Review Article

Scope of Biodiesel and Role of Homogeneous Catalysts: A Review

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Abstract: The biodiesel was the best alternative of petroleum diesel. The 1st generation feedstock would create the food shortage. The second-generation yield was comparatively less and from third generation feedstock the process was complicated and expensive. The fourth-generation feedstock produced from genetically modified algae or by artificial photosynthesis in plants to produce the raw material for biodiesel production The fourth generation was not available on commercial scale. The biodiesel produced by esterification (one step) and Transesterification process (two step). The catalysts used were homogenous, heterogenous and enzymatic. The homogenous were alkaline and acidic. The alkaline catalyst undergoes saponification reaction when free fatty acid concentration was high. The acidic catalyst preparation was expensive and complicate exhibited slow rate of reaction. The biodiesel used in blend form and diesel engines required the modification. The biodiesel sustainable and release no greenhouse gas.

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Introduction

Energy is essential to run the economic wheel and perform socio-economic activities. The energy demand is increasing with the passing time because of industrialization, population growth and man-made activities. This increased from 6 to 15 GTOE (Gigatons of Oil Equivalent) during the 1970-2015. The energy was derived from renewable and nonrenewable sources. The coal, coke and petroleum products were main nonrenewable sources of energy and they were commonly known as fossil fuels. The fossil fuel consumption was high in primary energy supply. In 1973 the fossil fuels contributed 86% of total energy supply (Banković-Ilić, 2012). Worldwide the oil consumption was 42% in 1973 in and 64.5% in 2014. The consumption rate was increased 43.33% in last 41 years (Key World Energy Statistics, 2016).

The fossil fuels organic in nature formed by long geological process carried out under earth crust at high pressure and temperature. The presence of carbon, hydrogen, volatile matter nitrogen and sulfur compounds they release the particulate matter, unburnt particulates, Carbon monoxide, Carbon dioxide NO_X and SO_X during combustion process. The fossil fuel reservoirs limited in nature are being depleted day by day. The environmental concerns

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raised globally regarding the greenhouse gas emission and depletion of reservoirs in last few decades (Popp, 2014). That was why the attention paid to renewable sources. Further the economic growth of any country relates prices of petroleum products in markets which is hiking continuously in international markets. The fossil fuels specially petroleum products prices are hiking by increase demand. The economical growth relates with the prices of prices of petroleum products. The need of today is to minimize the dependency of fossil fuels and switch to renewable, alternative and sustainable sources of energy (Oh *et al.*, 2002; Uma and Kim, 2009).

The wind, solar, geothermal, biomass energy and hydrothermal energy are renewable sources of energy (Demirbas, 2005). Among all the solar and biomass are the most practiced globally. Biodiesel is environmentally sustainable and cannot produce toxic gases (Haris *et al.*, 2022). The biofuels generated from biomass was the best alternative source of energy. The biofuels had potential role in minimization of greenhouses gases. The biofuels were produced from the first- and second-generation crops, vegetables oils, waste cooking oils. The biofuels popular in many developed countries as Brazil, USA, China, and others. The Brazil is famous for bioethanol production. The various aspects of commercialization of biofuel were under study by different researchers and planners. Those were the development of safe and economical generation process. Secondly the land was used for fuel crops and blending ratio of biofuels to the conventional fuels. Thirdly they focus the application and usage of biofuels and its commercialization strategies (Glenister and Nunes, 2011).

The biofuels exists in liquid, gaseous and solid forms. The biodiesel is liquid biofuel and the best alternative of petroleum diesel. It synthesized from animal fats, edible oil and non-edible oils. It is nontoxic, biodegradable and environment friendly (Ranjitha *et al.*, 2019). The main advantages are ecofriendly nature, renewability, high flash point, and nontoxicity (Shi *et al.*, 2013). It had potential to minimize the carcinogens preferable in close chamber emission (Krawczyk, 1996). The biodiesel production carried out the transesterification reaction. The Biodiesel is a combination of fatty acid methyl easter (Reddy *et al.*, 2016). The biodiesel is used in blended form in diesel engines.

The Rudolf Diesel was the inventor of diesel engines, experimented the peanut oil as fuel. It was found that vegetable oils can be used as alternative of petroleum diesel without modification in engines. The petroleum exhausted the smoke, particulate matter, unburned hydrocarbons, CO, and NOx. the oxide of Nitrogen most harmful (Senthikumar and Gunasekaran, 2014). In emergency situation during the decade of 1930 to 1940 the vegetable oil used in diesel engines.

In present situation the more attention is paid to biodiesel production from non-edible oils and fats to meet the increasing demand. Simultaneously it is need to reduce the greenhouse gases emission (Shay, 1993). The Government of various countries is encouraging the public and private sectors to launch the new ideas for enhancement and utilization of biodiesel on commercial scale (Gumus, 2009). The biodiesel is used in blended or pure form injection in compression engines by doing some modification in compression engines (Shahabuddin *et al.*, 2013). The performance can be enhanced by improving the brake thermal efficiency, brake torque and brake power (Gumus, 2009; Ruhul *et al.*, 2016). Besides all advantages of biodiesel there were a few drawbacks of biodiesel that were its high pour point viscosity and cloud point. The biodiesel had low calorific value, less volatile matter content, poor spray characteristics and emits greater amount of nitrogen oxide (Demirbas, 2008). Those draw backs can be eliminated by appropriate modification in diesel engines, addition of particular additives and selection of feedstock (Shi *et al.*, 2013).

The catalyst played important role in biodiesel production. Different parameter was consider during the biodiesel production like as Methanol to oil ratio, reaction time, reaction temperature and catalyst loading (Adriana *et al.*, 2022). In broad spectrum the catalysts were in homogenous or in heterogenous phase and had acidic or alkaline characteristic. The other one was the enzymatic catalyst. The nature of catalyst affects the transesterification reaction and played key role to convert the triglycerides to biodiesel. The researcher worked to explore the catalytic activity of various homogeneous and heterogeneous catalysts to get better yield under optimum conditions. The Chemicals catalysts are prominent because of their selectivity, better catalytic activity and yield, and fast reaction rate (Vivek, 2011).

Feedstock for biodiesel production

The biodiesel is a combination of fatty acid methy easter (Reddy *et al*., 2016). It is renewable, biodegradable, environmental eco-friendly and non-toxic (Ranjitha *et al*., 2019). It produce from edible oils seed, non edible oil, animal fats, waste cooking oil and algae (Deepak *et al*., 2016). Source of fatty acid can produce biodiesel (Rummi, 2017). The oil and free fatty acids content are dissipated in Tables 1 and 2.

Table 1: *The oil content of various feeds talk for biodiesel production.*

First generation (Edible oil)	Oil content (%)	2nd generation (Non-Edible)	Oil content (%)
Rapseed	38-46	Rubber seed	53.74-68.35
Soybean	15-20	Karanja	27-39
Sunflower	25-35	Jatorpha	30-40
Linseed	40-44	Castor	45-50
Canola	40-45	Chinese tallow seed (stillinga)	15-44
Peanut	45-55	Neem	20-30

The oil and fats are differentiated by saturated and unsaturated fatty acids content. The fats had high saturated bonds of free content. That was why the vegetable oil was turned to biodiesel easily and employed in biodiesel engines. While the saturated bonds deposited the carbon in engines and fuel lines hence the durability of engines were at risk.

The feedstock used in biodiesel production varies region to region directly depends on climatic and geological conditions. The other influence factors were the crop yield and availability. The biodiesel is generated from various sources those sources were 1st generation, 2nd generation 3rd generation and 4th generation. The waste cooking oils/ frying oil from homes and restaurants were also the source. In these cases, the composition should be assured otherwise the difficulties arise in purification process.

The first-generation feedstock was the edible oils used in foods. These were the sunflower oils, palm oil, corn oil, olive oil, cottonseed oils, walnut oils and etc. (Mahdavi *et al*., 2015). In early era of biodiesel production, the edible feed stalks were used as fuel crops this because of their availability round the year but there was the probability of food scarcity and high food prices. The land used for cultivation of crop were another social issue arises. To ensure the food supply the attention was diverted to second generation fuel crops (Tariq *et al*., 2012).

The second generation was the non-edible oils. Those were the Neem oil, rubber oil, jatropha oil, castor oil and etc. The plus point of 2nd generation feeds talk was the less cost required on biodiesel production and had high resistance towards the harsh climatical condition. Mostly the 2nd generation fuel crop was grown up on barren lands and in arid zones as well. The less water availability put no effects or less effects on their growth rate. It was worthful to express here that socio economic issues reported from various regions of world regarding the land utilizations for cultivation of 2nd generation feed stalks. It was noted that these needs comparatively more alcohol quantity for transesterification reaction (Tariq *et al*., 2012).

It was reported that the third generation feed stock of biodiesel production is waste cooking oil and micro algae etc. (Puneet and Sharma, 2016). They had more advantages than prior ones. There was importance of having no land need for cultivation and no scio-economic issue raised. The time and efforts were saved for cultivation and no influence on food chain. The merits included its fast growth rate high productivity and less greenhouse gas emission (Tariq *et al*., 2012). Besides all the large investment was required and the biodiesel production process was complicated. The sun lightis mandatory for run the process. The huge amount is required to establish on large scale. Only on small scale it was viable but not on large scale.

Table 2: *The Free fatty acid content of various feeds talk for biodiesel production.*

Vegetable oil	Free fatty acid %	Vegetable oil	Free fatty acid %	Vegetable oil	Free fatty acid %
Tobacco oil	35.0	Rubber oil	17.0	Ponagamia oil	0.64
Rape seed oil	2.0	Palm oil	5.3	Salvadora oil	1.76
Cottonseed oil	0.11	Crude soybean oil	0.4–0.7%	Tung oil	9.55
Jatropha oil	14.0	Mahua oil	21.0	Polanga oil	22.0
*WPO	>20%	**RWG	0.7–41.8%	Trap grease	50–100%
Karanja oil	2.53	Municipal sludge	Up to 65%	Waste oil	46.75%
# UCO	2–7%	Sorghum bug oil	10.5	Animal fat	5–30%

*WPO= Waste palm oil **RWG= Restaurant waste grease # UCO= Used cooking oil

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The fourth-generation of bio fuels was generated by Photo biological Process. In these processes the solar energy converts to biomass that was required in biodiesel generation. This process is also known as artificial photosynthesis and photobiological hydrogen production. In the last ten years the solar fuel was designed to discover the less expensive, efficient and viable method of biofuel generation. The solar energy stored in solar fuel cell and can be used on need.

The fourth-generation feedstock also refers to genetic modification in algae to boost the biodiesel production

The biodiesel production technique

There were many techniques many techniques adopted to produce the biodiesel. The first and most common technique were transesterification. This need refined oil free or less content of free fatty acid otherwise goes to soap formation (Khan, 2007). The other reported method, pyrolysis (cracking), microemulsion (Khan, 2007) and blending (Keskin, 2008). The recommended feedstock's acid value > 4.0mg/KOH for esterification reaction. It was further stated that heterogenous catalyst worked well on low quality feedstock convert free fatty acid on biodiesel. While enzyme do well given high percentage purity (Hideki *et al*., 2001).

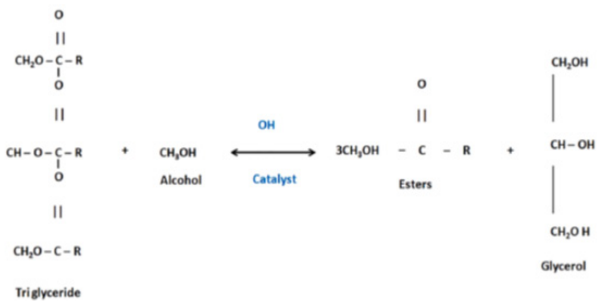

Figure 1: *The fats and alchol reaction biodiesel formed.*

The biodiesel syntheses was from animal fats and vegetable oils. The oil and fats were composed of 3 moles of fatty acid and 1 mole of glycerides. That was why commonly known as triglycerides (Sonntag, 1979). The fats and oil were not soluble in water. They make the immiscible layer because of their hydrophobic nature. The fatty acid was composed of unsaturated double bonds and long carbon chain. The chain varies molecule to molecule. The biodiesel was the fatty acid methyl esters. The diesel fuel refers to diluted form of biodiesel with solvent. The biodiesel was refined by thermal depolymerization. The pathway of biodiesel production of different generation is shown in Figure 2.

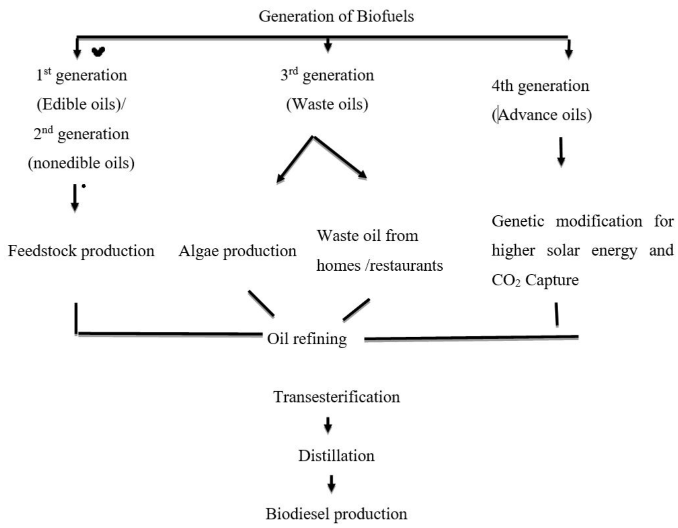

Figure 2: *The biodiesel production pathway of different generations.*

Catalyst for biodiesel production

The homogeneous catalysts were the acid or base expedite the esterification and transesterification reaction for biodiesel production.

The alkali homogonous catalysts

The alkali homogonous catalyst were hexoxide of sodium, potassium sodium methoxide, sodium ethoxide, sodium propoxide, potassium methoxide, sodium butoxide and carbonates. The sodium hydroxide was more popular than potassium hydroxide because of its cost effectiveness, had high purity and solubility in methanol. Its less quantity was utilized compared to potassium hydroxide for esterification/ transesterification reaction (Jitputti, 2006; Fukuda, 2001). It reported that alkali metal alkoxides more effective than alkalioxides for biodiesel production (Saydut *et al*., 2016). The CH_3ONa or CH_3OK gave better results than NaOH or KOH (Atadashi *et al*., 2013).

In alkali transesterification the sodium hydroxide reacts with methanol result the water produced in certain quantity even in water free reactant used as vegetable oil and free fatty acid. That minimized the biodiesel production and reaction switch to soap formation which directly influenced the quantity.

The researcher proposed to employ the two-step esterification reaction. The reason behind that was alkali and Free fatty acid tend to adopt the saponification route and formed the soap. This happens when concentration of free fatty acid is less than 1%. In that case soap acts as inhibitor to biodiesel and glycerin production. It was recommended to treat prior to acid in order to reduce the effectivity towards the soap formation and made it ready for alkali treatment (Thangaraj *et al*., 2014; Ghadge and Raheman, 2005).

Fukuda *et al*. (2001) reported that the alkaline catalyst gave faster rate of reaction around 4000 times faster than acid catalyst in same amount. The advantages and disadvantages of acidic and alkaline are shown in Table 4.

The acidic homogonous catalysts

In biodiesel formation the sulphonic acid, sulfuric acid, hydrochloric acid and phosphoric acid were employed but most preferable was the sulfonic acid in both esterification and transesterification reaction (Fukuda *et al*., 2001). One drawback of acid catalysts was their slow reaction rate sometimes took less than one day for completion of reaction. They offered gave high yield but higher oil to alcohol ratio required (Zheng *et al*., 2006; Marchetti, 2005).

It was suggested that the high percentage of free fatty acid can be eliminated by the treatment with p-toluene-4-sulphonic acid followed but prior the treated with potassium hydroxide (Meher *et al*., 2006; Hayyan *et al*., 2010). The obtained biodiesel neutralized by sulfuric acid prier were washed with distilled water, then treat with sulfuric acid in order to neutralize. Finally washed and used any suitable de hydrated to remove the moisture (Hayyan *et al*., 2010; Meher *et al*., 2006).

Table 3: *The merits and demerits of different generation feedstock used in biodiesel production.* (Digambar *et al*., 2020).

Generation for biodiesel production	Merits	Demerits
First generation	• The biodiesel conversion process easy • The feedstalk available round the year	• Directly influence the food supply • The crop yield was low • Limited area for cultivation • The adoptability of crop to environmental condition
Second generation	• Not effect on food supply • The feedstalk grow on less fertile or non-arable land • Feedstalk had High resistance towards harsh climatic condition less water supply and pests. • The cultivation cost very less.	• In some case low crop yield obtained • The biodiesel production technology was less cost effective.
Third generation	• The waste cooking oils utilized as feedstalk for biodiesel production. • No effect on food supply • The wastewater and sea water provide medium for algae grow. • The rapid growing rate of algae	• High investment and energy required for algae cultivation • Not feasible to run on large scale. • The oil extraction technology was neither cost effective nor easy and simple. • In open pond the lipids content in algae were low
Fourth generation	• The lipid content and energy were higher • The CO2 absorption ability were higher • High-rate high initial investment	• The biodiesel extraction technology on available on commercial scale.

Table 4: *The advantages and disadvantages of different homogenous catalyst used in biodiesel production.*

Homogenous catalyst	Catalysts name	Advantages	Disadvantages
Alkaline catalyst	• NaOH • KOH • CH_3ONa • CH3OK	• High reaction rate • less corrosive	• Formation of saponified Products, • Emulsion formation • High water and energy consumption • Huge wastewater discharge • High purification cost • Feedstocks are limited to weight 5% • Not recycle
Acid catalysts	• H_2SO_4	• Zero soap formation • Catalyst can be used for both trans-esterification and esterification	• Leaching effects • Catalyst preparation is complicated and expensive • Slow rate of reaction

Table 5: *The yield of various acid and alkaline homogenous catalyst used for biodiesel production.*

Feedstock	Alcohol type	Acidic homogenous catalyst	Amount	Biodiesel yield
Karanja oil	Methanol	H_2SO_4	0.5% w/v	80%
Karanja oil	Methanol	H_2SO_4	1ml	98.6%
Jatropha oil	Methanol	H_2SO_4	0.5% w/v	80%
Honne oil	Methanol	H_2SO_4	0.5 ml	89%
Corn oil	Methanol	H_2SO_4	0.5% w/v	80%
Canola oil	Methanol	H_2SO_4	0.5% w/v	80%
Alkaline homogenous catalyst				
Animal tallow fat	Methanol	NaOH	2g	-
Koranja	Methanol	NaOH	28.5	84%
Koranja	Methanol	KOH	2% w/v	90-95%
Jatropha	Methanol	KOH	2% w/v	90-95%
Jatropha	Methanol	KOH	2.09%w/w	80.5%
Honne oil	Methanol	KOH	0.75-1.5w/v	89%
Mahua oil	Methanol	KOH	0.7%w/v	98%
Mahua oil	Methanol	KOH	1%w/v	95.71%
Corn	Methanol	KOH	2% w/v	90-95%
Canola	Methanol	KOH	2% w/v	90-95%
Waste frying oils	Methanol	NaOH	0.6%w/v	98%

Conclusions and Recommendations

This paper reveals the review of various research studies on biodiesel production. The focus would be on role of homogenous catalyst used in biodiesel production. The feedstock of biodiesel production and its techniques would also be reviewed. The biodiesel is the best alternative of fossil biodiesel. This paper covers the scope of biodiesel in energy sector, the production techniques and role of catalysts. The first (edible), second (non-edible), third (waste cooking oil and algae) and fourth generation (genetically modified biomass) feedstock used for biodiesel production. The fourth generation is not common still under research. The homogenous and heterogenous catalysts played important role in biodiesel production. There were alkaline and acidic catalyst. The alkaline homogenous catalyst undergoes the saponification reaction when free fatty acid concentration high. The various alkali catalysts used include the NaOH, KOH, sodium methoxide, sodium ethoxide, sodium propoxide, potassium methoxide, sodium butoxide, and carbonates. The selection based on recovery of yield. The acidic homogenous catalyst is more expensive but played slow rate of reaction. The biodiesel releases no greenhouse gases its environment friendly but needs modification in diesel engines. I recommended that government get action to support the researcher to find new sources of energy to overcome the requirement of country demand.

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Novelty Statement

The study is novel to find new source of energy and to produce sustainable environmental fuel.

Author's Contribution

All authors equally contributed.

Conflict of interest

The authors have declared no conflict of interest.

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