Production of Biodiesel from a Low-Grade Second- Generation Oil Using Heterogeneous Catalyst - Waste to Energy Conversion

Dr. T KALYANI[1], Dr. P VIJAYA KUMAR[2], K. DURGA GOUTAM[3], B. PRADEEP[3], K.S.M GOPI[4], P. BHASKHAR RAO[5], U. SAMPATH SAI SURYA[6].

[1,2] Faculty, Department of Mechanical Engineering, Raghu Engineering College(A), Visakhapatnam, Andhra Pradesh 531162, India.

[3,4,5,6] Student, Department of Mechanical Engineering, Raghu Engineering College(A), Visakhapatnam, Andhra Pradesh 531162, India.

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Abstract - In this study, an attempt is made to produce biodiesel from waste cooking oil (WCO) via a transesterification process. Furthermore, a heterogeneous catalyst is prepared from the waste orange peel (WOP) extract by calcination at 600 °C for 120 minutes. Using transesterification process the waste cooking oil biodiesel (WCOBD) was obtained and the maximum yield achieved was 91.1%. The significant fuel oil properties such as viscosity, density, flash point, fire point, calorific value, cloud, pour points were determined. The results show that neat waste cooking oil biodiesel (WCOBD) biodiesel and diesel-biodiesel blend (B20) fuel oil properties are in close agreement with the ASTM standards. A cost estimation was conducted for the preparation of waste cooking oil biodiesel. Therefore, the cost analysis of waste cooking oil biodiesel was low than the standard diesel fuel cost. Thus, the waste cooking oil biodiesel could be used as a fuel in the existing diesel engine, an option to replace the fossil fuels.

Key Words: Waste cooking oil biodiesel, Heterogeneous Catalyst (HC), Waste Orange Peel, Transesterification

1. INTRODUCTION

Biofuels are fuels produced from biomass, which encompasses a wide range of sources including agricultural crop residues, forestry biomass, energy crops, livestock manure, municipal solid waste, sewage sludge, industrial effluents, and other organic waste streams. These waste materials are rich in organic matter that can be converted to fuels through a variety of thermochemical and biochemical technologies.

Unlike fossil fuels, biofuels are renewable because they are derived from organic materials that can be replenished over time. They are often promoted as cost-effective and environmentally friendly alternatives to fossil fuels. The development of biofuels is categorized into four generations, based on the feedstock used for their production: first, second, third, and fourth, each representing advancements in technology and sustainability [1].

Since the discovery of fire, humans have been utilizing biofuels Due to a significant rise in the number of cars and the depletion of global petroleum reserves, there is now a high demand for petroleum products. This has led the world to explore alternative sources of energy due to an increase in energy demand over the past two decades. India, as a developing nation, is looking to produce bio-diesel from non-edible oils that can be grown extensively in the country's wasteland. The use of bio-diesel has resulted in a decrease in carbon monoxide (CO), hydrocarbons (HC), and particulate matter (PM) emissions from vehicle exhausts. Biodiesel presents a capable substitute for traditional diesel oil. vegetable oils are a promising alternative to diesel since they are renewable and possess similar properties. Researchers have extensively studied the use of vegetable oils in diesel engines, which have yielded almost the same power output but with a slightly lower thermal efficiency. With the growing concern for environmental protection and increasingly strict exhaust gas recirculation regulations, reducing engine emissions has become a critical aspect of engine development research. Biodiesel made from Neem, Jatropha, Karanja, sunflower, rapeseed and other popular sources such as waste cooking oil, are currently being considered as substitutes for diesel.

Clean and renewable transportation fuels that are non-toxic, biodegradable, and eco-friendly can be used as neat fuels or blended with petroleum-based diesel in diesel engines. Among these, vegetable oils, waste cooking oils obtained the low-cost, second-generation biodiesels are considered as the most suitable alternative to diesel [2]. Diesel engines are known to have a harmful impact on the environment due to the high concentration of Sulphur and aromatics in their emissions.

The main objective of the present investigation is to produce biodiesel from waste cooking oil (WCO) using heterogeneous catalyst from waste orange peel (WOP) is considered an eco-friendly, non-corrosive, and reusable catalyst for producing waste cooking oil biodiesel (WCOBD). Heterogeneous catalyst especially WOP is also limited mooted this experimental investigation. Furthermore, the utilization of heterogeneous catalyst is checked and by using transesterification process the waste cooking oil biodiesels was prepared and finally the WCOBD is obtained. The biodiesel was blended with neat diesel fuel to examine the significant fuel oil properties such as viscosity, calorific value, flash point and fire point, as per the ASTM standards. Finally, the cost estimation was conducted to estimate how low the cost to produce waste cooking oil biodiesel.

2. ALTERNATIVE FUELS

Alternative fuels are defined as non-petroleum energy sources used to power transportation vehicles, which include options such as natural gas, ethanol, hydrogen, and electricity, aimed at reducing the reliance on petroleum-derived fuels. Alternative fuel is one of the widely used fuel substitutions for both petrol and diesel in the field of internal combustion engine Fig. 1. The increase in the demand for alternative fuel is currently driven by the requirement of decreasing engine fuel consumption and fulfilling the stringent engine exhaust emissions pollutant regulations [3].

In order to lessen the dependence of the globe on traditional fuels like petroleum, coal, and natural gas, alternative fuels are becoming more and more popular. The term "these fuels," often referred to as "non-conventional fuels" and "advanced fuels Key," refers to any chemicals or materials that can be utilised as fuel, but does not include nuclear materials like Other options for alternative fuels include bio-diesel, bio alcohol (methanol, ethanol, and butane), refuse-derived fuel, chemically stored electricity (batteries and fuel cells), hydrogen, non-fossil methane, non-fossil natural gas, and vegetable oil, in addition to uranium, thorium, propane, and other sources of biomass.

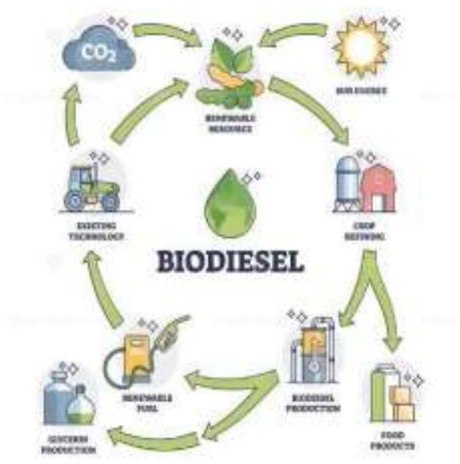

Fig - 1 Alternative Fuels

2.1 TYPES OF GENERATIONS

With the increasing use of fossil fuels, rising demand for energy, fluctuating fuel prices, and growing greenhouse gas emissions, a shift from fossil fuels to renewable fuels is more critical than ever. In this context, biofuels have emerged as a crucial component in reducing our reliance on fossil fuels. Derived from organic materials, biofuels are considered carbon-neutral because the CO_2 emissions from their combustion are absorbed by plants during photosynthesis, resulting in no net increase in atmospheric CO_2 levels. The use of biofuels, produced from renewable and biogenic materials, helps mitigate greenhouse gas emissions, meet growing energy needs, improve the overall energy efficiency of existing fuel systems, and create jobs in bio-based sectors.

Biofuels have been developed through four generations, each with distinct characteristics. This article explores the different types of first, second, third, and fourth generation biofuels, emphasizing their biomass sources, general characteristics, production processes, advantages, and disadvantages

2.2. BIO DIESEL SOURCES

Non-Edible Oil Seed Feedstocks for Production of Biodiesel

Non-edible biodiesel is a renewable fuel derived from non-food sources like Jatropha, Karanja (Pongamia), Neem, and waste cooking oils (WCO), avoiding competition with food supplies. Produced through transesterification, these oils are environmentally friendly, cost-effective [4], and suitable for diesel engines, though they often require high FFA treatment

2.2.1 Non-Edible Feedstock

Jatropha curcas (Ratanjyote): Grows in harsh conditions, widely used in tropical areas.
Pongamia pinnata (Karanja): Thrives in poor, saline soils.
Waste Cooking Oil (WCO): Economical and abundant, reducing waste.
Other Sources: Neem (*Azadirachta indica*), Rubber Seed (*Hevea brasiliensis*), Mahua, and algae.

Advantages and Characteristics

No Food Conflict: Uses crops grown on non-arable/wasteland.
Sustainability: Lower sulfur content and high biodegradability compared to petroleum diesel.
High Efficiency: High oil content in certain seeds allows for efficient conversion.

Production Process

Non-edible oils generally have higher Free Fatty Acids (FFA), necessitating a two-step process: esterification (to reduce FFA) followed by transesterification (using alcohol and a catalyst) to convert oil into biodiesel

Challenges

Higher Viscosity: Non-edible oils need significant reduction in viscosity to match diesel standards.

The utilization of these feedstocks is crucial for energetic independence and rural development, particularly in nations like India.

2.3 WASTE COOKING OILS

Waste cooking oil (WCO) is considered a significant feedstock for biodiesel production due to its availability and low cost. According to [8], a large quantity of edible oil is consumed globally for cooking purposes, and after usage, it is discarded as waste, which contributes to environmental pollution.

The improper disposal of WCO increases ecological problems, and its effective utilization is essential to address environmental and waste management issues.

Furthermore, the use of waste cooking oil as a raw material for biodiesel production helps in reducing production cost and supports sustainable energy development. As reported by Kolakoti and Satish (2020) [1], the use of low-cost feedstocks such as WCO, along with eco-friendly and reusable heterogeneous catalysts, can improve the economic feasibility of biodiesel production. Therefore, waste cooking oil is widely preferred as a second-generation biodiesel feedstock.

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3. MATERIALS AND METHODS

3.1. Materials

Waste cooking oil (WCO) was obtained from Raghu engineering college hostel canteen. Oranges were acquired from the fruit vendor. The chemical Methanol (CH_3OH) of analytical grade was obtained from Sigma-Aldrich chemicals, Visakhapatnam, India. The equipment's and apparatus used for the production of the biodiesel are conical flask, thermometer, retort stand, pipette, measuring cylinder, separating funnel, magnetic stirrer, feed stock, conical flask, drying equipment, stop watch, hot plate, catalyst waste orange peel (WOP), methanol, and waste cooking oil.

3.2 Methods

Steps in biodiesel production: the following steps are used in the production of the biodiesel are:

(i) Collection of waste cooking oil
(ii) Reduction of fatty acid
(iii) Catalyst preparation
(iv) Transesterification

3.2.1 COLLECTION OF WASTE COOKING OIL

Waste cooking oil (WCO) falls under second generation biodiesel, obtained from vegetable oils. The waste cooking oil, was obtained from the hostel canteen located at Raghu Engineering College which is obtained at a low cost Fig.2.

Fig – 2. Waste Cooking oil

3.2.2 REDUCTION OF FATTY ACID

The high concentration of free fatty acids (FFAs) in waste cooking oil makes difficult to produce biodiesel, due to the presence of high kinematic viscosity. To operate the biodiesel in engine, the kinematic viscosity value must fall under 5 (mm^2/sec). The raw waste cooking oil kinematic viscosity is > 5 (mm^2/sec), which is not suitable to operate in the diesel engine. This there FFAs have the potential to interact with the catalyst employed in the transesterification process, decreasing its efficiency and lowering biodiesel yields.

Several methods may be used to lower the FFAs in waste cooking oil. Esterification of acids: In this procedure, an alcohol, such as methanol, is reacted with an acid catalyst, such as sulfuric acid, to release the FFAs from the neem oil.

The FFAs are changed into esters as a result of the process, which may subsequently be transesterified into biodiesel with the aid of a base catalyst Pre - treatment: Prior to transesterification, the FFAs in neem oil can be converted into esters by pre-treating the substance with a catalyst such sodium hydroxide or calcium oxide. By doing this, you may be able to produce more biodiesel while producing less trash Enzymatic esterification:

Enzymes are used to catalyze the reaction between FFAs and alcohols to create esters in the enzymatic esterification process. Although this approach could be more costly than standard acid esterification, it might potentially be more ecologically friendly.

Blending: Another choice is to combine neem oil with a feedstock that has a lower FFA content, like soybean oil or canola oil. This can lessen the detrimental effects on the transesterification process and dilute the FFAs in the waste cooking oil. It's important to note that each of these approaches has pros and cons, and the best course of action may depend on elements like the accessibility of feedstocks, the cost of production, and the required level of biodiesel quality.

3.2.3 CATALYST PREPARATION

Catalysts play a significant role in biodiesel production, and two types of catalysts are widely used in the application.
Homogeneous and heterogeneous catalysts like sodium hydroxide (NaOH) and potassium hydroxide (KOH) give a better biodiesel yield during production [5] [6]. However, the homogeneous catalyst cannot be reused [7]. The comparison between homogeneous and heterogeneous catalyst was presented in the Table 1 below.

Table 1. Comparison of Homogeneous & Heterogeneous Catalyst

Homogenous catalyst	Heterogeneous catalyst
Advantages	Advantages
High selectivity	Excellent stability and easily accessible
High activites	Easily separable
High yield	Minmization of metal traces
Disadvantages	Disadvantages
Difficulty in production purification	Reaction time is more
Difficulty in catalyst recovery	Inferior catalyst performance
Many efficient systems cannot be ommercialized	Reduced efficiency

Heterogeneous catalysts emerged to overcome this challenge [3] Heterogeneous can be obtained from different potassium and calcium-rich materials, such as waste orange peel**,** waste chicken egg shells, banana fruit peel, sea shells, moringa leaves, Etc. This study uses the waste by-product of orange peel oil extract as a heterogeneous catalyst. The oil extract from discarded orange peels must be dried in a hot air oven for 24 hours to remove any moisture; after that calcination process is initiated to prepare the catalyst.
Calcination is a popular technique that helps improve chemical compounds by heating to high temperatures without melting and under a restricted supply of atmospheric oxygen.

In this study, orange peel extract is calcinated up to 600oC for 120 minutes, and the different stages of the calcination process are highlighted in Fig.3.

Fig -3. Preparation of waste orange peel catalyst using Muffle Furnace.

3.2 4 TRANSESTERIFICATION PROCESS

The aim of the transesterification process is to reduce the high viscosity of the oil without affecting its properties. There are different methods available to reduce viscosity. However, transesterification [9] is widely used and popularly known for an easy and high conversation of yield. Therefore, in this endeavor transesterification technique is employed.

The step-by-step approach used in the production of the biodiesel is given below.

The Waste cooking oil (WCO) obtained from Raghu engineering college hostel canteen and was heated up to 110 ºC. Initially, the raw (WCO) oil was collected in a conical flask and positioned on a magnetic heater with a hot plate.

Add the heterogeneous catalyst (calcinated waste orange peel) to the mixture. The amount of catalyst needed will depend on the quality of the oil and the amount of methanol used. Stir the mixture vigorously using a using a magnetic stirrer until the catalyst is completely dissolved. Heat the mixture to a temperature of around 60-70°C, depending on the catalyst used. The catalyst (CaO) was built up with an oxygen anion, which initiated to form a strong methoxide anion, thereby assisting the presence of triglycerides in the oil to transform diglycerides to monoglycerides.

Continue stirring the mixture for about 1-2 hours, or until the reaction is complete. The hot mixture of biodiesel and heavy glycerin was transferred into a separatory flask. The biodiesel was then poured into a separate beaker, while the lower layer was collected from the bottom of the separating funnel. Later, the glycerin was collected into a beaker, and the desired Waste cooking oil biodiesel (WCOBD) was obtained. Transfer the biodiesel to a clean container and wash it with distilled water to remove any remaining impurities.

Finally, neat biodiesel was produced by heating the washed biodiesel to a temperature of 100 ºC using a magnetic heater. Let the biodiesel dry for a few hours, then it will be ready to use. The experimental approach of biodiesel yield (%) was calculated using Equation 1.

$$\textbf{WCOBD } Yield \textbf{ (\%)} = \frac{Weight\ of \textbf{ waste cooking oil biodiesel}}{Weight\ of \textbf{ waste cooking oil}} \qquad \text{Eq 1.}$$

4. BLENDS MIXING

The biodiesel obtained was prepared for blends mixing of WCOBD 10 to WCOBD 100 and presented in Table xx.

Table 2: Composition Of Waste Cooking Oil Biodiesel (WCOBD)-Diesel Blend

Blend Name	Description
WCOBD 10	10% waste cooking oil biodiesel + 90% diesel
WCOBD 20	20% waste cooking oil biodiesel + 80% diesel
WCOBD 30	30% waste cooking oil biodiesel + 70% diesel
WCOBD 40	40% waste cooking oil biodiesel + 60% diesel
WCOBD 50	50% waste cooking oil biodiesel + 50% diesel
WCOBD 60	60% waste cooking oil biodiesel + 40% diesel
WCOBD 70	70% waste cooking oil biodiesel + 30% diesel
WCOBD 80	80% waste cooking oil biodiesel + 20% diesel
WCOBD 90	90% waste cooking oil biodiesel + 10% diesel
WCOBD 100	100% waste cooking oil biodiesel

Pictorial representation of the waste cooking oil biodiesel blends mixed with the diesel fuel are represented in the figure 4 below

Fig -4. Mixing of Blends (WCOBD10-WCOBD100)

5. CHARACTERIZATION OF WASTE COOKING OIL BIODIESEL

Thermal fuel properties of waste cooking oil biodiesel:

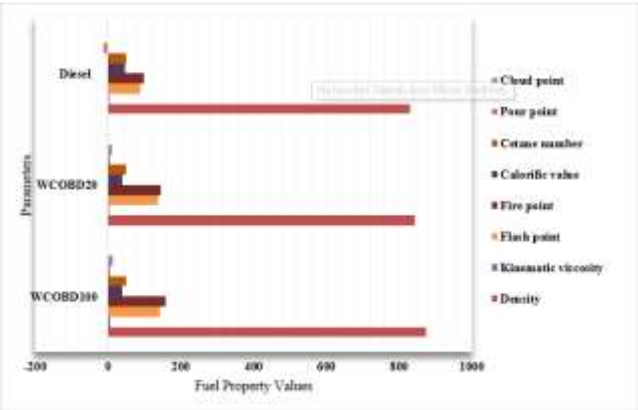
5.1.1 Kinematic Viscosity The internal resistance of a fluid to flowing under the influence of gravity is known as kinematic viscosity. It is calculated by timing in seconds how long it takes for a fixed volume of fluid to travel a specific distance by gravity via a capillary inside of a calibrated viscometer at a precise temperature.

5.1.2 Flash Point The lowest temperature at which a liquid (often a petroleum product) will produce a vapour in the atmosphere at its surface that will "flash," or momentarily ignite, when in contact with an open flame. The flash point is a broad indicator of a liquid's combustibility or flammability.

5.1.3 Fire Point: The temperature at which a mixture of vapour and air must be heated for the product to burn continuously under the parameters specified by the method is known as the fire point.

5.1.4 Density A substance's density is defined as its mass per unit volume (more specifically, the volumetric mass density; also known as specific mass). Although the Latin letter D may also be used, the sign most frequently used for density is (the lower-case Greek letter rho). Density is mathematically defined as mass divided by volume.

5.1.5 Calorific Value Calorific value, also known as heating value or heat of combustion, is a unit of measurement used to determine how much total energy is released as heat when a substance totally burns with air or oxygen. The table below displays the pure neem biodiesel's thermal fuel characteristics. The thermal fuel property values are presented in the graph 1.



Graph 1: Fuel Property Values

The results show that neat biodiesel and diesel-biodiesel blend (B20) fuel oil properties are in close agreement with the ASTM standards.

6. COST ESTIMATION

The production cost of the biodiesel is mainly dependent on the raw oil cost and the catalyst which are used in the transesterification process. The present study focusses on the raw oil which is available abundantly after their usage. An internal survey was conducted in the college campus regarding the availability of oil after their usage. It is observed that around 85 liters of oil per day is dumped. Hence, by using the WCO and waste orange peel (WOP) the overall production cost of the biodiesel was reduced. The cost of biodiesel is which is lower than the present diesel cost.

7. CONCLUSIONS

This study shows an effective way to use waste cooking oil for biodiesel production and heterogeneous catalyst preparation. The results show that the current energy and environmental challenges, especially non-conventional petroleum products, can be mitigated with renewable energy sources. From the experimental investigation, the following conclusions are illustrated.

- The catalyst was eco-friendly and can be reused.
- The important fuel properties are observed within the ASTM standards
- The waste cooking oil is successfully converted into waste cooking oil biodiesel with the transesterification process.
- The heterogeneous catalyst is prepared by calcination technique (heating up to 600°C 700°C)
- The cost analysis of waste cooking oil biodiesel was low than the standard diesel fuel cost.
- Hence, waste cooking oil can be considered as most suitable for biodiesel production and it will reduce the initial raw oil cost of the oil during the transesterification process.

Therefore, using Waste orange peel (WOP) catalyst for biodiesel production especially for waste cooking oils was economically cheaper and eco-friendly, also will promote sustainable biodiesel production.

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NOMENCLATURE

WCO	Waste Cooking Oil
WOP	Waste Orange Peel
WCOBD	Waste Cooking Oil Biodiesel
HC	Heterogeneous Catalyst
ASTM	American Society for Testing and Materials

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