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Biodiesel Production Using 2nd Generation Feed Stocks: A Review

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ABSTRACT

Continuous use of petroleum intensifies air pollution which increases global warming. As per environmental stringent, crude oil prices and depletion of fossil fuels (like petroleum, coal and natural gas) many researchers are looking forward to find an alternative source of renewable energy. As biodiesel is promising as a renewable source from the feed stocks like vegetable oils, animal fats and fried cooking oil, prepared by a common and most satisfactory way of producing maximum yield at low cost through transesterification process. In general vegetable oils are of two types. They are edible and non-edible oils. Out of all varieties of oils, waste cooking oil and non-edible oils (second generation feed stocks) are more preferably considered for biodiesel production without diminishing useful resource for mankind and to minimize fuel cost. The major parameters of producing biodiesel using transesterification process depends on free fatty acids (FFA) content, molar ratio, catalyst concentration, reaction temperature, reaction time and moisture content. Biodiesel is derived from mono alkyl esters of free fatty acids produced from animal fats or vegetable oils with small chain alcohols in the presence of catalyst. This review concerns about the factors affecting the biodiesel production and various methods to its production using 2nd generation feed stocks.

Keywords: Biodiesel; Transesterification; Non-edible oil; Pyrolysis; Micro emulsion; Reaction time.

INTRODUCTION

Energy is being the only one criteria now every country is confronting. Because, in every part of world, energy is consumed in terms of transportation, electrical power generation sectors, industries, marine, space research centers etc. Natural energies like wind, solar, tidal, crude oil reserves (gasoline, conventional diesel, coal and natural gas). In every aspect of day to day life rely on energy , fuels are major sources as being burnt in various systems to get converted into useful energy. Fossil fuels contribute energy in major parts of the world needs. Majority of industries, transportation and other sectors consume particularly significant amounts of diesel and gasoline, this might become strong requirement of fossil fuels in everyday life. Fossil fuels are produced from micro organisms and biodegradable bodies. Thus formation takes millions of years to convert the fuels which reveal fossil fuels are non renewable energy sources [1-3].

According to recent estimates, population of India in the present year is 1.34 billion, represents almost 17.85% of world's population. Hence, energy requirement is unremitting. People and income of individuals are the key drivers behind growing demand for energy.

Oil prices arose $52.39 for barrel in 2015 from that to $46.56 per barrel from the past year. Increasing oil prices might lead to economic recede of every individual. Consumption of oil resources grew by 1.9 million barrels per day nearly double the recent historical average and significantly stronger than the increase of 1.1

million barrels per day seen in past year 2014. On and average in US, 2,90,000 barrels/day (b/d) oil consumption is increased while in India, it is raised to 3,10,000 b/d. Whereas, global oil production increased even more rapidly than the consumption by 2.8 million b/d. Eventually, developed countries in fossil fuel sources, will be consumed with in five decades. (Statistical review of world energy-2016)

NECESSITY OF ALTERNATIVE SOURCES

The following are the major drawbacks of diesel fuel and dependency of renewable energy sources.
Formerly large growth in industries and transportation sectors there is a huge demand in petroleum products and on other side depletion of world petroleum resources in few decades. Thus made many researchers to find alternative sources.
Secondly using petroleum based fuels leads to atmospheric pollution particularly conventional diesel. In addition 98% of carbon emissions are to serve the net production of carbon dioxide (CO2), oxides of nitrogen (Nox), oxides of sulphur (Sox), carbon monoxide (CO), volatile organic matter and Particulate matter are emitted by conventional diesel causing damage to ozone layer and global warming. Globally all countries facing several problems due to global warming issues [4-5].

ADVANTAGES OF BIODIESEL

Virtually all of which in the form of biodiesel produced from raw vegetable oils or animal fats through a simplified way of transesterification process.[6-7] Biodiesel can be only one proven best replacing alternative fuel due to the following advantages:

- Biodiesel can be replaced diesel fuel without any engine modifications, as its physical-chemical properties of biodiesel such as oxygen content, cetane number, viscosity, density and heating value are closer to conventional diesel which further influence engine performance, combustion and emission characteristics.
- As it is derived from vegetable oils (renewable sources), they are sulphur free, no aromatic hydrocarbons, metals and residues.
- Biodiesel is more oxygenated fuel so that emissions and soot emitted from diesel engines are well reduced rather than diesel fuel. Thus controls global warming problems.
- The life of conventional diesel engine can be improved by using biodiesel, produced from vegetable oils and animal fats contain gummy nature which improves lubricating characteristics [8].
- The Occupational Safety and Health Administration approved biodiesel as non-flammable liquid.
- The required raw oil for biodiesel production can create employment in different countries.

Out of all these benefits, there are few drawbacks such as biodiesel production cost per unit quantity is higher, slightly higher fuel consumption due to lower calorific value, higher nitrogen oxide emissions at high temperatures and higher freezing point compared to diesel fuel which can be resolved by water emulsion and cold flow modifiers. All these problems can be improved significantly when biodiesel is blended with diesel fuel or some alcohols [7].

BIODIESEL AND IT'S PROPERTIES

Biodiesel is derived from natural oils and animal fats. Biodiesel, promising substitute for conventional and modern diesel engines, has become major role using in diesel engines due to its biodegradability and low emissions. Fueling raw vegetable oils in diesel engines is not a modern technique. It was developed by Rudolf Diesel (1858-1913) who invented a very first engine fueled with peanut oil.[9] Vegetable oils are substitute to diesel since they are renewable and posses similar properties. Using raw vegetable oils is the best way of producing energy but it creates several problems due to high density, high viscosity (ranging from 10 to 20 times more than petro-diesel.), low volatility and difficulty in cold starting which causes pumping, atomization, combustion and lastly high cost of raw oils. Chemical properties of various vegetable oils are given in Table 1 [7,10-13].

Table 1. Chemical properties of various Raw vegetable oils.

Vegetable oil/properties	Kinematic Viscosity at 38℃ (cSt)	Density (kg/l)	Flash Point (°C)	Pour Point (°C)	Cloud Point (°C)	Calorific value (MJ/kg)	Cetane No.
Std Diesel	3.06	0.855	76	-16	---	43.8	50
Edible oils:							
Corn oil	34.9	0.9095	277	-40	-1.1	39.5	37.6
Cotton seed oil	33.5	0.9148	234	-15	1.7	39.5	41.8
Linseed oil	27.2	0.9236	241	-15	1.7	39.3	34.6
Peanut oil	39.6	0.9026	271	-6.7	12.8	39.8	41.8
Rapeseed oil	37.0	0.9115	246	-31.7	-3.9	39.7	37.6
Safflower oil	31.3	0.9144	260	-6.7	18.3	39.5	41.3
Soybean oil	32.6	0.9138	254	-12.2	-3.9	39.6	37.9
Palm oil	39.6	0.9180	267	---	31.0	---	42.0
Waste Cooking oil (WCO)	45.34	0.9184	305	9	24	42.11	53
Sunflower oil	33.9	0.9161	274	-15	7.2	39.6	37.1
Caster oil	13.75	0.9245	120	---	---	---	50
Rice-bran oil	6.29	0.920	---	-3	7	37.9	---
Non-Edible oils:							
Karanja oil	27.84	0.912	205	---	---	34.0	---
Jatropha oil	49.9	0.918	240	---	---	39.7	45
Cieba Pentandra	30.42	0.916	297	---	---	41.62	49
Thumba oil Ref. [13]	40.2	0.927	225	6	3.5	8742	---
Jojoba oil Ref. [14]	24.75	0.863	295				53.5

There by direct use of vegetable oil is unpreferable. The conversion of raw vegetable oil to biodiesel is necessary to reduce the problems as discussed. In general vegetable oils are two types. They are edible and non-edible oils. Due to several benefits of biodiesel using in diesel engines, Fatty Acid Methyl Esters (FAME) is of particular reorganization. It is obtained mainly from vegetable oil, contains hydrophobic properties which results insolubility in water. Triglycerides (Vegetable oils) have 1 mol of glycerol and 3 mol of fatty acids. Carbon chain length and number of unsaturated bonds are varied based on fatty acid fractions.[4,12 and 14] The typical fatty acids content in different vegetable oils are given in Table 2 and 3 [10 and 15-18].

Table 2. Contents of Fatty Acid properties in various Edible oils.

Fatty Acid/Edible oils	Soy bean	Cotton Seed	Palm	Tallow	Peanut	Sesame	Olive
Lauric	0.1	0.1	0.1	0.1	0.1	0.1	0
Myristic	0.1	0.7	1	2.8	0.3	0.3	0
Palmitic	10.2	21.1	42.8	23.8	12.3	9.2	18.5
Stearic	3.7	2.6	4.5	19.4	4.6	4.8	4.5
Oleic	22.8	19.2	40.5	42.4	53.6	43.6	65.2
Linoleic	53.7	55.2	10.1	2.9	29	41.9	11.2
Linolenic	8.6	0.6	0.2	0.9	0.1	0.1	0.6

Table 3. Contents of Fatty Acid properties in various Non-Edible oils.

Fatty Acid/Non-Edible oils	Rice bran	Rape seed	Thumba Ref. (13)	Soap nut	Jatropha	Rice bran
Lauric	0.2	---	0.018	---	0.31	0.2
Myristic	0	---	0.084	---	---	0
Palmitic	11.2	1-3	10.07	4.67	13.38	11.2
Stearic	1.6	0.4-3.5	7.890	1.45	5.44	1.6
Oleic	46.5	12.24	18.19	52.64	45.79	46.5
Linoleic	40	12.16	56.89	4.73	32.27	40
Linolenic	0.5	7.10	---	---	---	0.5

Depending on climate and soil conditions these vegetable oils are produced in different countries. Based on availability of raw vegetable oils in different places in the world, research scholars are concentrating on different types of biodiesel productions. Table 4 shows availability of vegetable oils in different countries around the world [4].

Table 4. Availability of Raw vegetable oils in and around different countries.

Country Name	Available Raw Vegetable Oil		Country Name	Available Raw Vegetable Oil
India	Jatropha and Palm		**Finland**	Rapeseed and Animal Fat
Malaysia	Palm		**Germany**	Rapeseed
Indonesia	Palm and Jatropha		**Italy**	Rapeseed
Australia	Waste Oil and Animal Fat		**Swedon**	Rapeseed
Newzealand	Waste Oil and Animal Fat		**UK**	Rapeseed and Waste Oil
Thailand	Palm, Coconut and Jatropha		**France**	Rapeseed and Sunflower
Philippine	Coconut and Jatropha		**Spain**	Sunflower
Korea	Waste Oil		**Brazil**	Soybean, Palm, Caster and Cotton Oil
Japan	Waste Oil		**USA**	Soybean and Waste Oil
China	Jatropha and Waste Oil		**Canada**	Canola and Animal Fat
Russia	Rapeseed, Sunflower and Soybean		**Mexico**	Animal Fat and Waste Oil

Biodiesel is defined as "mono alkyl esters of long chain fatty acids derived from vegetable oils in the presence of catalyst". Biodiesel can be prepared by several methods such as Transesterification, Pyrolysis, Micro emulsion, Blending and Direct use. Mostly biodiesel is produced from transesterification process rather than other methods. So it is the transesterification of triglycerides of vegetable oils (edible /non edible oils) or waste fried oils using alcohols (methanol/ethanol) with acid or alkali/base catalyst (NaOH / KOH) [10, 19]. Biodiesel appear to be most popular diesel substitute as it's properties are similar to standard diesel. Different properties of biodiesel prepared from various vegetable oils (edible/non edible oils) are seen and correlated with standard Diesel and biodiesel standards in Table 5 [4,14,20 and 21].

Table 5. Biodiesel properties produced from different vegetable oils.

Vegetable Oil (Fuel)/Properties		Density (kg/l)	Kinematic Viscosity (mm^2/s)	Cetane number	Calorific value (MJ/kg)	Cloud Point (^{o}C)	Pour point (^{o}C)	Flash point (^{o}C)
Std Diesel		0.855	3.06	50	43.8	---	-16	76
Biodiesel standards	**ASTM D 6751-01**	870-900	1.9-6.0	48-60	---	---	-15-10	130
	DIN EN 14214	875-900	3.5-5.0	49	42	---	-15-10	120
Edible oils:								
Peanut		0.883	4.9	54	33.6	5	---	176
Rice bran		0.82	5	---	42.5	-6	3	---
Rapeseed		0.880	5.70	---	37.5	---	---	---
Soybean		0.885	4.5	45	33.5	1	-7	178
Babassu		0.875	3.5	63	31.8	4	---	127
Sunflower		0.870	4.6	49	33.5	1	---	183
Palm		0.880	5.7	62	33.5	13	12	164
Waste Cooking Oil (WCO)		0.884	4.5	57.2	32.9	1	-5	180
Almond		0.820	5.09	---	---	---	---	126
Non-Edible oils:								
Karanja		0.876	9.60	---	36.12	8	---	187
Jatropha		0.880	2.37	61	39.2	---	2	135
Jojoba Ref. [14]		0.860	8.84	53	45.5	---	---	198
Neem		0.873	6.81	---	36.4	---	---	168
Thumba Ref. [13]		0.830	4.78	41.7	37	2	-6	164
Cieba Pentandra		0.885	4.36	49	41.79	---	---	158
Pongamia [22]		0.874	19		29.44			156

MATERIALS USED IN BIODIESEL PRODUCTION

Biodiesel is more effectively receiving attention as a sustainable alternative produced from raw vegetable oil, animal fats and unused fried oils from the past few decades. Biodiesel production is significantly derived from different feed stocks. Former type is based on animal fats and edible oils such as corn, soybean, linseed, sesame, rapeseed, palm, sunflower oil etc. Around 95% of biodiesel production takes place from edible oils due to their availability. Biodiesel produced from these feed stocks are said to be first generation bio fuels [23]. Even though first generation biodiesel has several merits such as reduction in green house gas emissions, low FFA content for simple alkali/base catalysed transesterification and increasing domestic energy security, first generation biodiesel are not relevant in long term. Because of land usage impacts, price of edible oil, biodiesel cost per unit. In addition to this continues use of food based feed stocks may lead to scarcity of oils for human beings and deforestation. Keeping this in view, many researchers focused on second generation biodiesel from non-edible oils such as karanja, jojoba, jatropha, pongamai, neem, thumba etc. These oils have high potential to overcome the demerits caused with first generation biodiesel. Non edible oil crops grow in forests (unused lands) and cultivation is easy at low cost. These factors make many researchers to initiate biodiesel production from low cost non edible oils as alternative feed stock. Among the non edible feed stock, castor, jatropha, karanja and micro algae oils are strongly considered as high oil content seeds.

After many tests being conducted using non edible oils to yield biodiesel, researchers revealed problems associated with higher level of FFA and viscosity. Firstly, due to high FFA content in non edible oils, alkali catalysed transesterification process shows uncertainty. Because FFA reacts with catalyst to form soaps which is leading to emulsification and separation problems. In addition to this, excessive soap formation decreases biodiesel yield and restricts water washing and drying process [24]. However, the maximum limit of FFA in non edible oil for alkali catalysed transesterification is bench-marked by many scientists. As reported by scholars, FFA content should not be grater than 2-3% respectively. Finally FFA was suggested that it should never exceed more than 1% for alkali catalysed transesterification. Secondly, Non edible oils posses 10-20 times highly viscous compared to petroleum diesel which causes instability to use in diesel engines. High viscous fuel leads to poor atomization, incomplete combustion and chocking of the fuel injectors etc. These disadvantages together with the use of unsaturated oils (non edible oils), that may result production of biodiesel and performance of conventional diesel engines [25].

These two difficulties restrict to a simple alkali/Base catalysed transesterification process, A pre-esterification (Acid catalyzed transesterification) process is necessary before alkali catalysed transesterification. Several alkali catalysts have been invented for low FFA feed stocks such as homogeneous catalysts (potassium hydroxide (KOH), sodium hydroxide (NaoH), and sulfuric acid etc) and heterogeneous catalysts (metal oxides, carbonates, alkoxides and calcium oxides etc) [8, 20]. Out of these, NaoH or KOH are actively being used due to low cost and high product yield. Whereas acidic catalysts are macro-reticular organic resins, alkane alumina, phase transfer catalysts, sulphuric acids, P-toluene sulphonic and dehydrating agents as a co-catalyst. Among all these sulphuric acid is most commonly used. Alcohols (methanol, ethanol, proponol and butanol etc.) are widely used. Comparatively, methyl alcohol is preferred due to its low cost.

METHODS OF BIODIESEL PRODUCTION

Several techniques were developed for the production of biodiesel to suit well in our conventional engines without any modifications. Raw oil seeds contain fatty acids generally called as triglycerides of long chain fatty acids. The molecular weight of these triglycerides is normally 800 Kg/m^3 or even more. Obviously, higher molecular weight results higher viscosity thus affecting many problems using in diesel engines. These long chain molecules of fatty acids are separated into small chain similar molecules thus reducing viscosity and other properties of the product can be brought close to diesel fuel. In order to produce biodiesel several methods implemented are Direct use or Blending with diesel fuel (dilution), Micro-emulsification, Thermal cracking (pyrolysis) and transesterification [7,8 and 25]. Out of many biodiesel production methods transesterification is most widely accepted due to high conversion efficiency, simplicity, can be carried out in normal ambient conditions, low conversion cost and grate fuel qualities from the yield.

Direct use or Blending with Diesel fuel (Dillution)

Vegetable oils are not recommended to use in engines directly due to high viscosity leads to other problems. So as to solve these problems vegetable oils can be mixed directly with diesel fuel in some limited proportionals. After several experiments, Caterpillar Brazil, in 1980, had run an engine with 10% vegetable oil and 90% diesel fuel to attain maximum power without any engine modifications and later it was stated that only a blend of 20% of vegetable oil and 80% of diesel fuel was successful. Other blend ratios were also tested on engine. 50/50 and 25% of sunflower and 75% of diesel etc. Finally it was concluded that blends containing less viscosity could prove better performances and it can be achieved by higher amount of diesel (up to 80%) blended with lower amount of vegetable oils (up to 20%) [26].

Micro-Emulsification

Micro-emulsion is defined as the colloidal equilibrium dispersion of optically isotropic fluid micro structures with dimensions generally in the range of 1-150nm formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphiles [27]. The problem caused due to high viscosity of vegetable oil can be minimized by micro-emulsion using solvents such as methanol, ethanol hexanol and 1-butanol. This process includes diesel fuel, vegetable oil, alcohol, and surfactant and cetane improver in various suitable proportions. Methanol, ethanol are used as alcohols to reduce viscosity, higher alcohols are used as surfactants and alkyl nitrates are used as cetane improvers. The oil contains different hydrocarbons and olefins. This ternary phase can improve spray properties by explosive vaporization of low boiling constituents in the micelles. Continues use of micro-emulsified fuel causes injection needle stickings, carbon deposit formation and incomplete combustion [28-29].

Thermal cracking (pyrolysis)

Thermal cracking is a method of conversion of one substance onto another by means of heat or heating with the acids of catalyst in the absence of air or oxygen to yield small molecules. This process is simple, waste less, pollution freeand effective compared to other cracking process. The pyrolasis of vegetable oil to produce bio fuels like alkanes, alkenes, alkadienes, aromatics and carboxylic acids in different proportions. The drawbacks of this process are high equipment cost, removal of oxygen during thermal pyrolysis. It also removes environmental benefits of using an oxygenated fuel, it requires separate distillation equipment for separation of the various fractions, viscosity of pyrolysed non edible oil distillate is quite higher than standard diesel oil and product obtained is similar to gasoline containing sulphur which makes it less Eco-friendly[29].

Transesterification

Transesterification is defined as a chemical process in which triglycerides (vegetable oils/animal fats) react with alcohol (methanol/ ethanol) under acid or alkali/base catalyst (NaOH/KOH), producing Fatty Acid Esters (Biodiesel) and Glycerol. The long chain triglycerides are modified to short chain mono esters and glycerin . The total methanolysis of triglycerides is as shown in figure 1.

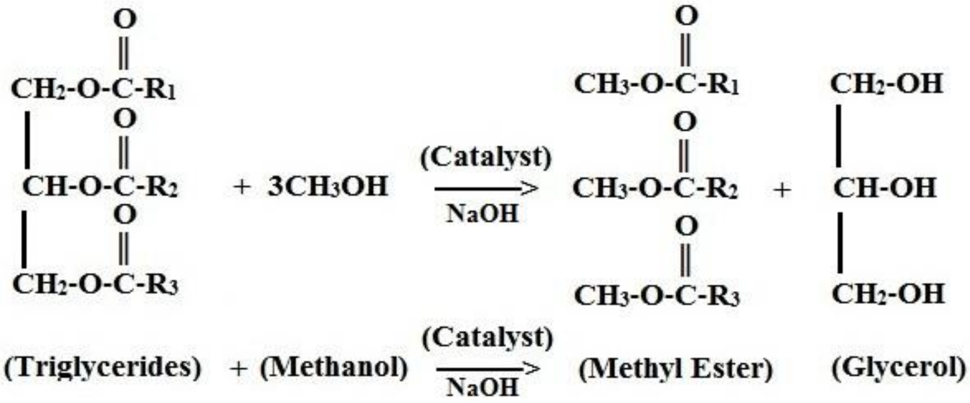
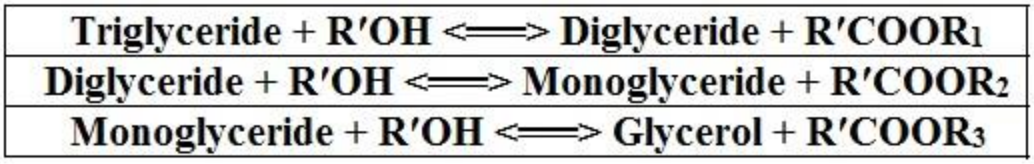


Figure 1: Represents methanolysis of triglycerides.

This process mainly reduces the viscosity of triglycerides. The general equation of transesterification process is referred in figure 2.

$$RCOOR' + R''OH \leftrightarrow RCOOR'' + R'OH$$

Figure 2: General equation of transesterification.



Triglyceride + R′OH <==> Diglyceride + $R'COOR_1$
Diglyceride + R′OH <==> Monoglyceride + $R'COOR_2$
Monoglyceride + R′OH <==> Glycerol + $R'COOR_3$

Figure 3: Transesterification reaction of triglyceride to esters and glycerol.

Transesterification process principle is most similar to alcoholysis and hydrolysis (except water is instead of an alcohol). Transesterification process can be reversible, even though the equilibrium lies in order to produce end product. Principle of transesterification process can be evaluated in 3 simple steps [30]. First step is conversion of triglycerides to diglycerides, diglycerides to monoglyceride and lastly, monoglyceride to glycerol. Producing one ester molecule from each glyceride for every step. A successful Transesterification process could result maximum yield and minimum glycerol. The Transesterification reaction in three simple steps is seen in Figure 3 [8, 30].

A flow chart of Biodiesel production is represented in Figure 4. It starts from raw feed stocks/animal fats. Acid value of raw feed stock determines FFA content. Based on FFA value, production of biodiesel starts to either pre-esterification or transesterification and other methods.

Acid Catalyzed Transesterification Process: Raw feed stocks/animal fats consisting higher value of FFA

(>1%), is esterified till its value is <1%. After this process the product is forwards to alkali transesterification process. Esterification process can be eliminated for low FFA feed stocks such as edible oils. In this process acid catalyst (most commonly sulphuric acid is used) is first mixed with alcohol (methanol) before adding in to high FFA content feed stock. These solvents stirred until the mixture become murky. This process is continued around $60^{O}C$ or higher for 2 hours [31]. It generally requires high temperature and faster stirring speed thus results faster conversion to esters. After few hours of this process, bottom fatty methyl esters and upper methanol are settled due to the density difference and separated using separating funnel. If the fatty methyl esters contain <1% FFA value then the solvent is further proceeded to Transesterification process or same method is repeated till its value reaches <1%.

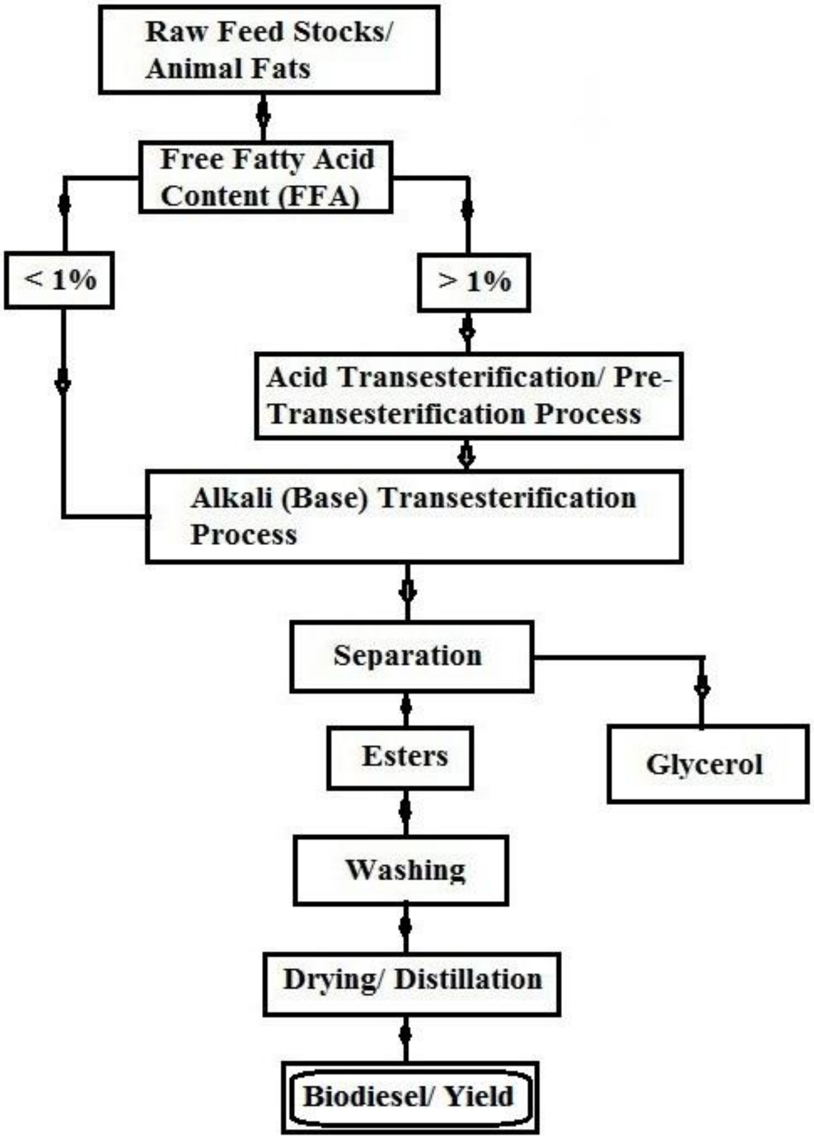


Figure 4: Flow Process of Biodiesel Production.

Alkali Catalyzed (Base) Transesterification process: Alkali transesterification process needs a strong homogeneous catalyst (considering sodium hydroxide (NaOH)), combines with alcohol (say methanol) for chemical reaction of triglycerides in order to convert FAME. The chemical reaction of alkali-catalyzed transesterification of triglycerides with alcohol is shown in Figure 5. The mechanism for this process is formulated in 4 steps. First step is an attack on the carbonyl carbon atom of triglyceride molecule by alkoxide ion to create tetrahedral intermediate. In second step, the tetrahedral intermediate reacts with an alcohol to regenerate alkoxide ion. In third step, rearrangement of the tetrahedral intermediate turns to fatty acid ester and diglyceride. Finally, the similar step is repeated to diglyceride and monoglyceride.

This method generally reduces viscosity of biodiesel. This process is conducted for the feed stock consisting FFA <1%. Concentration of catalyst has great impact on maximum yield production [32]. 1% of NaOH is used as catalyst due to low cost throughout the process. Initially NaOH is mixed with methanol and then added directly to the vegetable oils (edible oils/acid catalyzed product) (20). These products are stirred until it is found to be murky. This process is completely done at 50-60℃ for 1-2 hours. After 8 hours of this reaction, two layers are observed. Upper layer is biodiesel (non polar compound) and bottom layer is found to be glycerol (polar compound) and other sediments. Once methyl ester is separated, is washed with warm water till it is purified from glycerin, soaps, excess methanol and finally it is dried and stored. After washing with water, some fraction of water is left in biodiesel. So to remove this water content drying is necessary. The water is removed by boiling up to a temperature of 120℃. In some cases water washing is eliminated and directly taken to drying or distillation. Exact concentration of catalyst and molar ratio in esterification and transesterification process produce maximum yield of biodiesel and very less percentage of glycerol.

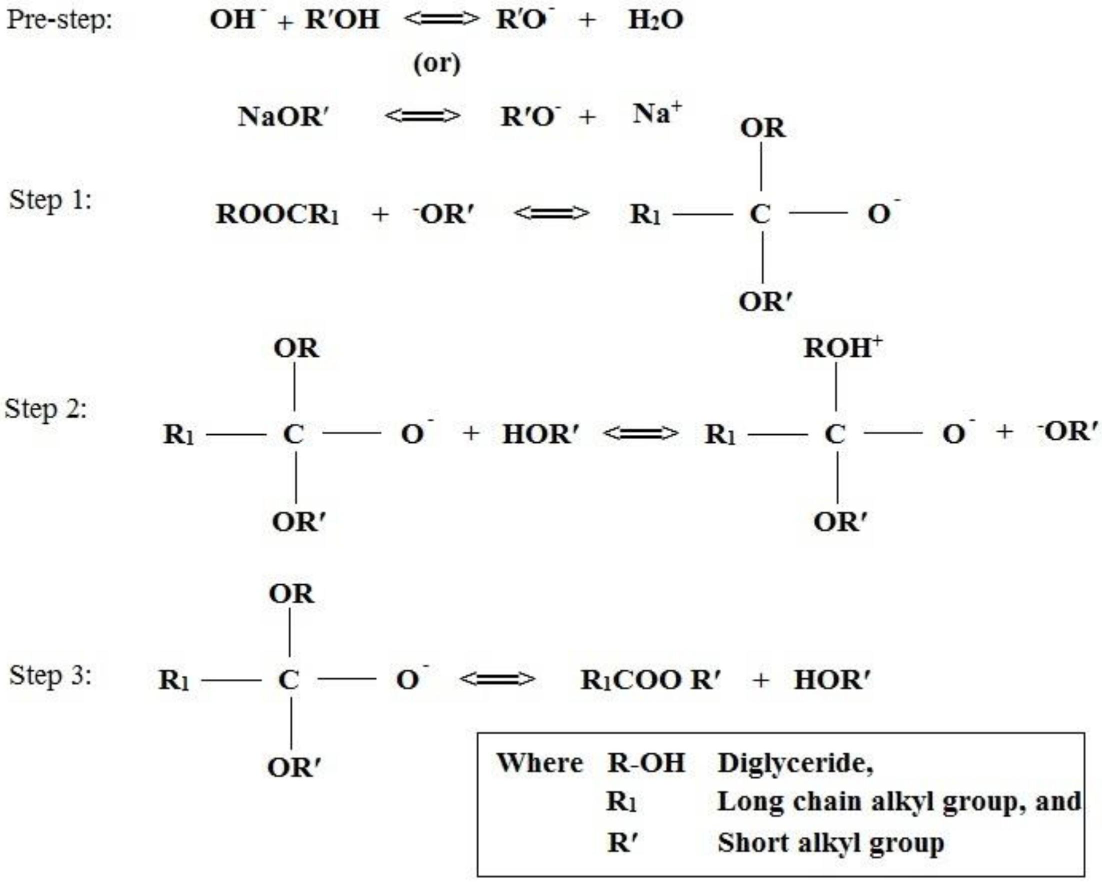


Figure 5: The mechanism of alkali-catalyzed transesterification of triglycerides in the presence of alcohol.

VARIOUS FACTORS INFLUENCING TRANSESTERIFICATION PROCESS

Free Fatty Acids (FFA) content

Based on acid value of fats in the vegetable oil there are two types of reactions. They are Alkali catalyzed transesterification and acid catalyzed transesterification. For alkali catalyzed reaction, the vegetable oils used should be free from fats. If any small percentage is present, alkali catalyst (NaOH) is utilized in neutralizing the FFA. This only absorbs the catalyst and slows down the reaction. For alkali catalyzed transesterification process the acid value of triglycerides should not exceed 1%. If it is more than 1%, then acid catalyzed transesterification is done. This reaction needs large amounts of alcohol under controlled conditions (high temperate (≥100℃) and pressure (5 bar)) for a long period [20]. Thus reducing acid value of triglycerides to lower value. Then allowed for alkali catalyzed transesterification.

Molar ratio of alcohol (methanol) to triglycerides

Most widely alcohol (methanol /ethanol) are used among different varieties of alcohols due to low cost and performance considerations. For stachiometric transesterification process, 3 moles of alcohol (methanol) per 1 mole of triglyceride to yield 3 moles of methyl esters and one mole of glycerol [20]. But in actual practice, molar ratio for alkali catalyzed transesterification can be higher considerably 6:1 as suggested by researchers in order to drive reaction for grater conversion in short time. Where as in acid catalyzed transesterification more alcohol is required under controlled conditions (high temperature (≥ 100℃) and high pressure 5 bar) and since this process is slow generally it takes more time. The suggested molar ratio for this reaction is 20:1 [23, 33].

Concentration of catalyst

Transesterification process needs a basic or acid catalyst as discussed earlier. In basic catalysts sodium methoxide and potassium methoxide are mostly proved to be successful. Where as in acid catalysts (sulphuric acid) is popular. As the catalyst concentration increases, conversion of triglycerides to ester and yield produced is increased. Excess concentration may effect the equilibrium reactions in production of esters, leads to form soaps and separations of esters are difficult.

According to research work it was concluded as: 90-98% conversion takes place from jatropha oil to methyl ester when 1.0-1.4% of NaOH concentration is used [8]. simillarly, best yield is achieved from jojoba methyl ester with the molar ratio of 6:1 when 0.5% of KOH catalyst involves in the reaction [14]. Nearly 90% yield is obtained from transesterification of thumba oil with the molar ratio of 8:1 and 0.75% of KOH catalyst [13].

Reaction temperature

High temperature during the process enhances the rate of reaction as more energy being stirred thus reducing viscosity of oils. For transesterification process suggested reaction temperature is (60-80℃) at a molar ratio of 6:1 to produce maximum yield [20]. Maximum temperature during the reaction is only limited by alcohol boiling point (60-70℃). Otherwise it will accelerate to the saponification reaction or evaporation of alcohol. Hence Reducing end product [14]. If fatty acids are more in triglycerides, it is pre-esterified and requires high temperature (more than 100℃) and pressure (5 bar).

Reaction time

Reaction time mainly influences the end product. Initially the reaction is slow due to mixing and dispersion of alcohol in to the oil. After few minutes, the reaction proceeds faster. Nearly it takes less than 2 hours for base catalyzed transesterification. Where as acid catalyzed transesterification takes (nearly 8-10 hours) more time than that of alkali catalyzed transesterification time [8, 25]. The yield produced from karanja oil methyl ester is found to be 94%, when the optimum temperature for base catalyzed transesterification is maintains 70℃ and takes 30 min. time [34].

Moisture content

Moisture content in triglycerides initiate reaction to form soap and reduces catalyst ability. This effect greatly impact on quantity of biodiesel to be produced. In case of acid catalyzed transesterification due to the effect of moisture the amount of biodiesel produced is greatly reduced than alkali catalyzed transesterification.

CONCLUSION

Biodiesel is potentially sustainable for diesel engines and good alternative as they are renewable in nature and environment friendly. There are several methods present in the investigation of biodiesel production. Transesterification of triglycerides is most popular method. The importance of this process is to reduce viscosity of oil. Direct use or blending with oils and micro emulsion processes can also reduce viscosity of oil but several problems associated during the usage in diesel engine such as engine performance, carbon deposits, injector plugging problems etc. Where as pyrolysis produces biogasoline rather than biodiesel.

Transesterification is a consecutive method. In which it first converts triglycerides to diglycerides, then diglycerides are converted to monoglycerides and lastly monoglycerides to esters and glycerol. This reaction mainly varies with reaction parameters. The main factors influencing this reaction are FFA content, molar ratio, concentration of catalyst, reaction temperature, reaction time and moisture content. Acid catalyzed transesterification is done before base/alkali catalyzed transesterification. Most commonly accepted molar ratio is 6:1-8:1 and 16:1 for alkali and acid catalyzed transesterification reaction respectively. The recommended alkali catalyst (NaOH or KOH) concentration is 0.5-1.2% based on type of oil. Higher reaction temperature reduces reaction time. Higher temperature is generally required for acid transesterification and normal temperature and pressure are sufficient for alkali transesterification reaction to produce maximum yield.

Many researchers concentrated production of biodiesel from edible oils but its production is better and at low cost with non edible oils. Properties of biodiesel from non edible oils are well correlated as per ASTM standards of diesel. As biodiesel is more oxygenated fuel, combustion properties are more similar to diesel fuel and emissions are reduced to lower values.

The government should protect crude oil reserves as long lasting supplements and make complete use of second generation biodiesel resources without deploying food resources.

REFERENCES

[1] Agarwal AK. *Prog Energy Combust Sci*. **2007**, 33, 233-271.
[2] Demirbas A. *Energy Convers Manag*. **2009**, 50, 2239-2249.
[3] Bull SR. *Renewable Energy*. **1996,** 9, 1019-1024.
[4] Daming Huang; Haining Zhou; Lin Lin. *Renewable Energy*. **2012**, 16,1874-1885.
[5] Mulimani H; Hebbal OD; Navindgi MC. *International Journal of Advanced Scientific Research And Technology*. **2012**, 2(2), 242-250.
[6] Ramadhas AS; Jayaraj S; Muraleedharan C. *Renewable Energy*. **2004**, 29, 727-742.
[7] Jaichandar S; Annamalai K. *Journal of Sustainable Energy and Environment*. **2011**,1, 71-75.
[8] Amit Agarwal; Pankaj Gupta; Rajdeep. *International Journal of Emerging Engineering Research and Technology*. **2015**, 3(1), 8-16.
[9] Demirbas A. *Prog Energy Combust Sci*. **2005**, 31, 466-87.
[10] Balasubramanian KR; Kannan GR; Anand R. *Petrotech.* **2010.**
[11] Kathirvelu S; Shenbaga Vinayaga Moorthi N; Neela Krishnan S; Mayilsamy K; Krishnaswamy T. *ARPN Journal of Engineering and Applied Sciences*. **2014**, 9(12).
[12] Arjun B; Chhetri; Martin S Tango; Suzanne M; Budge K Chris Watts; Rafiqul Isslam M. *Int J Mol Sci*. **2008**, 9, 169-180.
[13] Chavan SB; Kumbhar RR; Sharma YC. *Advances in Applied Science Research*. **2014**, 5(3), 10-20.
[14] Abdel fatah M; Farag HA; Ossman ME. *An International Journal of Engineering Science and Technology*. **2012**, 2(4),2250-3498.
[15] Joel Lindstrom. Use of straight vegetable oil as a fuel in appropriately equipped compression ignition (Diesel) engines, Harvesting Clean Energy Conference IX January, **2009**, 25-27.
[16] Khalisanni K; Khalizani K; Rohani MS; Khalid PO. *Global Journal of Environmental Research*. **2008**, 2(2), 81-83.
[17] Hanbey Hazar; Huseyin Aydin. *Appl Energy*. **2009**.
[18] Agarwal AK; Rajamanoharan K. *Appl Energy*. **2009**, 86, 106-112.
[19] Nithyananda BS ; Anand A; Dr. G.V. Naveen Prakash. *Int J Eng Res Appl*. **2013**, 3(4), 1778-1781.
[20] Alemayehu Gashaw; Amanu Lakachew. *International Journal of Science, Environment and Technology*. **2014**, 3(4), 1544-1562.
[21] Kannahi M ; Arulmozhi R. *Asian Journal of Plant Science and Research*. **2013**, 3(5), 60-64.
[22] Gaurav Dwivedi; Sharma MP. *International Journal of Renewable Energy Research*. **2013**, 3(2).
[23] Mohammad I Jahirul; Wenyong Koh; Richard J Brown; Wijitha Senadeera; Ian O"Hara ; Lalehvash Moghaddam. *Energies*. **2014**, 7, 5317-5331.
[24] Alemayehu Gashaw; Amanu Lakachew. *International Journal of Science, Environment and Technology*. **2014**, 3(4), 1544-1562.
[25] Vivek; Gupta AK. *J Sci Ind Res*. **2004**, 63, 39-47.
[26] Singh SP; Singh D. *Renewable and sustainable Energy Reviews*. **2010**, 12, 200-16.

[27] Alemayehu Gashaw; Tewodros Getachew; Abile Teshita. *Journal of Forest Products and Industries*. **2015**,2325-4513.
[28] Arifin SF. Production of biodiesel from waste cooking oil and Rbd palm oil using batch transesterification process, Universiti malaysia pahang, thesis, **2009**.
[29] Parawira W. *Scientific Research and Essays*. **2010**, 5(14), 1796-1808.
[30] Suresh Kumarm; Gupta AK; Naik SN. *J Sci Ind Res*. **2003**, 62, 124-132.
[31] Nor Hazwani Abdullah; Sulaiman Haji Hasan; Nurrul Rahmah Mohd Yusoff. *International Journal of Materials Science and Engineering*. **2013**, 1(2).
[32] Urvi patel; Amar Vaghela; Patel NM. *International Journal of Research in Information Technology*. **2013**, 1(4), 17-30.
[33] Tanzer Eryilmaz; Murat Kadir Yesilyurt. *Renewable energy*. **2016,** 95, 233-247.
[34] K V Yathish; Dr. R Suresh; Amruth E. *IOSR Journal of Applied Chemistry*. **2013**, 3(6), 09-15.