



Research Article

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Biodiesel production from waste cooking oil

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ABSTRACT

Due to the awareness of adverse effects of conventional fuels to environment and the frequent rise in crude oil's price, the need for sustainable and environment friendly alternate source of energy has gained importance in recent years. Biodiesel is proved to be the best replacement for diesel because of its unique properties like significant reduction in green house gas emissions, non-sulfur emissions, non-particulate matter pollutants, low toxicity and biodegradability. This paper reviews the pretreatment step, the physical and chemical properties of waste cooking oil, Esterification, Transesterification and production of Biodiesel from waste cooking oil by various methods and catalysts reported so far. The factors affecting the process parameters reported are studied and the point of interest focuses on their Alcohol to oil ratio, Reaction temperature, Catalyst both qualitative and quantitative scope. The optimum condition is investigated and the exhaust emissions of Biodiesel and Petroleum diesel are compared.

Keywords: Biodiesel, Esterification, Transesterification, FAME (Fatty Acid Methyl Ester), FFA (Free Fatty Acid), WCO (Waste Cooking Oil), WVO (Waste Vegetable Oil), WFO (Waste Frying oil).

INTRODUCTION

21st century has been facing many problems like energy sustainability, environmental problems and rising fuel prices. Conventional fuels are known for polluting air by emissions of sulfur dioxides, carbondioxides, particulate matter and other gases. This has resulted to increased research in alternate fuels and renewable source of energy [1-7]. Moreover, energy consumption of the world is ever increasing, this has caused the fuel resources dwindle. The transport sector worldwide has considerably increased the fuel consumption reaching 61.5% of the total, especially in the last decade [8]. Recent research expects that the amount of petrol in the world can be used merely for next 46 years. Hence, interest in research for an effective substitute for petroleum diesel is increasing [9]. Currently, India produces only 30% of the total petroleum fuels required for its consumption and the remaining 70% is imported, which costs about Rs. 80,0000 million per year. It is evident that mixing of 5% of biodiesel fuel to the present diesel fuel can save Rs.40, 000 million per year [10]. –

Over last few years, Biodiesel (fatty acid methyl esters) has become the part of the equation in the 1990's as the effects of global warming began to get political acknowledgement, because of its benefits over petroleum diesel like significant reduction in greenhouse gas emissions, non-sulfur emissions and non-particulate matter pollutants, low toxicity, biodegradable and is obtained from renewable source like vegetable oils, animal fat etc [1,2,8,9,11-15]. Biodiesel is superior to fossil diesel fuel in terms of exhaust emissions, cetane number, flash point and lubricity characteristics, without any significant difference in heat of combustion of these fuels [16]. Moreover, biodiesel returns about 90% more energy than the energy that is utilized to produce it [5]. Biodiesel mixed with conventional

diesel in some proportions can be used to run any existing conventional compression ignition engine and does not require any modifications to be done to the engine [9,11]. Due to benefits like renewable in nature, low cost and green house gas reduction potential, biodiesel is nowadays incorporated all over the world especially in developed countries like USA, France, Brazil in different proportions with diesel. It is also estimated that India can supplement 41.14% of its total diesel fuel consumption, if resources like waste cooking oil and other bio wastes were used as raw material for biodiesel production [10].

Biodiesel can be processed from different mechanisms.

Some of them are

1. Direct use or blending in diesel fuel, 2. Micro emulsions in diesel fuel, 3. Thermal cracking of vegetable oils and 4. Transesterification[6]. In this review, transesterification is focused.

Transesterification is the most common process, in this process an ester compound is exchanged by an alcohol in the alkyl group[11,17]. Biodiesel can be defined as fatty acid methyl esters (FAME) derived from the Transesterification of triglycerides (vegetable oils or animal fats) with alcohol and suitable catalyst [1,2,8,11,13]. Biodiesel is used as mix constituent of petroleum diesel in proportions for running a diesel engine, since using neat biodiesel has some engine issues[17,18]. Production rate, yield, product quality were the key performance indicators assessed. Biodiesel can be produced from different triglyceride sources such as vegetable oils (that can be edible, non-edible or waste oils), animal fats (mostly edible fats or waste fats) and microalgae oil [8,12]. The crops identified for biodiesel are corn, sunflower, palm, olive, canola, soybean, rape and peanut oils, and animal-based lipid (e.g. butter)[8]. Waste animal fat is also identified to be a good feedstock for biodiesel. Economic feasibility of biodiesel depends on the availability of low-cost feed stocks [19]. The key issue for large scale application of biodiesel as compared to petroleum diesel is the high cost of biodiesel which is mainly concerned with cost of feedstock oils as both the edible and non-edible oils are limited. Moreover, it has been reported that nearly 70-95 % of the total production cost is related to the cost of raw materials. This issue can be overcome by the use of WASTE COOKING OIL (WCO) as raw material which can effectively reduce the feedstock cost to 60-70%. Likewise, the cost of catalyst also affects the overall production cost. Several studies have been made to use waste materials for low cost catalyst preparation to develop sustainable biodiesel production process [5,13].

2. WASTE COOKING OIL (WCO)

Waste cooking oil refers to the used vegetable oil obtained from cooking food. Repeated frying for preparation of food makes the edible vegetable oil no longer suitable for consumption due to high free fatty acid (FFA) content [10]. Waste oil has many disposal problems like water and soil pollution, human health concern and disturbance to the aquatic ecosystem [8,10], so rather than disposing it and harming the environment, it can be used as an effective and cost efficient feedstock for Biodiesel production as it is readily available[1,3, 5,8, 10, 13,14, 18,20]. Furthermore, Animal fats with high acid value and fat-containing floating sludge discharged in water systems are subject to environmental concern due to their high pollutant potential and it is a challenge for wastewater treatment plants to purify it. Therefore, conversion of low quality lipid-rich sources from slaughterhouses into commercial grade biodiesel is an opportune strategy for minimizing environmental damages while it can help meeting the energetic challenge[19]. WCO collected can also be used to prepare soaps and additive for lubricating oil [8]. Many researchers have successfully converted used vegetable oil into biodiesel[2].

Vegetable oil contains saturated hydrocarbons (triglycerides) which consist of glycerol and esters of fatty acids [8]. Used vegetable oil (UVO) is a by-product from hotels, fast food restaurants and shops selling fritter and by-product of an operating vegetable oil refinery[11]. For serving better quality food, they usually throw this waste cooking without any treatment [2,4]. In some places, UCO from restaurants were re-used by street sellers to fry their food, this waste oil is termed as second-used cooking oil can also be utilized by converting to biodiesel[3]. Distillate that is produced by deodorization of palm oil (DDPO) is also a promising and cost effective feedstock [23]. In fact, using waste vegetable oil reduces the need for biodiesel-producing crops and the competition with food[3,5,14]. UCOs have different properties from those of refined and crude vegetable oils [3]. The chemical and physical properties of WCO are different from those of fresh oil since some changes due to chemical reactions - such as hydrolysis, oxidation, polymerization, and material transfer between food and vegetable oil occur during the frying process. The typical chemical and physical characteristics of WCO are shown in Table 1. The usual values for Properties like density, kinematic viscosity, saponification value, acid value and Iodine value are shown in the table.[8].

Table -1 Main properties of WCO [8]

Property	Units	Value
Density	g /cm ³	0.91-0.924
Kinematic viscosity (40 ⁰ C)	mm ² /s	36.4-42
Saponification value	mgKOH/g	188.2-207
Acid value	mgKOH/g	1.32-3.6
Iodine number	gI ₂ /100g	83-141.5

The properties of WCO can change depending on the frying conditions, such as temperature and cooking time. Indeed a vegetable oil subjected to thermal stress such as during frying can completely vary its chemical and physical original characteristics [8]. The cooking process causes the vegetable oil, Triglyceride to break-down to form, Diglycerides, Monoglycerides, and free fatty acids (FFAs)[14].The amount of heat and water in the frying increases the hydrolysis of triglycerides, therefore it causes a growth of the Free Fatty Acids (FFAs) in the WCO. [3,8]. Moreover, because of oxidation and polymerization reactions, there is an increase in the viscosity and the saponification number of the WCO when compared with the original oil .Furthermore the transport of matter and heat between the frying food and the vegetable oil occurs and causes a higher content of water in the WCO .During the transesterification reaction, the presence of water in the WCO samples often lead to hydrolysis, whereas high FFA content and high saponification number can lead to saponification reactions. Both hydrolysis and saponification reactions cause low biodiesel yield and high catalyst consumption[8].The information on the physical–chemical properties of the many biodiesel sources available is a key issue to decide on investments for the development of crop production, processing, quality control, and engine adequacy[17].

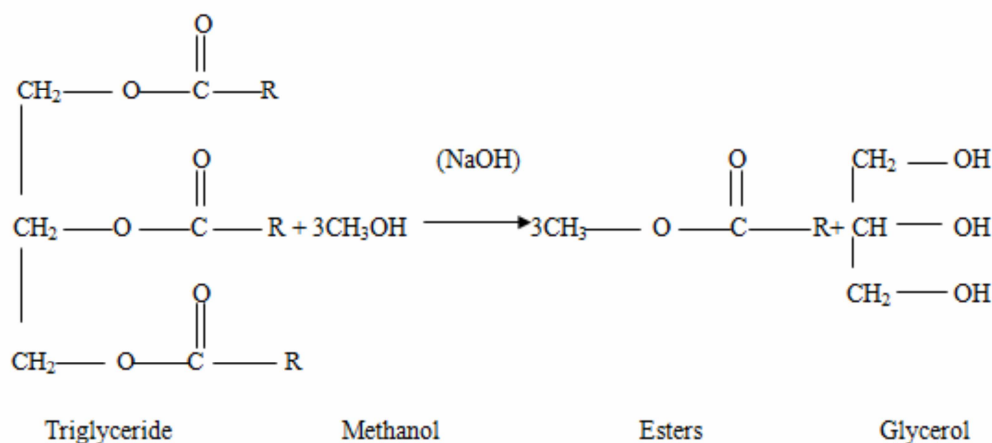
In a study on the fatty acid profiles [2] , it was concluded that the vegetable oil contains acids like Myristic (Tetradecanoic), Palmitic(Hexadecanoic), Stearic (n-Octadecanoic), Oleic , Linolenic, Arachidic and other special fatty acids. Among these oleic and linolenic were identified to be in major amounts.The most used vegetable oils for frying purposes are generally olive, sunflower and peanut ones. As for these oils, the fatty acid composition is dominated by oleic and linoleic fatty acids in addition to smaller quantities of stearic and palmitic acids [2,8].

Another study [9] concluded that to obtain a better yield of product (above 90%) , the concentrations of palmitic, oleic and linoleic acids should be about 37, 50 and 12% v/v and more.In terms of concentrations of triglyceride, diglyceride and monoglyceride, an investigation shows that used a WCO with FFA (wt/wt%) 8.42 and Acid value (mg KOH g⁻¹) 16.6 , had Triglyceride concentration (%) of 84, Diglyceride concentration (%) of 7.0 Monoglyceride concentration (%) of 0.3 [14].The characteristics of second UCO were found to have similarity to UCO but the FFA value is found to be higher in the second UCO [3].As the time spent for the frying of oil is increased, the product yield is decreased [9].

3.TRANSESTERIFICATION OF WASTE COOKING OIL

In transesterification reaction, the triglyceride component of oil reacts with the alcohol in the presence of NaOH or any other catalyst to give ester and glycerol as shown in the scheme -1 [7].

In general, there are three systems of transesterification with vegetable oil or an animal fat as a starting material, they are homogeneous ,heterogeneous systems and enzymatic based on the catalyst employed in the process. UVO is reacted with alcohol, In most of the cases methanol is used because of better efficiency[1-18, 21-24]. However ethanol and isopropyl alcohol can also be used, Ethanol is used for animal fats [19].It has been reported that, transesterification process depends upon several parameters which are reaction temperature and pressure, reaction time, rate of agitation, type of alcohol used and molar ratio of alcohol to oil, type and concentration of catalyst used and concentration of moisture and FFA in the feed oil. The optimal values of these parameters largely depend on the physical and chemical properties of the feedstock oil for attaining higher conversion [3,8]



Where, R is long chain hydrocarbons.

Scheme-1 A schematic representation of the transesterification reaction[7]

The majority of biodiesel today is produced through homogeneous alkali-catalysed transesterification of edible vegetable oils [1,2,3,6,7,9,11,12,18,24]. Homogeneous catalysts are those which are soluble during the reaction, they may be liquid or gaseous. They are of two types : Acidic and Alkaline. Acidic catalysts like H_2SO_4 are used widely for Esterification[7,11] while Alkaline catalysts like NaOH and KOH are used for Transesterification [1,2,3,7,9,15,18]. The advantages of homogenous catalysts are (i) ability to catalyze reaction at lower reaction temperature and atmospheric pressure; (ii) high conversion can be achieved in less time, (iii) availability and it is economical [3]. This process enables a good product quality and a relatively shorter reaction time [12]. The effective use of Alkaline homogenous catalyst is limited only for refined vegetable oil with less than 0.5 wt.% FFA or acid value less than 1 mg KOH/g. [3]. Moreover, the separation of these catalysts after the reaction is completed, requires the washing of biodiesel with water which might result in loss of Fatty acid alkyl esters, energy consumption and generates large amount of waste water. This also increases the overall biodiesel production cost as catalyst is difficult to recover and catalysts may cause reactor corrosion [5]. The triglyceride and alcohol should be anhydrous and a Low free fatty acid (FFA) content of raw material is required to avoid the soap production (by alkaline catalyst consumption) and low product yields [7,12].

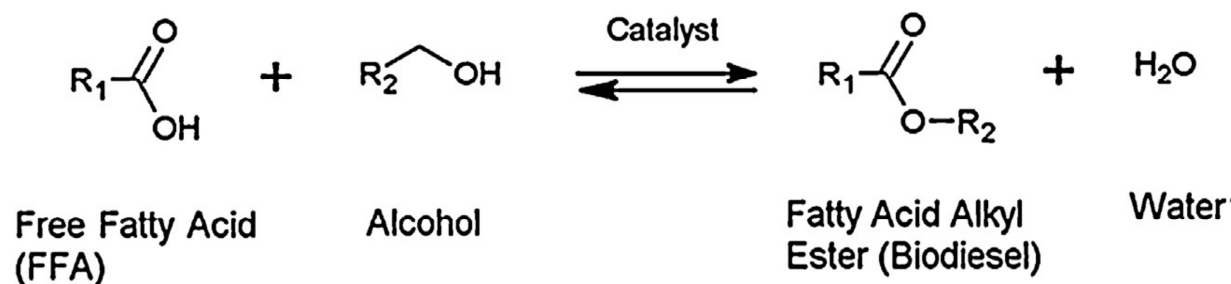
Heterogeneous catalysts are the solids and are insoluble during the reaction. Most of them are Metal oxides like KBr/CaO, chitosan, $\text{SrFe}_2\text{O}_4/\text{SiO}_2\text{-SO}_3\text{H}$ and catalyst derived from chicken bones[5,15,16,22]. From economic point of view, Heterogeneous (solid) catalysts are preferred over homogenous as they can be reused, allow a better separation and better quality of the final products[12]. Solid base catalysts are considered to be promising catalysts for transesterification as they have advantages such as easy separation of catalyst from reaction mixture, can tolerate high FFA, no washing is required, easy regeneration, less corrosive character of the product, low in cost and it is a more environment friendly approach[21]. However, there are also some disadvantages of the heterogeneous catalysts like they require extreme reaction conditions (higher temperature and reaction times are generally used) for preparation compared to homogeneous process. The calcinations temperature for catalyst obtained from chicken bones is 900°C [5]. Homogeneous catalysts might be needed to be characterized by sophisticated equipment's techniques like Fourier Transform Infrared spectrometry (FTIR), X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) techniques [5,16]. Furthermore, methods like Response Surface Methodology (RSM) using Central Composite Design (CCD) were employed to study the effects of process variables on the reaction yield[16]. Solid acid catalysts like zeolites, mixed oxides, sulfated zirconia and ion exchange resins might be very interesting for the production of biodiesel from feedstocks with high FFA contents, but still their activity is low as it depends upon the reaction conditions and higher amount of catalyst consumption compared to homogeneous catalysts.. Furthermore in some of the cases, soap formation is also seen using heterogeneous catalyst and purification is still required in most of the cases to ensure the required quality of fuel[12].

Enzymatic catalysts are becoming one of the most promising catalysts for the biodiesel production. They can tolerate high FFA and simultaneous Esterification and Transesterification takes place in these reaction. Enzymatic

catalysts are known for being cost effective catalysts shorter reaction time and lower reaction temperature .However they need more amount of catalyst and production yield is less compared to homogeneous and heterogeneous [20].

4. ESTERIFICATION OF WCO

Most biodiesel specifications impose an upper limit on the FFAs content as FFA can cause deposits and engine damage .Esterification can be used to convert the FFAs to biodiesel and reduce the FFA as shown in scheme-2. In this reaction , fatty acid reacts with alcohol in the presence of catalyst to give fatty acid alkyl ester (Biodiesel).[14].



Scheme-2 Schematic representation of the esterification reaction [14]

The aim of esterification step is to minimize the acid value of WCO. Usually the esterification process is an acid catalysed homogeneous process in which acids such as sulphuric acid, hydrochloric acid, butyl-methyl imidazoliumhydrogensulfate(BMIMHSO₄) and sulfonic acid are usually selected as the traditional acid catalyst[7,8,11].However some Heterogeneous catalysts like SrFe₂O₄/SiO₂-SO₃H also shows good catalytic activity for esterification and can be very easily separated after the reaction using magnetic field.[15].

Acid value of the oil is determined by the titration of mixture of oil with ethanol and diethyl ether (1:1) against KOH using phenolphthalein as indicator . It is calculated by the formula Acid value =56.1*CV/m; while V is the volume of KOH (mL);C is the concentration of KOH (M) AND m is the weight of oil sample (g).[9].This titration method followed official methods AOCS Cd 3d-63 and ASTM D-664 [6,9] .Based on acid value, the catalyst is selected. For FFA less than 1%, the feedstock can be transesterified with an alkali catalyst without any pretreatment step[3].

Results from an investigation [11] shows that maximum conversion is obtained at 2% v/v H₂SO₄ . The main inhibitor in the completion of esterification reaction is equilibrium as the reaction is reversible. Reducing water by preheating in an oven can minimize the FFA[11,18].The main parameters affecting Esterification reaction are identified to be Alcohol to methanol ratio, Catalyst and its amount used and the reaction temperature[3,11,14,18]

5. BIODIESEL PRODUCTION PROCESS

Biodiesel production can be done both in batch scale and in continuous scale . Since, the batch scale process is simple , inexpensive and required less skilled workers, Most of the Industries prefer Batch scale production. There are many methods in which Transesterification can be carried out. Among them the lab scale batch reactor is most commonly used .

Pretreatment of WCO

Before proceeding for the reaction, Pre- heating of oil is done at 50⁰C and 1 atm Pressure and incase of used oil a titration is done to determine the amount of catalyst required for the reaction as well as the amount of catalyst required to neutralize the FFAs. Now the oil is filtered to remove any chunks of food particles passing the oil through a cotton cloth. The preheating depends on the type of oil used for the reaction whether fresh or used [1].

5.1 Lab scale Batch reactor method

These reactors mostly employ round bottom flask with 3 necks or 2 necks with a magnetic stirrer and a reflux condenser. This type of reactor is used in laboratories for the preparation of biodiesel .Figure-1 shows the Three necked round bottom flask which is connected with condenser , thermometer and Erlenmeyer [3].

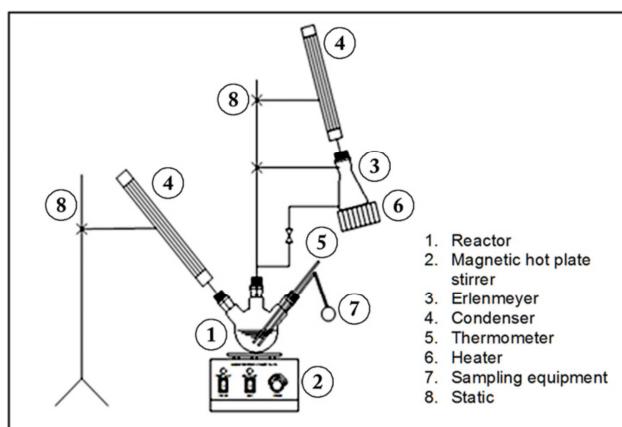


Figure 1: Transesterification batch reactor [3]

After the titration that determines the amount of catalyst required for the reaction, the catalyst is mixed with alcohol, this is mixed with oil in the reactor and continuously stirred. Once the reaction is completed, the product formed is of two layers which was separated by separating funnel[1,2,9]. The upper layer is Biodiesel and lower layer is Glycerol. After this separation, the produced biodiesel is washed with water to remove unreacted alcohol and catalyst[1-3]. The water present in the product can be removed by reacting with Na_2SO_4 [5]. In most of the cases the reaction temperature maintained is between $55 - 65^\circ\text{C}$ using methanol as alcohol [1-5,9-12,14-19,21,23,25]. A reaction temperature of 30°C is used for ethanolysis of animal fat [19].

It was reported in a study [1] that 80 % yield of Biodiesel can be obtained from WCO with methanol to oil ratio of 6:1, NaOH 1% wt/wt as catalyst, and $60 \pm 1^\circ\text{C}$ temperature for 1 - 3 hours by continuously stirring at 300 rpm in a lab scale batch reactor.

Another investigation

Another investigation [2] used WFO from fritter selling shops as a raw material and obtained a yield of 94% using methanol to oil ratio 15:1, NaOH (0.5-1 % wt/wt) at 55°C for 1-1.5 hours. It was also concluded that lower amount of catalyst can lead to unreacted product and higher amount results in the soap formation. The final product yield is strongly dependent on the component free fatty acids present in the feed.

In an investigation [3], second used cooking oil was selected as feedstock and a maximum yield of 92.76% was obtained with a methanol to oil molar ratio of 6.18:1, KOH 1% wt/wt as catalyst at 66.5°C in a batch scale three necked round bottom flask. Kinetic reaction of second used cooking oil for transesterification was determined to be $k = 0.0251 \exp(-15.29/RT) \text{ dm}^3/(\text{mol} \cdot \text{min})$. The biodiesel product obtained was of density 877 kg/m^3 , Viscosity Kinematic $4.971 \text{ mm}^2/\text{s}$, Flash Point 180.5°C and Pour Point 3°C .

In another study [5] heterogeneous catalyst derived from chicken bones calcined at 900°C was used for Transesterification of WCO and a product yield of 89.33% was obtained when 5% wt/wt catalyst was used with methanol to oil ratio 15:1 at 65°C for 4 hours in a 3 necked round bottom flask. The catalyst was found to have good catalytic activity, could be recycled for 4 times and can tolerate moisture and high FFA.

A glycerol enriched catalyst was used in an investigation[12] for production of biodiesel from WCO and soybean oil. It was concluded that using CaO, glycerol and methanol at a mass ratio of 1:1.6:13.4 as catalyst at 0.4% wt/wt with 7:1 methanol to oil molar ratio under ambient atmosphere during 2 h at 60°C obtained a good quality product (EN 14214). It was also mentioned that catalyst could be reused for 4 times.

Waste animal oil was converted to biodiesel in an investigation[19] with a conversion of 83% at 30°C with 7:1 ethanol to fat molar ratio and 0.96 wt.% KOH as catalyst for 30 minutes in a tubular glass reactor surrounded with thermostated bath and equipped with a mechanical stirring. The biodiesel formed was by elution through a silica gel column under vacuum.

An investigation [21] on Alkali metals (Li, Na, and K) supported by rice husk silica as catalysts for methyl esters production was conducted and a conversion of 96.5- 98.2% in 1hour was obtained using 3% catalyst ,methanol to oil molar ratio 9:1 at areaction temperature of 65⁰C.

It was also concluded that the catalyst is able to tolerate free fatty acid upto1.25w/w % and moisture content up to 1.75w/w %.

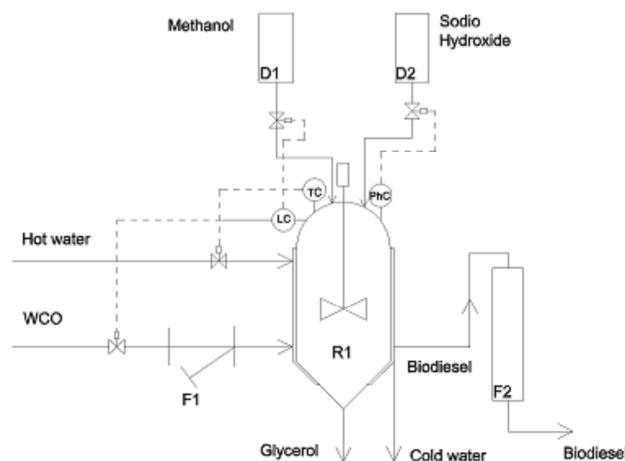
A feedstock which is a distillate that is produced by deodorization of palm oil (DDPO) was utilized in a study [23] for biodiesel production using a catalyst prepared from a waste material, Amazon flint kaolin. A conversion of 92.8% was obtained at 160 ⁰Cfor 4 hours with methanol molar ratio of 1:60 with 5% wt/wt of solid catalyst activated with sulfuric acid.

5. 2 Pilot Scale Reactor method

A pilot scale plant is used to process around 100 liters of biodiesel. In an investigation [8], a pilot scale plant was used for the production of biodiesel and the parameters affecting the reaction were studied namely reaction temperature, type and quantity of alcohol used, agitation rate, catalyst type, and original oil characteristics. An optimization process was carried out to obtain a yield of 94.3% biodiesel with density of 0.875 g/cm³ using UVO with 3% FFA with methanol to oil molar ratio of 6:1 and catalyst NaOH with concentration of 0.5% w/woil.

Figure-2 and Figure-3 shows the layout and photograph of pilot plant. As shown in scheme-4, a pilot plant is composed of stainless steel reactor jacketed of 100 liters capacity R1. WCO is filtered through filter F1 before it is loaded to the reactor, this process is an automatic process. Catalyst and reagent are placed into two tanks, D1 and D2, and are automatically moved to the reactor depending on the volume and the FFA percentage. The produced biodiesel is passed through an ionic resin filter F2 in order to remove residues of waste material and wastes resulting from the reaction are removed from the bottom of the reactor. All parameters are monitored by a computerized system with a touch screen interface.

Figure-2 Pilot Plant layout [8]



5.3 Bubble column reactor method

This type of reactor is very useful for conversion from low value alcohol and low-value lipids into biodiesel. Hence, potentially lowering the feedstock cost and the production cost.

A bubble column reactor was used in an investigation [6] and a conversion of 95% was achieved in less than 2 hours with a low quality vegetable oil containing higher content of water and FFA and Methanol to oil molar ratio of less than 3:1 at a temperature of 120 ⁰C and ambient pressure. The bubbling alcohol vapor through the reactor was at a flow rate of 0.034 moles of alcohol per mole of FFA in the oil present per minute into liquid.

Figure-3 Pilot plant for biodiesel production [8]



Figure-4 shows a schematic representation of a bubble column reactor showing bubbling action of reactor and water and methanol transfer between liquid and vapor phase. Bubble column reactor is jacketed with glass column. Reactor is operated typically at a temperature of 120 °C and 180 ml of feedstock lipid. The top of the column is exposed to the atmosphere to allow alcohol and water to bubble through the reactor to exit into a fume hood where experiments are performed. Sulfuric acid was mixed with small volume of alcohol to make a catalytic solution. This solution is added to the reactor at the top by a peristaltic pump during the first 5 minutes of the reaction. The heat exchangers are used for vaporizing methanol. The syringe pumps are used for pumping alcohol.

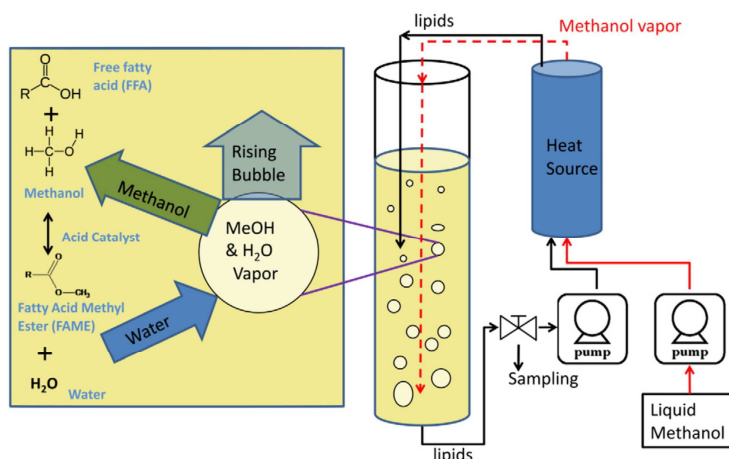
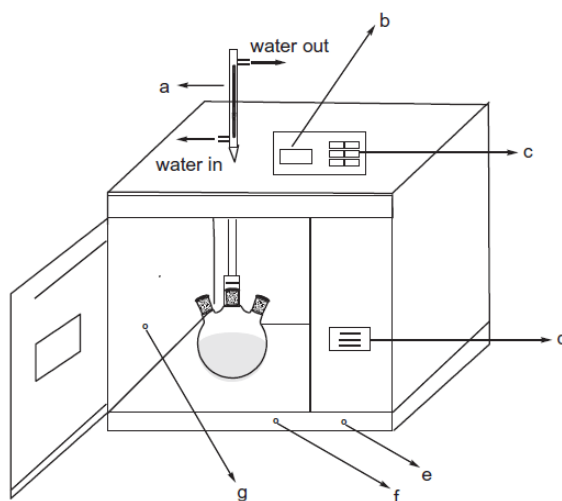


Figure-4 Schematic of reactor showing bubbling action of reactor and water and methanol transfer between liquid and vapor phase [6]

5.4 Microwave Technique

In this method, the heat supplied to the reaction is supplied by Microwave oven. Figure-5 shows the set up of the micro wave reactor.

Figure-5: Schematic diagram of the microwave accelerated reaction system. (a) Condenser pipe; (b) display panel; (c) control panel; (d) reaction chamber switch; (e) main switch; (f) magnetic stirring knob; (g) infrared temperature measurement. [13]

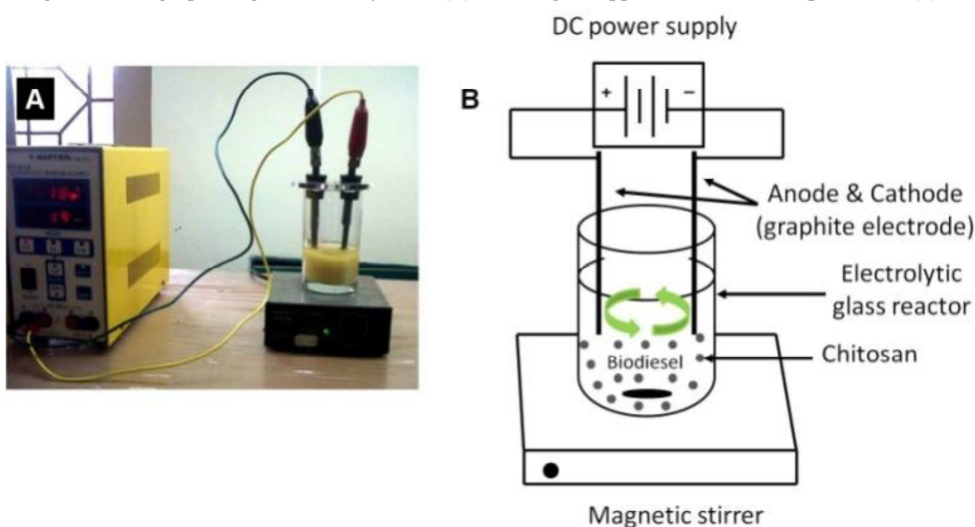


A study [11] compared traditional heating esterification (THE) with microwave assisted esterification (MAE) using cation ion exchange resin particles (CERP)/PES catalytic membrane and concluded that MAE needs less reaction time, lower reaction temperature, less energy and lower methanol additive. The FFAs conversion reached 97.4% under the optimal conditions of reaction temperature 60 °C, methanol/acidified oil mass ratio 2.0:1, catalytic membrane (annealed at 120 °C) loading 3 g, microwave power 360W and reaction time of 90 min. Thus, manufacturing biodiesel using microwave results in a fast, green way, easy and effective route with advantages of a short reaction time, a low methanol/acidified oil mass ratio, an ease of operation, reduced energy consumption and all with lower production cost. In this process, heterogeneous catalysts can be used to overcome the shortcoming of liquid acid catalyst.

5.5 Electrolysis method

Feedstocks with high water content can be directly used in this method where the hydrolysis of water at anode and cathode takes place. The photographic images of electrolytic cell and the apparatus used for biodiesel production is shown in Figure-6. The photograph shows that there are two graphite electrodes separated by a distance of 15 mm. The reactants are filled in the electrolytic-assisted cell.

Figure-6 Photograph images of electrolytic cell (A) and designed apparatus for biodiesel production (B) [13]



An investigation[13] on use of Chitosan (Organo metallic catalyst) for Biodiesel was analyzed using Electrolysis method. A conversion of 59.1% was obtained from the combined use of electrolysis process and 10 % chitosan applied in 4 h. the reaction mixture containing used cooking oil, methanol, Tween 80, chitosan, deionized water and NaCl as a supporting electrolyte was filled in the electro –assisted cell. The molar ratio of methanol to oil was adjusted to 24:1 and co-solvent to methanol to 100 : 1. NaCl concentration was 0.56% wt/wt. Electrolysis was carried out at room temperature using a constant voltage of 18 V (DC). The reaction mixture was agitated using a magnetic stirrer.

6. Purification of Biodiesel

Once the reaction is completed, the mixture of product is transferred to a Separating funnel where the mixture is allowed to settle down at room temperature [1-9,12,16,19] or centrifuging [5,18]. The mixture is separated to 2 layers in most of the cases[1,2]. When ionic liquid is used as catalyst , the product formed was in 3 layers [18] based on the catalyst used. The upper layer is always biodiesel and the lower layer is glycerol. This separation is based on density difference. Biodiesel is separated and washed by distilled water or ethyl acetate for removal of minor impurities[1,2,9,14]. The washed biodiesel was heated to remove any moisture present [2] It can also be treated with Na_2SO_4 to remove water to yield the biodiesel which is a yellow liquid[9] .

In an investigation [24] it was reported that after the separation of glycerol from biodiesel, the purification of crude biodiesel(methyl esters) using activated carbons produced from spent tea waste can result in higher yield of product and better fuel properties compared to the conventional methods of water washing and use of silica gel. Furthermore, this spent activated carbon can be regenerated and reused.

The ASTM standards for the produced Biodiesel are shown in the table-2 [1]. Biodiesel produced from various methods should be in its limits.

Table 2: ASTM STANDARDS [1]

Property	Standard value	units
Density	0.87	g/cc
Viscosity	1.9-6.5	mm ² /s
Cetane index	>47	No units
Carbon residue(100% sample)	0.050	Wt%
Acid Value	0.50(max)	Mg KOH/g

7. Engine emissions fuelled with biodiesel from waste cooking oil

In the current scenario, biodiesel has been identified as a potential alternative fuel for CI Diesel engine as its use can cut down the fossil fuel consumption as well as engine out emissions. Many researchers have studied on the emission characteristics of biodiesel and concluded the benefits of Biodiesel[4,10,17,25]. The ideal diesel fuel characteristics include good fluidness in the engine operating temperature range, contamination-free and wax-free, easy ignition, clean, and efficient combustion[17].

An investigation[4] done on the combustion characteristics of Engine fuelled with Biodiesel showed that the biodiesel provided significant reductions in CO, and unburned HC, but the NO_x emission was increased. Biodiesel has a 5.95 % increase in brake-specific fuel consumption due to its lower heating value.

It was reported [10] that biodiesel shows similar characteristics to that of diesel. The brake thermal efficiency, carbon monoxide, unburned hydrocarbon and smoke opacity are observed to be lower in the case of WCO biodiesel blends than diesel. But specific energy consumption and oxides of nitrogen of WCO biodiesel blends are found to be higher than diesel.

Another study[17] reported that Fuel blends with up to 20% waste cooking oil biodiesel or 35% castor oil biodiesel concentration in diesel fuel will meet present specifications for biodiesel density and kinematic viscosity. Fuel density and viscosity increased with increasing biodiesel concentration in the diesel-biodiesel blend, while fuel sulfur content was reduced.

Another investigation[25] analyzed the performance and emission characteristics for diesel engine (without any modifications) using different blend fuels such as DF (100% diesel fuel), JB5 (5% jatropha biodiesel and 95% DF),

JB10 (10% JB and 90% DF) and J5W5 (5% JB, 5% waste cooking oil and 90% DF). It was reported that exhaust emissions of JB5, JB10 and J5W5 had reduction in HC, CO and CO₂ emissions compared to that of DF. Whereas, NO_x emissions for all fuel blends was increased compared to DF. Furthermore, .In comparison with the diesel fuel, blend fuels produced lower sound levels due to many factors including increase in oxygen content, reduction in the ignition delay, higher viscosity, lubricity etc.

CONCLUSION

Biodiesel is an effective alternative fuel for conventional diesel and can be directly used as fuel in a diesel engine without any modifications to the engine. It has many positives like high biodegradability, reduction in green house gas emissions, non-sulfur emissions, non-particulate matter pollutants, low toxicity, excellent lubricity and is obtained from renewable source like vegetable oils, animal fat etc. Transesterification is the most common method for biodiesel production. Waste cooking oil is a cost effective and promising feedstock. WCO with higher FFA content results in decrease in the overall yield. In this case, esterification is to be done before Transesterification. Homogeneous catalysts like NaOH and KOH are known for having less reaction time and moderate reaction conditions but oils with high FFA may result in soap formation which reduces the overall yield and the recovery if catalyst is difficult. Heterogeneous catalysts have better separation and better quality of product but they have extreme reaction conditions. For carrying Transesterification, batch reactors are preferred over continuous because of easy assemblage, maintenance, inexpensive and easy to design. Obtaining higher yield of product depends upon the quality of oil used. The parameters affecting the reaction were identified to be methanol to oil molar ratio, the catalyst used and its amount and the reaction temperature. The produced biodiesel mixed with proportions of petroleum diesel (B20 : 20% biodiesel and 80% petroleum diesel) showed significant reduction in CO, HC and smoke emissions.

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