

A Systematic Review of Biodiesel Production with Sustainable Feedstock Using Assorted Catalyst

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Abstract: This research is focused on methodical appraisal and long lasting use of feed stocks for manufacture of biodiesel. Biodiesel is a good substitute to petroleum diesel because of its environmentally friendly constituents. They are renewable, sustainable with high oxygen content. Production of biodiesel from various feedstock's using a suitable and affordable catalyst have also been reported in this review. They are produced by the reaction of a free fatty acid with an alcohol using a suitable catalyst at appropriate conditions with suitable parameters. Consideration of sundry or assorted materials for production of biodiesel became necessary in order to have an idea of quality yield of biodiesel from different materials. It is equally important to note that one of the most common input parameters for accelerating the yield of biodiesel is feed stocks. The most prevalent is catalyst, which vary for biodiesel production. There are various catalyst for biodiesel production ranging from base catalyst, acid catalyst and many more. This research delves into sustainable production of biodiesel from diverse categories and the effects of the produced biodiesel on the fuel properties. Various breakthroughs have been recorded from different researchers to increase biodiesel as a vital fuel for engines. In addition to its tremendous capacity to evacuate various problems from the environment like the greenhouse gases and global warming, they are also very affordable and renewable. Biodiesel will play a vital role in the energy investment and contribute tremendously to the increase in the local and industrial automobile economy for the future.

Keywords: Biodiesel Production, Assorted Catalyst, Feedstock

1. Introduction

Biodiesel production, findings, exploration and usage in various diesel engines is of enormous importance in some energy discoveries that are continuous and imaginative [1]. The depletion of fossil fuels, concerns for protection of our environment and steady increase for the market values of these fuels from fossils are moving researchers for greater quest for different fuel sources. Biodiesel is generally accepted as a major source of diesel in transportation and the quest for these diesels is on the increase. Their oxygen content is high with controlled amount of toxicity, little or no pollution and they are biodegradable. Furthermore, it does

not need to be adaptable before it can be used to run an engine [2]. A research in 2014, which was reported globally had it that biodiesel yield was over 25.2 million tons, European Union (EU) which produced a yield about 37.1% with a range of 16.7% produced in the United States, 10.7% in Argentina and 11.9% in Brazil [3].

In consideration of global total energy utilization, transportation has acquired the 3rd place with reference to the industry. The rate of consumption is assumed to increase by a rate of 60% in 2030 which would be as a result of industrialization, increment in population and good living standards [4]. Biodiesels are distinct owing to their high sustainability while fossil fuels are sparse resource. Biodiesels have the tendency of powering several diesel

engines irrespective of the conditions of the atmosphere. Raising the level of biodiesel production, will necessitate the accessibility of clean and affordable source of energy which is striking different from fuels from fossils.

Transesterification method has been significantly recognized as a method of biodiesel production. The reaction which converts triglycerides of oils using alcohol, in the presence of an acid or a basic catalyst produces biodiesel. It also involves reaction of triglycerides in order to form diglycerides, monoglycerides and glycerol, by three sequential, reversible method [5]. Free fatty acid (FFA) content, catalyst type and its concentration, type of alcohol used and molar ratio (alcohol: oil), reaction temperature and time are the basic five determinants to biodiesel production [6]. The feedstock character are determined by different transesterification techniques. Some techniques can handle very delicate feedstock with small quantity of FFA as well those with high FFA [7].

Contemporary research reckons on cheap, available feedstocks, current production process and purification technologies for biodiesel production. The cheap and gross reusability nature of heterogeneous catalyst makes it ever viable. Again, it hardly releases waste water nor undergo saponification and has few stages for processing [5]. The enzyme catalyzed processes has lots of benefits in conjunction with their conversion, yield and reusability. The lipase catalyzed transesterification has increased the reaction rate accompanied by increased conversion, irrespective of the fact that the actions of the free enzyme is decreased as the stability also decreases. Nanobiocatalyst relies mostly on the transesterification of oils using methanol to produce fatty acid methyl esters [8].

There are novel approaches to biodiesel production by catalytic conversion of oils and fats. Some of them includes using nano catalyst and ionic liquid catalysts in biodiesel production which are more beneficial in comparison to the conventional acid/base catalysts. Varieties of homogeneous and heterogeneous catalysis are been used by these nanomaterials as catalysts for a variety of applications. Catalysts from nanoscale have large definite surface area and surface energy leading to high catalytic activity. Nano catalysts promotes the selectivity of reactions by increasing reaction at a lower temperature, decreasing the effect of side reactions, higher recycling rates and recovery of energy usage. Nano catalysts are viable substituent for effective production of biodiesel from oils and fats because they have increased definite surface area with increased catalyst activities removing the definite problem of mass transfer resistance associated with conventional catalysts [7].

Biodiesel has been designed to make our energy investment significant and an addition to the industrial and domestic economy. The worldwide technological acceptance of these biodiesel has been recorded according to their production rate, usage and legislation supporting the economic viability of these diesel engines that are appropriate for biodiesel with little or no alteration. It is clear that biodiesel is designed to make our future remarkable with the progress made so far by many scientist to demonstrate biodiesel as a feasible engine fuel,

together with their ability to remove environmental issues like global warming and sustainability [9].

2. Feedstocks for Production of Biodiesel

Varieties of both organic and agricultural products have been investigated for the production of biodiesel. Some of them includes jatropha, soyabean oil, palm kernel oil, groundnut oil, rapeseed oil etc. Some food resources are under consideration for the production of biodiesel because they may deplete the food chain supply. Therefore, there is paramount reason to deliberate on other sources which do not challenge the use of our domestic farmland as well as the food chain supply, it calls for huge equilibrium between our economic, social and benefits from our environment in a comprehensive way. Many developed countries like the U.S.A and Brazil have stopped the usage of these food crops for production of biodiesel [1]. Biodiesel realized from these food crops cannot be compared to the diesel from petrol in terms of their cetane number, density and viscosity [12].

Several feedstock like the jatropha curcas, xanthoceras sorbifolia, cornus wilsoniana and pistacia chinensis have been researched on for production of biodiesel. Wastes from oils have also been assessed as an acceptable feedstock for production of biodiesel in some developed countries like Spain, China, and Austria e.t.c. [13]. The quantity of wastes from these oils is above 10 million tons per year and just 20% of it can be used again specifically in China (Shields-Menard *et al.*, 2018). The total worldwide demand for these diesel fuel from waste oils are quite minimal. The major setback in highly commercialized countries is the accessibility of huge sparse of land for the plantation of these feedstock. Some oleaginous heterotrophic microbes have been recorded to have very likely results [14]. This implies that there should be strong assessment of these microbial oils from oleaginous heterotrophic microbes as feedstock for biodiesel production.

Fuels from biological feedstock are biodegradable, oxygenated, and less toxic with little or no pollution coupled with ease of adaptation with engines [2]. Carbon dioxide and sunlight through the effect of photosynthesis fosters the growth of microalgae. Microalgae oil content as compared with other vegetable oils is on the high side. They can be planted in a designed system with sewage or water from the sea as a culture medium with carbon source obtained from the carbon dioxide in the coal-fired power plants and other factories. [15] Eriola is of the opinion that biodiesel is environmentally friendly than the fuels gotten from petrol as a result of their low content of aromatic compounds and sulphur. [16]. Again, these increased population rate has resulted to a continuous rise in the quest for energy demand and also a continuous struggle for lands used for agriculture and crops owing to the fact that first generation biodiesel makes use of edible oils. These growing demand for food and effects from the environment motivates scientists to proffer better solution concerning enough availability of feedstock with respect to the non-edible oils and biotechnological processes [16].

Table 1. Process parameters for various non-edible feedstocks oils.

Feedstocks Oils	Optimal Biodiesel yields	Design	Independent variables
<i>Sesamum indicum</i>	96.62%	ANN and RSM	Rate of reaction, amount of catalyst, temperature, molar ratio of methanol to oil
<i>Vitellaria paradoxa</i>	99.65%	ANN coupled with GA and RSM	Rate of reaction, amount of catalyst, temperature, molar ratio of methanol to oil.
<i>Jatropha curcas</i> , <i>Pongamia pinnata</i> and <i>Calophyllum inophyllum</i>	93%, 91%, and 85%	NM	Reaction pattern condition, amount of catalyst, temperature, molar ratio of alcohol to oil, type of alcohol, time, temperature and reactants purity
<i>Jatropha curcas</i>	>99%	RSM	Quantity of methanol, concentration of the acid and time of reaction
WCO	96.03%	NM	Temperature, time, methanol-to-oil mole ratio
<i>Hura crepitans</i>	93.97%	D-Optimal	Temperature, time, catalyst concentration, catalyst type
<i>Thevetia peruviana</i>	81%	RSM	Temperature, time, ratio of alcohol-to-oil
<i>Parinari polyandra</i>	95.62%	RSM	Temperature of reaction, amount of catalyst, rate of reaction,
<i>Pongamia pinnata</i>	98%	NM	Concentration of catalyst, molar ratio of oil/methanol, temperature, mixing intensity
Oleic acid	82.1%	ANN-GA	Loading of catalyst, rate of reaction, methanol to oleic acid molar ratio, temperature.
Castor oil	94.19%	RSM	Reaction temperature, concentration of catalyst, molar ratio of alcohol: castor oil.
Castor oil	99.81%	RSM	Reaction temperature, molar ratio of methanol/oil, catalyst concentration
Mahua oil	92.7%	RSM	Concentration of the catalyst, Amount of methanol, temperature of the reaction, rate of reaction
WCO	98%	GA	Humidity, Impurity, speed, rate of reaction, amount of catalyst, temperature, molar ratio of methanol to oil
<i>Pongamia glabra</i>	95%	NM	Molar ratio, catalyst, time, speed, Molar ratio of alcohol to oil, concentration of catalyst, temperature, time
Shea Butter	92.16%	RSM	Temperature, agitation speed, molar ratio of alcohol: oil, loading of catalyst
Fly larvae of black soldier	96.15%	RSM	Loading of enzyme, temperature of reaction, molar ratio of methanol: fat, time
Sterculia oil	90.2%	RSM coupled with ANN	Concentration of catalyst, temperature, molar ratio of methanol to oil, speed of agitation
<i>Jatropha curcas</i> - <i>Ceiba pentandra</i>	93.47%	ANN-GA	Concentration of catalyst, molar ratio of methanol to oil, speed of agitation.
<i>Brucea javanica</i>	94.34%	RSM	Concentration of catalyst, molar ratio of methanol to oil, temperature
Cantaloupe	90.5%	NM	Loading of catalyst, molar ratio of methanol to oil, temperature.
Loofah	84%	RSM-ANN	Quantity of alcohol and KOH, time, temperature.
<i>Bauhinia monandra</i>	91.34%	RSM	Loading of catalyst, molar ratio of dmethanol to oil, time

[8]

The various feedstocks are the major determinants of the quantity of biodiesel yield because of their various sources, physico-chemical properties and the process variables. Modern technologies are justified in the research field of bioenergy. Novel researches concentrate on affordable, inexhaustible feedstock, modern production and purifying technologies for biodiesel [9].

3. Catalyst Used in Biodiesel Production

Catalyst increases the rate of chemical reaction. It requires a little change in the rate of a reaction most times. Catalyst speeds the rate of chemical reaction by providing a substitute reaction medium that has a lower activation energy to the non-catalyzed process.

There are various applications of catalysts ranging from heterogeneous to nano catalyst for the production of biodiesel owing to their numerous economic and environmental benefits. Homogeneous catalysts like the hydroxides of sodium and potassium, sulfuric acid, and supercritical fluids, enzymes like lipase are mostly used. There are various benefits and practicability of these catalyst in production of biodiesel, these are economically and environmentally feasible. Catalysts plays a vital role in vegetable oils transesterification. Presently, biological and chemical catalyst are been studied because of their various advantages

and disadvantages. These catalyst are anticipated to be cheap and friendly to the environment in applications involving large scale. The homogeneous catalyst in their physical forms is more essential than the heterogeneous catalyst, although their separation are more intrinsic. These heterogeneous catalyst in some cases are been effected by intense reaction conditions. Presently, nanocatalysts which show high effectiveness are been researched on. These nanoparticles show efficiency in lipase immobilization using biological catalysts as solid carriers. Production of biodiesel by lipase immobilization on magnetic nanoparticles has also proven to be a sustainable biocatalyst.

4. Classifications of Catalyst

4.1. Base Catalyzed Processes

The base catalyst can be categorized into two major types namely - the homogenous and the heterogeneous base catalyst.

Homogeneous Based Catalysis

Several homogeneous bases such as potassium hydroxide (KOH), sodium hydroxide (NaOH), sodium methoxide (NaOCH₃), and sodium ethoxide (NaOCH₂CH₃) are continuously utilized as catalysts. Homogeneous catalyst are usually faster in reaction rates than acid catalyzed

transesterification. They have high FFA content and are relatively cheap. Saponification of oil is the main problem of this method due to variety in quality of feedstocks. The recovery of the glycerol is difficult; thus requiring further treatment. They occur at mild reaction condition, low energy intensity and widely available with less corrosive tendency [7]. Different forms of oils such as the refined, frying or crude oil can be used to elucidate the activities of these catalyst. [23]. Conducive temperature, pressure state and a brief time of reaction are required for the performance of a transesterification reaction. The process reactants purity, water content and employed fatty acids are the major constraint to this technology. Excessive water may lead to the triglyceride hydrolysis into diglycerides and FFA (free fatty acids)), but the moisture should be managed in the procedure to get a biodiesel with high quality. Care must be taken in the use of a base catalyst in the production of biodiesel to avoid large amounts of FFA capable of causing saponification (soap production) which will promote the formation of an emulsion thereby increasing the recovery from downstream and raising the purifying cost process and giving rise to great accumulation of polluted liquid effluent [16].

Heterogeneous Base Catalysis

Recently, the use of heterogeneous catalyst has been on the high side because of their usability, reduced corrosion problems and lasts longer [17]. The base of these heterogeneous catalyst are used with feedstock requiring high purity with little amount of water and FFA content. (Fonseca *et al.*, 2019). Usage of some metal oxides, alkaline zeolites and several clays have been studied in present studies to show their efficacy in the use as heterogeneous based-catalyst [18-21]. These processes may be done together with other methods or can also be done alone [22]. The major setback in the use of these catalyst that are heterogeneous based is that they have low quantity of FFA, excessive oil proportion and molar alcohol, limiting diffusion, expensive when related to the old reactions and catalyst leaching skills which makes the marketability of the catalyst a major hindrance [18, 23].

The benefits of base catalyst that are oil heterogeneous in transesterification is that it lowers the stages for the methods and wastes which helps in catalyst separation and reusability. This process occurs at low energy intensity and at reduced conditions of reaction. There will be soap formation if there is large quantity of FFA. The soap formed as a result of this reduced biodiesel yield might cause problem in the purification of this product while leaching the catalyst's active sites can cause contamination of the product.

4.2. Acid-catalyzed Processes

The acid-catalyzed process can be categorized into the heterogeneous and homogeneous acid catalyst.

Homogeneous Acid catalyzed

The most widely used catalyst for acid-catalyzed transesterification are hydrochloric acid (HCl) and sulphuric acid (H₂SO₄). A homogeneous acid catalyst has more benefits in comparison to the alkali-catalyzed methods

because it can catalyze both esterification and transesterification at the same time, making it insensitive to the presence of FFA and thus allowing its use on low-cost feedstocks such as waste frying oils to reduce the acidity of the process. [24, 25]. The problem with this process is the need for intense conditions when compared to the alkaline method, such as temperature, reaction time, and oil to alcohol ratio [24].

Homogeneous acid catalyzed gives high yield. They are not sensitive to the content of FFA in the feedstock, thus chosen process if low-grade feedstock is used. Esterification and transesterification occur at once with low energy intensity. The corrosiveness of these acids may destroy the equipment. Huge quantity of free glycerol in the biodiesel during heterogeneous catalysis needs high temperature operation although lower than that of the supercritical which is not simple to separate the catalyst from the product. It has lower production rate which takes a relatively longer time.

Heterogeneous Acid Catalysis

Inorganic polymeric materials such as heteropoly acid and sulfonated carbons are examples of inorganic polymeric materials are mostly used with heterogeneous acid catalysis, which enhances the continuity of the technology because it helps in their separation from the reaction medium, reusability and prevents the corrosion of the equipment from homogeneous acid catalyst [23]. Metal-organic frameworks (MOFs) and covalent-organic frameworks (COFs) have advantages over other catalysts, such as a greater surface area and regular pore structure, which leads to an enhanced capacity for storing ions. Highly cross-linked amorphous covalent-organic polymers (COPs), such as the mesoporous melamine-formaldehyde polymer (MMFP), are regarded as exceptional chemicals because of their hydrothermal stabilities, as well as the features seen in MOFs and COFs. Low surface area, high solubility, low heat stability, and problems in fabricating chemically antagonistic functionalities are only a few of the drawbacks to using the HPA. [25].

4.3. Enzyme-catalyzed Processes

Under the enzyme catalyzed process, discussion shall focus on the Lipase catalyzed.

Lipase catalyzed

Biodiesel and glycerol are produced by lipase which are heterogeneous biochemical catalyzers mostly produced by microorganisms. They have wide application in the industries since they can be used as catalyst for lipidic feedstocks, acting at low temperature and conditions of pressure with high yields of reaction [26]. Lipases are environmentally friendly method because of their biocompatibility and biodegradability ability which promotes its use in agriculture and medical applications. Some microorganisms have been researched on in the literature as the effective producers of lipase which are mostly used in the production of biodiesel. For the production of lipase B, *Candida antarctica* is reported to be the most important yeast. Other *Candida* species are reported as good producers of lipases [26]. Lipases can also be produced from other sources like *Rhizomucor*, *Thermomyces*, *Aspergillus* and

Penicillium [27]. (Amoah *et al.*, 2016). Also, bacterial species like *Proteus* and some *Streptomyces* also reported to produce lipases and the produced lipases were utilized effectively for production of biodiesel [26]. Again, recombinant heterologous lipases with increased thermostability and tolerance to methanol denaturation have been produced. This is because lipases are normally found in free form, numerous support materials, including as alginate, chitosan, and silica gel, have been created to immobilize them. [28]. Some methods like the physical adsorption, ionic bonding or covalent bonding, entrapment cross-linking techniques, etc. can be used effectively for immobilization of lipases [29]. Novel biodiesel production methods have been investigated, such as whole-cells, which have a number of advantages, including a streamlined operation procedure and lower production costs. Another technology connected with solid state fermentation (SSF) is solid enzymatic preparation (SEP), in which fungal cells grow spontaneously in immobilization structures to secrete lipases that will be employed as biocatalysts. [30]. The issues with enzyme-catalyzed transesterification are mostly linked to lipase manufacturing, such as enzyme robustness, yields, purification, and stability. [26]. Furthermore, in comparison to alkali catalysis transesterification, enzyme-catalyzed transesterification has higher enzyme manufacturing costs and a longer enzymatic reaction time. [30].

Use of supercritical conditions

Supercritical methanol method has a high rate of reaction and transesterification efficiency without the need for catalysts [31]. This process needs an increased temperature and pressure with specified system control. The Sinopec Research Institute of Petroleum Processing's supercritical methanol process (SRCA) has recently been evaluated for industrial-scale biodiesel synthesis. The SRCA method employs several types of feedstocks without requiring any acid pretreatment, and the biodiesel generated meets BD100 diesel specifications. The percentage of glycerol can be as high as 90%, which helps to reduce the cost of purification. A significant reduction in purification, although the wastewater generation and solid residue can be decreased by 60% and 80%, respectively. Furthermore, due to severe conditions of reactions like increased temperature and pressure, the high cost of operation and capital are indispensably incurred in the SRCA process, which may delay its large-scale application. Enzymatic catalysis and supercritical alcoholysis are still in their early stages of development when compared to traditional homogeneous and heterogeneous catalysis processes, but they are becoming increasingly appealing in terms of process simplicity, strong adaptability, environmental friendliness, and high biodiesel yield. [32].

Table 2. Various Biodiesel Production Processes are compared.

Process Index	Homogeneous Catalytic Process	Heterogeneous Catalytic Process	Enzyme Catalytic Process	Supercritical Alcoholysis Process
Yield of Biodiesel (%)	>90	80-90	80-85	>90
Time of reaction	Low	High	High	Low
Temperature (°C)	50-90	55-150	10-40	200-250
Reused catalyst	Usable	Good reusability	Good reusability	No need catalyst
Deacidification	Need before alkali catalysis	Need before alkali catalysis	No need	No need
Generation of wastes	Acid-alkali wastewater	Nil	Nil	Nil
Separation	Complicated	Simple	Simple	Simple
Preparation	Simple	Hard	Simple	Nil
Cost of catalyst	Cheap	Expensive	Expensive	Nil
Byproducts	Less purification	High purification	Higher purification	Higher purification
Development	Industrialization	In-depth study	In-depth study	Preliminary study

[32]

Nano catalyzed transesterification

Nanocatalysts have several benefits when compared to other catalysts employed in the production of biodiesel like their increased reactivity, good selectivity and the optimum yield. Heterogeneous catalytic reactions are more feasible for the production of biodiesel because of the fast and easy recovery process of the catalyst from their reaction mixtures. The nano-catalyst-expedited esterification gives significant benefits, like the high rate of reactants mixing, saving of time of the reaction, simple and fast method of separation from the reaction mixture. Changing the physical and chemical properties of the catalysts can help in the monitoring of the catalytic activity and selectivity. Alkaline-catalyzed methods (NaOH, KOH), acid catalyzed methods (HCl, H₂SO₄) and enzyme- (lipase) catalyzed methods are in vogue. Lipases are heterogeneous biochemical catalysts that are solely produced by microorganisms. Homogeneous acid catalysts have more

benefits when compared to alkali-catalyzed methods [16].

There are several current innovations in catalytic conversion of fats and oils to biodiesel. Nano catalyst and Ionic liquid catalysts have more benefits than the conventional acid/base catalysts. Nano catalysis makes use of nano materials as catalysts for various homogeneous and heterogeneous catalysis applications. The high catalytic activity of the nanoscale catalyst is as a result of their high surface energy and specific surface area. In general, nano catalysts promotes the selectivity of the reactions by permitting reaction at a reduced temperature, thereby lowering the occurrence of side reactions, increasing the recycling rates and recovering of energy consumption [7]. Nano catalysts are very essential in biodiesel production from oils and fats because of their high catalysis activities and high surface area which eliminates the problems of mass transfer resistance related with conventional catalysts [7].

In biological catalysts, nanoparticles are used as solid carriers for lipase immobilization. Lipase immobilized on magnetic nanoparticles has been demonstrated to be a true biocatalyst for biodiesel synthesis. [33]. Nano-catalysts serve as a link between homogeneous and heterogeneous catalysts, allowing solid-acid or solid-base catalysts to be developed. Because of the small particles, traditional filtration and centrifugation are insufficient to recover the components following synthesis. A magnetic field could be used to swiftly recover magnetic nanoparticle-supported catalysts. [34].

5. Nanocatalysts in Biodiesel Production

Nanotechnology can be considered as one of the most relevant technology because of its wide range of applications in numerous fields. It involves the atomic or molecular accuracy in the size range of 1–100 nm in the synthesis, production, and applications of matter [35]. Several new and distinguished properties from nanotechnology have their building blocks from nanomaterials. Some nanomaterials such as the metal nanoparticles have been recorded to have surface area several hundred times more than their equal weight of macro scale materials. Apart from the extensive increase in surface area, other properties like tenacity, elasticity, catalytic activity, electricity, strength, etc. were discovered to be more developed at the nanoscale [36]. Current development in the area of nanotechnology and some remarkable studies proposed that the potential catalytic efficacy of nanomaterials makes them the most renowned catalysts in production of biofuel especially in biodiesel production. Some of the important solid nano catalysts which have been used in biodiesel production are metal oxides (CaO, MgO, Fe₃O₄, Ca/Al/Fe₃O₄, KF/Al₂O₃, SnO₂, etc.), sulfated oxides, hydrotalcites, zeolites, zirconia, etc [37].

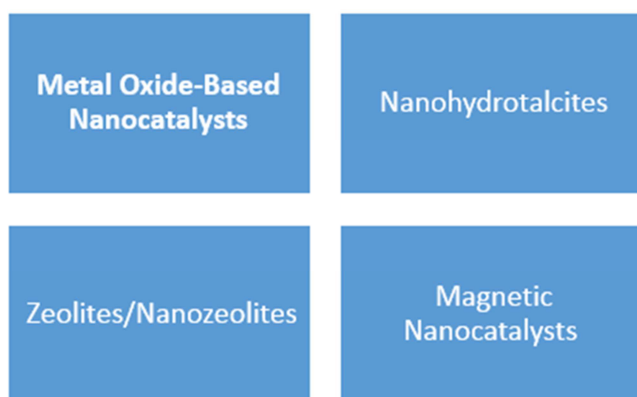


Figure 1. Block Chain Showing important nano catalysts frequently employed in production of biodiesel.

5.1. Metal Oxide-Based Nanocatalysts

The most promising heterogeneous nanocatalysts are the metal oxide-based nanocatalysts. The nanocatalyst from CaO were found to be a beneficial catalysts for the transesterification process of several oil feed stocks for the production of biodiesel [38]. (Bankovic-Ilic et al., 2017).

There are basically four types of nanocatalyst from CaO. They includes: neat CaO, doped CaO, loaded CaO and waste CaO. They are employed as efficient noncatalyst in synthesis of biodiesel from different oil feedstocks. Doped CaO and loaded CaO based catalyst are preferred to the neat CaO as a result of their quick formation of hydrogen bond with methanol and glycerol [39]. (Kumar *et al.*, 2018). The production of biodiesel from waste cooking oils, using nanoparticles from CaO and MgO synthesized by sol-gel self-combustion methods were investigated, CaO nanoparticles expressed remarkable rise in the yield of biodiesel compared to the nanoparticles obtained from MgO [11]. Metal oxide based nanocatalysts can be classified as the most effective heterogeneous catalysts for the production of biodiesel from several feedstocks.

5.2. Nanohydrotalcites

Hydrotalcites are common in nature and they have wide range of viable applications. They are best prepared using the co-precipitation methods [40]. Modern researches focus on the production of nanohydrotalcites which are usually known as anionic clays or aluminum-magnesium layered double hydroxides as a result of their wide range of applications. The hydrotalcite compounds are a sort of two-dimensional nanostructured anionic clay that comprises two types of metallic cations in a positively charged brucite-like layer, which are helped by a close packed configuration of OH groups. [40]. These nanohydrotalcites are used efficiently in biodiesel production which are environmentally friendly as a result of the process been carried out at room temperature [40].

5.3. Zeolites/Nanozeolites

Zeolite is a type of catalyst employed in industrial production of biodiesel. Their relevance are made known as a result of their promising work in the existence of strong acid sites, specific molecular sieving properties, elevated surface area and shape selectivity. Recently the scientific community are focusing on the advancement and usage of nanozeolites for improved effectiveness [41]. Nanozeolites have high external surface areas with high distributive ability in both aqueous solutions and organic media which enables improved passage of the enzymes to the substrate. The complexes from nanozeolites-enzyme have proven to be the most effective catalyst for biodiesel production. Also various mediums which are enzyme-catalyzed requires the usage of lipases enzymes which are efficient in transesterification of triacylglycerides. The rise in the catalytic activity of the immobilized enzymes are as a result of their improved stability to higher temperature and other environmental conditions. Their ease of reusability makes the application of nanozeolite very important. It is easy to reuse and retrieve them in consecutive cycles of transesterification of triacylglycerides because of the immobilization of catalytic enzymes on solid nano supports [42].

5.4. Magnetic Nanocatalysts

Magnetic nanocatalysts have remarkable magnetic properties. In their cycle of transesterification, they can be used more than once. Various magnetic nanocatalysts were evolved and used in the transesterification of different feedstocks for biodiesel production. The economic feasibility of magnetic nanocatalyst are as a result of their reusable ability and they are also easy to recover [43] have developed new magnetic nanocatalyst which he noticed have the same magnetic nano catalysts and can be reused up to 14 times without much loss in its activity and it is feasible to recover more than 90% of catalyst. Recently, the synthesis of ZnO/BiFeO₃ magnetic nanocatalyst by co-precipitation method was displayed for their use in biodiesel production from canola oil through a transesterification reaction. The high yield of biodiesel reported from this catalyst have proven its catalytic effectiveness [43]. Furthermore, the synthesis of a magnetic core-mesoporous shell KOH/Fe₃O₄ @ γ -Al₂O₃ nanocatalyst using the Fe₃O₄@ γ -Al₂O₃ core-shell structure as support and KOH as active component. The high biodiesel production yield of (97.4%) demonstrates the catalytic efficacy of this magnetic catalyst, which was attained through transesterification of canola oil under certain optimal reaction conditions. [44].

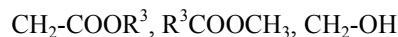
6. Transesterification

The most important process to the use of oils in replacement to fossil diesel is by transesterification. It creates biodiesel with very close viscosity and cetane index [45]. The catalyst-assisted approaches are the most ancient approach to produce biodiesel which can be employed with the use of heterogeneous or homogeneous methods. Homogeneous catalysis is easy, quick, the process gives high yield with a strong catalytic agent and less limitations [24]. Selectivity and eco-friendly ability of the heterogeneous catalysis makes its approach to production of biodiesel interesting. [23]. Transesterification of different oils can be used to produce esters and glycerin by adding alcohol, usually methanol or ethanol. [17]. Addition of catalyst helps in the breakdown of triglyceride into diglyceride and then monoglyceride. From the produced monoglyceride, glycerin is obtained. The most used catalyst used in production of biodiesel are alkali, acid and enzymatic. For effective utilization of the oils, some important variables as reported in the literature like the various alcohols, catalysts, reaction temperature, mixing intensity, and the alcohol to catalyst ratio are all factors to consider. [23].

Chemical Reactions

The oil is transesterified to make biodiesel, helping in the esterification of fatty acids. In the presence of an alcohol and a catalyst, transesterification and esterification of oils and fatty acids can be completed. This process is elucidated stoichiometrically by the process of the reaction shown below. The alcohols employed in this method are short chain

alcohols, like methanol and ethanol while chemical catalysts, biocatalysts, and non-enzymatic heterogeneous catalysts are all commonly utilized in this process.



Triglyceride, Methanol, Methyl ester, Glycerol

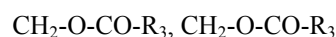
Triglyceride Transesterification: The unutilized FFA can cause formation of soap with the use of catalyst which may decrease the yield. The main disadvantage in carrying out the alcoholysis of oil is to curtail the presence of water and free fatty acids (FFA) in the oils.



FFA, Sodium Hydroxide, Soap, Water

Soap formation /Saponification

This determines the quality of product obtained. The rate at which a triglyceride is transesterified by hydrolysis is delayed by water in the reaction system, thereby raising the FFA content of the system.



Triglyceride, Water, Diglyceride, FFA

The hydrolysis of triglyceride produces acid molecules which leads to the production of soap. The free fatty acid present in the acid catalyzed system may react with alcohol, leading to the formation of esters. This gives rise to the formation of two stage catalyzed process. Oils with free fatty acid exceeding 3.0%, requires acid catalyzed treatment.

Emissions from cars

Various feedstocks determine the emissions from biodiesel combustion [9]. Earlier on, hydro treating of animal fats, vegetable oils and used cooking oils are good substitute to transesterification in the production of biofuels. This method has been proposed as another process to produce bio-based diesel with high quality fuels that have no effect on fuel logistics, engines or emissions after treatment devices. HVO, a fluid fuel containing a sulfur-free and aromatic-free blend of paraffinic hydrocarbons with a high cetane number [46]. Biofuel is developed by hydro treating catalysis of triglyceride-based biomass like vegetable oils, waste cooking oils or animal fats. Innovative selection has been detailed which relates to generation rate, utilization and enactment favoring the financial plausibility of diesel motors that are compliant for biodiesel with small or no moderation. Many researchers have made tremendous progress to institute biodiesel as a critical engine fuel, along with its ability to address environmental challenges such as global warming and sustainability, is a win-win situation, it is obvious that biodiesel is intended to be a long-term energy investment

as well as a significant contributor to the home and industrial automobile economies [47].

7. Opinion and Analysis of Biodiesel for the Future

In the period of biodiesel usage, economic importance should be merged with their benefits from the environment in order to attain such fits. Some vital problems should be deliberated on properly such as searching for cheap and environmentally friendly feedstock for production of biodiesel, highly effective and reusable catalysts that are cheap, eco-friendly transesterification agents and use of nano particles in biodiesel production.

The worldwide request for catalysts in 2014 was assessed around US\$33.5 billion. With the fast inception within the automotive and chemical industries generally, the global catalyst trade is anticipated to experience quick development in the coming years. Vladimir Ipatieff performed some of the earliest mechanical scale response, counting the revelation and commercialization of oligomerization and the improvement of catalysts for hydrogenation [48].

A dramatic changing market with threats and opportunities arises from the catalyst industry with regulations from the environment, increase in prices of materials, denser feedstocks which attracts the attention of green chemistry as an incentive. Huge expenditure have been made or arranged for building of new production equipment in emergent nations and industrialized regions to meet the increasing demands from the market. Increased prices of precious metals, reduced supply of rare-earth have led the global producers of leading catalysts into tremendous research and improvement of new processes, technologies and products [48]. It is of paramount reason to deliberate that production of biodiesel should not affect the use of farm lands for agriculture and successive supply of food. The economy, social and welfare of the environment should be at equilibrium in a complete way. This has caused some countries to avoid the use of crops meant for food to produce biodiesel [9].

8. Conclusion

Biodiesel is generally known as a substitute fuel which is environmentally friendly, although there are problems which needs to be handled in terms of preparation of biodiesel for future purposes. The use of different catalyst ranging from base catalyzed to acid catalyzed and use of supercritical conditions has been studied with their respective parameters were discussed to guide other researchers. Also, the use of nano particles in biodiesel production was also researched on which proves it to be a very feasible technology because of its transforming uses in various fields making it the best catalyst for biodiesel production. Different feedstocks determine the emissions from biodiesel combustion. The different feedstock oils were researched on in terms of their biofuel yield, design and their independent variables [49].

Finally, I believe that we need to standardize renewability and sustainability of produced biodiesel by employing policies and grants supports from the government.

References

- [1] Oyetola, O and Noor, A. A. (2019). A review of global current scenario of biodiesel adoption and combustion in vehicular diesel engines *Energy Reports*. vol. (5). pp. 1560-1579.
- [2] Eloka-Eboka, A. C., Igbum, G. O. and Inambao, F. L. (2017) Biodiesel methyl ester production and testing from selected African tropical seed oil feedstocks. *Energy Procedia*, vol. (142) pp. 755–767.
- [3] Zhang, X. L., Yan, S., Tyagi, R. S. and Surampalli, R. Y. (2013). Biodiesel production from heterotrophic microalgae through transesterification and nanotechnology application in the production. *Renew. Sustain. Energy Rev.* vol. (26) pp. 216–223.
- [4] Bhuiya M. M. K., Rasul M. G., Khan M. M. K., Ashwath N. and Azad A. K. (2016). Prospects of 2nd generation biodiesel as a sustainable fuel—Part: 1 selection of feed stocks *Renew. Sustain. Energy* vol. 55 pp. 1109-1128.
- [5] Otori, A. A., Mann, A., Suleiman. M. A. T., and Egwim, E. C (2019). Synthesis of Heterogeneous Catalyst from Waste Snail Shells for Biodiesel Production using *Afzelia africana* Seed Oil. *Nigerian Journal of Chemical Research* vol. (23) pp. 35-51.
- [6] Puneet, V and Sharma M. P. (2016). Review of process parameters for biodiesel production from different feedstocks. *Renewable and Sustainable Energy Reviews* vol. (62) pp. 1063-1071.
- [7] Shemelis N. G. and Jorge Mario M. (2017) Review Biodiesel production technologies: review *AIMS Energy*. vol. (5) 425-457.
- [8] Tayari S., Abedi R., Rahi A. (2020). Comparative assessment of engine performance and emissions fueled with three different biodiesel generations *Renew. Energy*. vol. (147) pp. 1058-1069.
- [9] Knothe, G., Krahel, J. and Van G. (2015). *The Biodiesel Handbook*, Elsevier, Salt Lake City.
- [10] Efe, M. A. Ceviz, H. Temur. (2018). Comparative engine characteristics of biodiesels from hazelnut, corn, soybean, canola and sunflower oils on DI diesel engine, *Renew. Energy* vol. (119) pp. 142–151.
- [11] Tsoutsos, T. D., Tournaki, O., Pararba S. D., Kaminaris. (2016). Used cooking oil-to-biodiesel chain in Europe assessment of best practices and environmental performance, *Renew. Sust. Energy. Rev.* vol. (54) pp. 74–83.
- [12] Yellapu, S. K., Kaur, R. and Tyagi D. (2017). Detergent assisted ultrasonic nation aide institute transesterification for biodiesel production from oleaginous yeast wet biomass, *Bio-resource. Technol.* vol. (224) pp. 365–372.
- [13] Ren, H., Tuo, J., Addy, M. M., Zhang, R., Lu, Q. and Anderson, E. (2017). Cultivation of *Chlorella vulgaris* in a pilot-scale photobioreactor using real centrate wastewater with waste glycerol for improving microalgae biomass production and wastewater nutrients removal, *Bio- resource Technol.* vol. (245) pp. 1130–1138.

- [14] Gaurav, A.; Dumas, S.; Mai, C. T. Q.; Ng, T. T. (2019). A kinetic model for a single step biodiesel production from a high free fatty acid (FFA) biodiesel feedstock over a solid hetero poly acid catalyst *Green Energy Environ. J.* vol. (4), pp. 328–341.
- [15] Avinash P. I., Anuj K. C., Rafael P., Sabrina E., Martiniano and Silvio S (2020). Advances in Nanocatalysts Mediated Biodiesel Production: A Critical Appraisal. *Symmetry*, 12, 256; doi: 10.3390/sym12020256.
- [16] Bouaid, A., Vázquez, R., Martinez, M. and Aracil, J. (2016). Effect of free fatty acids contents on biodiesel quality. Pilot plant studies. *Fuel* vol. (174), pp. 54–62.
- [17] Quah, R. V., Tan, Y. H., Mubarak, N. M., Khalid, M., Abdullah, E. C. and Nolasco-Hipolito, C. (2019). An overview of biodiesel production using recyclable biomass and non-biomass derived magnetic catalysts. *J. Environ. Chem. Eng.* vol. (4) 103219.
- [18] Knothe, G.; Steidley, K. R. (2018). The effect of metals and metal oxides on biodiesel oxidative stability from promotion to inhibition. *Fuel Proc. Technol.*, 177, 75–80.
- [19] Abukhadra, M. R., Ibrahim, S. M., Yakout, S. M., El-Zaidy, M. E. and Abdeltawab, A. A. (2019) Synthesis of Na⁺ trapped bentonite/zeolite-P composite as a novel catalyst for effective production of biodiesel from palm oil; Effect of ultrasonic irradiation and mechanism. *Energy Convers. Manag.* vol. (196) pp. 739–750.
- [20] Jung, J. M., Oh, J. I., Park, I. K., Lee, J. and Kwon, E. E. (2019). Biodiesel synthesis from fish waste via thermally-induced transesterification using clay as porous material. *J. Hazard. Mater.* vol. (371) pp. 27–32.
- [21] Li, Z.; Ding, S.; Chen, C.; Qu, S.; Du, L.; Lu, J.; Ding, J. (2019). Recyclable Li/NaY zeolite as a heterogeneous alkaline catalyst for biodiesel production: Process optimization and kinetics study. *Energy Convers. Manag.* vol. (192) pp. 335–345.
- [22] Kalavathy, G.; Baskar, G. (2019) Synergism of clay with zinc oxide as nanocatalyst for production of biodiesel from marine *Ulva lactuca*. *Bio resource. Technol.* vol. (281) pp. 234–238.
- [23] Fonseca, J. M., Teleken, J. G., de Cinque Almeida, V. and da Silva, C. (2019). Biodiesel from waste frying oils: Methods of production and purification. *Energy Convers. Manag.* vol. (184) pp. 205–218.
- [24] Farobie, O. and Matsumura, Y. (2017) State of the art of biodiesel production under supercritical conditions. *Prog. Energy Combust. Sci.* vol. (63) pp. 173–203.
- [25] Jeon, Y., Chi, W. S., Hwang, J., Kim, D. H., Kim, J. H. and Shul, Y. G. (2018). Core-shell nanostructured heteropoly acid-functionalized metal-organic frameworks: Bifunctional heterogeneous catalyst for efficient biodiesel production. *Appl. Catal. B: Environ.* vol. (242) pp. 51–59.
- [26] Hama, S., Noda, H. and Kondo, A. (2018) How lipase technology contributes to evolution of biodiesel production using multiple feedstocks. *Curr. Opin. Biotechnol.* vol. (50) pp. 57–64.
- [27] Amoah, J.; Ho, S. H.; Hama, S.; Yoshida, A.; Nakanishi, A.; Hasunuma, T.; Ogino, C.; Kondo, A. (2016) Converting oils high in phospholipids to biodiesel using immobilized *Aspergillus oryzae* whole-cell biocatalysts expressing *Fusarium heterosporum* lipase. *Biochem. Eng. J.* vol. (105) pp. 10–15.
- [28] Lee, J. H.; Lee, J. H.; Kim, D. S.; Yoo, H. Y.; Park, C.; Kim, S. W. (2019). Biodiesel production by lipases co-immobilized on the functionalized activated carbon. *Bioresour. Technol. Rep.*, 7, 100248.
- [29] Zhao, X., Qi, F., Yuan, C., Du, W. and Liu, D. (2015). Lipase-catalyzed process for biodiesel production: Enzyme immobilization, process simulation and optimization. *Renew. Sustain. Energy Rev.*, 44, 182–197.
- [30] Aguiéiras, E. C. G., Cavalcanti-Oliveira, E. D. and Freire, D. M. G. (2015). Current status and new developments of biodiesel production using fungal lipases. *Fuel*. vol. (159) pp. 52–67.
- [31] Sakdasri, W., Sawangkeaw, R. and Ngamprasertsith, S. (2018). Techno-economic analysis of biodiesel production from palm oil with supercritical methanol at a low molar ratio, *Energy* vol. (152) pp. 144–153.
- [32] Yingqun, M. and Yu L. (2019). Biodiesel Production: Status and Perspectives. *Elsevier Inc. Academic Press*. Chapter 21. pp. 503-537.
- [33] Prabhu, M., Manikandan, M., Kandasamy, P., Kalaivani, P. R., Rajendiran, N., Raja, T. Synthesis of biodiesel using the Mg/Al/Zn hydrotalcite/SBA-15 nanocomposite catalyst. *ACS Omega* 2019, 4, 3500–3507.
- [34] Thangaraj, B., Solomon, P. R., Muniyandi, B., Ranganathan, S., Lin, L. (2019). Catalysis in biodiesel production—A review. *Clean Energy* vol. (3) pp. 2–23.
- [35] Khan, I.; Saeed, K.; Khan, I. (2019). Nanoparticles: Properties, applications and toxicities. *Arab. J. Chem.* vol. (12) pp. 908–931.
- [36] Zhang M., Gao, Z., Zheng, T., Ma, Y., Wang, Q. and Gao, M. (2018). A bibliometric analysis of biodiesel research during 1991-2015, *J. Mater. Cycles Waste Manage.* vol. (20) pp. 10–18.
- [37] Zuliani, A.; Ivars, F.; Luque, R. (2018). Advances in nanocatalysts design for biofuels production. *ChemCatChem*, vol. (10) pp. 1968–1981.
- [38] Bankovic'-Ilic', I. B., Miladinovic', M. R., Stamenkovic', O. S. and Veljkovic', V. B. (2017) Application of nano CaO-based catalysts in biodiesel synthesis. *Renew. Sustain. Energy Rev.* vol. (72) pp. 746–760.
- [39] Kumar, D., Sharma, S., Srivastava, N., Shukla, S. and Gaurav, K. (2018). Advancement in the utilization of nanocatalyst for transesterification of triglycerides. *J. Nanosci. Tech.*, 4, 374–379.
- [40] Shekoohi, K.; Hosseini, F. S.; Haghighi, A. H.; Sahrayian, A. (2017). Synthesis of some Mg/Co-Al type nano hydrotalcites and characterization. *Methods X* vol. (4) pp. 86–94.
- [41] Al-Ani, A., Darton, R. J., Sneddon, S. and Zholobenko, V. (2018). Nanostructured zeolites: The introduction of intracrystalline mesoporosity in basic Faujasite-type catalysts. *ACS Appl. Nano Mater* vol. (1) pp. 310–318.
- [42] Kim, K. H., Lee, O. K. and Lee, E. Y. (2018). Nano-immobilized biocatalysts for biodiesel production from renewable and sustainable resources. *Catalysts* vol. (8) pp. 68.

- [43] Hu, S., Guan, Y., Wang, Y. and Han, H. (2011) Nano-magnetic catalyst $\text{KF/CaO-Fe}_3\text{O}_4$ for biodiesel production. *Appl. Energy* vol. (88) pp. 2685–2690.
- [44] Ghalandari, A., Taghizadeh, M. and Rahmani, M. (2019) Statistical optimization of the biodiesel production process using a magnetic core-mesoporous shell $\text{KOH/Fe}_3\text{O}_4 @\text{g-Al}_2\text{O}_3$ nanocatalyst. *Chem. Eng. Technol*, vol. (42) pp. 89–99.
- [45] Giakoumis, E. G. and Sarakatsanis, C. (2019). A comparative assessment of biodiesel cetane number predictive correlations based on fatty acid composition. *Energies*, vol. 12 pp. 422.
- [46] Hartikka T, Kuronen M, Kiiski U. (2012) Technical Performance of HVO (Hydrotreated Vegetable Oil) in Diesel Engines, SAE Technical Paper 2012-01-1585.
- [47] SY. (2014). Application of hydrotreated vegetable oil from triglyceride based biomass to CI engines – a review. *Fuel* vol. (115) pp. 88–96.
- [48] Nicholas, C. P. (2018). Dehydration, Dienes, High Octane, and High Pressures: Contributions from Vladimir Nikolaevich Ipatieff, a Father of Catalysis. *ACS Catalysis*. vol. (8) pp 8531–8539.
- [49] "Market Report: Global Catalyst Market" (3rd ed). *Acmite Market Intelligence*.