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Biofuel: An Environmental Friendly Fuel

Adeola Suhud Shote

Abstract

Various types of biofuels and feedstocks are considered and discussed in terms of their environmental and economic feasibilities. Biofuel is gaining the centre stage as human activities keep rising and the consequent increase in the discharge of lethal emissions is also a subject of concern. The need to cut down greenhouse gas emissions (i.e. CO₂, N₂O, CO, NO, SO₂) is imperative to preserve our natural biodiversity. Biodiesel and bioethanol are the most common, viable alternatives and infinite green fuels that can be used in internal combustion engine. Biodiesel (commonly from waste cooking oil, nonedible vegetable oil, animal fat and tallow) and bioethanol (usually from forestry waste, Lignocellulosic biomass, starchy and sugary vegetable sources, and agricultural residues) are synthesized from straight vegetable feedstocks to bring their characters close to that of the fossil diesel and gasoline. The candidates as green fuels have the potential to significantly reduce the greenhouse gas emissions by as much as 30% from their combustion in internal combustion engine. The various possible methods used for their productions determine the fuel sensitivity to the environment and the energy balance. In general, the energy balances are positive for both fuel substitutes.

Keywords: biofuel, biodiesel, bioethanol, emission, combustion

1. Introduction

The serious concerns of the global climate change, the rising trend of environmental pollution among others have necessitated researchers and industries to develop renewable alternative and cleaner energies across the world. The need for alternative and sustainable energy sources also arises from the global rise in population and the consequent increase in energy demand even as industrialization keeps on expanding. Therefore, the need to drive the world with efficient and eco-friendly energy carriers is paramount. Biofuels are one of the renewable, sustainable sources of energy carriers that can drive the modern day world with the high prospect and potential of reducing greenhouse gas emissions [1–5]. This reduction in this greenhouse gas emission will certainly be in line with Kyoto Protocol. Yet, no fuel system is completely free of environmental concerns [6]. The high dependency and pressure on finite fossil fuels will be shifted due to the global call to look into renewable eco-friendly fuel carriers.

The key sectors that need to be driven by efficient and cleaner fuel substitutes are the aviation, transportation and the manufacturing industries. Over the last two decades, a number of biofuels have been developed. These include bioethanol,

biodiesel, biogas, synthetic fuel, hydrogen and so on. Most of these fuels can be blended or used directly in internal combustion engine (ICE) [7, 8]. The cost of production of some these fuels is still relatively on the high side even despite the fact that they have lower environmental consequences when compared with fossil fuel. The various production methodologies could be responsible for the high cost of these biofuels [9]. Syntheses like fermentation, alcoholysis, Saccharification, acidolysis, hydrolysis, esterification, gasification, liquefaction and extraction have been used to produce biofuels.

The combustion of hydrocarbon fuel with O_2 from the atmosphere gives equivalent amount of CO_2 and H_2O . The other discharges are carbon monoxide (CO), nitrogen oxides (NO, N_2O) and nitrogen compounds (NH_3 and HCN), sulfur gases (SO_2 , CS_2 , OCS), compounds of halogens and carbons (CH_3Br and $CHCl$). Combustion of these finite fossil fuels and other biomass led to the global alteration in the atmosphere with respect to huge emissions discharges from these two main contributors [10]. Combustion from automobile, stationary sources are largely responsible for most of the greenhouse gas emissions to date (through CO_2 , stratospheric O_3 , and soot) and also some opposing effects (through SO_2). It has had minimal effect on stratospheric O_3 (through CH_3Cl , CH_3Br , CH_4) but has likely influenced the stratospheric oxidant levels (through CO, NO_x , NMHC), specifically the Northern Hemisphere [10]. Even though energy is key to drive the daily and economic activities but it should not be to the detriment of humanity.

Bioethanol, biogas and biodiesel are the most widely used biofuels. Bioethanol production is very high in Brazil and USA due to large volume of production of sugar cane and corn respectively. Research is also directed to the use of cellulose to produce ethanol [11]. Cellulose is converted to sugar and thereafter to ethanol. However, biodiesel is common in the Scandinavian countries and Germany in Europe. Biodiesel is usually blended using about 5–20% in these countries [12]. Germany is one of the top countries known for the production of biodiesel. Biogas on the other hand is usually produced from animal waste. The leading countries in the production of biogas in Europe are Germany and Great Britain. As the production of biofuel is gaining interest, bio-refineries are being cited in advanced countries like the USA, Germany to produce biofuels and other associated products.

Gasification of biomass to produce methanol, ethanol, dimethylether, syn-diesel could also result in the production of hydrogen and methane which may be used in vehicles. Largely, all these conversion processes are still relatively high in cost.

1.1 Biofuel as an alternative fuel

Researches are going on in the use of sustainable alternative fuels for automobile and stationery machines. The most prominent of those technologies being under investigation are the use of electric and hybrid automobiles, compressed natural gas (CNG), dimethylether, hydrogen, liquid biofuel, liquefied petroleum gas (LPG) and liquefied natural gas (LNG) among others. The centre of discussion here will focus on two prominent liquid fuels which are biodiesel and bioethanol. Their environmental impact and their sensitivity analysis will be looked into in detail.

These fuels are sourced mainly from vegetable feedstock chain supplies. These may include edible and nonedible vegetable sources that are sustainable [1].

2. Bioethanol

The feedstocks include sorghum, sugar beet, wheat, cassava and so on. Bioethanol can be used in straight or even blended form with premium motor spirit

(PMS) in spark ignition engine (SIE). Engine modification is not necessary for blends between 5 and 20%. The blend is often represented as E(percentage)G, that is E15G. The middle term '15' represent the percentage of the blend. However, higher blends may require engine modification. This adds to the final cost of the use of bioethanol in SIE. Besides, many advantages are associated with the candidate's use in SIE. The blends help in engine lubrication, thereby reducing the wear rate and reducing the engine temperature. It also has the advantage of cutting down the greenhouse gas emissions [13].

2.1 Pre-treatment for bioethanol

The production and quality of bioethanol produced is significantly boosted by the pretreatment procedures. Various pretreatment methods are presented in [14, 15] for lignocellulosic substrates and the merits of employing a pretreatment procedure. Pretreatment is necessary for the substrate feedstock because it gives direct yield of fermentable sugar ready for hydrolysis and heating. It also inhibits degradation and retards the activities of inhibitors for the final conversion to ethanol [15]. It gives a positive energy balance at the long run as the pretreatment process reduces the production cost, wastage of materials and time before the final fermentation process [15, 16]. The pretreatment processes involve the reduction of the size of the feedstock matrix-fraction (some time through the use of enzyme called amylase or through the mechanical means like milling). Hydrolysis and heating can then follow so that the enzyme can easily acts on the pretreated substrate [15].

Microorganisms like fungi can also be employed for the pretreatment of feedstocks particularly lignocellulosic materials. This involves breaking of the lignin structure. This pretreatment method is usually used on a laboratory scale because the process is slow and does not require much energy input as chemical processes are not involved [17].

The chemical pretreatment (alkaline/acid) is desirable for large scale industrial production due to the availability and affordability of chemical which are not affected by ambient changes unlike biological pretreatment agents [14]. Diluted acid pretreatment is usually preferred due to the draw backs of the use of concentrated acid pretreatment like corrosion of production line components. Within a short period of time and at about 160°C, sugar monomers are formed. The common agents used for acid pretreatment include nitric acid (HNO₃), hydrochloric acid (HCl), sulfuric acid (H₂SO₄), organic acid (lactic/acetic acids) and that of the alkaline are sodium hydroxide (NaOH), calcium hydroxide (Ca(OH)₂) ammonium hydroxide (NH₄OH) [14]. The various pretreatment methods and effects are summarized in **Table 1**.

2.2 Synthesis of bioethanol

The traditional method involves liquefaction and saccharification of starch. Saccharification involves the hydrolysis of cellulose or starch (polysaccharides) to simple monosaccharides. Carbohydrates (such as sucrose, maltose) are broken down to give simple sugar (like glucose, fructose, galactose).

The process is usually catalyzed using biological method (an enzyme) or chemical method (acid/base) [15, 18]. The saccharification procedure is very important because it determines the time, quality and quantity of the final product which is the bioethanol. Crystalline nature of cellulose fiber, lignin and hemicellulose content, porosity of lignocellulosic substrate affect the hydrolysis process [19]. Some drawbacks like increase in process cost from the chemical obtained, acid recovery, corrosion of production line components are associated with the use of chemical

| Pretreatment method | Effects | Pros | Cons |
|--------------------------------|--|--|--|
| Diluted acid | Hydrolyses hemicelluloses; Alters the structure of lignin Reduces cellulose more amenable for additional enzymatic treatment | Less corrosion effect than the conc acid Low formation of inhibitors | Generation of degradation products due to high temperature Low sugar concentration exit stream |
| Concentrated acid | Hydrolyses both hemicelluloses and cellulose | High glucose yield Operational cost reduction due to moderate operating temperature Low formation of degradable products No enzyme are required | Acid recovery is mandatory Equipment corrosion Generation of inhibitory compounds |
| Alkali | Removes lignin and hemicelluloses Increases accessible surface area | High lignin removal High digestibility | Long residence time Irrecoverable salt formation |
| Biological | Degrades lignin and hemicelluloses | Low energy consumption | Low hydrolysis rate |
| Mechanical | Reduces cellulose crystallinity | No formation of inhibitors | High power and energy consumption |
| Ammonia fiber explosion | Increases accessible surface area Slightly removes lignin and hemicelluloses to an extent | Low formation of inhibitors | Not efficient for biomass with high lignin content High cost due to large amount of ammonia |
| Ammonia recycled percolation | Removes lignin | Highly selective delignification | High energy consumption |
| Ionic liquids | Reduces cellulose crystallinity Removes lignin | High digestibility Green solvent | Large-scale application still under investigation |
| Ozonolysis | Reduces lignin transformation | No formation of inhibitors Mild operational conditions | High cost due large amount of ozone required |
| Steam explosion | Causes lignin transformation Causes hemicellulose solubility | Cost effective High yield of glucose and hemicellulose | Generation of inhibitory compounds Partial hemicellulose degradation Incomplete disruption of the lignin carbohydrate matrix |
| Supercritical fluid technology | Increase accessible surface area | Cost effective No formation of inhibitor | Does not affect lignin and hemicelluloses Very high pressure requirements |
| Wet oxidation | Removes lignin | Low formation of inhibitors | High cost of oxygen and alkaline catalyst |
| Organosolv | Hydrolyses linin and hemicelluloses | Pure lignin recovery High digestibility | Solvents need to be drained and recycled High cost |

Table 1.
Pretreatment methods for lignocellulosic feedstocks in bioethanol synthesis [14].

catalysis [20]. However, the use of dilute acid is often preferred as it contributes to less impact on the environment. The enzymatic approach is mostly carried out in an orbital shaker (120–150 rpm) at about 40–50°C for 120 h [21]. β -Glucosidase, *Cellulase* are commonly used for the hydrolysis of complex starch [22]. Thereafter, the fermentation of sugar extracted from starch plant, followed by distillation. Enzyme, bacteria or yeast are used during the fermentation process to accelerate the formation of the product in an anaerobic environment. The simple sugar is converted to ethanol and carbon dioxide. Some time, saccharification and fermentation are considered simultaneously due to low cost, reduced process time, prevention of cellulose inhibition, high yield of ethanol [22]. Most of the world's ethanol is produced in Brazil and USA. Corn is used to synthesize bioethanol in the USA while sugar cane is used substantially in Brazil [13]. However, in Spain, bioethanol is produced from barley and in France it is obtained from beet. Agricultural biomass or residue from waste paper or corn stalks can also be used to obtain bioethanol [13]. Other agricultural produce that can be used to generate ethanol are wheat, potato, maize cassava etc.

Ethyl tertiary butyl ether (ETBE) is also worthy of mentioning here since it can also be obtained from some of the agricultural produce like barley, wheat which can be blended with PMS. They are usually produced in the refinery. Lignocellulose residue is gaining more research interest due to the reduction in the cost of production [14]. The lignocellulose contains cellulose, hemicelluloses and lignin. Hydrolysis are used to fractionalize some agricultural produce like maize so that complete conversion to ethanol and carbon dioxide can be obtained easily and efficiently with reduced wastage.

2.3 The ethanol conversion process

The schematic process of production chain of bioethanol is depicted in **Figure 1**. The process starts with milling of the feedstock for easy extraction of the starch. Yeast is added to make the extraction easy. The next stage is hydrolysis. Enzyme is added to obtain single sugar (glucose) and starch before fermentation by bacteria or microorganisms. Thereafter, distillation is followed to remove large volume of water in the product and then dehydration to further remove the water content so that the outcome concentration will increase. There are various pretreatment methods that can be used to obtain high quality ethanol [14, 23]. **Figure 2** presents the summary of the pretreatment and conversion methods while **Table 1** presents the pretreatment methods and the various merits and drawbacks from the use of

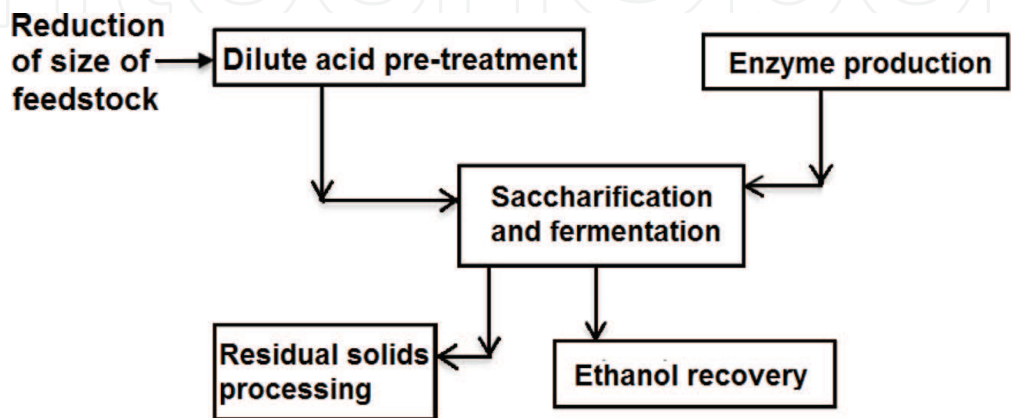


Figure 1.
Bioethanol conversion scheme [29].

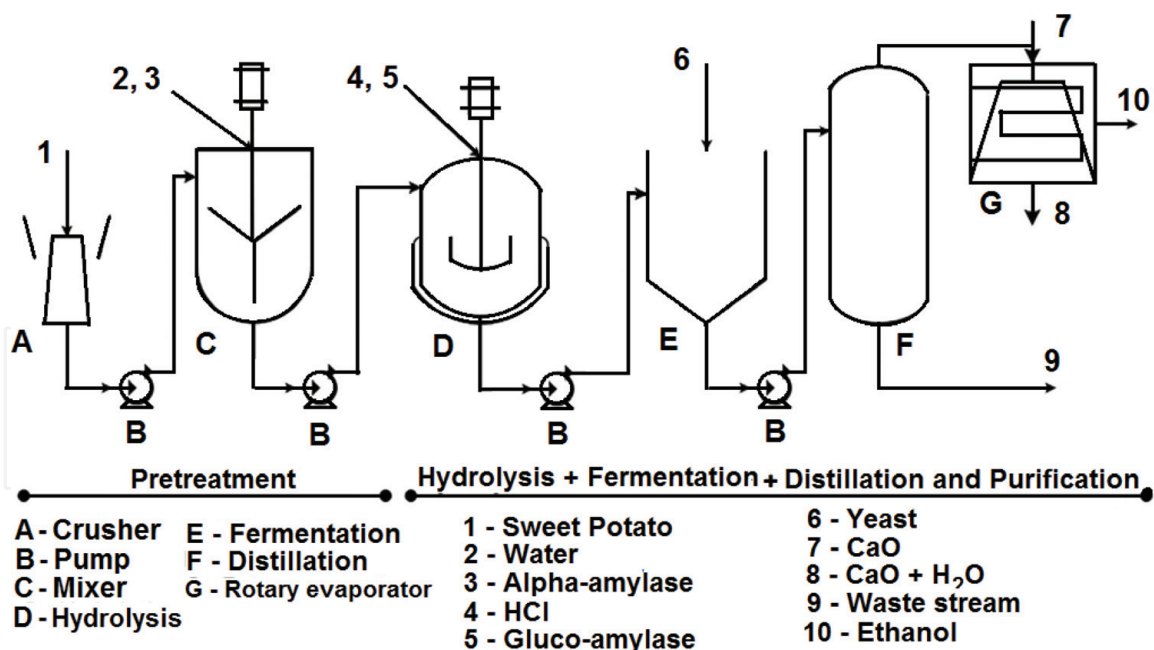


Figure 2.
Pretreatment and bioethanol conversion processes [27].

respective pretreatment method. In more recent time, response surface methodology (RSM) and artificial neural network (ANN) have been used to optimize the production of bioethanol [24]. ANN is used to perform complex cognitive procedurals which mimic the biological function of human brain. ANN genetic algorithm is used to simulate the biological processes in the ethanol production so that the major parameters can be varied to obtain a much desired output.

2.4 Impact of bioethanol and its sensitivity on the environment

This is related to the emission pattern compared with the fossil premium motor spirit (FPMS) and the energy balance for the synthesis of the ethanol. The energy balance involves the input feedstock and the by-product. Bioethanol has a huge potential to reduce the hazardous gas emissions due to its vegetable source. It helps in the complete combustion process because it is oxygenated thereby reducing the emissions by as much as 30%. Bioethanol from lignocellulosic biomass resource has huge strategic potential in cutting down of greenhouse gas emissions into the environment and reducing the consumption of crude fuel [21]. It can be blended with PMS due to its characteristics such as low cetane number, high octane number, high heat of vaporization that are close to that of the fossil gasoline [25]. The use of this large lignocellulosic biomass has the potential to reduce transportation cost which will contribute tremendously to positive energy balance [26]. Ethanol production from lignocellulose also has advantages over first generation biofuel in that it makes use of low cost biomass and employs a production process that is environmentally friendly [27].

Various methods of biofuel feedstocks, production loading methodologies and the environmental and economic viability of biofuel production are issues that are attracting and promoting the use of biofuels. However, biofuels combustion in ICE were found to have the prospect of reducing the greenhouse gas emissions [28] thereby lowering the average mean temperature of the atmosphere in the long run. This is in line with Kyoto protocol. The global pressure on the finite premium motor spirit (PMS) and automotive gas oil (AGO) will reduce significantly by using biofuel in straight or blended forms. Biofuels also have the merits of renewability and sustainability. The energy balance of most biofuels is positive as production is maximized.

3. Biodiesel

Biodiesel is currently gaining more and more interest as the desire to use eco-friendly fuel substitute keeps increasing because of the increase in the fluctuations in the crude-fuel prices internationally and the environmental consequences of fossil fuel. There are numerous ways of producing biodiesel from different feedstocks and different catalysts. Some of the feedstock include but not limited to grapeseed, camelina, lupin, linseed, rapeseed, sunflower, peanut, palm oil, palm kernel oil, poppyseed, olive, chestnut, karanja, pongamia, soybeans, canola, corn, crambe, jatropha, cottonseed and so on. Animal fat can also be used to synthesize biodiesel. The common methods of production are transesterification (alkaline catalyzed), the use of enzyme (e.g. lipase) catalyst, supercritical method of production (under high temperature and relatively high pressure) and the use of acid catalyst [30]. However, the commonly used method for the production of biodiesel is the transesterification method because of its simplicity and ease of handling.

Vegetable oils normally contain fatty acids which makes the properties (like viscosity, density, flash point, pour point cloud point, cetane number) to be high in value and mostly unsuitable to be used in internal combustion engine (ICE) without engine modification. So, the essence of the conversion to biodiesel is to remove or lower the effect of the fatty acid composition in **Table 2** [30]. The chemical structures of common fatty acids are also presented in **Table 3**. Some oils that are having lower fatty acid content can be used directly or in blended form as biodiesel fuel in compression ignition engine (CIE) which may require modification. This makes the whole chain of production more costly.

‘xx’ indicates number of carbons, and ‘y’ number of double bonds in the fatty acid chain.

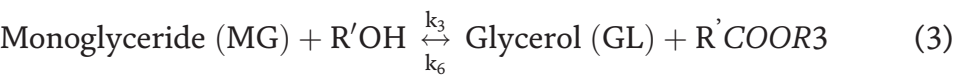
The production of biodiesel starts with oil extraction (usually with hexane). The high fatty acid oil containing triglycerides reacts with alcohol (usually methanol or ethanol) to produce esters and glycerol in the presence of a catalyst (KOH or NaOH). The whole processes are reversible processes and are in three steps as shown in Eqs. (1)–(3) [16]. Excess alcohol is desirable to accelerate the reaction towards the products side. The kinetics parameter k_x are in Nouredini and Zhu [32].

Transesterification of rapeseed oil in the supercritical methanol method shows that at temperature of 239°C and a pressure of 8.09 MPa, glycerin and methyl esters are produced as the principal products [31].

The main product is biodiesel and the by product is glycerol which are mainly used in the cosmetics and pharmaceutical industries. The basic conversion scheme of the vegetable oil is shown in **Figure 3**.

| Fatty acid | Lauric | Myristic | Palmitic | Stearic | Oleic | Linoleic | Linolenic |
|-------------|--------|----------|----------|---------|-------|----------|-----------|
| Soybean | 0.1 | 0.1 | 10.2 | 3.7 | 22.8 | 53.7 | 8.6 |
| Palm | 0.1 | 1.0 | 42.8 | 4.5 | 40.5 | 10.1 | 0.2 |
| Cotton seed | 0.1 | 0.7 | 20.1 | 2.6 | 19.2 | 55.2 | 0.6 |
| Tallow | 0.1 | 2.8 | 23.3 | 19.4 | 42.4 | 2.9 | 0.9 |
| Coconut | 46.5 | 19.2 | 9.8 | 3.0 | 6.9 | 2.2 | 0.0 |
| Lard | 0.1 | 1.4 | 23.6 | 14.2 | 44.2 | 10.7 | 0.4 |

Table 2.
Fatty acid in vegetable oil [30].



3.1 Impact of biodiesel and its sensitivity on the environment

This centers on the emissions comparison of the finite fossil diesel with biodiesel. Shote et al. [5] conducted a research on the emission patterns of the biodiesel blends compared with petroleum diesel. One hundred percent biodiesel was found to have lowest impact on the environment in terms of the hazardous emissions (CO, NO, NO₂, NO_x). Besides, the result also shows gradual reduction of the emissions pattern as the concentration of PKO-based biodiesel increases in the blend.

| Fatty acid | Chemical name of fatty acids | Structure (xx:y) | Formula |
|------------|--------------------------------------|------------------|--|
| Lauric | Dodecanoic | 12:1 | C ₁₂ H ₂₄ O ₂ |
| Myristic | Tetradecanoic | 14:1 | C ₁₄ H ₂₈ O ₂ |
| Palmitic | Hexadecanoic | 16:0 | C ₁₆ H ₃₂ O ₂ |
| Stearic | Octadecanoic | 18:0 | C ₁₈ H ₃₆ O ₂ |
| Arachidic | Eicosanoic | 20:0 | C ₂₀ H ₄₀ O ₂ |
| Behenic | Docosanoic | 22:0 | C ₂₂ H ₄₄ O ₂ |
| Lignoceric | Tetracosanoic | 24:0 | C ₂₄ H ₄₈ O ₂ |
| Oleic | cis-9-Octadecenoic | 18:1 | C ₁₈ H ₃₄ O ₂ |
| Linoleic | cis-9,cis-12-Octadecadienoic | 18:2 | C ₁₈ H ₃₂ O ₂ |
| Linolenic | cis-9,cis-12,cis-15-Octadecatrienoic | 18:3 | C ₁₈ H ₃₀ O ₂ |
| Erucle | cis-13-Docosenoic | 22:1 | C ₃₂ H ₄₂ O ₂ |

Table 3. Chemical structure of common fatty acids [31].

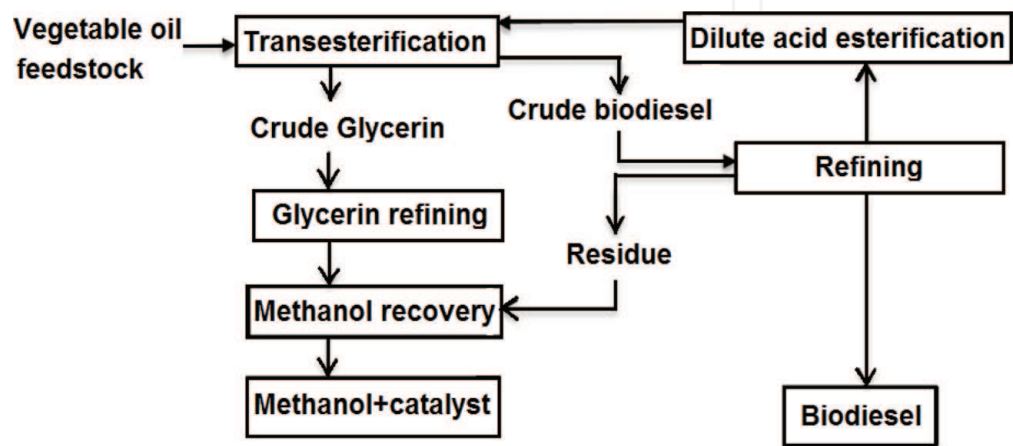


Figure 3. Biodiesel conversion scheme [16].

In general, the energy balance of most biodiesels is positive depending on the source of the vegetable oil, production, extraction and esterification. Zhang et al. [9] found out that the plant capacity, feedstock of oil and the method used to synthesize biodiesel are the most significant factors determining the final cost of biodiesel. The use of glycerol in the cosmetics and pharmaceutical industries will boost the energy balance of the biodiesel significantly. Since biodiesel is gaining more ground in terms of the usage, then the energy balance tends to be more positive. Biodiesel are found to reduce greenhouse gas emissions [5, 7]. Biodiesels also have the advantage of lubricating and bringing down the temperature of ICE. The generic NO_x emissions are not significantly affected as the concentration of the blends increase in the fuel mixture [5]. NO_x formation is governed by Zeldovich mechanism.

Acid catalyst (tetraoxosulphate VI acid) is also used instead of alkali catalyst (NaOH or KOH) to lower the activation energy for quick formation of esters and glycerin. However, the reaction takes longer time (about 2 days) to complete. The molar ratio is kept at 30:1 and the temperature range is between 60 and 80°C. The triglyceride is usually used with one mole of sulfuric acid to give 90% conversion to ester and glycerin in about 2 days [16].

Other methods involve the use of enzyme to fast track the rate of chemical reaction and the formation of esters. This method is very expensive because of the cost of enzyme which invariably affects the energy balance of the entire chain of production processes.

The summary of the common methods used for the production of biodiesel are presented in **Table 4**.

3.2 The summary of technologies at developmental stage dealing with biofuel production

a. *Pyrolysis of oil*: lignocellulosic biomass is usually used to synthesize bioethanol. The process normally starts with pretreatment procedures. However, any of the biomass substrates can be used to produce biodiesel. Research is till on going in the development of reactor for accelerated pyrolysis processes. A lot of investment and researches are still needed in this area so that the process and the end results will be economically reliable [33].

| Variable | Alkali catalyst | Lipase catalysis | Supercritical alcohol | Acid catalysis |
|----------------------------------|----------------------------|----------------------|-----------------------|----------------------------|
| Reaction temperature (°C) | 60–70 | 30–40 | 239–385 | 55–80 |
| Free fatty acid in vegetable oil | Saponified products | Methyl esters | Esters | Esters |
| Water in vegetable oil | Interference with reaction | No influence | — | Interference with reaction |
| Yield of methyl esters | Normal | Higher | Good | Normal |
| Recovery of glycerol | Difficult | Easy | — | Difficult |
| Purification of methyl esters | Repeated washing | None | — | Repeated washing |
| Production cost of catalyst | Cheap | Relatively expensive | Medium | Cheap |

Table 4.
Different techniques for ester production [16].

- b. *Hydrothermal upgrading process*: this process involves hydrolysis of biomass at high pressure and moderate temperature to produce bio-crude. It is also at the development stage just like pyrolysis process.
- c. *Dimethylether*: this is produced from gasification of biomass. It could also be obtained from natural gas. It is one of the conventional diesel fuel substitutes that is capable of cutting down NO_x emissions from its combustion in CIE. It is commonly synthesized from methanol.
- d. *Fischer-Tropsch*: synthetic gas is produced from fossil fuels. Research is still on going to produce synthetic gas from biomass feedstock. In the past, the primary feedstock for its production is fossil fuel. The origin of this synthetic fuel can be traced to Germany. Production of synthetic fuel through pyrolysis of biomass is still under investigation.
- e. *Synthetic fuel*: this fuel is synthesized by recycling organic waste. A lot of work is going on in this area to optimize the processes. It can be blended with conventional fuel.

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