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Microwave-based Transesterification of Waste Cooking Oil using Waste Aluminium Foil (NaOH/γ-Al_2O_3) as Catalyst

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In present study, the waste aluminium foil a menace to the environment and human health has been converted into catalyst. The prepared catalyst NaOH/γ-Al_2O_3 (3% by wt. of oil) has been used to transesterify waste cooking oil (WCO) in combination to methyl alcohol (CH_3OH) having a methyl alcohol to oil molar ratio of 15:1 for a reaction time of 1 hour in microwave based processor. The effect of different process affecting constraints such as catalyst amount, reaction temperature/time, the molar ratio of methyl alcohol to oil are also studied. The bio-diesel yield has been recorded as 98% and the physicochemical properties of bio-diesel found in reasonable agreement with ASTM bio-diesel standards.

Keywords: Biodiesel, Waste aluminium foil, Microwave, Transesterification

1 Introduction

The economic growth of the world is being severely hurt as fuel prices are rising high due to the high rate of fuel consumption and depletion of fossil fuel reserves with time. The uncertainty in the availability of fossil fuel is another concern which initiated the efforts for a search of alternative fuel. Rudolf Diesel, the father of the diesel engine, was first to use the engine to run on groundnut (peanut) oil in the year 1893 for farmers having a source of vegetable oil readily available. The high viscosity of the vegetable oil makes it not suitable to use directly in the internal combustion engine. There are various methods to reduce the viscosity of oil like mixing vegetable oil with diesel, thermal cracking, micro-emulsions and transesterification. Transesterification method is the best method to lower the oil viscosity and producing bio-diesel[1]. Therefore, an alternative fuel like bio-diesel becomes a necessity of the time for the energy security necessary for the economic development of a nation[2].Bio-diesel is biodegradable, sustainable and discharges fewer amounts of greenhouse gases. In Figure 1, unlike the petro-diesel, the oxygen content in the molecular structure of bio-diesel is 10-15%[3] which fastens the combustion process in compression ignition engines with less or nil emission of pollutants like oxides of Sulphur, oxides of Carbon and particulates[4-6]. The cetane value of bio-diesel is higher than diesel due to which ignition delay is smaller. The higher lubrication properties of bio-diesel reduce wear of the fuel injection pump and injectors resulting in an increased life[7]. The flashpoint of bio-diesel (100-170°C) is higher than petro-diesel oil (60-80°C) making it safe in storage, transportation and handling[8]. Thus, bio-diesel seems to be a better alternative substitute to petro-diesel fuel.

Bio-diesel has been vegetable oil/animal fat-based fuel composed of a long chain of fatty acid alkyl esters. Bio-diesel has many remarkable and favourable advantages over the other internal combustion engine fuel alternatives due to its physical characteristics very close to those of petro-diesel fuel and the production process is relatively easy and simple[9]. In addition to this bio-diesel can be ignited directly in conventional unmodified compressed ignition engines, with least deposition[10]. The viscosity of vegetable oil has been high enough to make it not

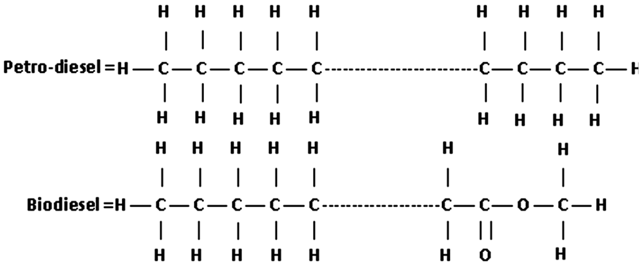

Fig. 1 — Dissimilarity in molecular structure of bio-diesel and petro-diesel.

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*Corresponding author (E-mail: naveengarg452@gmail.com) suitable to use in CI engines. Therefore, the viscosity of the oil is reduced by the transesterification reaction using methyl alcohol[11]. In addition to that, the properties of bio-diesel nearly similar to diesel fuels. According to ISO norms, bio-diesel is characterized by its properties like specific density, viscosity, cetane number, pour / cloud points, ignition points and high heating value (HHV) etc.

In the transesterification process, triglyceride in vegetable oil reacts with ethanol/methanol in the presence of alkaline catalysts as shown in Fig. 2. The use of a different type of catalyst in the transesterification reaction is a deciding factor in the conversion of triglycerides into bio-diesel. So the different types of catalysts are experimented to convert triglycerides into bio-diesel fuel. In general, there are two types of catalysts used to catalyze transesterification reaction i.e. homogeneous and heterogeneous catalysts. KOH and NaOH are popular base homogeneous catalysts soluble in methanol that give a higher yield of bio-diesel in transesterification reaction. But it generates a huge quantity of wastewater required for water-washing to neutralize and separate the catalyst from the methyl esters (bio-diesel). The byproduct of reaction i.e. glycerol is also obtained of poor quality due to the presence of water. These problems are easily rectified with the use of heterogeneous catalysts in the reaction due to its insolubility in methanol. The heterogeneous catalysts can be separated from the product of the reaction very economically. The recycling and reusability of the heterogeneous catalysts further make it more suitable than homogeneous catalysts leading to lower cost of production.

2 Materials and Methods

The vegetable oil after repeated frying becomes nonedible, is referred to here as waste cooking oil (WCO). On repeated frying of oil, total polar compounds (TPC) is formed in oil and the toxicity of TPC leads to diseases like hypertension, Alzheimer's diseases[12] and liver disease. A huge quantity of WCO is produced by caterers all over the world. Therefore it is essential to check the quality of vegetable oil during repeated frying[13]. As per the Food Safety and Standards Authority of India (FSSAI), the Total Polar Compounds (TPC) in vegetable oil should not be more than 25%. From 1st Jul 2018, all Food Business Operators (FBO) are required to monitor the quality of vegetable oil and comply with the regulations. In this work, WCO was collected from reputed caterers in kamla nagar, Delhi. WCO contains moisture and food particles. Food particles were removed by filtering through sieves and moisture was removed by heating the oil to 120°C. The WCO was then cooled and kept in an airtight glass container after filtration. FFA, iodine value, saponification, value, etc. of WCO were determined and recorded in table 1 by using standard methods. The Aluminium food wrap foil discarded from the lunch box was collected from local offices and educational institute, DTU in Delhi. The foil was used to convert into the catalyst required for the transesterification of WCO.

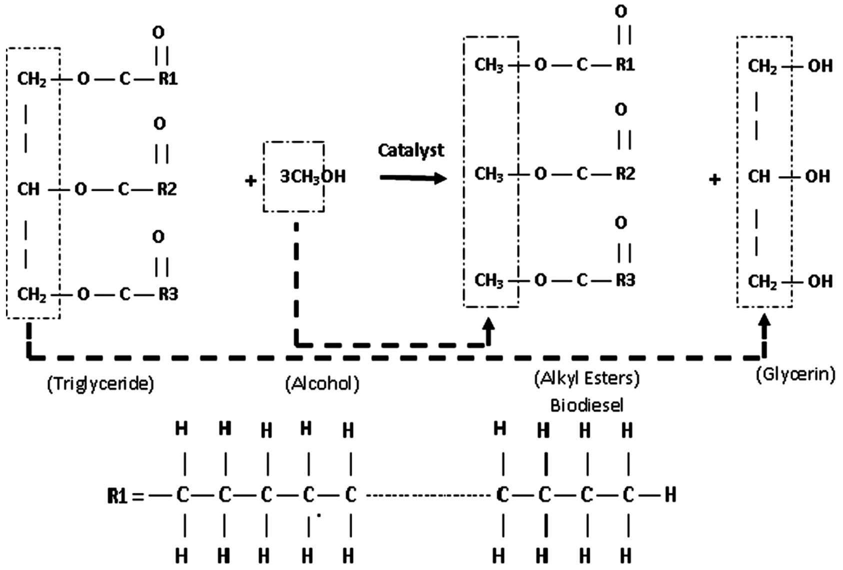

Fig. 2 — Transesterification reaction using alcohol and catalyst.

Table1 — Properties of WCO

Properties	Measured Value
Kinematic viscosity @ 40°C	51.5 mm^2/s
Acid Value	5.4 mg KOH/g
Iodine number	58.7 g I_2/100g
Saponification Value	203.7 mg KOH/g
FFA	1.04%

2.1 Catalyst from waste aluminium foil

Aluminium foil is emerging out as one of the most consumed aluminium products across the world due to its versatility and multiple uses. The demand of Aluminium foil may rise to 6.4 MMT by 2020. As per Aluminium Foils Market intelligence, aluminium foil is also used in the packaging of beverages and other liquids whose demand is also expected to grow at 4-5 percent by 2022. Growth in the consumption of aluminium foil is increasing due to the change in lifestyle and food habits. The high demand for ready to eat confectionaries and pharmaceutical products is also a reason for the growth of the aluminium foils industry. As per aluminium association, out of total aluminium foil produced in the world, more than 75% is used for food packaging which ends up in the local landfills Fig. 3.

The aluminium producing industries are optimistic to recover and recycle aluminium from the used foil. They want to get back all of the used metal at the expense of less energy than that is required to produce the pure metal. Industries are making significant efforts and investment to explore the different ways to recycle the aluminium from foil over several years. There are many companies in the world supplying the thin foils, used as laminates in drinks cartons. They have carried a feasibility study that shows the possibility to remove the aluminium from laminating material and return the used aluminium to produce more foil.

Aluminium oxide (Al_2O_3) known as alumina, is a compound of aluminium and oxygen. The oxides of aluminium are good in hardness, chemical inertness, high melting point, resistance to oxidation and corrosion, so broadly used in making ceramic refractory and abrasives[14]. The alumina as a catalyst is used in many chemical reactions. Aluminium oxide because of its properties like high dielectric constant, favourable thermal conductivity, excellent stability, low refractive index, and high hardness is used in electric batteries, thermal machinery, optics, and microelectronics. There are seven phases of polymorphs of transition alumina identified till now. These are named as phase γ (gamma), η (eta), δ (delta), θ (theta), χ (chi), κ (kappa), and ρ (rho). The phase-γ of transition alumina has a larger surface area in comparison to other phases and also has better structural stability. So it is widely used in industries for catalysis processes. The phase γ-alumina is formed conventionally by thermal dehydration of aluminium oxy-hydroxide above 450°C temperature. The γ-phase is a metastable phase which upon heating will form α-phase. The phase-γ of alumina is used as a catalyst in various processes due to its high surface area and mesoporous properties. Phase γ-alumina is usually used as a catalyst in various chemical processes such as ammonia synthesis, production of hydrogen gas, hydrogenation of oils, refining of petroleum, emissions control of automotive, etc.

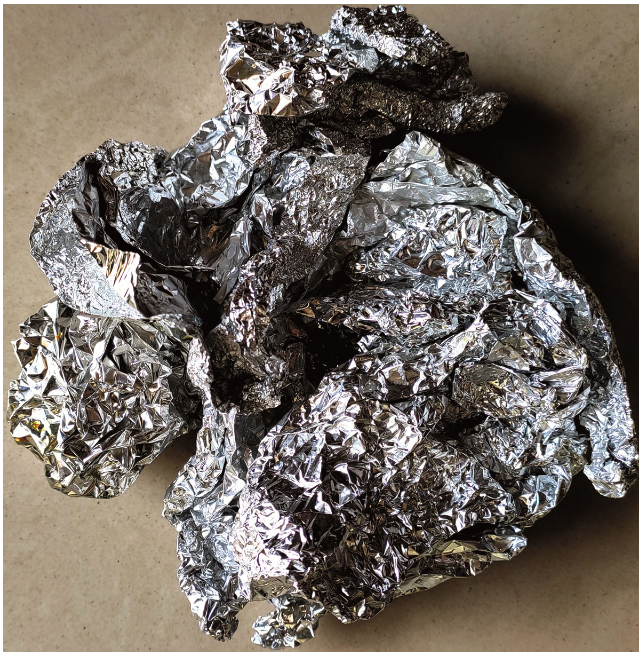

Fig. 3 — Waste Aluminium Foil.

2.2 Preparation of $AlCl_3.6H_2O$ from waste aluminium foil

Waste aluminium foil was cleaned using water and detergent to remove any dirt or oil. Dried foil was dissolved in a hydrochloric acid (HCl) solution containing 6 moles of hydrochloric acid. As aluminium being amphoteric, so can react with acid as well as with base. While reacting with acids, aluminium dissolves in hydrochloric acid to form solution of aluminium chloride and colourless gas hydrogen.

$$2Al + 6HCl = 2AlCl_3 + 3H_2$$

Aluminium chloride solution is kept for drying under desiccators to form crystalline aluminium chloride hexahydrate ($AlCl_3.6H_2O$). These crystals were dissolved in distilled water and the solution is filtered to remove any soluble chloride. The solution is again dried to re-crystallize. The process of purifying the crystal is done 2-3 times. The complete removal of chloride was verified by adding a drop of silver nitrate ($AgNO_3$) in the sample of the solution. The presence of any chloride content will be indicated by a turbid solution. Finally, pure $AlCl_3.6H_2O$ is obtained.

2.3 Preparation of catalyst γ-Al_2O_3 from $AlCl_3.6H_2O$

The obtained precipitate of aluminium chloride hexahydrate was dispersed in distilled water. The pH value of the solution was regulated with ammonia solution NH_4OH drop by drop. The solution was stirred continuously at a speed of 200 rpm with a magnetic stirrer.

$AlCl_3(aq) + 3\ NH_4OH(aq) \dashrightarrow Al(OH)_3(s) + 3NH_4Cl\ (aq)$

The pale off-white precipitate of $Al(OH)_3$ was filtered, washed, and dried at 120°C. The substance was further calcined at 500°C and 600°C for a period of 2 hours in a muffle furnace to obtain γ-Al_2O_3.

2.4 X-Ray diffraction analysis

The crystalline phase was verified using X-ray diffraction (XRD) patterns, obtained with CuK radiation of λ = 1.54 A° in 2θ range varying from 20° to 80° at room temperature as shown in Fig. 4 and Fig. 5. The diffractograms for the samples at a calcination temperature of 500°C and 600°C have shown three distinctive reflections of 311, 400 and 440 at angle 2θs of 37.2°, 45.6°, and 66.8° respectively. These reflections are found in line with the gamma Al_2O_3 standards. The further increase in the calcination temperature did not have any effect in the position of peaks, therefore indicating no further change in the structure of γ-Al_2O_3.

2.5 Preparation of catalyst γ-Al_2O_3/NaOH/Na

The catalyst was prepared by employing the impregnation method using phase γ-Al_2O_3 and a solution of sodium hydroxide. The phase γ-Al_2O_3 was impregnated with 15 ml of sodium hydroxide solutions (50 wt.%). This impregnated γ-Al_2O_3 was then dried at a temperature of 120°C. The catalyst was then calcined at 650°C for 2 hours.

2.5.1 Transesterification of waste cooking oil (WCO)

a) A WCO sample was collected in a glass beaker. To eliminate any solid contaminants, it was filtered with a clean cloth. To eliminate any moisture existing in the oil, the oil was heated to 105°C. The oil was then allowed to cool to 60°C before being treated further.

b) The catalyst (γ-Al2O3 / NaOH) powder (3 % by weight of oil) was stirred in a molar ratio of 15:1 with heated methyl alcohol (CH_3OH) and poured into the glass beaker carrying oil.

c) 100 gm WCO sample was transferred to a round bottom flask. It has been treated with a CH_3OH solution and the prepared catalyst. The reactant mixture in the flask was treated in a microwave reactor[15]. The reaction temperature was recorded at 60°C. Throughout the reaction, the solution was constantly agitated. The speed of the turntable stirring was kept constant at 5 rpm throughout the process.

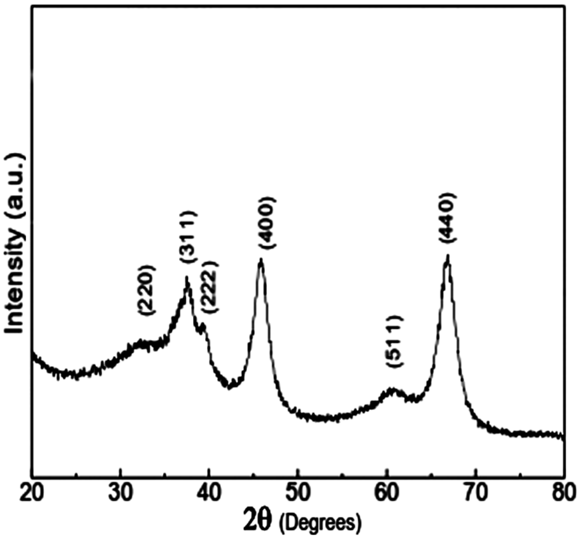

Fig. 4 — XRD pattern of γ-Al_2O_3 calcined at 500°C.

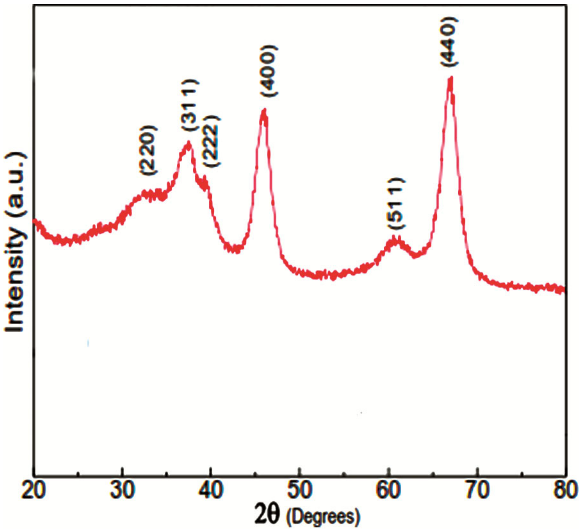

Fig. 5 — XRD pattern of γ-Al_2O_3 calcined at 600°C.

d) To avoid alcohol boiling, the reaction temperature of the solution was not allowed to increase over 60°C. The procedure was repeated for 60 minutes.

e) The reaction catalyst was removed from the reaction product. The remaining solution was allowed to settle in a separate funnel. The reaction products, bio-diesel, methyl alcohol, and glycerin, were separated based on their specific weight.

f) Because bio-diesel and methyl alcohol are lighter in weight, they settled on top of the solution, leaving glycerin at the bottom. The distillation procedure was used to extract the methanol from the bio-diesel.

g) Bio-diesel's physicochemical qualities were investigated. The bio-diesel's specific gravity (0.8849) and density (0.884 gm/cm^3) were determined using the DMA 4500 (Anton Paar) instrument, which was found to be in fair compliance with ASTM bio-diesel specifications. The product's kinematic viscosity was also determined to be 5.694 centistokes using a Stabinger Viscometer.

3 Results and Discussion

3.1 The Effect of Methanol/oil Molar Ratio

The molar ratio has been the most important element in the transesterification reaction, influencing both the bio-diesel output and the production cost. Three moles of methanol react stoichiometrically with one mole of triglyceride to form three moles of fatty acid methyl ester and one mole of glycerin. Because the reaction is seen as being reversible in nature, an excessive amount of methanol was required to drive the reaction towards the product side. The use of an excessive quantity of methanol in the process may increase the cost of bio-diesel, therefore it became critical to determine the ideal molar ratio to limit production costs. The addition of the methanol-oil molar ratio increased the bio-diesel output, as seen in the Fig. 6. A molar ratio of 15:1 produced the highest output. When the molar ratio exceeded 15, the yield % declined. This might be owing to an incomplete reaction and residual glycerol in the bio-diesel form.

3.2 The Effect of Catalyst Amount

The impact of catalyst loading on the reaction has been investigated. The method was evaluated by adjusting the amount of catalyst from 1 to 5 (wt%) of oil weight, and the effect on bio-diesel yield is shown in Fig. 7.

The yield increased when the catalyst was increased from 1 to 3 (wt %). A further increase in the amount of catalyst has lowered the yield. The addition of catalyst apparently made the liquid viscous enough to minimise the likelihood of reactants coming together for the reaction.

3.3 Reaction Time's Effect

For different samples, the reaction time ranged from 5 to 90 minutes. It was discovered that with a reaction period of 60 minutes, a maximum yield of 98 % was achieved. There was no apparent increase in yield afterwards.

3.4 The influence of Reaction Temperature

The transesterification reaction gets influenced by the reaction temperatures. The temperature of the reaction may vary depending on the type of alcohol and catalyst used. Figure 8 illustrates an example of the mixture prepared at five different temperatures. It can be noticed that the yield was decreased at a lower

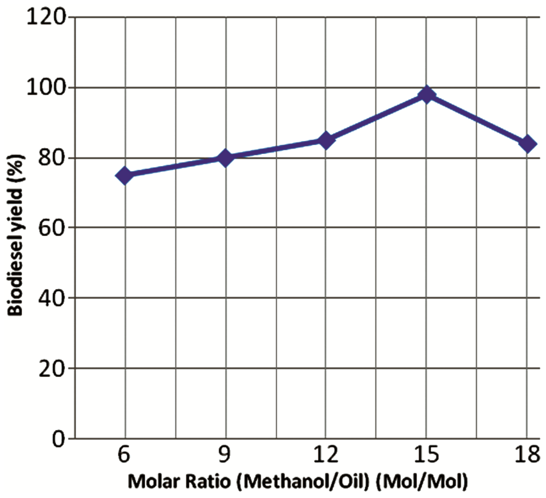

Fig. 6 — Impact of the molar ratio on yield.

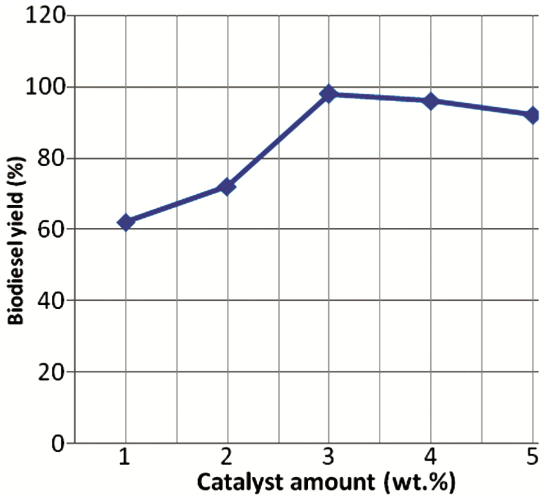

Fig. 7 — Impact of the catalyst on yield.

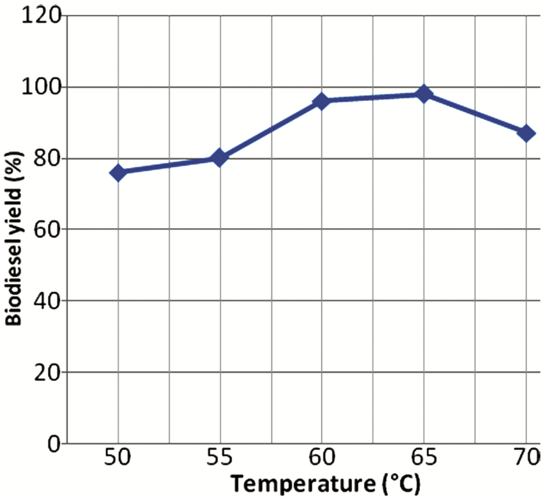

Fig. 8 — Impact of reaction temperature on bio-diesel yield.

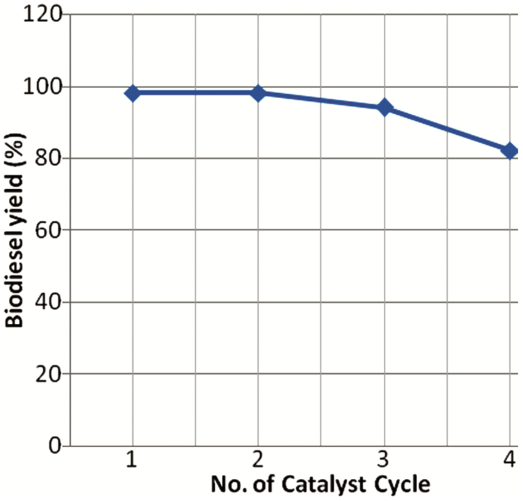

Fig. 9 — Reusability of catalyst.

temperature range of 50-55°C due to mass transfer and solubility issues.

The viscosity of the mixture was found to be reduced at higher temperatures, which is sufficient to increase the kinetic energy of the reactant and provide good mass transfer between oil and methanol to improve yield. The highest yield was found at reaction temperatures ranging from 60 to 65°C. Methanol began to boil at around 65°C, and methanol evaporate from the mixture, lowering the molar ratio and resulting in a reduced bio-diesel yield.

3.5 Reusability of catalyst

The cost of producing bio-diesel has been a determining element in bio-diesel manufacturing technologies. The cost of production can be lowered to some extent by reusing the same catalyst. The recovered catalyst γ-Al2O3 / NaOH has been washed with n-hexane and calcined again at 650°C temperature.

In the same experiment, the utilised and rejuvenated catalyst was employed in four successive transesterification reactions with similar regeneration strategies. No substantial loss of catalytic activity was seen in the first three consecutive uses of the catalyst, while catalytic activity was observed to be lowered in the fourth run of the experiment, as shown in Figure 9. This reduction of catalytic activity could be owing to the absorbed organic molecule blocking active sites on the catalyst surface, resulting in less surface area accessible for the reaction site.

3.6 Bio-diesel Properties and Their Significance

The characteristics of bio-diesel are mostly determined by the quality of the feedstock and the amount of free fatty acid present in it. In the laboratory of Delhi Technological University, the bio-diesel made from WCO has been tested for its chemical and physical attributes. As demonstrated in Table 2, the sample satisfies the ASTM D6751 standards.

Table 2 — Properties of bio-diesel produced

Parameter	Measured Value
Calorific Value	39MJ/kg
Flash point	146°C
Pour point	6°C
Kinematic viscosity @ 40°C	4.5 mm^2/s
Density at 30°C	0.884 g/cm^3
Specific gravity	0.8849
Acid value	0.77 mg KOH/g
Iodine number	86.4 g I_2/100g

The flash point would be a critical factor in the safe storage and handling of bio-diesel for fire safety. The minimal temperature at which the vapour of a liquid fuel forms an ignitable composition when mixed with air and produces a short flash in the presence of a small flame has been defined as the flash point. The flashpoint of bio-diesel produced in this study was determined to be 146°C, which is greater than the flashpoint of petro-diesel fuel (52 to 96°C)[16]. The pour point of fuel determines its ability to flow in the engine at lower temperatures. Fuels with a high pour point should not be used in engines at low temperatures[17]. When subjected to external forces, a fluid's resistance to flow is caused by internal friction. The viscosity of the fuel influences its atomization (spray properties and droplet volume). For the fuel injection system to function properly, the kinematic viscosity of the fuel should be close to that of petro-diesel[18]. At 40°C, the kinematic viscosity of the bio-diesel produced in this investigation was determined to be 4.5mm^2/s. Bio-diesel with a higher density consumes more fuel, resulting in higher nitrogen oxide emissions. The higher the acid value of the fuel, the more likely it is to induce corrosion in the engine's fuel supply system. The acid value in this investigation was 0.77 mg KOH/g, which was close to the ASTM D-6751 norm of 0.8 mg KOH/g. The iodine number represents the occurrence of double bonds in bio-diesel, indicating the extent of unsaturation[19]. The iodine number has an effect on the oxidation stability of bio-diesel.

4 Conclusions

- Waste aluminium foil has been effectively employed to create a heterogeneous catalyst γ-Al_2O_3.
- The catalyst has been utilised to convert WCO into methyl ester, and a maximum yield of 98% is reached utilising a catalyst amount of 3 wt. %, a molar ratio of 15:1, and a reaction temperature of 60°C for 60 minutes.
- The catalyst has been optimally reutilized multiple (four) times in the bio-diesel conversion process.
- The microwave centred transesterification along with waste aluminium foil based catalyst has been effectively used to synthesize bio-diesel from WCO.
- The cost of bio-diesel production can be reduced to great extent by combination of microwave centred transesterification along with waste aluminium foil based catalyst and WCO.

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