INTERNATIONAL JOURNAL OF PHYTOFUELS AND ALLIED SCIENCES
(A Journal of the Society for the Conservation of Phytofuels and Sciences)
(http://www.phytofuelsciences.com) (ISSN 2354 1784)

The Chemistry of Biodiesel Production

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Abstract
Biodiesel has gained importance as an alternative fuel for diesel engines. The best starting materials for the production of biodiesel are the vegetable oils from plant sources because of their high conversion rates and relatively short reaction time. This writes up review the various methods by which biodiesels may be produced.

INTRODUCTION

Energy is the most fundamental requirement for human existence and activities. As an effective fuel, petroleum has been serving the world to meet its need of energy consumption. It has been projected that global energy consumption will increase by 28% between 2015 and 2040, with fossil fuels providing the bulk (77%) of the energy consumption (Showstack, 2017). But the dependence of mankind entirely on the fossil fuels could cause a major deficit in energy production future. The need for energy is increasing continuously due to increased industrialization activity and population growth. In addition to the issue of global warming, scientists are encouraged to develop fuel substitutes that are renewable and sustainable (Kulkarni and Dalai, 2006; Prafulla *et al.,* 2012).

Meanwhile, escalating oil prices and depletion of oil reserves has necessitates better alternatives energy from fossil fuels, in addition, the rise in concern for pollution caused by fossil fuels such as petroleum, coal and natural gas has made biodiesel a popular alternative fuel and renewable sources of energy (Ogunwole, 2012; Garlapati *et al*., 2013).

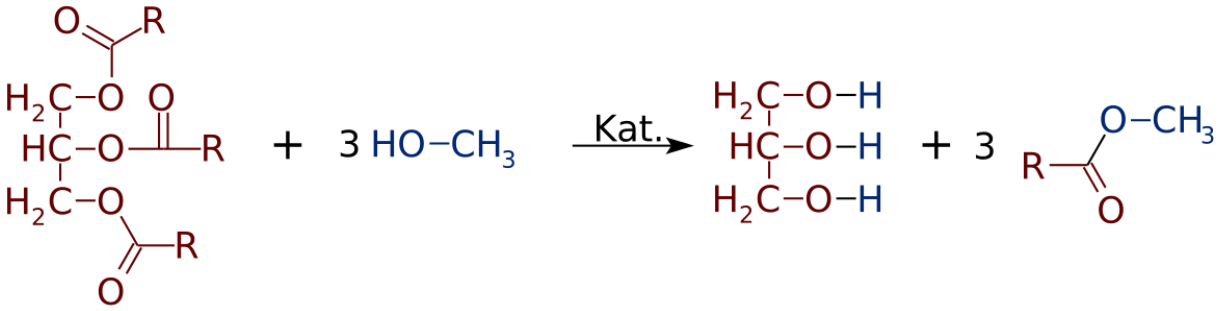
Over the last few years biodiesel has gained importance as an alternative fuel for diesel. Vegetable oil from plant sources is the best starting material to produce biodiesel because the conversion of pure triglyceride to fatty acid methyl ester is high and the reaction time is relatively short. The most common way to produce biodiesel is by transesterification, which refers to a catalyzed chemical reaction involving vegetable oil and an alcohol to yield fatty acid alky esters and glycerol (Thirumarimurugan *et al.,* 2012). The use of edible vegetable oils and animal fats for biodiesel production has recently been of

great concern because they compete with food materials. As the demand for vegetable oils for food has increased tremendously in recent years, it is impossible to justify the use of these oils for fuel purposes such as biodiesel production. Moreover, these oils could be more expensive to use as fuel (Ameen *et al.*, 2014; Belewu *et al.*, 2018).

Spent oils both (domestic and industrial) could constitute a serious environmental pollution problem. Their use for the production of biodiesel has thus allayed this fear and has added to the advantage of their low price (Thirumarimurugan *et al.*, 2012). Used vegetable oil is described as a 'renewable fuel' as it does not add any extra carbon dioxide gas to the atmosphere, as opposed to fossil fuels, which cause changes in the atmosphere. In addition, the contribution of non-edible oils from plants such as Jatropha, Castor, Thevetia, Soapnut, etc have also shift attention from the food crops oil (Ameen *et al.*, 2014).

1.1 Biodiesel

Biodiesel is the name for a variety of ester-based oxygenated fuels from renewable biological sources. Chemically, biodiesel is defined as the monoalkyl esters of long-chain fatty acids derived from renewable biolipids.. Fatty acid methyl esters or biodiesels from processed organic oil are produced from a vegetable oil or animal fats. Biodiesel is similar to petroleum diesel in many aspects of its chemical and physical properties (Demirbas, 2008a; Soon *et al.*, 2013; Vashist and Ahmad 2014).



Fatty Acid **Methanol** **Glycerol** **Fatty Acid Methyl Ester**

Fig 1: Chemical Structure of a Fatty Acid Methyl Ester (Biodiesel)

(Source: en.m.wikipedia.org/wiki/Fatty_acid_methyl_ester)

2.0 TECHNOLOGIES IN BIODIESEL PRODUCTION

2.1 Sources

Biodiesel production is the process of producing biodiesel, through the chemical reactions of transesterification and esterification. This involves vegetable or animal fats and oils being reacted with short-chain alcohols (typically methanol or ethanol) (Anastopoulos *et al.*, 2009). The fractions of biomass that have been used and are still enjoying renewed attention as feedstock for production of liquid biofuels are from agricultural sources, like: lipids, simple sugars and polysaccharides sources (Adebayo *et al.*, 2011). Thus most crop seed rich in oil provide a good source for the raw material for the production of biodiesel, these crops include Soybean, Oil palm, Sunflower, Peanut, Flax, Safflower Castor

Seed, Tung, Cotton, Jojoba, Jatropha and Avocado **(**García Penela, 2007, Demirbas, 2007). Other sources of biodiesel raw material include Microalgae, (Chisti, 2007).

There are many current technologies or procedures employed in the production of Biodiesel. The procedures involved in these processes vary as:

1. Direct use and blending
2. Micro-emulsions
3. Pyrolysis of vegetable oil
4. Transesterification

2.1.1 Direct use and blending

Crude vegetable oils are found not much encouraging to be used directly as diesel engine fuels. Hence, crude vegetable oils are mixed directly or diluted with diesel fuel to improve the viscosity and to be used for diesel engines. Energy consumption in the case of these oils are found equivalent to diesel fuel. The ratios of oil to diesel 1:10 – 2:10 was found successful (Fukuda *et al.*, 2001). But at the end, the use of direct oils or blend of oils was not satisfactory with regard to direct or indirect usage as diesel fuels. Polymerisation during storage and combustion, carbon deposits and lubricating oil thickening are the problems encountered generally (Ma and Hanna, 1999).

2.1.2 Micro-emulsions of oil

The fuels of this kind are also termed as hybrid fuels. The problem of high vegetable oil viscosity can be overcome by micro-emulsification. A micro-emulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions in the range of 1–150 nm, formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphiles (Ma and Hanna, 1999). They exist as three components, namely an oil phase, an aqueous phase and a surfactant. The maximum viscosity limitation required for diesel engines can be met by mico-emulsions with butanol, hexanol and octanol (Jain and Sharma, 2010).

2.1.3 Pyrolysis of Oils

Pyrolysis is the conversion of an organic compound into another organic compound by means of heat with the help of catalyst. Animal fats, vegetable oils, natural fatty acids or methyl esters of fatty acids can be used as pyrolyzed material. In the case of animal fats and vegetable oils conversion, triglycerides play an important role and thus the thermal cracking reactions. It is a promising technology for biodiesel production. The pyrolysis reactions can be divided into catalytic and non-catalytic reactions. The points to be considered are the expensive equipment for the process and all possibilities of more gasoline production than diesel fuel, Fig 2 (Maher and Bressler , 2007).

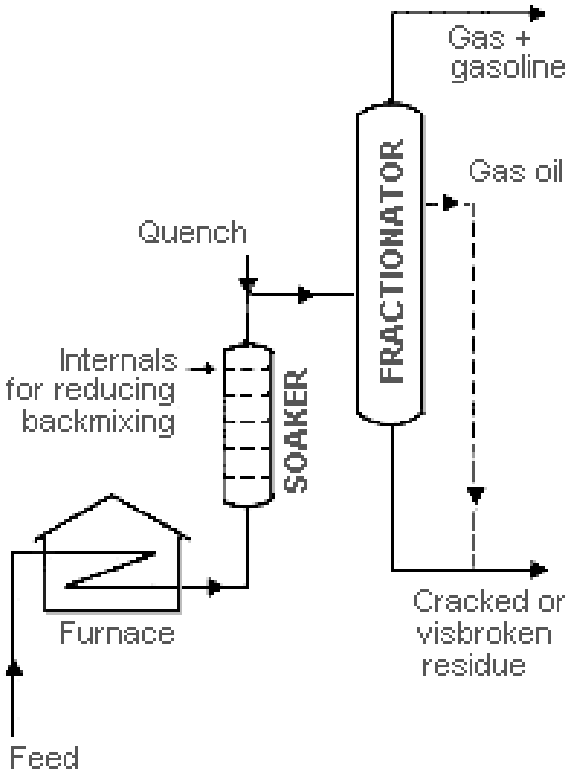
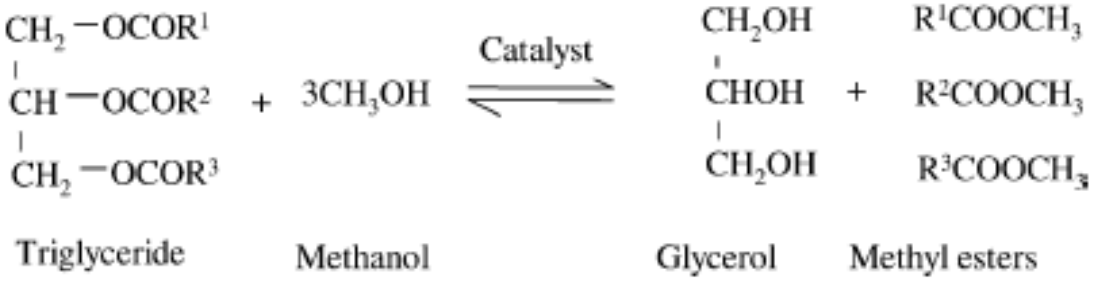


Fig 2: Thermal Cracking Process (www.setlab.com/resources/refining/thermal-cracking)

2.1.4 Transesterification of oils

The most important and effective current technology for biodiesel production is the transesterification of oils with alcohol to give biodiesel as main product and glycerine as by product (Meher *et al*., 2006).



Scheme 1: Transesterification Reaction (Meher *et al*., 2006).

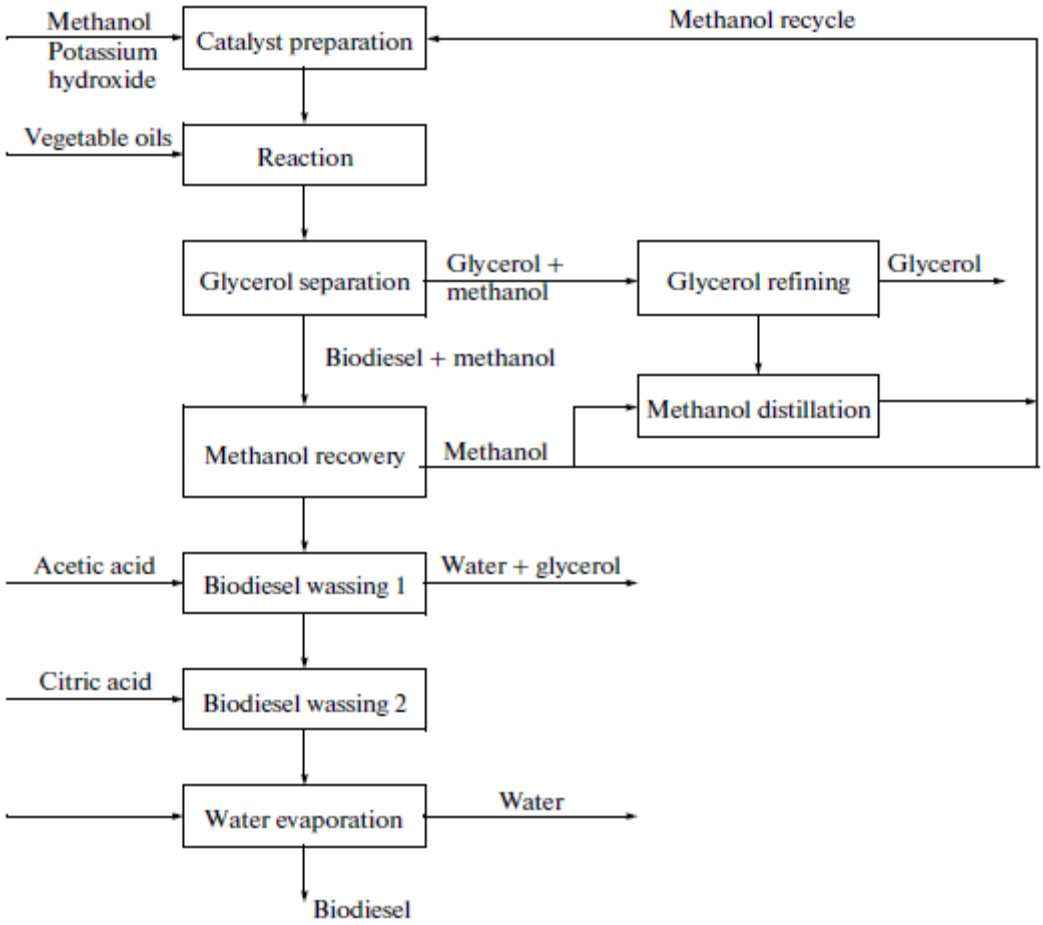


Fig 3: Transesterification Process (Source: Fabiano *et al.*, 2012)

The current technologies in use for production of biodiesel are catalytic and non-catalytic transesterification methods (Meher *et al*., 2006; Cerveró *et al*., 2008).

2.1.4.1 Catalytic Transesterification

The transesterification of vegetable oils by heating with an alcohol and using a catalyst is carried out in this process. Two types of catalysts are used in catalytic technique; one is by homogenous catalysts and the other one by heterogeneous catalyst. In the catalytic methods the selection of suitable catalyst is more important to reduce the cost of production (Meher *et al*., 2006; Cerveró *et al*., 2008).

a) The homogenous catalytic methods are again sub divided into two methods, one is homogenous base catalytic transesterificationa and the other, homogenous acid catalytic transesterification (Meher *et al.*, 2006).

i) **Homogenous base catalytic transesterification**: At present, this process is the most employed in commercial sectors. It uses homogenous catalysts such as an alkaline metal alkoxides and hydroxides, as well as sodium or potassium carbonates (Meher *et al*., 2006). In the method of basic methanolysis, almost in all the cases

sodium hydroxide or potassium hydroxide have been used, both in concentration from 0.4% to 2% w/w of oil. The reasons these catalysts preferred are best operative conditions, high conversion rate in minimum time, good catalytic activity and economical (Fabiano *et al.*, 2012).

ii. **Homogeneous acid catalytic transesterification**: An acid catalyst is used for the processing of triglycerides for biodiesel production. Sulphuric acid, sulphonic acid and hydrochloric acid are used as acid catalysts. The process starts by mixing the oil directly with the acidified alcohol, and then the separation and transesterification occur in one step, with the alcohol acting both as a solvent and as an esterification reagent (Cerveró *et al*., 2008).

b) **Heterogeneous catalytic transesterification**: These catalysts can act in different phases which can help in easy separation. The expensive method of homogeneous catalysts has called for heterogeneous methods. No soap formation takes place in heterogeneous processes. The process is as presented in Figure 4 (Kouzu and Hidaka 2011).

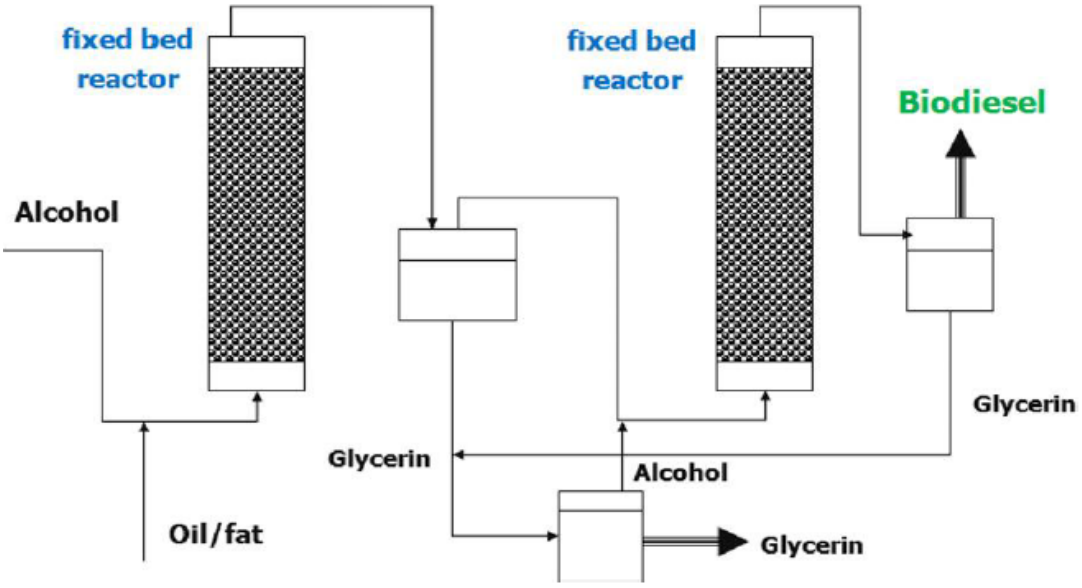
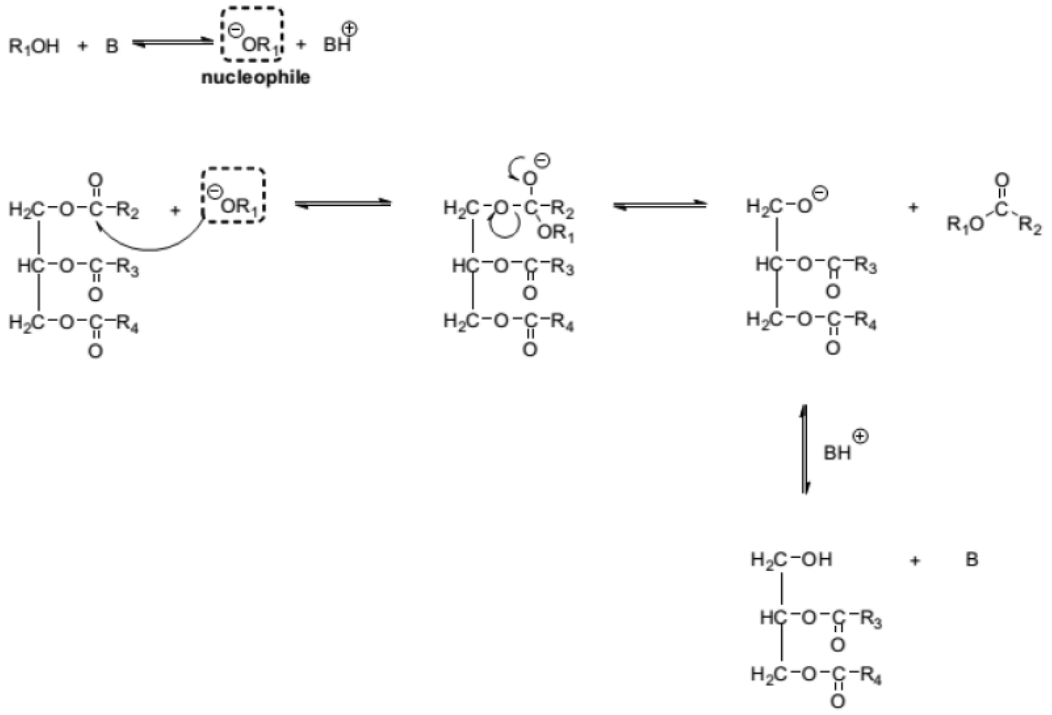


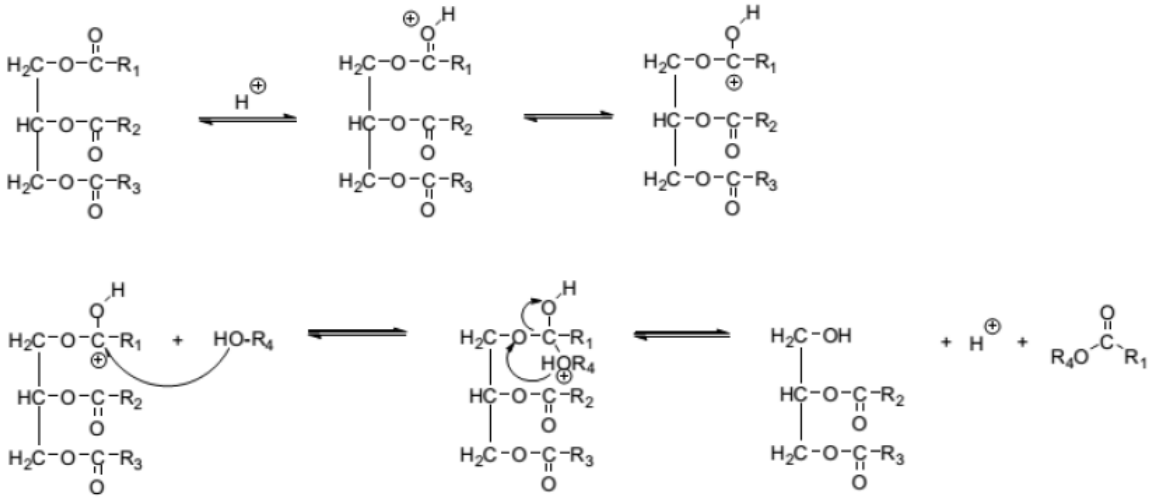
Fig 4: Heterogeneous Catalytic Transesterification (Kouzu and Hidaka 2011)

There are two more divisions in heterogeneous catalyst run reactions; they are heterogeneous solid base catalysts and heterogeneous solid acid catalysts. The former catalysts are base or basic oxides coated over large surface area. Solid-base catalysts are more active than solid-acid catalyst. The most common solid-base catalysts are Basic zeolites, alkaline earth metal oxides and hydrotalcites. Solid base can leads to the heterogeneous catalytic process, which promises the cost reasonable biodiesel production (Kouzu and Hidaka 2011).

Heterogeneous solid acid catalysts have different acid sites with varying strengths of Bronsted or Lewis acidity, compared to the homogenous acid catalysts. Heterogeneous Solid acid catalysts, such as Nafion-NR50, sulphated zirconia and tungstated zirconia have been chosen to catalyze biodiesel forming transesterification due to the presence of sufficient acid site strength (Dalai and Meher, 2006).



Scheme 2: Reaction Mechanism For Base-Catalyzed Transesterification during Biodiesel Production (Where B is a base and R1-4 are hydrocarbon groups)



Scheme 3: Reaction mechanism for acid-catalyzed transesterification during biodiesel production (Where R1-3 are hydrocarbon groups)

2.1.4.2. Non Catalytic Transesterification

There are few non catalytic methods too, these process render production of biodiesel through a conventional transesterification system complicated, thus giving a reason to investigate the production of biodiesel from triglycerides via non-catalytic reactions. Super critical alcohol esterification, and BIOX co-solvent transesterification are included in the non-catalytic processes (Ahmad *et al.*, 2012; Zakir, 2016).

3.0 DIFFERENT SOURCES OF BIOFUEL

3.1 Algae

Algae come from stagnant ponds in the natural world, and more recently in algae farms, which produce the plant for the specific purpose of creating biofuel. Advantages of algae include the reduction in the emission of CO_2, self-generating biomass, Algae can produce up to 300 times more oil per acre than conventional crops. Among other uses, algae have been used experimentally as a new form of green jet fuel designed for commercial travel. At the moment, the upfront costs of producing biofuel from algae on a mass scale are in process, but are not yet commercially viable (Adenle *et al.*, 2013; Kumar *et al.*, 2015; Farm Energy 2019)

3.2 Carbohydrate (Sugars) Rich Biomaterial

It comes from the fermentation of starches derived from agricultural products like corn, sugar cane, wheat, beets, and other existing food crops, or from inedible cellulose from the same crops produced from existing crops, can be used in an existing gasoline engine, making it a logical transition from petroleum. It used in Auto industry, heating buildings ("flueless fireplaces")

At present, the transportation costs required to transport grains from harvesting to processing, and then out to vendor's results in a very small net gain in the sustainability stakes (Murata and Kawai, 2016).

3.3 Oils Rich Biomaterial

It comes from existing food crops like rapeseed (e.g Canola), sunflower, corn, and others, after it has been used for other purposes, i.e. food preparation ("waste vegetable oil", or WVO), or even in first use form ("straight vegetable oil", or SVO). Not susceptible to microbial degradation, high availability, re-used material. It is used in the creation of biodiesel fuel for automobiles, home heating, and experimentally as a pure fuel itself. At present, WVO or SVO is not recognized as a mainstream fuel for automobiles. Also, WVO and SVO are susceptible to low temperatures, making them unusable in colder climates (Elkady *et al.*, 2015, Demirbas, 2007).

3.4 Agriculture Wastes (Organic and Inorganic Sources)

It comes from agricultural waste which is concentrated into charcoal-like biomass by heating it. Very little processing required, low-tech, naturally holds CO_2 rather than releasing it into the air. Primarily, biochar has been used as a means to enrich soil by keeping CO_2 in it, and not into the air. As fuel, the off-gasses have been used in home heating. There is controversy surrounding the amount of acreage it would take to make fuel production based on biochar viable on a meaningful scale. Furthermore, use of

agriculture wastes which is rich with inorganic elements can be used as compost (fertilizer) in agriculture (Awasthi, *et al.*, 2015; Panpatte and Jhala, 2019).

4.0 Biodiesel Production Processes

Transesterification is widely used for the transformation of triglyceride into fatty acid methyl ester. The base catalyzed production of biodiesel generally has the following processes.

4.1 Mixing of Alcohol and Catalyst

This typical process is mainly done by mixing alkali hydroxide (commonly potassium hydroxide and sodium hydroxide) with common alcohols (methanol and ethanol) in the mixer with standard agitator to facilitate thorough mixing. Alkali hydroxide is dissolved in the alcohol to produce alkoxide solution (Demirbas, 2008a; Adebayo *et al.*, 2011; Ameen *et al.*, 2014; Belewu *et al.*, 2018; Ameen *et al.*, 2019).

4.2 Chemical Reaction

The alcohol and catalyst mixture is then charged into a closed reaction vessel and the oil is added. The reaction system is totally closed to the atmosphere to prevent the loss of alcohol, since it easily vaporizable. The reaction mixture is kept just near the boiling point of the alcohol to speed up the reaction. Excess alcohol is normally used to ensure total conversion of the oil to its esters as there is no problem of recovering of the alcohol for later use after recycling (Demirbas, 2008b; Adebayo *et al.*, 2011; Ameen *et al*, 2014; Belewu *et al.*, 2018; Ameen *et al.*, 2019).

4.3 Separation

After the reaction is completed, there exists glycerol and biodiesel formation. Both have a significant amount of the excess alcohol that was used in the reaction which is in need of being recovered. The reacted mixture is sometimes neutralized at this step if the basic media that is caused by alkali hydroxide is occurred. The glycerol phase is much denser than biodiesel phase, making biodiesel to float. The two products can be separated by gravity using settling vessel. The glycerol is drawn off at the bottom of the settling vessel and biodiesel is drawn off at the top. In some cases, a centrifuge is used to separate the two materials faster by screening both phases (Demirbas, 2008b; Adebayo *et al.*, 2011; Mulimani *et al.*, 2012; Ameen *et al.*, 2014; Belewu *et al.*, 2018; Ameen *et al.*, 2019).

4.4 Alcohol Removal

After the glycerol and biodiesel phases have been separated, the excess alcohol in each phase is removed with a flash evaporation process or by distillation commonly. But currently extractive distillation can instead be used to fasten the process and to be more economical. On the other hand, the alcohol is removed and the mixture neutralized before the glycerol and esters have been separated to prevent the effect of basic media inside the reactor. After the alcohol is being recovered it is used as main raw material (Demirbas, 2008a; Adebayo *et al*, 2011; Mulimani *et al*, 2012; Ameen *et al.*, 2014; Belewu *et al.*, 2018; Ameen *et al.*, 2019).

4.5 Biodiesel Washing

After transesterification the upper ester layer may contain traces of NaOH, methanol and glycerol. Since the remaining unreacted

methanol in the biodiesel has safety risks and can corrode engine components, the residual catalyst (NaOH) can damage engine components, and glycerol in the biodiesel can reduce fuel lubricity and cause injector coking and other deposits. These being water soluble is removed by washing (4-6 times) the biodiesel with water maintained at 40-50ºC. Washing is carried out by spraying hot water over the biodiesel; precautions were taken to avoid soap formation (Mulimani *et al*, 2012). The washed biodiesel needs drying in order to remove trace impurities. In some processes washing step is not necessary depending on the quality of biodiesel produced (Demirbas, 2008a). After the completion of washing process the biodiesel may contain some traces of water. Biodiesel is heated to 110 ^{0}C to remove the trapped traces of water (Demirbas, 2008b; Adebayo *et al.*, 2011; Mulimani *et al.*, 2012; Ameen *et al.*, 2014; Belewu *et al.*, 2018; Ameen *et al.*, 2019).

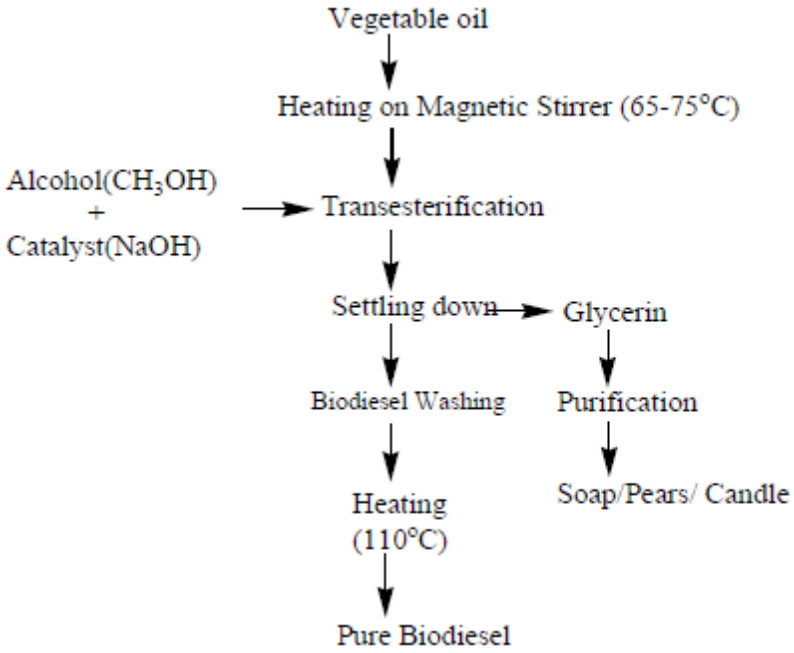


Fig 5: Flow Chart of Biodiesel Production Process

9.0 CONCLUSIONS

The importance of biodiesel and its production cannot be overemphasized; biodiesel has assumed a very prominent position in the energy development of both the developed and developing nations. This is so primarily because of climate change and the fear of the depletion of the fossil fuel. Biodiesel being not only clean fuel but also obtained from renewable sources is believed to be a better alternative to the traditional petro-diesel. Thus development geared towards the production and utilization of biodiesel will go a long way in conserving the ecosystem as well as serve as a source of income.

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