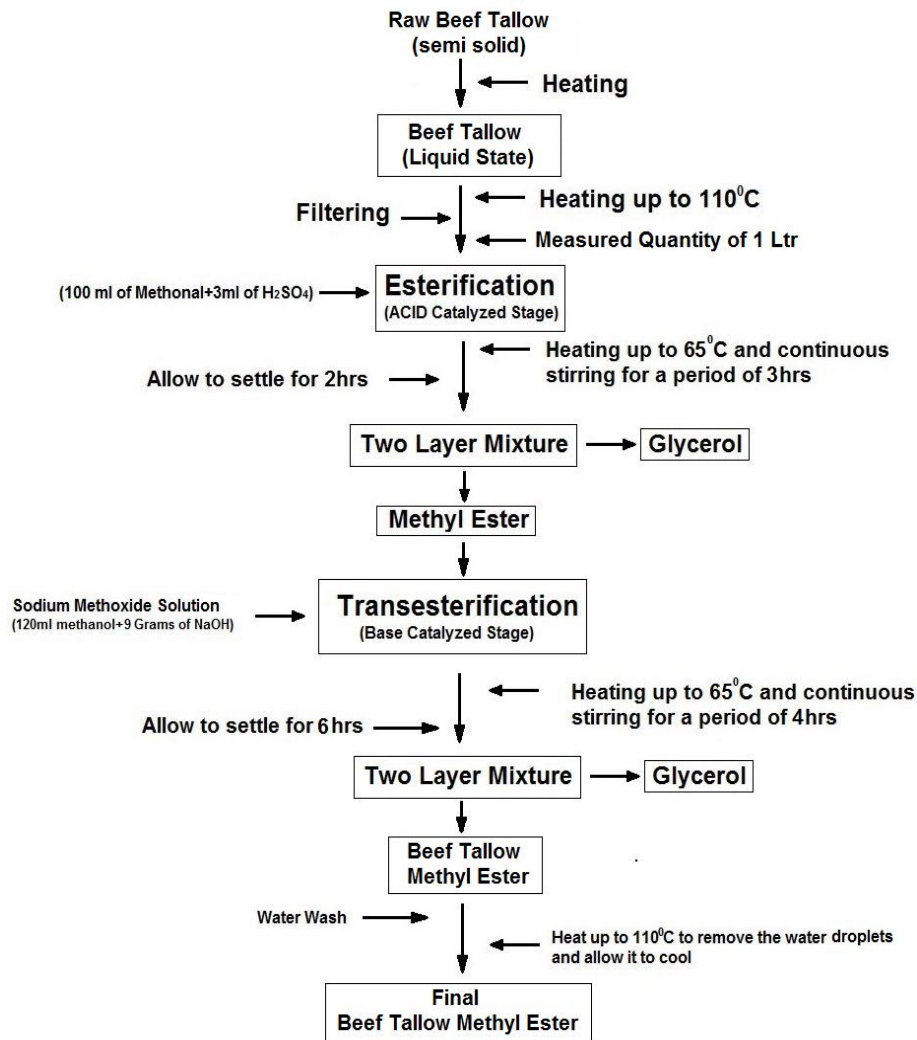


Figure 2. Process flow chart for preparation of methyl esters

3.1 Extraction of beef tallow from animal waste materials

The procedure for extraction of beef tallow from fatty materials depends on their characteristics and composition.

1. Milling and grinding of raw material.
2. Cooking on screw conveyor to a batch digester, where it remains for 4 to 5 hours to be cooked with saturated vapor at about 110°C, until it losses about 70% of its moisture content.
3. Separation of liquid fat from solids by percolation and sieving in a percolator tank heated by steam.
4. Centrifugation or filtration of the fat. Decantation for final separation of fat from the aqueous phase present.
5. Collection and separation of the solid material for pet food.

3.2 The processing of Beef Tallow Methyl Ester (BTME)

1. The inedible beef tallow is melted to liquid state (**Figure 4(b)**) and it is filtered by using surgical cotton to eliminate the traces of water and particulate matter.
2. One liter of beef tallow oil is taken for transesterification process.
3. The raw oil is heated to 100 °C temperature and maintained for 15 minutes to remove the remnant traces of water as shown in **Figure 4(c)**. For a successful reaction, the oil must be free from water; otherwise it may lead to soap formation.

3.3 Esterification (Acid-catalyzed stage)

The free fatty acids can be reduced to esters by adding methanol with acid catalyst. The reactions are depicted in the **Figure 3**.

1. One liter of treated oil is heated up to 65°C to melt the solid fats presented in it.

2. Methanol of 99.9% pure (**Figure 4(d)**) is added (0.1 liter/liter of oil) to the heated oil. And it is stirred continuously (Methanol is a polar compound, oil is strongly non-polar, hence a suspension will form).
3. Three milliliter of 95 % pure sulfuric acid (H_2SO_4) (**Figure 4(d)**) is added for each liter of oil using a graduated eye dropper.
4. The compound is stirred for three hours maintaining the temperature at $65^\circ C$ as shown in **Figure 4(e)**.
5. The mixture is allowed to settle for 2 hours in a decanter to remove glycerin and chemicalwater as shown in **Figure 4(f)**.

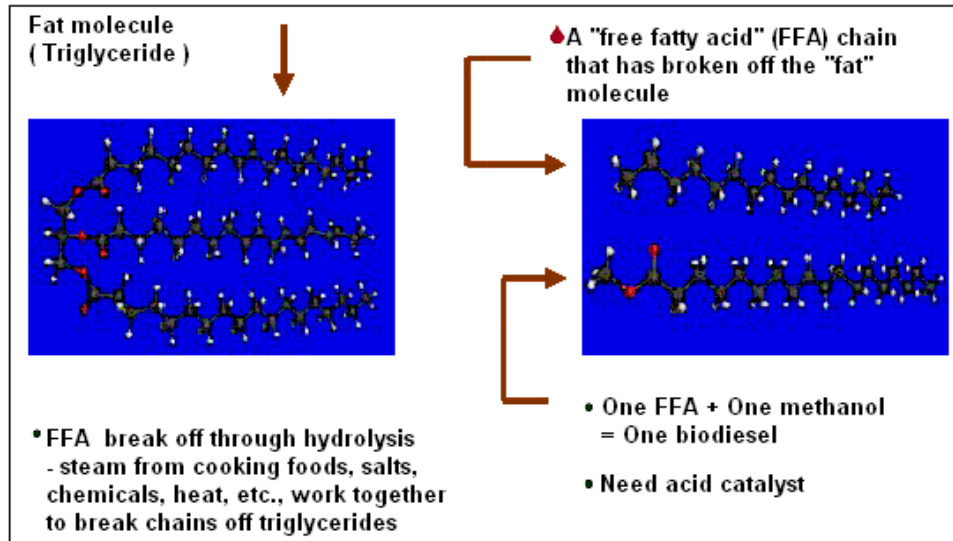


Figure 3.FFA break off with acid treatment

3.3 Transesterification (Base-catalyzed stage)

1. For each liter of beef tallow oil, 0.12 liter of methanol (12% by volume) is measured to which it is added 9 gram of sodium hydroxide (NaOH) as shown in **Figure 4(g)**. The mixture is stirred thoroughly until it forms sodium methoxide as shown in **Figure 4(h)**.
2. The prepared Sodium Methoxide is poured into the heated mixture and the mixture is stirred for continuous at low speed (i.e.500 to 600 rpm) in order to neutralize the sulfuric acid.
3. The mixture is heated to $65^\circ C$ and the whole reaction is maintained as shown in **Figure 4(i)**.
4. After four hours the mixture is poured into a decanter and allowed it to settle for 6 hours. As glycerin is heavier than the biodiesel, it will settle at the bottom as shown in **Figure 4(j)**. Glycerin finally is separated from the biodiesel (beef tallow methyl ester).

3.5 Waterwashing of the methyl ester

Methyl ester thus obtained possesses traces of sodium hydroxide and acid which will change the pH values of the biodiesel. By water washing, the above said acid and base traces can be eliminated ensuring almost neutral solution. Washing method is explained step by step as mentioned below.

1. Bubble wash method is used, but there is no need to monitor pH value of the oil any more. One milliliter of phosphoric acid (H_3PO_4) is added to the washing water first. This wash is repeated 2 to 3 times finally to remove sodium hydroxide and acid traces.
2. Oil is water washed using a proportion 1:3 (water: oil) as shown in **Figure 4(k)**.
3. The mixture is allowed to settle in a decanter for one hour as shown in **Figure 4(l)** and the water is drained off latter.
4. The biodiesel is heated to $100^\circ C$ (dehydration) to dispense with the traces of water and preserved as shown in **Figure 4(m)**.

Figure 4.(Indicate the processes one by one in chronological order to convert raw beef tallow into methyl ester.)



Figure 4(a).
Raw beef tallow



Figure 4(b).
Melted beef tallow



Figure 4(c).
Beef tallow oil



Figure 4(d).
Methanol+Catalyst(H_2SO_4)



Figure 4(e).
Esterification
(Acid-catalyzed stage)



Figure 4(f).
Separation after
esterification



Figure 4(g).
Methanol +Sodium
hydroxide



Figure 4(h).
Sodium methoxide



Figure4(i).
Transesterification
(Base-catalyzed stage)



Figure 4(j).
Separation after
transesterification



Figure 4(k).
Water washing



Figure 4(l).
Separation of methyl
ester and water



Figure 4(m).
Final BTME

Figure 4(a, to m). Beef tallow methyl ester making demonstrating step by step process

3.6 Properties of biodiesels

After making the required quantity of methyl ester of the oil, necessary properties of the ester can be established as per the ASTM (D6751), EN (14214) and IS test methods (IS: 1448). Characterization of the oil is taken up as per the standards at Hindustan Petroleum Corporation Limited, Visakhapatnam and Department of Marine Engineering, A.U. College of Engineering as per IS test methods. The results are tabulated in **Table 1**.

Table 1. Properties of diesel fuel, Beef Tallow Methyl Ester (BTME)

S.No.	Property	Diesel	BTME
1	Density at 33 ⁰ C(kg/m ³)	830	883
2	Calorific Value (kJ/kg)	43000	38570
3	Viscosity at 33 ⁰ C (cSt.)	2.75	4.5
4	Cetane Number	47	60
5	Flash Point(⁰ C)	62	170
6	Auto ignition temperature(⁰ C)	210	363
7	Latent Heat of Vaporization(kJ/kg)	250	300
8	Rams bottom Carbon Residue (Wt %)	0.17	0.27
9	Pour Point (⁰ C)	-4	-5 to 10
10	Acid Number (mg- KOH/g)	0.03	0.15
11	Cloud Point (⁰ C)	-15 to -5	-3 to 15
12	Stoichiometric air to fuel ratio (wt/wt %)	15	12.67

3.7 Fatty Acid Composition by Gas Chromatography of Beef Tallow Methyl Ester

The conversion of the transesterification reaction was confirmed by thin-layer chromatography (TLC) analysis and showed a spot for the triglycerol with an R_f (Retardation Factor) equal to 0.30 and another one for the biodiesel with an R_f equal to 0.71. The fatty acids present in biodiesel were measured by gas chromatography coupled mass spectrum (GC-MS) **Figure 5** and the results are presented in **Table 2**. In this case, it was found that the saturated fatty acids (SFA) are predominant with 66.545% and 30.775% of unsaturated fatty acids (UFA). The stearic (C18:0) and palmitic acids (C16:0) are predominant in this sample, and they are saturated fatty acids. The **Figure 6** clearly envisages the saturated fatty acid content of the BTME. **Figure 7** explains in general the saturated fatty acid content in various vegetable and fat raw oils.

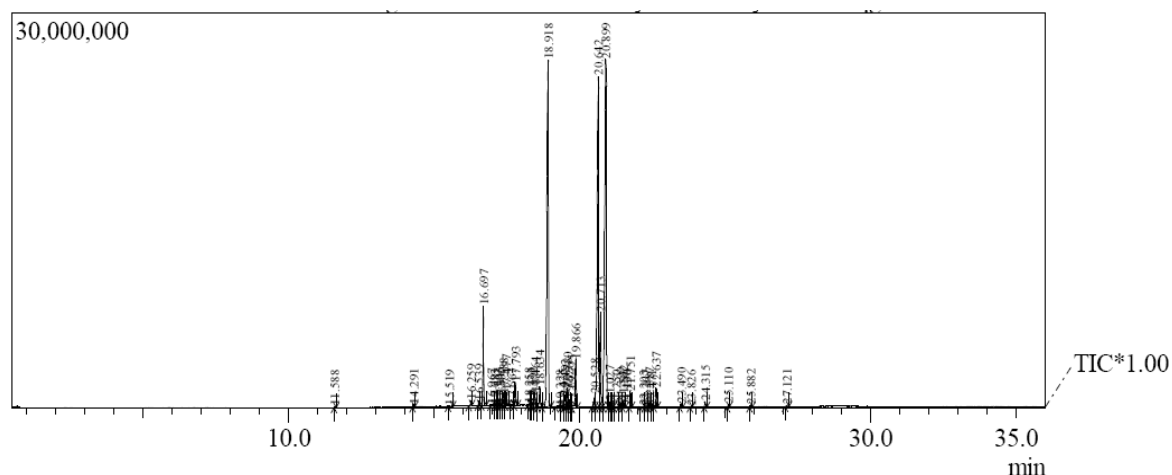


Figure 5. Abundance percentage verses mass to charge ratio of BTME

Table 2. Beef tallow methyl ester fatty acid composition

S. No	Lipid Number	Wt %	Status
1	C14:0	5.685	Saturated
2	C15:0	1.715	Saturated
3	C16:0	25.42	Saturated
4	C18:0	27.555	Saturated
5	C20:0	5.91	Saturated
6	C24:0	0.26	Saturated
7	C16:1	1.95	Monounsaturated
8	C18:1	28.825	Monounsaturated
9	C18:2	0.595	Poly unsaturated
10	C18:3	0.04	Poly unsaturated
11	Others	2.345	
	Total	100 %	

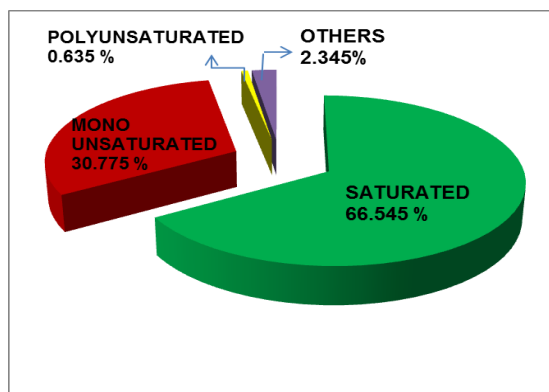


Figure 6. Pie diagram representing fatty acid composition of BTME

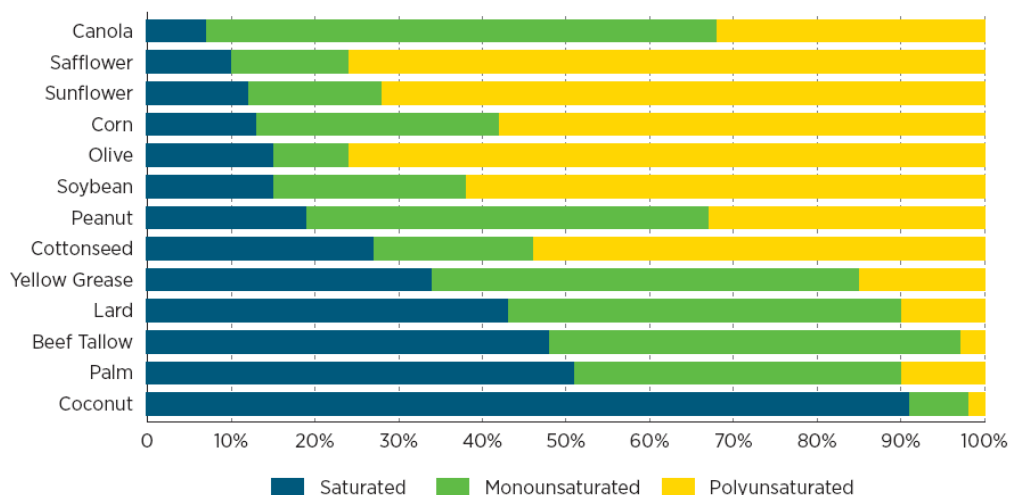


Figure 7. General composition of various biodiesel feed stocks in order of increasing saturated fatty acid content
"Teresa et al. (2016)"[15]

3.8 Elemental Analysis

The Figures 8&9 indicates the elemental analysis of the BTME fuel. The values are shown in Table 3.

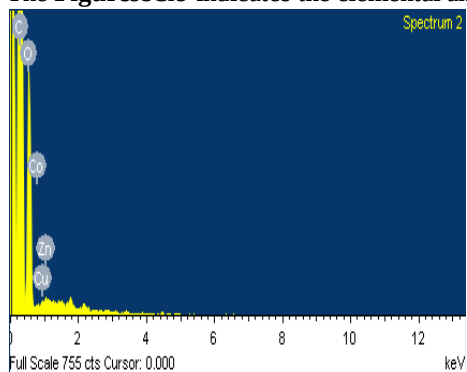


Figure 8. BTME Spectrum

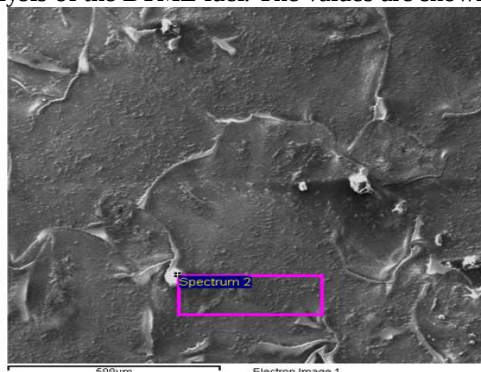


Figure 9. BTME Composition

Table 3. Elemental composition of Beef Tallow Methyl Ester (BTME)

S.No	Element	Weight %	Atomic %
1	Carbon (C)	74.05	79.63
2	Oxygen (O)	24.97	20.16
3	Cobalt (Co)	0.49	0.11
4	Copper (Cu)	0.25	0.05
5	Zinc (Zn)	0.25	0.05
6	Total	100	100

IV.CONCLUSIONS

This study analysis of fatbiodiesel from animal waste isevaluated andtheir sustainability in comparison to fossil diesel fuel. The following are the conclusions:

- BTME has met with the standards of diesel fuel after transesterification.
- The time consumed in conducting the transesterification is substantially reduced.
- The presence of saturated fatty acids in BTME is advantageous in reducing the emissions to appreciable level.
- The characterization as regards the saturated fatty acids is tallying with the general standard envisaged in the general fatty acid chart.

Furthermore, this study result indicates animal fats can be an interesting low-cost alternative feedstock to produce high quality biodiesel, and animal fats have a great potential to increase the biodiesel production amount.

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