

# Chemistry of Biodiesel and Its Environmental Impact

## A Review Article

Tekalign Kasa and Fisseha Gebrewold

Madda Walabu University, College of Natural and Computational Science, Department of Chemistry, Bale-Robe, Ethiopia; P.Box: 247

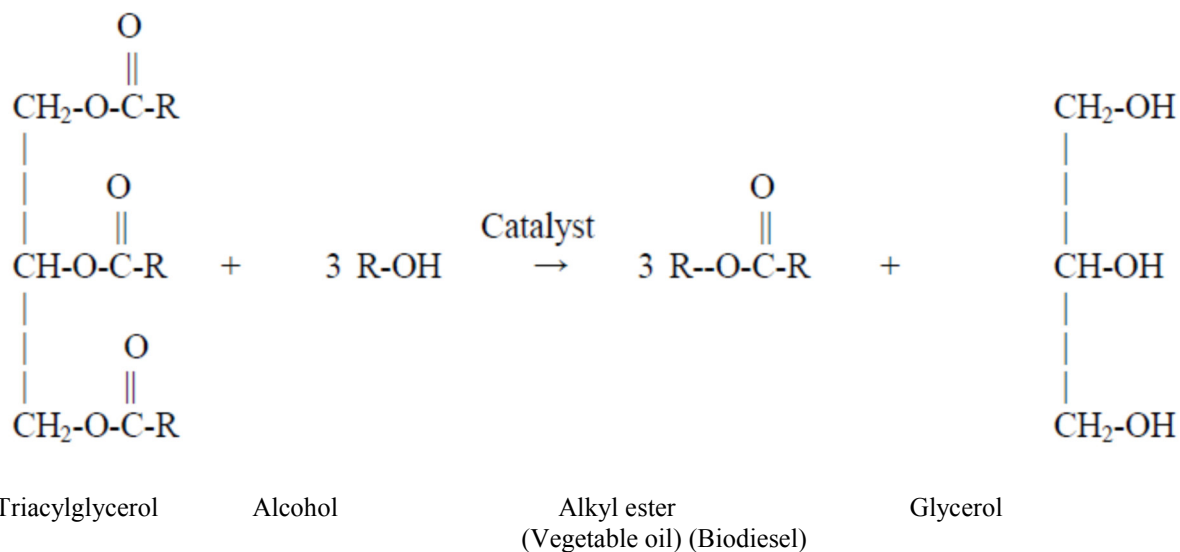
### Abstract

Biodiesel is a liquid obtained by chemical processes from vegetable oils or animal fats and an alcohol that can be used in diesel engines, alone or blended with diesel oil. It is one of the fuels that are being considered as an alternative to fossil fuels. The chemical reaction for producing biodiesel known as transesterification. Biofuel can be monoalkyl esters of fatty acids produced from animal fats or vegetable oils by transesterification or other methods with small chain alcohols, using different kinds of catalysts and they are drawing increasingly attention throughout the world as substitutes for petroleum-derived transportation fuels to address energy cost, energy security and global warming concerns associated with liquid fossil fuels. As the technology used in the conversion of feedstock into biofuel is more advanced, the second and third generation biofuels are more useful in environmental protection by greenhouse gas emission.

**Keywords:** biodiesel, environment, transesterification

### INTRODUCTION

Biodiesel is the name given to fuel for Diesel engines created by the chemical conversion of animal fats or vegetable oils. It can operate in compression ignition engines like petroleum diesel without requiring any essential engine modifications. Moreover, it can maintain the payload capacity and range of conventional diesel unlike fossil diesel, pure biodiesel is bio-degradable, nontoxic and essentially free of sulphur and aromatics (Indhumathi *et al.*, 2014). Chemically, most biodiesel consists of alkyl esters instead of the alkanes and aromatic hydrocarbons of petroleum derived diesel (Ariharan *et al.*, 2014). It is a renewable, biodegradable, environmentally benign, energy efficient, substitution fuel which can fulfill energy security needs without sacrificing engine's operational performance. Thus, it provides a feasible solution to the twin crises of fossil fuel depletion and environmental degradation. Any fatty acid source may be used to prepare biodiesel. Thus, any animal or plant lipid should be a ready substrate for the production of biodiesel. The use of edible vegetable oils and animal fats for biodiesel production has recently been of great concern because they compete with food materials - the food versus fuel dispute (Pimentel *et al.*, 2009; Srinivasan, 2009). There are concerns that biodiesel feedstock may compete with food supply in the long-term (Lam *et al.*, 2009; Metzger, 2009). Hence, the recent focus is the use of non-edible plant oil source and waste products of edible oil industry as the feedstock for biodiesel production meeting the international standards. (Refaat, 2010). It has similar fuel properties to diesel and therefore it can be used as a substitute for diesel fuel, either in neat form or in blends with petroleum diesel and also has the following advantages over petroleum-based diesel; it is renewable, carbon neutral, more rapidly biodegradable, less toxic, has a higher flash point and low sulfur content. Availability of feedstock and optimization of production process are, however, among the biggest challenges facing biofuel industry worldwide. The transesterification is carried out using homogeneous catalysts such as KOH, NaOH, and H<sub>2</sub>SO<sub>4</sub> (Ogbu and Ajiwe, 2013) or heterogeneous catalysts such as metal oxides or carbonates (Alemayehu and Amanu, 2014). It appears to be an attractive energy resource for several reasons. First, biodiesel is a renewable resource of energy that could be sustainably supplied. Second, biodiesel appears to have several favorable environmental properties resulting in no net increased release of carbon dioxide and very low sulfur content. The release of sulfur content and carbon monoxide would be cut down by 30% and 10%, respectively, by using biodiesel as energy source. Moreover, biodiesel contains no aromatic compounds and other chemical substances which are harmful to the environment and for the health of the society. Recent investigation has indicated that the use of biodiesel can decrease 90% of air toxicity and 95% of cancers compared to common diesel source. Third, biodiesel appears to have significant economic potential because as a non-renewable fuel that fossil fuel prices will increase inescapably further in the future. Finally, biodiesel is better than diesel fuel in terms of flash point and biodegradability (Huang, 2010). About 90-100 years ago, the major source of energy shifted from recent solar to fossil fuel (hydrocarbons). It is biodegradable and non-toxic has low emission profiles and so is environmentally beneficial. Alternative fuels, other than being renewable, are also required to serve to decrease the net production of carbon dioxide (CO<sub>2</sub>), oxides of nitrogen (NO<sub>x</sub>), particulate matter, and etc., from combustion sources (Niraj *et al.*, 2011).



Scheme 1: REACTION BETWEEN TRIACYLGLYCEROL AND ALCOHOL TO PRODUCE ALKYL ESTER

The oil is first charged to the system, followed by the catalyst and methanol. The system is agitated during the reaction time. Then agitation is stopped. In some processes, the reaction mixture is allowed to settle in the reactor to give an initial separation of the esters and glycerol. In other processes the reaction mixture is pumped into a settling vessel, or is separated using a centrifuge. The alcohol is removed from both the glycerol and ester stream using an evaporator or a flash unit. The esters are neutralized, washed gently using warm, slightly acid water to remove residual methanol and salts, and then dried. The finished biodiesel is then transferred to storage. The glycerol stream is neutralized and washed with soft water. The glycerol is then sent to the glycerol refining section (Gerpen *et al.*, 2004).

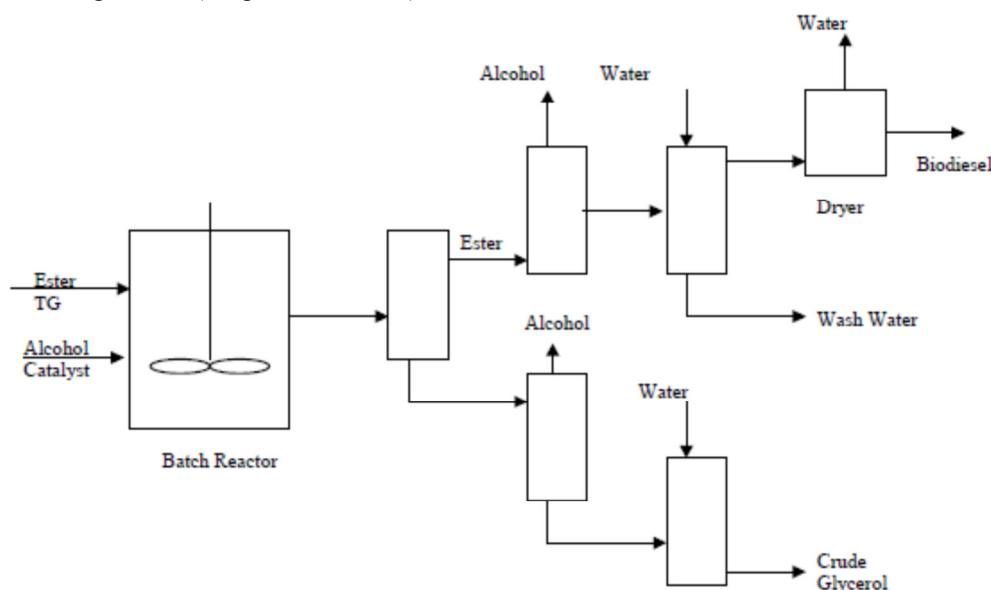


Figure 1: SHOWS A PROCESS FLOW DIAGRAM FOR A TYPICAL BATCH SYSTEM (Gerpen *et al.*, 2004).

The biggest difference between biofuels and petroleum feedstocks is oxygen content. Biofuels are nonpolluting, locally available, accessible, sustainable and are a reliable fuel obtained from renewable sources. Electricity generation from biofuel has been found to be a promising method in near future. First generation biofuels refers to biofuels made from starch, sugar, vegetable oils or animal fats using conventional technology. The basic feedstocks for the production of first generation biofuels are often seeds or grains such as wheat, which yields starch that is fermented into bioethanol, or sunflower seeds, which are pressed to yield vegetable oil that, can be used in biodiesel (Chauhan and Shukla, 2011).

TABLE 1: SHOWS THE CLASSIFICATION OF RENEWABLE BIOFUELS BASED ON THEIR PRODUCTION TECHNOLOGIES (NIGAM AND SINGH, 2010).

Generation	Feedstock	Example
First generation biofuels	Sugar, starch, vegetable oils, or animal fats	Bio-alcohols, vegetable oil, biodiesel, biogas
Second generation biofuels	Nonfood crops, wheat straw, corn, wood, solid waste, energy crops	Bio-alcohols, Bio-oil, Bio-DMF, Wood diesel
Third generation biofuels	Algae	vegetable oils, biodiesel
Fourth generation biofuels	vegetable oils, biodiesel	Biogasoline

Second and third generation bio fuels are also called advanced bio fuels. Second generation bio fuels are mainly made from non-food crops like wheat straw, corn, wood etc. On the other hand appearing the fourth generation is based in the conversion of vegoil and biodiesel into bio gasoline using the most advanced technology. Renewable liquids biofuels for transportation have recently attracted huge attention in different countries all over the world because of its renewability, sustainability, common availability, regional development, rural manufacturing, jobs, reduction of greenhouse gas emissions and its biodegradability. There are several reasons for biodiesel to be considered as relevant technologies by both developing and industrialized countries. They include energy security reasons, environmental concerns, foreign exchange savings and socioeconomic issues related to rural sector (Chauhan and Shukla, 2011).

First-generation fuels are already being produced in significant commercial quantities in a number of countries. Second-generation fuels are generally those made from non-edible lingo-cellulosic biomass either non-edible residues of food crop production (e.g. corn stalks or rice husks) or non-edible whole plant biomass (e.g. grasses or trees grown specifically for energy). Second-generation fuels are not yet being produced commercially in any country (WHO, 2006). Many industrialized countries are pursuing the development of expanded or new biofuels industries for the transport sector, and there is growing interest in many developing countries for similarly “modernizing” the use of biomass in their countries and providing greater access to clean liquid fuels (Goldemberg *et al.*, 2004).

#### Typical Oil Crops Useful for Biodiesel Production

The main characteristics of typical oil crops that have been found useful for biodiesel production are summarized in the following paragraphs (<http://www.springer.com/978>).

##### Rapeseed

Rapeseed adapts well to low fertility soils, but with high sulfur content. It is the most important raw material for biodiesel production. Moreover, low prices in comparison to wheat (its main competitor for crop rotation) and low production per unit area have limited its use.

##### Soybean

It is a legume originating in East Asia. Depending on environmental conditions and genetic varieties, the plants show wide variations in height. Leading soybean producing countries are the United States, Brazil, Argentina, China, and India. Biodiesel production from soybean yields other valuable sub-products in addition to glycerin: soybean meal and pellets (used as food for livestock) and flour (which have a high content of lecithin, a protein). Since the seeds are very rich in protein, oil content is around 18% (<http://www.springer.com/978>).

##### Oil Palm

Oil palm is a tropical plant that reaches a height of 20-25 m with a life cycle of about 25 years. Two kinds of oil are obtained from the fruit: palm oil proper, from the pulp, and palm kernel oil, from the nut of the fruit (after oil extraction, palm kernel cake is used as livestock food). Several high oil-yield varieties have been developed. Indonesia and Malaysia are the leading producers. It is important to remark that pure palm oil is semisolid at room temperature (20-22°C), and in many applications is mixed with other vegetable oils, sometimes partially hydrogenated (Agudelo *et al.*, 2004).

##### Sunflower

Sunflower “seeds” are really a fruit, the inedible wall (husk) surrounding the seed that is in the kernel. The great importance of sunflower lies in the excellent quality of the edible oil extracted from its seeds. It is highly regarded from the point of view of nutritional quality, taste and flavor. Moreover, after oil extraction, the remaining cake is used as a livestock feed. Sunflower oil has a very low content of linoleic acid, and therefore it may be stored for long periods.

##### Safflower

Safflower is low in the content of the oil; the seed has as high as 30 to 40%. Therefore, it has economic potential for arid regions. Currently, safflower is used in oil and flour production and as bird feed. There are two varieties, one rich in mono-unsaturated fatty acids (oleic acid) and the other with a high percentage of polyunsaturated fatty acids (linoleic acid). Both varieties have a low content of saturated fatty acids. The oil from safflower is of high quality and low in cholesterol content. It is extracted by means of hydraulic presses, without the use of solvents, and refined by conventional methods, without anti-oxidant additives. The flour from safflower is rich in

fiber and contains about 24% proteins.

**Avocado**

Avocado has a high nutritional value, since it contains essential fatty acids, minerals, protein and vitamins A, B6, C, D, and E. The content of saturated fatty acids in the pulp of the fruit and in the oil is low; on the contrary, it is very high in mono-unsaturated fatty acids (about 96% being oleic acid). The oil content of the fruit is in the range 12-30% (<http://www.springer.com/978>).

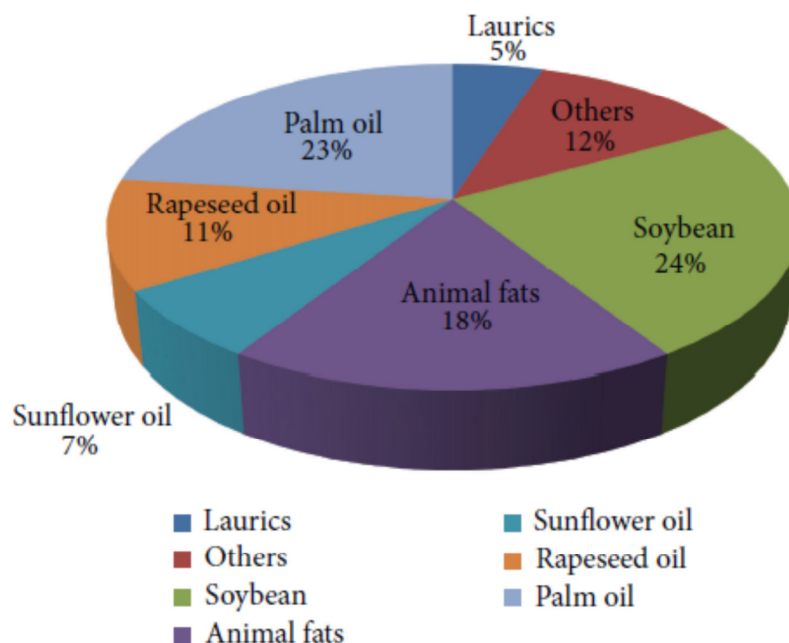
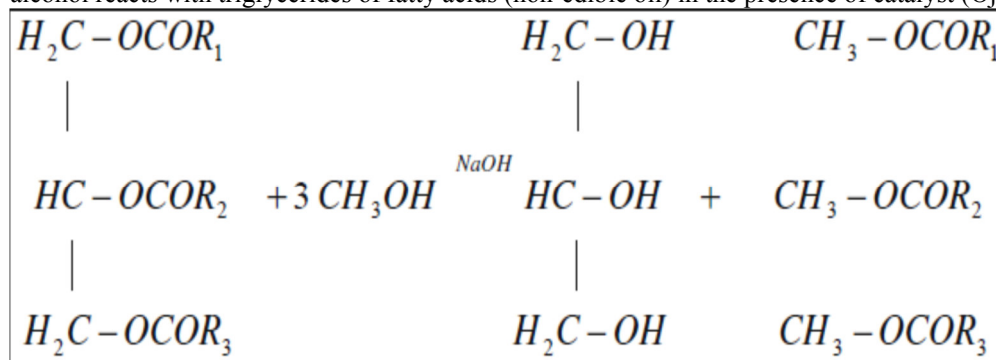


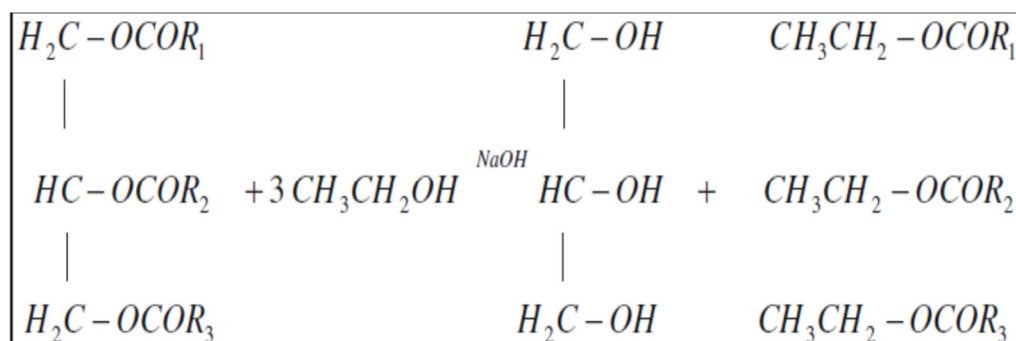
FIGURE 2: PRODUCTION OF BIODIESEL FROM DIFFERENT FEEDSTOCK (Gnanaprakasam *et al.*, 2013).

**Transesterification**

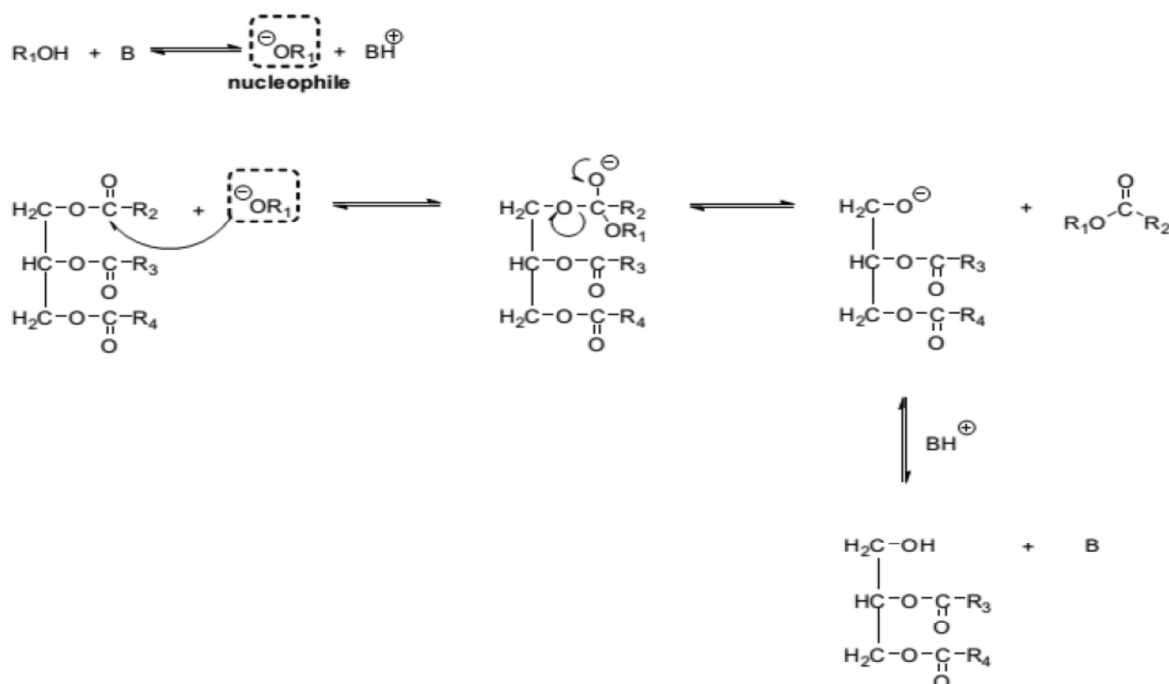
Biodiesel, an alternative diesel fuel is derived from a chemical reaction called transesterification of plant-derived oil. It is the chemical conversion of oil to its corresponding fatty ester in the presence of a catalyst. The reaction converts esters from long chain fatty acids into mono alkyl esters. Chemically, biodiesel is a fatty acid methyl ester. Transesterification process helps reduce the viscosity of the oil. The process proceeds well in the presence of homogenous catalysts such as sodium hydroxide (NaOH), potassium hydroxide (KOH), sulphuric acid (Demirbas, 2008). The formation of fatty acid methyl esters (FAME) through transesterification of seed oils requires raw oil, 15% of methanol & 5% of sodium hydroxide on mass basis. However, transesterification is an equilibrium reaction in which excess alcohol is required to drive the reaction very close to completion (Ahmad *et al.*, 2011). Transesterification transform the large branched molecule structure of the oils into smaller, straight chained molecules similar to the standard diesel hydrocarbons. Transesterification is the process of exchanging the organic group R'' of an ester with the organic group R' of an alcohol. These reactions are often catalyzed by the addition of an acid or base. Transesterification is common and well-established chemical reaction in which alcohol reacts with triglycerides of fatty acids (non-edible oil) in the presence of catalyst (Ojolo *et al.*, 2011).



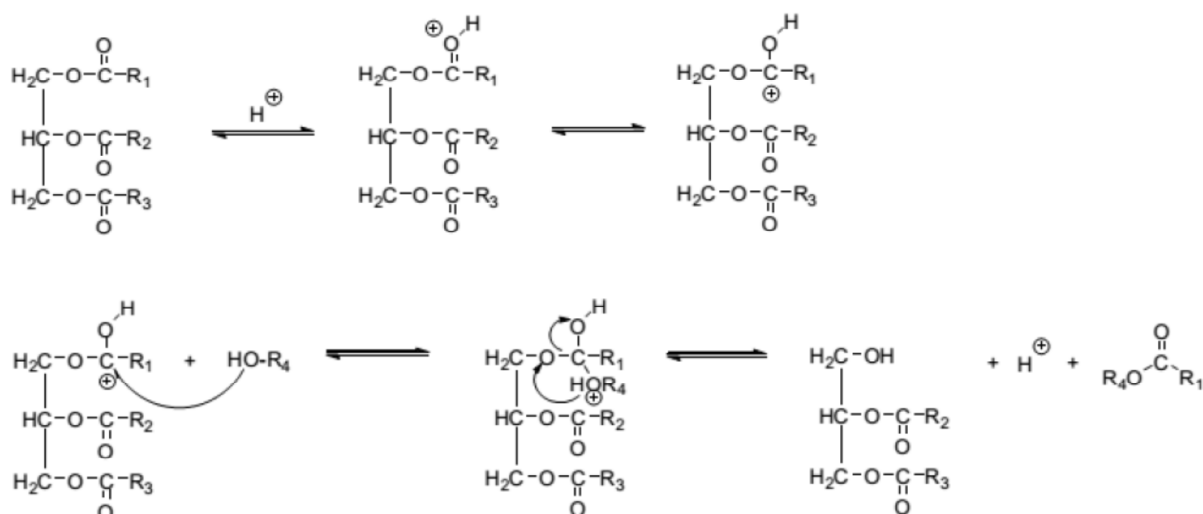
SCHEME2: BASIC TRANSESTERIFICATION REACTION WITH METHANOL (HOSSAIN *et al.*, 2010).



SCHEME 3: BASIC TRANSESTERIFICATION REACTION WITH ETHANOL (HTTP://WWW.SPRINGER.COM/978).



SCHEME4: REACTION MECHANISM FOR BASE-CATALYZED TRANSESTERIFICATION DURING BIODIESEL PRODUCTION (Alemayehu and Amanu, 2014).



SCHEME5: REACTION MECHANISM FOR ACID CATALYZED TRANSESTERIFICATION DURING BIODIESEL PRODUCTION (Alemayehu and Amanu, 2014).

## **Biodiesel Combustion**

The waste gas emissions associated with the biodiesel Combustion must be considered when determining its overall environmental impacts. Biodiesel would be blended with fossil diesel by a petrochemical company according to a given fractional volumetric ratio (1:19) for vehicle use (Khan *et al.*, 2013). The level of exhaust emissions that results from the burning of ethanol and biodiesel depends upon the fuel (e.g. feedstock and blend), vehicles technology, vehicle tuning and driving cycles. Most studies agree that using biofuels can significantly reduce most pollutants compared to petroleum fuels, including reductions in controlled pollutant as well as toxic emissions. NO<sub>x</sub> emissions have been found to increase slightly as blend level rise, although the levels of emissions differ from study to study (Chauhan and Shukla, 2011).

Oxygen in its molecular form enables a relatively low-temperature combustion, which also reduces the emissions of CO, NO<sub>x</sub> and volatile organic compounds (VOC). If a large amount of fertilizers is used to grow the feedstock, bioethanol could lead to increased N<sub>2</sub>O emissions on a life cycle basis. Biodiesel is a high-cetane fuel, which can be fully blended with fossil diesel to run compression ignition engines. It offers low emissions of GHG, sulphur compounds and particulate matter compared with fossil diesel. Over the last ten years, liquid biofuel production has been growing rapidly in many countries, boosted by mandates and tax incentives for blending biofuels with fossil fuels for road transport. The global production (mostly based on conventional biofuels) has grown from 16 billion liters in 2000 to about 105 billion liters in 2010 (i.e. 82% bioethanol and 18% biodiesel), accounting for about 3% of today's transport fuel on an energy basis (IEA, 2011) and using almost 3% of global arable land. Leading bioethanol producers in 2011 are the US (i.e. 63% of the global production, mostly from corn) and Brazil (i.e. 24%, mostly from sugarcane).while 58% of world biodiesel is produced in the EU (i.e. mostly in Germany from rapeseed oil), also with important production in Thailand and Malaysia (palm oil biodiesel) (REN21, 2012).

## **Impacts of Biodiesel on the Environment**

The world is presently confronted with the twin crises of fossil fuel depletion and environmental degradation. Gasoline and diesel-driven automobiles are the major sources of greenhouse gases (GHG) emission. Scientists around the world have explored several alternative energy resources like biomass, biogas, primary alcohols, vegetable oils and biodiesel. These alternative energy resources are highly environment-friendly but need to be evaluated on case-to-case basis for their advantages, disadvantages and specific applications. Excessive use of fossil fuels has led to global environmental degradation effects such as greenhouse effect, acid rain, ozone depletion and climate change. Due to the environmental problems caused by the use fossil fuels, considerable attention has been made to biodiesel production as an alternative to petro diesel and is an ecofriendly, alternative diesel fuel prepared from domestic renewable resources i.e. produced from vegetable oils and animal fats. It is a renewable source of energy seems to be an ideal solution for global energy demands including Ethiopia as well. The general method to produce biodiesel is transesterification of non-edible oil with methanol in the presence of either base or strong acid catalysts. An ideal transesterification reaction differs on the basis of variables such as fatty acid composition and the free fatty acid content of the oil. The worldwide worry about the protection of environment and the conservation of non-renewable natural resources, has given rise to alternate development of sources of energy as substitute for traditional fossil fuels. The major part of all energy consumed worldwide comes from fossil sources (petroleum, coal and natural gas). Thus, looking for alternative sources of new and renewable energy such as hydro, biomass (better sources of energy), wind, solar, geothermal, hydrogen and nuclear is of vital importance. Alternative new and renewable fuels have the potential to solve many of the current social problems and concerns, from air pollution and global warming to other environmental improvements and sustainability issues (Anitha and Dawn, 2010).

## **Environmental Benefits of Biodiesel**

### **Emissions**

The 20% biodiesel blended with 80% conventional diesel fuel reduced total hydrocarbons by up to 30%, Carbon Monoxide up to 20%, and total particulate matter up to 15%. Typically, emissions of nitrogen oxides are either slightly reduced or slightly increased depending on the duty cycle of the engine and testing methods used. Increases in NO<sub>x</sub> can be effectively eliminated with the use of normal mechanical remediation techniques (e.g. catalysts or timing changes). Pure biodiesel does not contain sulphur and therefore reduces sulphur dioxide exhaust from diesel engines to virtually zero. Biodiesel reduces GHGs by 41% compared with diesel, reduces several major air pollutants, and has minimal impact on human and environmental health through N, P, and pesticide release (Khan *et al.*, 2013).

### **Health Effects**

Biodiesel is safer for people to breath. Research conducted in the US shows biodiesel emissions have decreased levels of all target polycyclic aromatic hydrocarbons (PAH) and nitrated PAH compounds, as compared to petroleum diesel exhaust. PAH and nPAH compounds have been identified as potential cancer causing compounds (Khan *et al.*, 2013).

## Energy Balance

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. But the dependence of mankind entirely on the fossil fuels could cause a major deficit in future. The application of biodiesel to our diesel engines for daily activities is advantageous for its environmental friendliness over petro-diesel. The main advantages of using biodiesel is that it is biodegradable, can be used without modifying existing engines, and produces less harmful gas emissions such as sulfur oxide. Biodiesel reduces net carbon-dioxide emissions by 78% on a lifecycle basis when compared to conventional diesel fuel (Carvalho *et al.*, 2011). Biodiesel is an alternative fuel made from renewable biological sources such as vegetable oils both (edible and non-edible oil) and animal fats (Antony *et al.*, 2011). Currently, more than 95% biodiesel are produced from edible oil feedstock (soya bean oil, sunflower oil, Niger oil, rapeseed oil, palm oil, linseed oil and sesame oil), due to this there is a huge imbalance in the human nutrition chain versus fuel. Algae are an economical choice for biodiesel production, because of its availability and low cost (Basumatary, 2013). Biodiesel, (the mono alkyl (mainly methyl) esters of long-chain fatty acids, derived from a renewable lipid feedstock (Cholakov *et al.*, 2013), is advised for use as an alternative fuel for conventional petroleum-based diesel chiefly because it is a renewable, domestic resource with an environmentally friendly emission profile and is readily biodegradable. Biodiesel, a promising substitute as an alternative fuel has gained significant attention due to the predicted shortness of conventional fuels and environmental concern. The amount of greenhouse gas emissions, generating energy from renewable resources is being possessed a high priority gradually to decrease both over-reliance on imported fossil fuels (Hossain and Boyce, 2009).

Generally, biodiesel is produced by means of transesterification. Transesterification is the reaction of a lipid with an alcohol to form esters and a byproduct, glycerol. The first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides, and finally monoglycerides into glycerol, yielding one ester molecule from each glyceride at each step (Anitha and Dawn, 2010). Biodiesel production from waste cooking oil is found to be economically feasible method (Gnanaprakasam *et al.*, 2013). For every one unit of energy needed to produce biodiesel, 5.5 units of energy are gained. Because of this high energy balance and since it is domestically produced, biodiesel use can greatly contribute to domestic energy security. Among current food-based biofuels, soybean biodiesel has major advantages over corn grain ethanol. Biodiesel provides 93% more usable energy than the fossil energy needed for its production (Khan *et al.*, 2013).

## Greenhouse gas (GHG) emissions

The effectiveness with which greenhouse gas emissions (GHGs, including CO<sub>2</sub>, CH<sub>4</sub>, and others) can be avoided using biofuels is related to the amount and carbon intensity of the fossil fuel inputs needed to produce the biofuel, as well as to what fossil fuel is substituted by use of the biofuel. A proper GHG accounting considers the full life cycle of the biofuel, from planting and growing the biomass to conversion of the biomass to biofuel, to combustion of the biofuels at the point of use. The net emissions might be negative if perennial energy crops (which can build soil carbon) are established, replacing annual row crops that were being grown on carbon-depleted soil (Watson *et al.*, 2000). Higher GHG savings with biofuels are more likely when sustainable biomass yields are high and fossil fuel inputs to achieve these are low, when biomass is converted to fuel efficiently, and when the resulting biofuel is used efficiently (Karthi and Larson, 2000; Greene, 2004). One of the greatest advantages associated with biofuels and one of the main driving forces behind worldwide biofuel uptake are their alleged reduced GHG emissions, and hence their potential to help minimise climate change. The basic argument is that because growing feedstocks absorb CO<sub>2</sub>, the release of CO<sub>2</sub> emitted during biofuel combustion does not contribute to new carbon emissions since the emissions are already part of the fixed carbon cycle. However, there is considerable variation in GHG savings-ranging from negative to more than 100%. In addition to reduced GHG emissions, biofuels also have the potential to reduce emissions of key toxic substances usually associated with standard fuels (<http://www.ascensionpublishing.com/BIZ/HD41.pdf>).

## CONCLUSION

Biodiesel is a good alternative fuel for diesel engines because it is environmentally friendly and renewable in nature. Biodiesel an alternate diesel fuel is made from renewable biological sources by using different methods. From these methods which are used to produce biodiesel, transesterification of vegetable oil and fats are predominantly used. The main purpose of using transesterification process is; to lower the viscosity of the oil. Transesterification reaction process (usually with methanol and a basic catalyst) used to produce a mixture of fatty acids methyl esters (FAME) with glycerin as a co-product. At the end of transesterification, the mixture of methyl esters separated from the glycerin and purified in order to fulfill with the requirements set by international standards for biodiesel.

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