

Utilizing Waste Cooking Oil for Sustainable Biodiesel Production: A Comprehensive Review

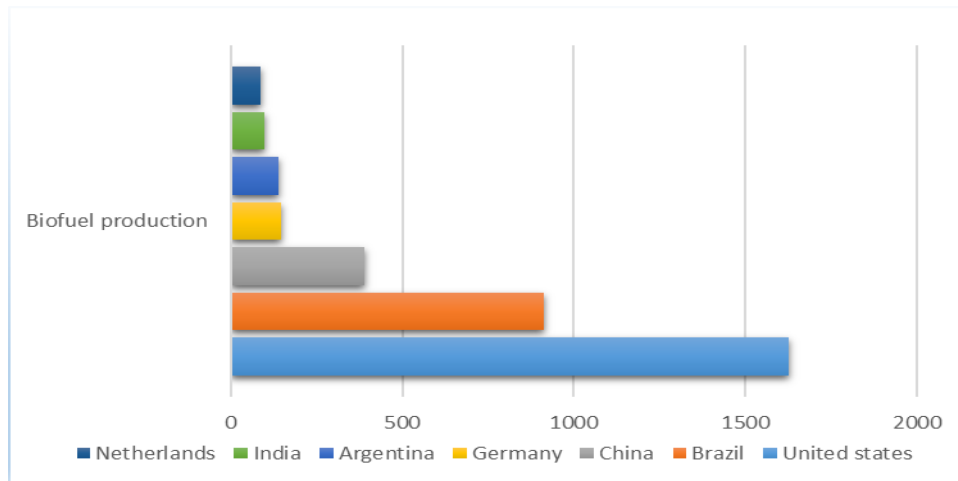
Abstract

The growing need for sustainable and eco-friendly energy sources has spurred research on alternative fuels, with biodiesel emerging as a viable contender. The current study focuses on turning used cooking oil—a commonly accessible but underutilized resource—into biodiesel. Transesterification, a proven technique for converting triglycerides into glycerol and biodiesel, is a part of the conversion process. The production of biodiesel includes key parameters such as reaction temperature, catalyst concentration, and reaction time to enhance biodiesel yield and quality. By turning a waste product into a valuable biofuel, using used cooking oil not only lessens the negative environmental effects of improper disposal but also supports the circular economy, lessens reliance on fossil fuels, and is in line with international efforts to create a more sustainable and environmentally friendly energy future.

INTRODUCTION:

Due to changes in the global environment caused by the high utilization of fossil fuel energy resources through **combustion** and depletion of resources, research has been shifted towards the production of alternate forms of fuel i.e., **BIODIESEL** production from waste vegetable oils, plants (Paratroop, castor, sunflower, etc) **(1)**. American Society For Testing and Materials defined biodiesel as “mono alkyl esters of long chain fatty acids that are derived from vegetable oil or used cooking oil” with an added requirement of having green house gas emission at least half of the baseline of green house gas emission **(5)**. India only produces 30-40% of total petroleum for its consumption and the remaining 70% is exported from other countries, which costs about 10,00000 million per year, this can be curtailed by replacing it with biodiesel **(2)**. Nearly one million species would become extinct if the global temperature accelerated above 1.5oC, in order to put a check over then, intergovernment pannel on climate change made the decision that there should be reduction of 40% of green house gas emission to sustain the increase in the global temperature. **(3,4)**. Used cooking oil can be used as a potential source of raw material for production of biodiesel, it consists of free fatty acids that reacts with alcohol and forms esters using relevant catalyst through transesterification process **(6)**. The combustion of fossil fuels increasing the the release of green house gases, ocean acidification, and sea level rise which is leading to climate change which is showing hazard impacts on agriculture. **(7)**. Petroleum refineries are the primary source of causing air, water and land pollution where they are constructed. They are also the major sources of air pollutants like Nitrogen oxide (NOx), Carbon mono oxide (COx), sulphur dioxide and

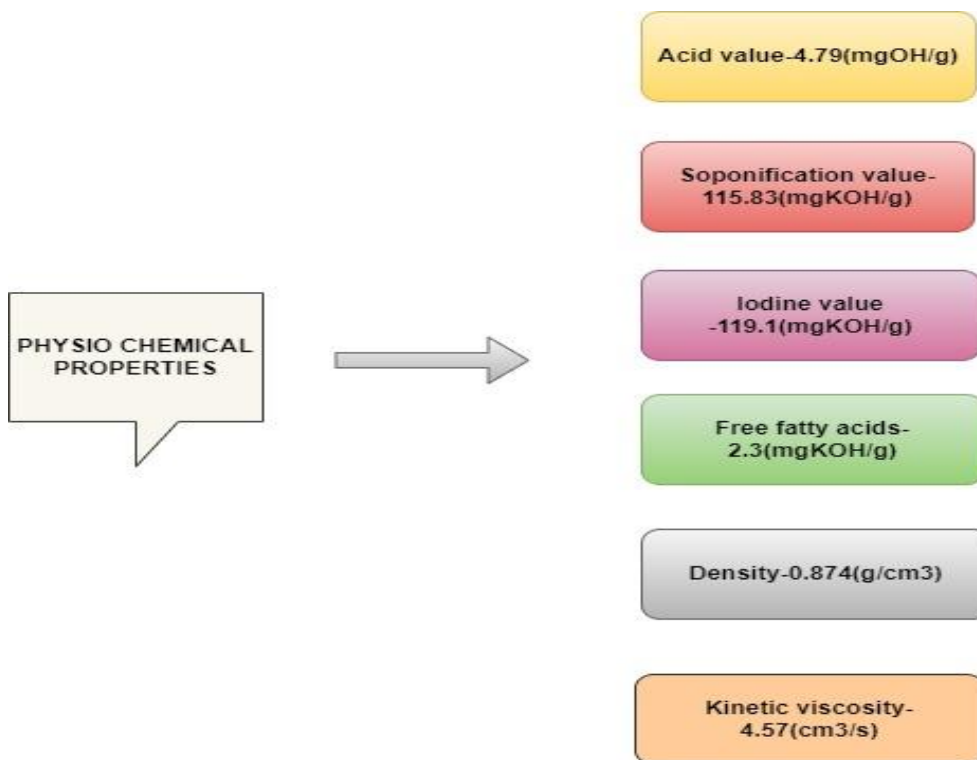
hydrogen sulphide, some of the chemicals released from these causes cancer , asthma and reproductive problems to the people. These refineries uses deep wells for depositing their waste into them but these deepwells with refinery waste waste water causes ground and surface water contamination.(8).Biodisel has become popular because it has environmental benefits compared to petrol and diesel because the biodisel made from plants and waste cooking oil which are renewable sources which cannot be replenished.



RAW MATERIALS THAT CAN BE USED FOR MAKING BIODISEL AND ITS PROPERTIES:

Biodisel has lower pollutant emission, biodegradable, enhances the engine lubricity and contribute sustainability (9,10).

NOTE: Cetane number indicates the measurement or quality of fuel. High the cetane number the better the fuel burns. No aromatics, Nosulphur, Contains 10-11% oxygen by weight , all these reduces the emission of green house gases (11).



Physio chemical properties of biodiesel

RAW MATERIALS:

1. WASTE COOKING OIL:

Vegetable oils produced from plants having vital use in manufacturing of soap, paints, varnishes, lubricants etc(18,19). Large amount of waste cooking oil is available throughout the world especially in developing countries, which will be discharged into lakes and rivers, management of these oils is difficult because of their disposable problem and contamination of land and water resources, some of the waste is being used in processing of soap but major portion of waste cooking oil is discharged into water which cause contamination of ground and surface water. 100 million gallons of waste cooking oil is produced per day in USA, where as average per capita of waste cooking oil is reported to be 9 pounds reported by Energy administration in United states.(12). Statistics Canada estimated the population of Canada 33 millions, the total waste cooking oil is 1,35,000 tons per year(13). In European countries waste cooking oil is approximately 700,000 to 1,000,000 tons per year(14). All the produced waste cooking oil is illegally dumped into rivers and lakes, which cause pollution, as these oils also contains free fatty acids which can be used for production of biodiesel which reduces the contamination of land and water resources(15). Lipolytic efficiency of lipase was determined by the total 22% C-18 fatty acid liberated from waste frying oil. Linoleic acid content in raw oil was originally between 55 and 60 percent; subsequent oil boiling lowered this to 28 to 32 percent.

2. Plant source

Cotton seed oil:

Cotton seeds have an oil content that can be extracted chemically or mechanically. However, in order to improve the quality of biodiesel, the gossypol concentration in the seeds must be reduced chemically. Cotton seed oil contains 70% unsaturated fatty acids, 18% monounsaturated fatty acids, 52% polyunsaturated fatty acids (oleic acid), and 26% steric acid (16)

Sunflower Oil:

It is possible to extract sunflower oil mechanically or chemically. High levels of linoleic acid in sunflower oil produce high-quality biodiesel and also include wax. The removal of wax from the oil can be achieved through centrifugation or by employing other solvents such as petroleum ether, acetone, etc. About 15% of sunflower oil is saturated, and the remaining 85% is unsaturated fatty acid, with oleic and linoleic acids making up 43% and 47% of the unsaturated fatty acid composition, respectively(80).

Palm oil

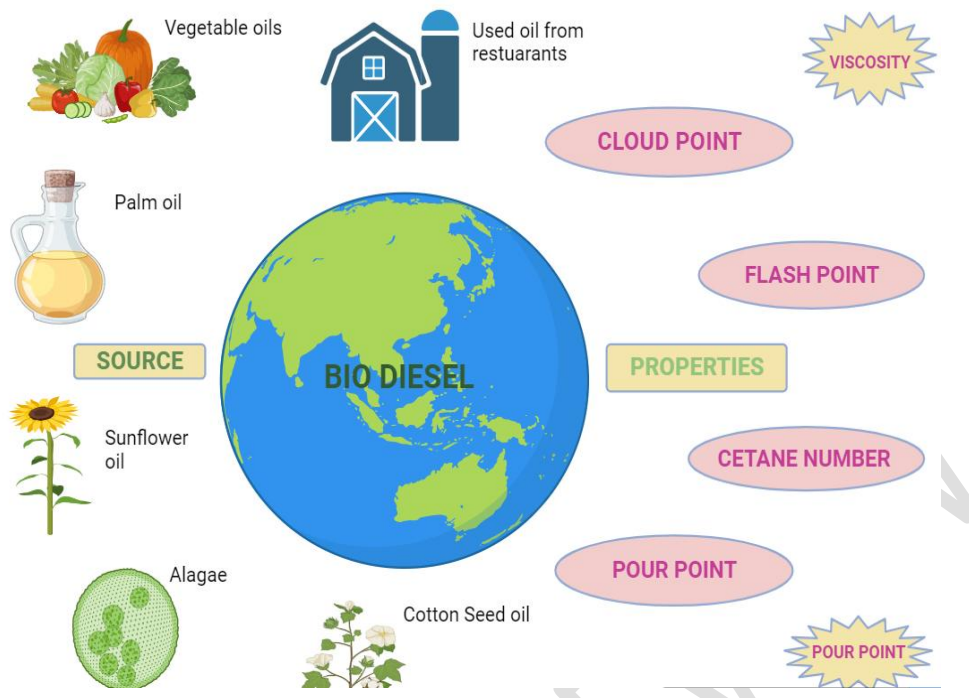
According to published reports, the cetane numbers for palm biodiesel range from 42 to 62, sometimes even surpassing those of pure diesel. The minimum cetane number of biodiesel allowed by ASTM D613 and EN ISO 5165 is 51(17). Like other biodiesel, the calorific value of crude palm oil is around 39.5 MJ/kg. The fossil diesel has a calorific value of roughly 43–45 MJ/kg. The high cetane number of biodiesel is a favorable property that indicates the quality of ignition. Due to its high cetane number, palm oil is widely utilized in the synthesis of biodiesel. About half of the saturated fatty acids in palm oil are made up of 44% palmitic acid (C16:0), 5% stearic acid (C18:0), and trace amounts of myristic acid (C14:0). Around 40% of the unsaturated fatty acids are oleic acid (C18:1), 10% are polyunsaturated linoleic acid (C18:2), and the remaining 10% are linolenic acid (C18:3)(81).

Jatropha :

Nigeris has wide diversity of flora having oil seed bearing capacity which can be used as source of biodiesel production, this also bring value to waste products(20). *Jatropacurcas* seeds have 27-40% of oil which can be processed for production of high quality biodiesel if oil seeds are well extracted (21). Oleic (41.5–48.8%), linoleic (34.6–44.4%), palmitic (10.5–13.0%), and stearic (2.3–2.8%) acids were the main fatty acids detected in the oil samples(82).

Neem oil:

The oil present in neem seed is 20-30%, density and viscosity of Neem oil, are 929 kg.m^{-3} (at $15 \text{ }^\circ\text{C}$) and $38,875 \text{ mm}^2.\text{s}^{-1}$ (at $40 \text{ }^\circ\text{C}$)(31). Neem oil mostly contains large amount of unsaturated fatty acids like oleic acid (25 to 54%) and linoleic acid (6 to 16%) and saturated parts like stearic acid (9 to 24%).(33)



Animal tallow

After soy oil, animal tallow is the most widely utilized raw material in Brazil for raw material production(34). Additionally, it generates 17–30% greater impact from fuel with low sulfur content, which is good for the environment and lowers greenhouse gas emissions(35). According to Bolonio et al., there are two steps involved in making bio-diesel from animal fat: first, the raw fat is hydrolyzed to release free fatty acids, and then those free fatty acids react with ethanol. The two-step method Suwannapa and Tippayawong utilized to produce bio-diesel from cow tallow(37). Tallow contains the following fatty acids: Acids that are saturated: 26% of palmitic acid (C16:0), 14% of stearic acid (C18:0), and 3% of myristic acid (C14:0), Fats that are monounsaturated: Palmitoleic acid (C16:1): 3%, and oleic acid (C18-1, ω-9): 47%, Fats that are polyunsaturated: 1% for linolenic acid and 3% for linoleic acid(83).

Algae oil:

Micro and macroalgae are grown in natural and artificial environments, as need light, carbon dioxide, nutrients, and other inorganic substances to grow(39). Better efficiency in the production of algae biomass was achieved through the cultivation of micro-algae in an open and closed system in the treatment of wastewater(40). After harvesting, algae can be used as an inedible source for bio-diesel production(41). Its lipid content (40-80% dry weight) is 15-300 times higher than in other cultures(42). In general, the most significant advantages of producing bio-diesel from micro-algae are less land use(43)

Algae oil comprises 14.6 weight percent of palmitic acid (16:0) and the unsaturated fatty acids oleic (26.9 weight percent), linoleic (22.8 weight percent), and linolenic (16.1 weight percent).(84)

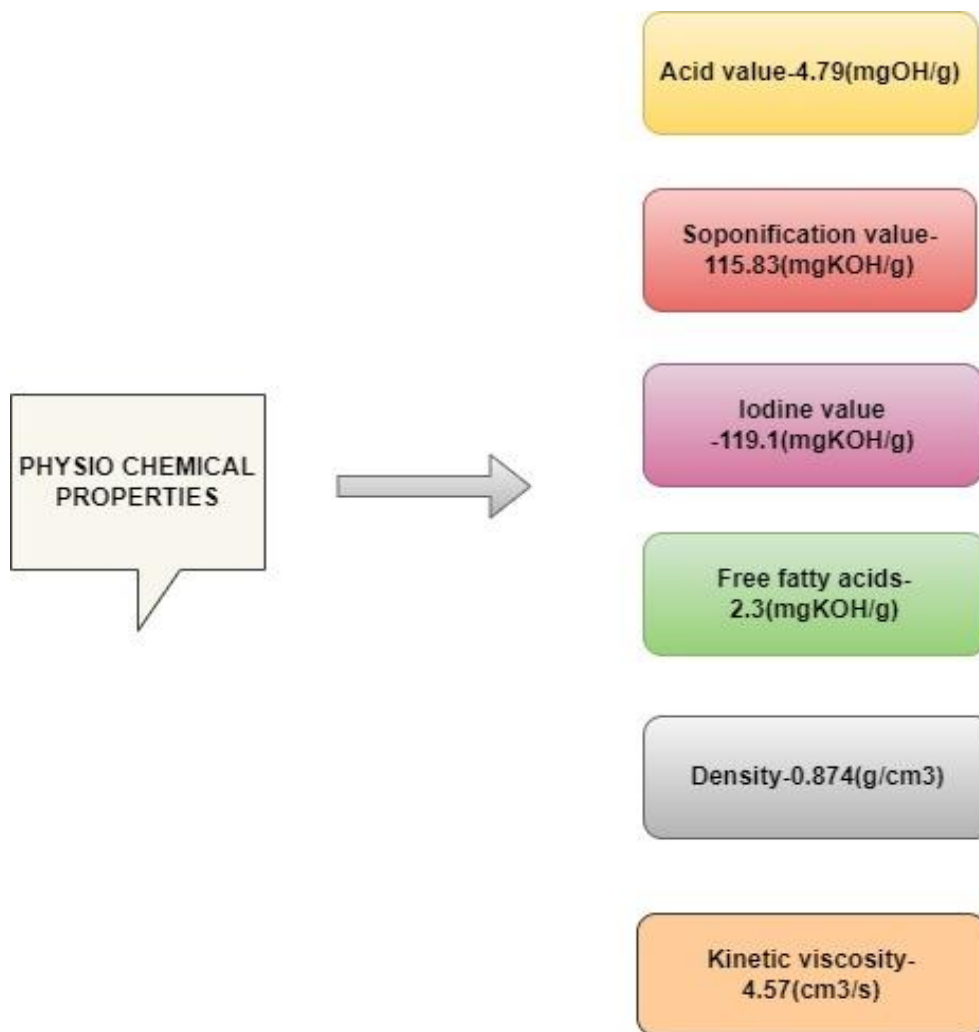
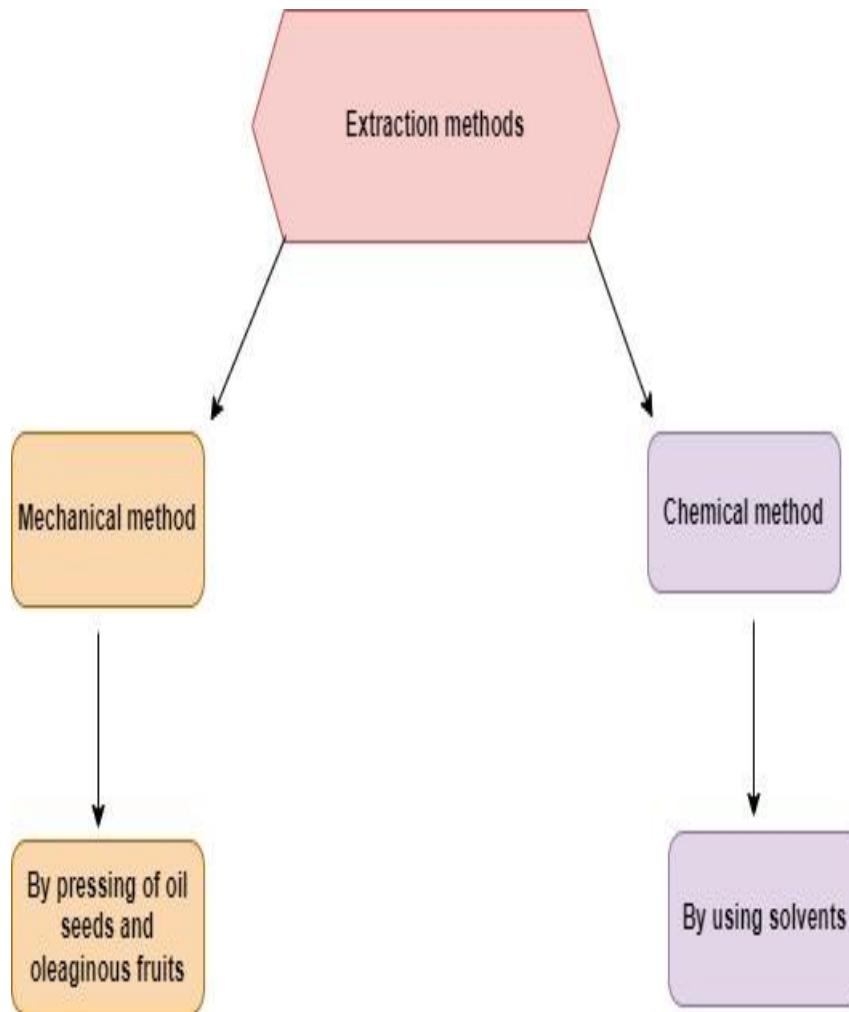


Table-8 Physio-chemical properties of biodiesel(44)

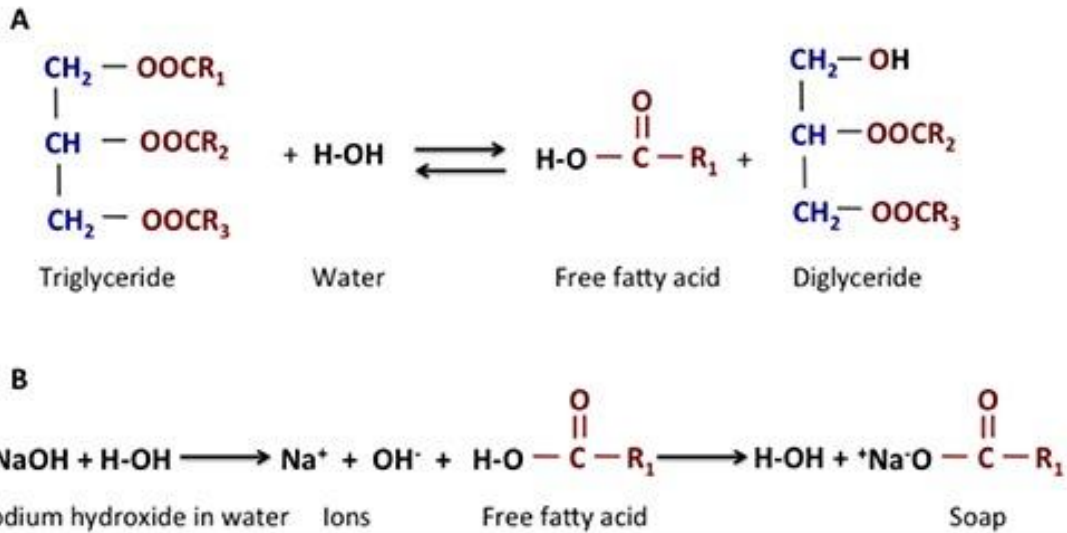
METHODS OF EXTRACTION OF BIODISEL:



Pre-Treatment of Waste cooking oil:

During the process of cooking heating causes oil to undergoes oxidation, hydrolysis and polymerization reaction. During this process many oxidative products such as hydro peroxides and aldehydes are produced which are absorbed into food and some remains as in oil. So in order to remove all these we have to pre treat our used vegetable oil by preheating it at 50oC and 1atm pressure(temperature and pressure depends on type of used vegetable oil take as raw material)and tit-ratation has to be made to know the amount of catalyst to be used in the reaction to neutralize the free fatty acids. The oil should be now filtered to remove any food remnants in it by using a cotton cloth.(10)

Transesterification:



A) TRANSESTERIFICATION REACTION AND
 B) SIDE REACTION SOPONIFICATION REACTION

In this reaction, triglycerides get reacts with alcohol in the presence of catalyst such as Na OH, or any other catalyst(H2SO4 -Acidic homogeneous catalyst- Esterification) to produce esters and glycerols. Three systems of transesterification is based on the catalyst used in the process, like homogeneous, heterogeneous and enzymatic catalyst.(45). Used vegetable oil is reacted with alcohol. Ethanol and isopropanol can be used in the process but in most of the cases methanol is used because of better efficiency(46). Transesterification process mainly depends on many factors like reaction time, temperature, pressure, type of alcohol used, molar ratio of alcohol to oil, catalyst concentration, concentration of free fatty acids and moisture in feed stock oil.(47)

1. ESTERIFICATION

In esterification reaction free fatty acids get reacts with alcohol in the presence of catalyst to produce Biodiesel (fatty acid alkyl ester). This process is endorsed as it reduces the amount of free fatty acid content which in turn reduces damage to the engine.(14)



The main aim of the esterification process is to reduce the acid value, as it is acid catalyzed homogeneous process. Some of the homogeneous catalyst used in the esterification reaction are hydrochloric acid, sulfuric acid and heterogeneous catalyst like SrFe2O4/SiO2-SoSH which shows good catalytic activity and can be easily separated by using magnetic field after reaction.(15)

PROCESS	MAIN PROCESS	PROS	CONS
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<p>1)Pyrolysis</p>	<ul style="list-style-type: none"> ● This technique, which involves preheating the oil and is based on the analysis on the boiling temperatures of various products, including gas and liquid, can be carried out with or without the use of a catalyst..(48) 	<ul style="list-style-type: none"> ● Free from environmental pollution and simple process.(49) 	<ul style="list-style-type: none"> ● Expensive because of the use of extremely sophisticated temperature equipment. ● Low level of biodisel purity.(49)
<p>2)Transesterification.</p>	<ul style="list-style-type: none"> ● In this process the oil get reacted with alcohol in the presence of catalyst.Glycerol is a byproduct of these processes.(50) 	<ul style="list-style-type: none"> ● The resulting biodiesel has a high conversion rate and gentle reaction conditions, making it comparable to petroleum and diesel and suitable for use in industrial production.(50) 	<ul style="list-style-type: none"> ● Separate purification procedures are necessary, and a significant volume of waste water is generated.(50)
<p>3)Micro emulsification</p>	<ul style="list-style-type: none"> ● The oil was made soluble using solvents until the desired viscosity was reached.(51) 	<ul style="list-style-type: none"> ● Simple and environmentally friendly process.(52) 	<ul style="list-style-type: none"> ● Sticking, partial combustion, and carbon deposition are caused by high viscosity and low stability.(51)

DIFFERENT TYPES OF CATALYST USED IN THE EXTARCTION OF BIODISEL.

1) HOMOGENOUS CATALYST:

This catalyst may be acidic or alkaline and they are soluble during the reaction. Acidic catalyst like H₂SO₄, which are usually used during esterification process, where as alkaline catalyst such as NaOH and KOH are used in transesterification process. Benefits of homogeneous catalyst are 1) easy availability and low cost, 2) high conversion in less time, 3) they can catalyse the reaction at lower temperature and pressure. The use of alkaline catalyst will be effective for refined oil with less than 0.5% fatty acids or acid value less than 1mgKOH per gram, but for removal of these fatty acids from produced biodiesel require washing it with water which generate large amount of waste water(53) which in turns increase the overall cost of biodiesel production and also causes corrosive reaction due to usage of water for removing catalyst. Alcohols and triglycerides should be anhydrous and for preventing soap formation free fatty acid content of raw material should be low.

2) HETEROGENOUS CATALYST:

These are solids and insoluble during reaction, mostly metal oxides are used as heterogeneous catalyst like SrFe₂O₄, KBr, CaO, chitosan and some of them derived from meat. These are more preferred than homogeneous catalyst because it can be reused, better separation and good quality of oil(54). Solid base catalyst of heterogeneous are preferred because these can be easily removed, no washing required, easy regeneration and less corrosive reaction as less water is used for separating of catalyst(55). Solid base catalyst such as mixed oxides, zeolites, sulfates, zircon and ion exchange resins mainly used for production of biodiesel from feed stocks having low free fatty acid content.(56).

3) ENZYMATIC CATALYST:

These are one of the most used catalyst for biodiesel production and both esterification and transesterification will be done during reaction.

COMPARISION OF THREE CATALYST

HOMOGENOUS	HETEROGENOUS	ENZYMATIC
<ul style="list-style-type: none">● Sophisticated equipment and techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR) were needed.● Statistical tools like Response surface methodology (RSM) using Central Composite	<ul style="list-style-type: none">● Heterogeneous catalysts are created using a variety of techniques, including base metal impregnation, precipitation, calcination, and co-precipitation.(58)● In order to produce biodiesel, Borges and Diaz employed a packed bed catalytic reactor in a	<ul style="list-style-type: none">● Compared to homogeneous and heterogeneous catalyst, the yield of biodiesel produced by enzymatic catalyst is relatively lower, while it is less expensive and requires less time for the reaction to occur.(58)

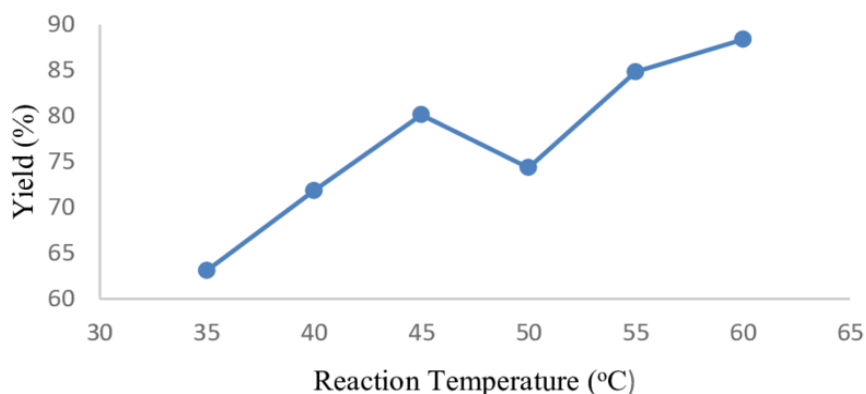
<p>Design(CCD) (experimental design) are essential to study the effects of process of variables in the reaction yield.(57)</p>	<p>recirculating system to use potassium-loaded pumice material as the heterogeneous catalyst in the transesterification process between waste oil and sunflower oil.(58)</p>	
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FACTORS EFFECTING BIODISEL PRODUCTION:

Vegetable oil changes viscosity throughout the transesterification process. Low viscosity fuels will be produced by removing glycerol and other high viscosity components. The biodiesel's flash point will drop and its cetane number will rise following the transesterification process. Many variables affect the quality of biodiesel, including temperature, catalyst utilized, reaction time, moisture content, free fatty acid content, and the molar ratio of alcohol to oil.(59)

1. TEMPERATURE:

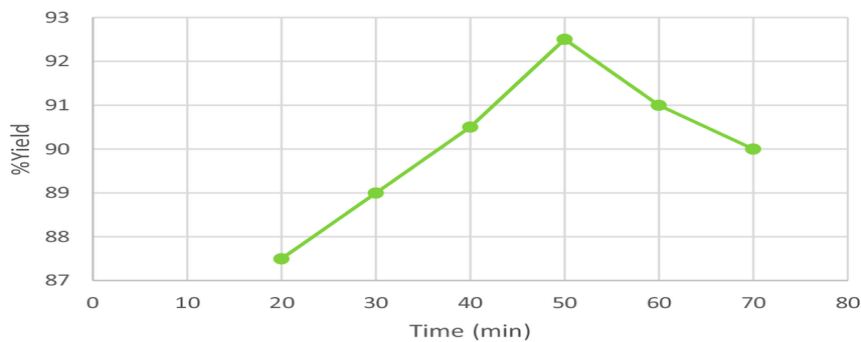
Good quality of biodiesel mainly depends on temperature. Higher the temperature the reaction rate also get increased by which the reaction time get decreased and the viscosity of the oil also decreases. When the temperature increased above the optimal level than the quality of biodiesel get decreased which eventually make Saponification of triglycerides(60) and also leads to vaporization of ethanol.(61) The reaction temperature depends on nature of oils and fats used and optimal temperature relays between 50-60oC. To stop alcohol from evaporating, the transesterification reaction temperature needs to be lower than the boiling point of alcohol.(60)



2. REACTION TIME:

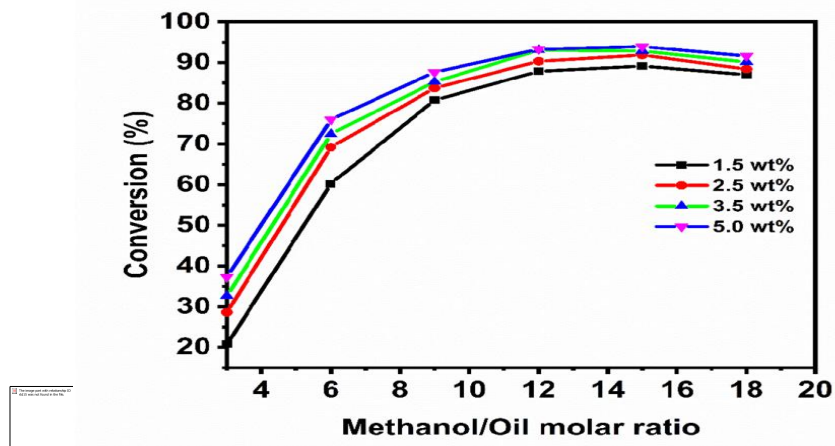
A quicker reaction time results in a quicker conversion of fatty acid esters. Because alcohol and oil disperse easily, the reaction will start out slowly but pick up speed later on and finish

in around 90 minutes. Increased reaction time won't result in a faster conversion; instead, the reversible nature of transesterification—which results in the loss of esters and the creation of soap—will eventually cause the yield of biodiesel to drop.(60)(61)



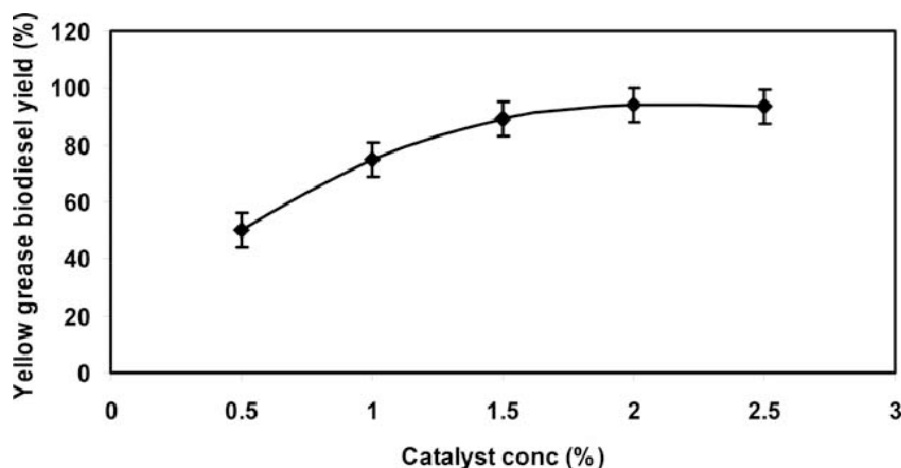
3. METHANOL TO OIL MOLAR RATIO:

Since esterification is a reversible reaction, more alcohol can be added to the mixture or extra product can be eliminated to boost the biodiesel output. The reaction rate will be maximum when all of the methanol is utilized. Because it is inexpensive, polar, and a short chain alcohol, methanol is generally chosen over other alcohols such as ethanol, propanol, and so on. However, ethanol is preferred in the transesterification reaction because it can be generated from agricultural products, is renewable, and poses less of a biological threat to the environment. 99.5% biodiesel output at an oil to methanol ratio of 1:6 is the maximum that can be achieved. The output of biodiesel has increased as methanol consumption has increased.(64)



4. TYPES AND AMOUNT OF CATALYST USED:

The kind and quantity of catalyst we utilize will vary depending on the type, alcohol content, and technique employed. The most widely utilized catalysts in the manufacture of biodiesel are potassium hydroxide (KOH) and sodium hydroxide (Na OH).(60) In the transesterification process, adding additional catalyst typically results in a higher ester yield; however, this is not profitable because catalyst is expensive. Therefore, producing biodiesel will require the best possible utilization of catalyst (65).



5. MIXING INTENSITY:

Mixing is essential to the transesterification process and the generation of esters since alcohol and oil are not easily miscible and reactions take place at the liquid-liquid interface. As a result, there needs to be a maximum amount of mixing between alcohols and oils; the amount of mixing varies depending on what is needed for the transesterification process. Vegetable oils require severe mechanical mixing due to their high viscosity, even though the intensity of the feed stock mixing can be increased to a consistent and acceptable degree (65). The majority of research indicates that during the transesterification reaction, the reactants first form a two-phase liquid system. It has been discovered that mixing significantly contributes to the reaction's slow rate; however, once phase separation ends, mixing's impact diminishes (70).

6. FREE FATTY ACID AND WATER CONTENT:

When utilizing a catalyst to transesterify glycerides with alcohol, the free fatty acids and water content have a big impact. A greater than 1%w/w percentage of free fatty acids causes soap production, complicates the separation of products (glycerol), and reduces the output of biodiesel (71). Because waste cooking oil has a higher water content, the hydrolysis reaction will rise and the amount of ester formation will decrease at the same time,(72) Therefore supercritical methanol approach is utilized to solve this issue because water has a much smaller impact in this process.(60) A maximum water content of 0.5% is required to get a 90% biodiesel production. More than 0.5% of water content makes acid-based catalyst reactions more hazardous than base catalyst reactions for producing biodiesel because alcohol combines with free fatty acids in these reactions, producing esters and water in the process (73).

PROCESS OF BIODISEL PRODUCTION FROM WASTE COOKING OIL:

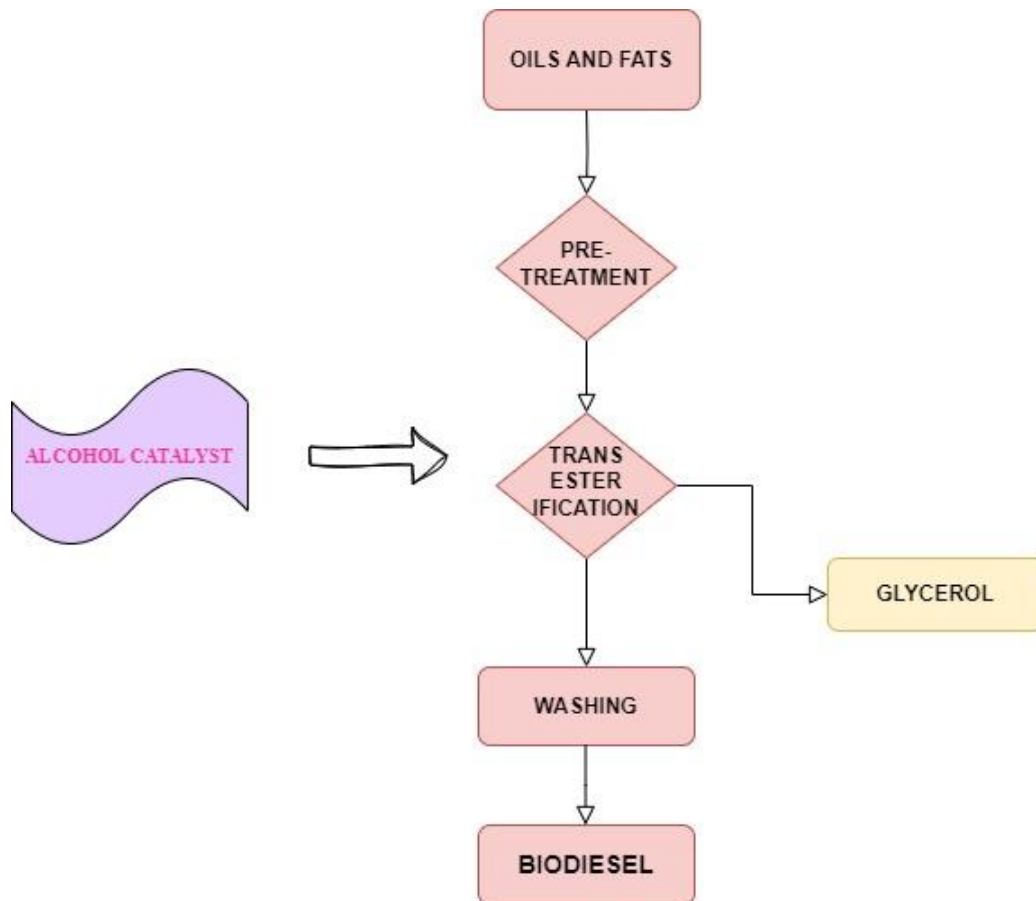
PROCESS -I:

- I. **FILTERING:**Heat exchangers are used to preheat waste cooking oil to 60 degrees Celsius in order to eliminate contaminants that are present in it. Alcohol and acid catalyst are thoroughly mixed at 60 degrees Celsius before this preheated oil is added to the esterification reactor. This creates an adequate number of esters for the manufacture of biodiesel. The esterification reaction occurs between 80 and 90 degrees Celsius and at atmospheric pressure of one.(74)
- II. **SETTLING TANK:**The esterification reactor's products were cooled to 45 degrees Celsius and the catalyst was removed before they entered the settling tank, where methanol and a combination of water were removed (56).
- III. **DISTILLATION COLUMN:** The methanol and water mixture at the top of the settling tank is collected, and the methanol is separated from the water mixture and reused in a distillation column.This column's bottom product is sent to the transesterification reactor.

PROCESS-II:

- I. **TRANSESTERIFICATION REACTION COLUMN:**After mixing the catalyst and alcohol in a mixer, the mixture is transferred to a transesterification reaction column, which is maintained at 65 degrees Celsius, one atmosphere pressure, and an oil-to-alcohol molar ratio of 1:6.
- II. **SEPERATOR II:**This separator receives products from the transesterification reactor. Alcohol and biodiesel, which are present in the product created, are distilled and separated in this separator.
- III. **SEPERATOR-III:**Biodiesel obtained is washed with hot water and moved to seperator to separate water and biodiesel.
- IV. **STORAGE TANK:**Biodiesel is transferred from the third separator tank into the storage tank. The glycerol and alcohol distillation column is located at the bottom of the second separation section (75).
- V. **Top of distillation column :**Methanol is repurposed and recycled.
- VI. **Bottom of distillation column :**Glycerin is produced as a result.

BIODISEL FLOW CHART (76)



PURIFICATION OF BIODIESEL:

SEPERATING FUNNEL:The resulting mixture is poured into this separating funnel, where it is centrifuged or allowed to settle at room temperature. The mixture separates into two layers after centrifugation; however, if an ionic liquid catalyst is applied, three layers will form in the separating funnel(77). Densities are the basis for separation; biodiesel is always at the top and glycerol is at the bottom. After being heated to eliminate any remaining moisture, biodiesel is cleaned with water or ethyl acetate to get rid of any remaining contaminants. Moreover, anhydrous sodium sulfate can be used to extract the water, producing a yellow liquid known as biodiesel(78).



Image(79)

CONCLUSION:

As biodiesel is a new, environmentally safe, nontoxic, renewable, and biodegradable alternative fuel for transportation, it has garnered a lot of attention worldwide. It can be produced using a variety of feedstocks that contain fatty acids, including animal fats, non-edible oils, leftover cooking oil, byproducts of vegetable oil refinement, algae etc. The process of transesterification is widely employed in the manufacturing of biodiesel. The most effective catalysts for this purpose are heterogeneous ones. Cooking oil waste can be used as feedstock to lower the cost of biodiesel. By first treating waste cooking oil with acid catalyst, the high fatty acid content in the oil can be decreased. The esterification process produces water, which could prevent acid catalyst from working. With a step-by-step reaction mechanism, it can be eliminated. The best alcohol is methanol because it's inexpensive and simple to separate from biofuel. However, there is still a need to choose the best process technology and use environmentally friendly catalysts to economically optimize the biodiesel process.

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