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Biodiesel from Waste Cooking Oil: Acidic Transesterification

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Abstract—*Waste cooking oil which has been reused again and again in roadside food stalls and dhabas after a certain number of times is not fit to be used and is generally discarded. Due to the consecutive process of deep frying, there are many chemical reactions which take place and degrade the oil. This leads to the loss in quality of oil and becomes darker in colour, off-flavoured and contains no nutritional properties. Many health risks are also related to the recycling of waste cooking-oil for food preparation. Thus, to put this waste to better use, acidic transesterification method was developed to convert it into biodiesel. The oil was transesterified using hydrochloric acid, methanol and toluene. Physical and chemical properties like colour, odour, physical state, specific gravity, refractive index, pH, free fatty acids, iodine value etc were determined and compared with the ASTM standards. Most of the parameters were within the expected range. GC-MS analysis was performed to detect the fatty acid composition of the biodiesel samples. Acid-catalysed transesterification was found to be an effective method for utilizing waste oil and producing useful biodiesel.*

1. INTRODUCTION

The world is facing several environmental issues today. The top most distressing and worrying issues regarding environment are energy crisis and the global warming. The foremost reason for global warming is the quick usage of non-renewable energy source assets [1], which thus commits to global crisis of energy and an increase in petroleum and oil costs [2]. Around 80% is the worldwide energy appeal, which is mainly reliant on petroleum derivatives alone, prompting environmental change, genuine medical problems and ecological contamination [3]. Hence for conquering these serious issues, it is necessary to find or discover some different sources for the creation of non-renewable energy sources [4]. As substitutes of petroleum products, there are numerous different renewable fuel sources, which might be chosen to defeat the energy sector perceptivity for example tidal, wind or sun powered assets [5].

Fuels derived from the biomass known as biofuels are an alternative for opposing energy emergency. **Biodiesel or biofuel** are known as an alternative fuel just like traditional or 'fossil' diesel [6]. Biodiesel can be prepared from different vegetable oil, animal oil/fat or tallow and waste cooking oil are mostly a mixture of fatty acid methyl esters (FAMEs). The method used for the conversion of these oils to biodiesel is known as transesterification. Though oil straight from the agricultural industry represents the greatest potential source, it is not being produced commercially simply because the raw oil is too expensive. After the cost of converting it to biodiesel has been added on, it is simply too expensive to compete with fossil diesel. Waste vegetable oil can often be sourced for free or already treated for a small price. The waste cooking oil must be treated before conversion to biodiesel to remove impurities. The result is Biodiesel produced from waste vegetable oil can compete with fossil diesel. The waste cooking oil which has been reused many times is generally discarded without any treatment, which in turn pollutes theenvironment. Many health risks are also related to the recycling of waste cooking oil for food production. Thus, transesterification method was developed to convert this reused waste cooking oil to biodiesel.

Biodiesels are classified into 3 generations. **"First generation"** or original biodiesels acquired from sources, for example, oils from vegetables and animals were mainly utilized in beginning. In any case, there are numerous adverse circumstances of utilizing food crops as options for biofuel, because of utilization of land, water for water system or irrigation and high cost and deficiency of nourishment [7]. Biodiesel was mostly formed from waste cooking oil and plant oils because of the occupancy of high percentage of triacylglycerols (TAGs), which are fundamental for the production of biodiesel. Issues related with oil originated from fuel source for the production of biofuel has made ready for **"second generation"** or age of biofuels [8]. They are basically created from non-edible material biomass, for example, woody yields, paddy straws, backwoods deposits,

bagasse and so on, yet the length of generation expanded the expense and limited their utilization. The **"third era"** biodiesel is generally considered as generation of biofuel from microbial oils extracted from microorganisms, for example, green growth, microscopic organisms, bacteria, algae, yeast, parasites by developing them in an appropriate growth media. Likewise, the creation of biofuels ought to be financially and in fact practical and savvy, for the improvement of natural concerns and in overall improvement of environment [9].

Biodiesel has various environmentally advantageous properties. The principal advantage of biodiesel is that it could be defined as 'carbon impartial or carbon neutral'. This implies that the fuel produces no net yield of carbon in the form of carbon dioxide (CO_2). Hence the production of amount of carbon dioxide is zero. Properties of biodiesel are very much similar and comparable to that of petroleum diesel, which is biodegradable, and has lower emissions and might not need any changes in the boiler engines besides having some more lubricative properties like non-toxicity, sustainability and renewability. In comparison with low sulphur diesel fuels, biodiesel has good lubricating properties and cetane ratings. The biodiesel colour varies from golden or yellow to dark brown depending on the method of production. Boiling point of biodiesel is high and has lower vapour pressure. It is found to be a little miscible with the water. Density of biodiesel is higher than that of petrodiesel. Chain length, stretching change and the level of unsaturation, kinematic consistency, oxidative stability and heat of combustion are few more important properties of biodiesels.

Transesterification of waste cooking oil:

Transesterification process also known as **alcoholysis**is used for the production of biodiesel. The process of transesterification is the reaction of triacylglycerol (waste cooking oils) named as TAG with the alcohol to produce ester and glycerol.[10] Mainly ethanol or methanol is used as alcohols because the molecular weight of alcohol used in the transesterification reaction should be low. Ethanol is mostly used due to its lower cost. However, higher conversion to biodiesel could be achieved by using methanol. Glycerol and the biodiesel itself are the products of the transesterification reaction

2. MATERIALS AND METHODS

Waste cooking oil, which has been reused again and again mostly for deep frying, was obtained from roadside food stalls, street sellers and dhabas. This oil needs to be treated before conversion to biodiesel to remove impurities.

Chemicals and reagents used:

Ethanol, methanol, toluene, phenolphthalein, sodium hydroxide, hydrochloric acid, potassium iodide, thiosulphate, iodine, chloroform and potassium hydroxide have been purchased from Thermo Fischer Scientific India Pvt. Ltd. (Mumbai, India) and Central Drug House Pvt. Ltd. (Mumbai, India).

Conversion of waste cooking oil to biodiesel by acidic-transesterification method:

The acidic transesterification was done by using methanol – toluene as a reagent for biodiesel production from the inedible oil. About 5 g ofoil was dissolved in 2 ml of toluene, then to this 15 ml methanol has been added, further followed by the addition of 3 ml of methanol – hydrochloric acid mixture. After addition of all the chemicals and reagents the mixture was vortexed for 2-3 minutes and kept for incubation for 24 hours at 45ºC in an incubator shaker. After incubation, the upper yellow layer containing biodiesel has been extracted by the addition of distilled water and toluene until the lower layer becomes colourless and clear. The transesterification reaction is said to be successful when it shows three different layers-upper yellow layer which contains biodiesel, middle cloudy white layer which contains glycerol content and the third clear layer of distilled water.

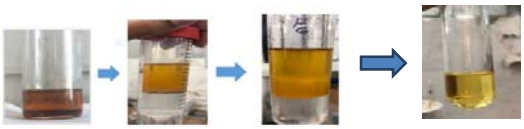


Figure 1: FAME and Glycerol layer separation after acidic-transesterification of waste cooking oil

Determinationof physicalproperties:

- **Smell, colour and physical state: -** All these physical properties like odour, colour and physical state of the waste cooking oil sample or biodiesel samples can be identified through sensory evaluation.
- **Specific gravity: -** Specific gravity expressed the density of a substance to that of water around 15ºC. Specific gravity can also be evaluated by using hydrometer.

Determinationof chemical properties:

- **pH:** The pH of the sample is determined with the help of a pH probe.
- **Free fatty acids and acid number:** The free fatty acid content and acid number were expressed according to the AOCS method. Weighed around 1g of filtered oil sample into a conical flask then 95% ethanol and few drops of phenolphthalein indicator were added into it. The content of the flask was heated to 70ºC for first bubbling and then titrated with NaOH. The ethanol gets neutralised by the addition of sodium hydroxide till a light pink colour appeared. Now this sample was titrated against sodium hydroxide until a permanent pink colour persists for at least 30 seconds during the titration. The acid number and the free fatty acid content can be calculated using the following formulae:

Free fatty acid (FFA %) = (28.2 × V × N)/weight of the sample

Where,

V= Volume of NaOH consumed

N= Normality of NaOH

- **Acid number** (mg NaOH/g) = 1.99 × FFA(%)
- **Iodine Value:**The iodine value was calculated using the AOAC official method. Two conical flasks were taken. One flask with the 1g of oil sample and the other flask without the oil sample as control were taken. Now add about 15 ml of Wij'ssolution and 10ml of chloroform in both the conical flasks and then keep the flasks in dark for around 1 hour at normal room temperature. After 1 hour, 10 ml of 10% KI was added in both the conical flasks. The solutions in both the flasks were titrated with against standard sodium thiosulphate till the colour of the solution becomes pale yellow. 2 ml of freshly prepared starch solution was added and then the titration was continued until the dark blue colour of the solution disappeared and the solution becomes colourless. The following equation can be used for the calculation of iodine value:

  Iodine value = (B – S) × N × 12.7 /W

  Where,

  B = Titre value of blank (ml)

  S= Titre value of the sample (ml)

  N= Normality of the hypo

  W= weight of the oil taken (g)

- **Refractive Index:** Abbe's refractometer was used to measure the refractive index of the samples just by placing the 1-2 drops of sample on the surface of the prism.

Cetane number: Cetane number of a fuel sample is derived as the percentage by volume of normal cetane in a mixture of α-methyl naphthalene and normal cetane which has the same ignition characteristics (ignition delay) as the test fuel (biofuel produced), when combustion is carried out in a standard engine under specified operating conditions. It was calculated with earlier two values obtained from saponification value and iodine value. The cetane number was calculated using the following equation:

Cetane number = 46.3 + 5458/SN – 0.225 × IV

Where,

SN is saponification number and IV is Iodine value.

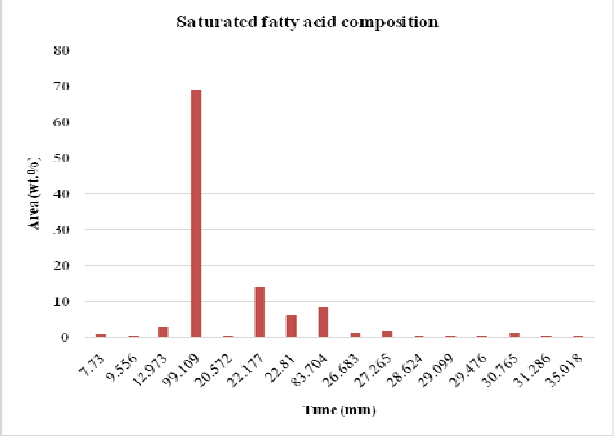
Gas chromatography-mass spectrographic analysis:

GC-MS analysis of the FAME sample obtained by acidic-transesterification of waste cooking oil was done which shows the different fatty acid peaks of biodiesel produced. A graph from the GC-MS data was plotted which showing fatty acid composition of biodiesel produced from waste-cooking oil.

3. RESULTS AND DISCUSSION

Physical and chemical properties

- The colour of the waste cooking oil changes from dark brown to golden-yellow.
- The obtained biodiesel had faint fuel like smell.
- Physical state of FAMEs obtained was liquid and transparent whereas waste cooking oil is muddy liquid and not transparent.
- The specific gravity of FAMEs was found to be 0.894 g/ml and that of the oil taken is 0.857 g/ml.
- The pH is 7 i.e., neutral for the waste oil taken and the pH was recorded as 8.9 after acidic-transesterification.
- Free fatty acids content expressed the amount of oils and fats and as the fatty acid chains breaks into smaller chains, the value of free fatty acids increases. The free fatty acid value of FAME and waste cooking oil was found to be 0.315% and 0.658% respectively.
- Acid number of FAME and waste cooking oil was found to 0.62 mg NaOH/g and 1.30 mg NaOH/g respectively.
- Refractive index determines the low degree of unsaturation. The refractive index of FAME and oil samples was found to be 1.481 and 1.469 respectively.
- Iodine value identifies the presence of unsaturated fatty acids or the number of double bonds in the oil. In this study, iodine value of waste cooking oil and FAMEs sample were found to be 12.14 g I^2/100g and 22.01 g I^2/100g respectively.



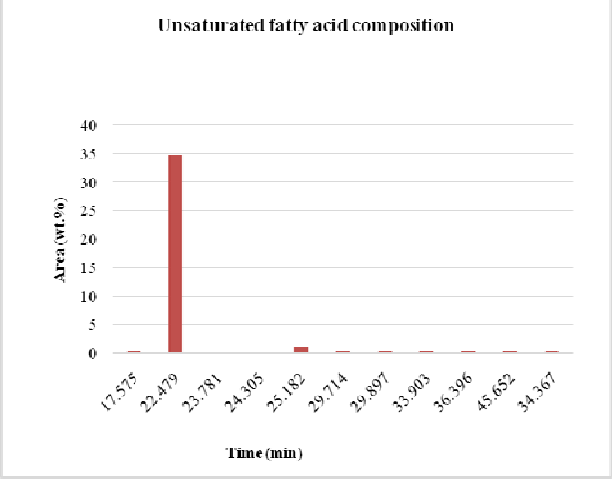


Figure 2: Fatty acid composition (FAMEs) as determined by GC-MS analysis of biodiesel produced from waste cooking oil by acidic-transesterification method

From the above graph, we conclude that unsaturated fatty acids, mostly oleic acid were present in large amount as compared to the saturated fatty acids which indicated that FAMEs obtained were appropriate and formation of biodiesel by acidic-transesterification process takes place.

4. CONCLUSION

GC-MS analysis results tell us about the presence of FAME profile. Presence of saturated and unsaturated fatty acids in a sample was determined with the help of GC-MS characterization. Physical and chemical properties of the FAME samples were recorded and compared with the ASTM standard values. In this present study, biodiesel produced from waste cooking oils was characterized for its physical and chemical properties and to determine its feasibility as a feedstock for biodiesel production. The FAME profile and physio-chemical properties of biodiesel reported in this study showed that refractive index, specific gravity and acid value are within the range of ASTM standards. However, some parameters such as FFA value and cetane value were slightly lower than compared to ASTM standard and parameters such as pH value were higher than the ASTM standard. Slight optimization during biodiesel production may be implemented to enhance fuel properties. Unsaturated fatty acids were found to be more in comparison to the saturated fatty acids.

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Table 1: Comparison of different physical and chemical properties of biodiesel produced from waste cooking oils by acidic-transesterification method with other reported sources

Properties	Min/max value (ASTM standards)	Biodiesel from acidic transesterification of waste cooking oil (this study)	waste cooking oil (this study)	Crude salmon oil (Dave et al. 2014)	Jatropha curcus oil (Sarker 2016)
Physical state	-	Transparent liquid	Muddy liquid	Clear liquid	Liquid
Colour	-	Golden-yellow	Dark brown	Orange	-
Specific gravity	0.87-0.90 g/cm^3	0.894 g/cm^3	0.857 g/cm^3	0.921 g/cm^3	-
pH	7	8.2	7	6.8	7.8
Iodine value	<120 gI^2/100g	20.01 gI^2/100g	12.14 gI^2/100g	116.79 gI^2/100g	94 gI^2/100g
Free fatty acid	<2.5%	0.315%	0.658%	1.23%	-
Acid value	<0.8 mg KOH/g	0.62 mg NaOH/g	1.30 mg NaOH/g	2.441 mg KOH/g	-
Refractive index	1447-1.48	1.48	1.469	1.47	-
Cetane number	>47	41	-	49.39	38