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Production and Optimization of Biodiesel from Microalgae using Banana Peel as Catalyst Through Response Surface Methodology (RSM) – a Review

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Abstract: Microalgae have emerged as a promising sustainable feedstock for biodiesel as the quest for alternatives to fossil fuels continue. When compared to standard biofuel crops, several species have high lipid content and need simple cultivation, requiring less freshwater and land space. Technological developments in the growing, harvesting, pretreatment, lipid extraction and transesterification subsystems have recently pushed microalgae biodiesel closer to becoming economically viable. Biodiesel can be produced through transesterification reaction, the transesterification reaction is influence by various factors such as molar ratio of alcohol to oil, catalyst concentration, reaction time, temperature, presence of water, free fatty acid content and mixing intensity or agitation speed. optimization of the production process is crucial to obtain highest yield and ensure material equalization. Transesterification processes are typically carried out in the presence of either a homogeneous or heterogeneous catalyst. The downsides of homogeneous catalysts include their one-time usage, slow reaction rate, and saponification concerns caused by the presence of fatty acids in the feedstock. The homogeneous catalysts' acidic nature causes equipment corrosion as well. Heterogeneous catalysts, on the other hand, provide several advantages, including reusability, higher reaction rate, and selectivity, ease of product/catalyst separation, and low cost. As a result of these factors, researchers are increasingly interested in developing solid-phase transesterification catalysts. The present review compares the usage of heterogeneous catalysts for biodiesel production from microalgae oil as a reliable feedstock to other accessible feedstocks. It also emphasizes the optimum reaction conditions for the highest biodiesel yield, solid catalyst reusability, affordability, and environmental impact. Microalgae higher lipid content, along with the solid acid-base catalysts effective concurrent esterification and transesterification, could lead to new biodiesel breakthroughs.

Key words: Biodiesel, microalgae, optimization, heterogeneous catalyst, homogenous catalyst, transesterification reaction, factors affecting biodiesel.

I. Introduction

Biodiesel is an alternative fuel made from monoalkyl esters formed by the transesterification of triglycerides (oils or fats) with light alcohols, which can be catalyzed or not (methanol or ethanol). Virgin or used edible oils such as soybean oil, palm oil, vegetable oil, or sunflower oil can be used as triglyceride sources. Even after being used in cooking, these discarded vegetable oils can be used as oil feedstocks. Biodiesel has some advantages, including high lubricity, high flash point, low viscosity, biodegradability, environmental friendliness, and reduced greenhouse gas emissions (Banković *et al*., 2017).

1.2 The effect of fossil fuels on the environment

Humans have relied on simple sources of energy for most of their existence, including muscle from humans and animals, as well as biomass like wood or crops. Fossil fuels, on the other hand, were made accessible during the Industrial Revolution. Fossil fuels have been a major force behind subsequent advances in technology, society, the economy, and development (Roser *et al*., 2020).

There has been and will continue to be a significant role for fossil fuels in global energy systems. They do, however, have several disadvantages. When fossil fuels are burned, they release carbon dioxide (CO_2) and other greenhouse gases, which in turn trap heat in our atmosphere, making them the primary contributors to global warming and climate change (Roser *et al*., 2020).

Fossil fuels and the environment are inextricably linked, as evidenced by the chemicals and substances they contain. Carbon, methane, and other greenhouse gases are abundant in the atmosphere, making it difficult to overlook their negative impact on the environment. Plastics, for example, are derived from fossil fuels, the production of plastics has a wide range of environmental consequences, including the degradation of the environment's cleanliness and the release of chemicals into the atmosphere and waterways because of their biodegradable nature (Nunez, 2019).

Perhaps more ostensibly, fossil fuels have the greatest impact on the atmosphere, given the type of substances they are composed of. Carbon dioxide, which enters the atmosphere when fossil fuels are burned, and methane, which is emitted during the production and transportation of fossil fuels, are both greenhouse gases (GHGs). This is due to the greenhouse effect, which occurs when GHGs are released into the atmosphere. The greenhouse effect is a natural phenomenon that contributes to the warming of the Earth's surface. When solar energy reaches the earth, it is absorbed and re-radiated in part by greenhouse gases. This is essentially what maintains the earth's temperature. Thus, increased GHG emissions increase gases that absorb heat from the sun, increasing the earth's average temperature. This results in climate change, which affects weather patterns in the short run and completely alters climate patterns in the long run.

Today, climate change is mostly a result of human activity, and it is accelerating. According to the World Metrological Organization (WMO) Greenhouse Gas Bulletin, worldwide averaged carbon dioxide (CO_2) concentrations reached 407.8 parts per million (ppm) in 2018, up from 405.5 ppm in 2017 (World Metrological Organization, 2019). The Intergovernmental Panel on Climate Change (IPCC), likewise anticipates a 2.5-to-10-degree Fahrenheit temperature increase over the next century (NASA, 2019). Continuous temperature increases would exacerbate climate change, resulting in droughts and heatwaves, sea-level rise, desertification, forest fires, storms, and hurricanes, as well as further repercussions on land, water, and ecosystems.

Unlike land, fossil fuels have the potential to interact with the water that is always flowing. As a result, dangerous chemicals are added to fresh water, which then serves as a drinking water supply. The pollution caused by fossil fuels has a knock-on effect on marine life and the ecosystem, including humans and other species who are reliant on it. Fossil fuels, contributes heavily to water pollution. To put it another way, water pollution happens when harmful substances pollute an area of water (such as a river, lake, ocean, or aquifer), decreasing the water quality and posing a threat to human health or the environment. There are numerous ways for pollution to occur, oil spills are one major issue that nations around the world are continuously grappling with (History, 2018).

1.3 On the focus now

Countries throughout the world are working to reduce greenhouse gas emissions from fossil fuels to avert the worst impacts of global warming. Other entities including cities, governments, and oil companies have made their commitments as part of the 2015 Paris Agreement and committed to carbon reduction objectives. Most of these initiatives aim to increase energy efficiency by switching from fossil fuels to renewable energy sources (Nunez, 2019).

Biodiesel has been promoted as a potential replacement for existing petroleum-based fuels one of many obtained from the refining of crude oil. Aside from that, biodiesel is a renewable, biodegradable, and environmentally beneficial fuel. Plant biomass, which emits no greenhouse emissions, is a cost-effective feedstock for biofuels (Gimbun *et al*., 2013). The feasibility of first and second-generation biofuels, mostly derived from edible and non-edible crops, to meet targets for biofuel production, climate change mitigation, and economic growth is being vigorously discussed around the world.

II. Advantages of using Biodiesel

There are numerous advantages to using biodiesel, including the following:

1. Biodiesel is the world's most diverse fuel. Different types of fat and oil like Soybean oil, animal fats, and leftover cooking oil are all used in its production. Since biodiesel can repurpose fats and oils, it is an excellent advanced biofuel, cutting emissions by more than 50% when compared to petroleum-based fuels. It also encourages the development of novel feedstocks. Microalgae, for example, is a future feedstock that may help meet the world's energy needs (https://www.biodiesel.org/what-is-biodiesel, 2021).
2. Biodiesel reduces greenhouse gas emissions by an average of 80% compared to petroleum diesel, even when land-use consequences are considered. It has been established by government agencies and national laboratories that biodiesel reduces greenhouse gas emissions significantly across its whole lifecycle (https://www.biodiesel.org/what-is-biodiesel, 2021).
3. With ultra-low sulfur heating oil, biodiesel can be blended to form bioheat, a fuel for home heating. It is a simple decision that provides better fuel for the home and the environment. Bioheat is heating oil for the future, and it is currently sweeping the industry. Bioheat fuel blends range from B20 up to B100, with most businesses now offering blends from B20 on up (https://www.biodiesel.org/what-is-biodiesel, 2021).
4. It fits seamlessly with today’s diesel infrastructure. In other words, it fits in existing vehicles and technologies, biodiesel blends provide performance characteristics like conventional diesel, such as

fuel economy, horsepower, and torque. Depending on the fuel type and concentration, biodiesel may also provide the following extra performance advantages like longer engine life due to improved lubricity. Enhanced combustion because of increased Cetane numbers, emissions reductions when compared to petroleum-based alternatives (https://www.biodiesel.org/what-is-biodiesel, 2021).

In conclusion, biodiesel can be said to have the potential to provide some perceived advantages over the conventional diesel derived from fossil fuel including political, economic, and agricultural benefits, as well as environmental (due to its biodegradability, lower toxicity, and renewability) and health benefits (greenhouse gas-saving, less harmful exhaust emissions).

2.0 Biodiesel feedstocks

The first and second-generation biofuel sources are primarily food crops, making biofuel production unsustainable. The negative impact of first-generation biomass feedstock on global food prices has prompted researchers to investigate the usage of lignocellulosic biomass resources, also known as second-generation biomass feedstock. Crop residues, wood residues, and dedicated energy crops developed specifically for biofuel generation are examples of these feedstocks. Because they are not food crops and hence are not in competition with food, the second-generation biomass feedstock is gaining popularity around the world as a sustainable alternative to fossil fuels. However, the second-generation feedstock also competes with arable lands (Cherubini, 2010).

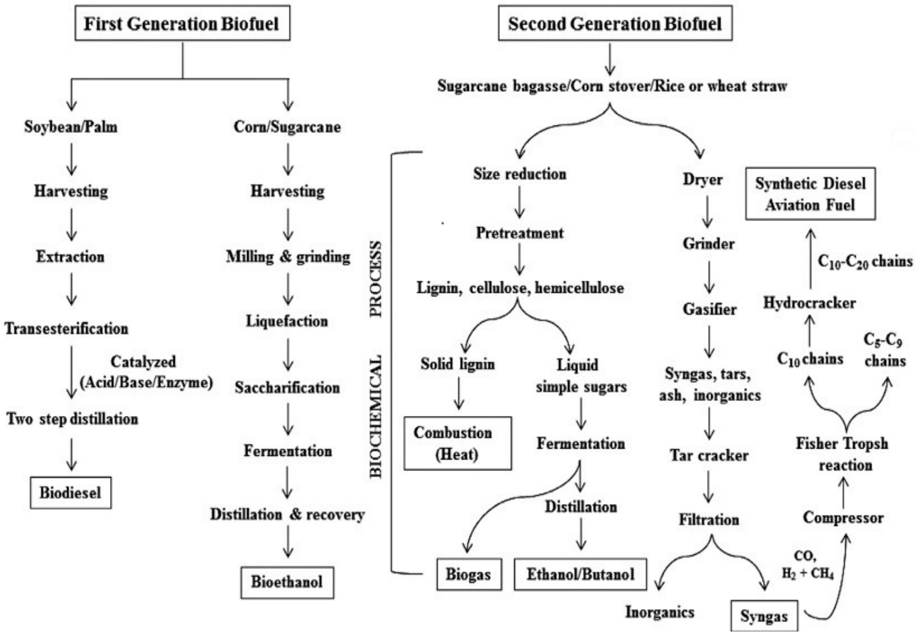

Figure 1: The first and second-generation biofuel sources are primarily (Dutta *et al.*, 2014)

Because of their high carbohydrate or lipid/oil content, a range of photosynthetic and fermentative bacteria and algae are currently being investigated as biocatalysts and feedstock for biofuel production. These microbial cells are classified as biomass feedstock of the third generation (Dutta et al., 2014). These microbial cells are more sustainable than first- and second-generation biofuel feedstock since they do not require arable agricultural lands or other farming inputs (such as fertilizers, pesticides, and water) for growing, and hence do not compete with food or at least minimize the competition.

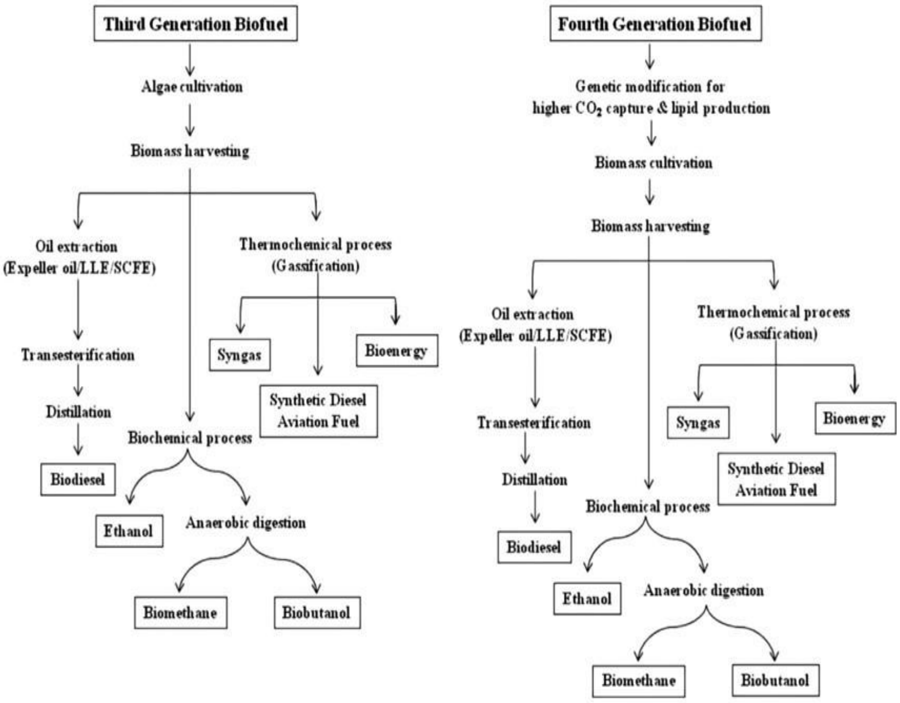

Figure 2: Third and Fourth Generation Biofuels (Dutta *et al.*, 2014)

2.1 Why microalgae for biodiesel production

In comparison to other accessible feedstocks, various research reports and articles outlined many advantages of employing microalgae for biodiesel synthesis (Li *et al.*, 2008). They are simple to cultivate, can grow with little or no attention, and use water that is unfit for human use. They are also easy to collect nutrients. They can also grow practically anywhere with just sunlight and a few simple nutrients, though growth rates can be boosted with the addition of nutrients and adequate aeration (Aslan *et al.*, 2006). Other benefits of employing microalgae include:

i. They have fast growth rates; for example, they can double in 24 hours (Rittmann, 2008).
ii. By modifying the composition of the growing medium, their lipid content could be altered (Naik *et al.*, 2006).
iii. They could be harvested multiple times per year (Schenk *et al.*, 2008).
iv. You might utilize salty or wastewater (Schenk *et al.*, 2008).
v. Microalgae use atmospheric carbon dioxide as a carbon source (Schenk *et al.*, 2008).
vi. Microalgae lipid biodiesel is non-toxic and very biodegradable (Schenk *et al.*, 2008).
vii. On an area basis, microalgae produce 15–300 times more oil for biodiesel production than conventional farming (Chisti, 2007).

2.2 Microalgae Oil Content and Biodiesel Yield

Some microalgae produce large amounts of lipids and can be driven to create even more lipids by altering their development circumstances, usually by depleting them of nitrogen or through genetic modification (Mata *et al.*, 2010).

Table 1 compares the oil content and biodiesel yield of various marine and freshwater microalgae species, revealing considerable variances among them.

Table 1: Oil Content and Biodiesel Yield of Some Different Microalgae Species

Marine and freshwater microalgae species	Lipid content (mg g^{-} dry weight)	Biodiesel yield (mg g^{-} dry weight)
Amphidinium sp.	189	141.0
Biddulphia sp.	249	109.0
Phaeodactylum tricornutum	217	187.5
Picochlorum sp.	305	274.8

Nannochloropsis oculata	410	267.1
Extubocellulus sp.	270	116.9
Scenedesmus dimorphus	-	84.3
Chlorella vulgaris	281	75.9
Chlorella sp.	279	93.2
Chlorella pyrenoidosa	212	74.3
Franceia sp.	-	79.7
Mesotaenium sp.	-	76.5
Ankistrodesmus falcatus	165	17.5
Ankistrodesmus fusiformis	207	27.3
Kirchneriella lunaris	173	30.5
Chlamydomonas sp.	151	14.1
Chlamydocapsa bacillus	135	19.2
Coelastrum microporum	206	49.1
Desmodesmus brasiliensis	180	37.0
Scenedesmus obliquus	167	4.4
Pseudokirchneriella subcapitata	284	36.7
Botryococcus braunii	455	58.9
Botryococcus terribilis	490	16.7

Source: Muhammad *et al.*, (2013); Nascimento *et al.*, (2013).

In summary and based on literature, using microalgae as biodiesel feedstocks has received unprecedentedly increasing interest, including but not restricted to microalgal strain selection and genetic engineering, mass cultivation for biomass production, lipid extraction and analysis, transesterification technologies, fuel properties, and engine tests. Considering all these and due to their unique characteristics, microalgae have been considered as the most promising feedstock of biodiesel that has the potential to displace fossil diesel without or at least with minimal competition between food and fuels.

2.3 Biodiesel Production Process

Biodiesel can be made from vegetable oils or animal fat in one of four ways. The four methods are direct use and blending, transesterification process, pyrolysis, and microemulsion. However, biodiesel is mostly produced through the transesterification reaction of vegetable oil or animal fats with an alcohol in the presence of a catalyst.

Catalyzed reactions can be divided into three categories: homogeneous catalysts, heterogeneous catalysts, and enzymatic catalysts. Biodiesel is commercially manufactured using a homogenous catalytic reaction using currently available technology, namely transesterification (Tan *et al.*, 2018). With the presence of a homogeneous catalyst, the reaction is considered quite quick and can reach high conversion in a short period. Despite this, it has significant flaws. Because the catalyst cannot be regenerated or recovered, it must be neutralized and removed immediately after the reaction is completed. During the purification step, this will result in a huge amount of wastewater (Wang *et al.*, 2018). Furthermore, separating homogenous catalysts from products is a difficult and time-consuming operation. As a result, additional equipment will be required, resulting in greater capital costs (Banković *et al.*, 2017).

Some potential technologies have suggested that using a heterogeneous catalyst in the transesterification process can help to alleviate the problems that homogeneous catalysts can cause. Natural-based heterogeneous catalysts are generally non-corrosive and non-polluting. It is significantly easier to separate the heterogeneous catalyst from the mixture than it is for homogeneous catalysts (Tan *et al.*, 2018). Furthermore, using heterogeneous-based catalysts in the transesterification reaction can improve the yield and purity of the biodiesel produced (Goli *et al.*, 2018).

Humans produce garbage regularly; for example, banana peels generate a substantial amount of waste, which has a physical and chemical influence on the environment. These environmental consequences will result in increased energy use, solid waste output, pollution, and greenhouse gas emissions. These wastes can be converted into usable materials or used as the starting material for heterogeneous K_2O/CaO-based catalyst production. Furthermore, waste reuse and recycling allow these wastes to be fully utilized, resulting in a reduction in waste disposal.

2.4 Biodiesel catalyst

Numerous technologies can be utilized to make biodiesel. For example, the transesterification of edible or non-edible oils with alcohols such as methanol, with or without the use of a catalyst. Catalysts are divided into two categories: homogeneous catalysts and heterogeneous catalysts. The majority of biodiesel is produced with the help of a homogeneous catalyst using current transesterification technology. However, there are several drawbacks to using a homogeneous catalyst in a chemical reaction, including difficulty in separating the biodiesel mixture and the production of a considerable amount of effluent (Fan *et al.*, 2016). As a result, scientists have improved existing technologies and are now able to handle connected challenges by using a heterogeneous catalyst in the biodiesel synthesis process. The heterogeneous catalyst can be made from a variety of materials, including biomass and non-biomass sources, such as building debris. Table 2 shows the advantages and disadvantages of homogeneous and heterogeneous catalysts.

Heterogeneous catalysts synthesized from biomass or non-biomass are now being researched actively due to their potential to reduce capital production costs. Biomass will be chemically converted into carbonaceous material by high-temperature treatment, and this carbon-based material, which contains the anticipated functional groups, can be used as a catalyst (Maneerung *et al.*, 2016). Furthermore, the calcium carbonate component in some biomass waste can be transformed into a calcium/potassium oxide-based catalyst for use in transesterification (Maneerung *et al.*, 2016).

Table 2: Comparison of homogeneous and heterogeneous catalyst based on advantages and disadvantages

Type of catalyst	**Advantages**	**Hitches**
Homogeneous base catalyst	a. There is no water formation in the transesterification process (Atadashi *et al.*, 2013) b. Alkaline catalytic (2 steps) transesterification reaction from waste vegetable oil is economical in producing biodiesel (Okwundu *et al.*, 2019) c. Sodium hydroxide (NaOH) and potassium hydroxide (KOH) are easily obtainable and economically feasible (Lam *et al.*, 2010) d. The reaction occurred at trivial reaction which reduces the usage of energy (Atadashi *et al.*, 2013) e. The rate of reaction is roughly 4000 times faster than the transesterification process using an acidic catalyst (Lam *et al.*, 2010).	a. There is an occurrence of saponification when the free fatty acids composition in the oil is more than 2 wt% which will decrease the biodiesel yield and cause difficulties in the purification process (Atadashi *et al.*, 2013) b. There will be more wastewater eliminated through the purification stage (Sagiroglu *et al.*, 2011) c. The catalyst can only be used once d. High sensitivity towards free fatty acids content (Lam *et al.*, 2010).
Heterogeneous base catalyst	f. The catalyst is reusable and recyclable (Okwundu *et al.*, 2019) g. The separation process from the product is easier (Okwundu *et al.*, 2019) h. The reaction rate is much faster than acid-catalyzed reaction (Lam *et al.*, 2010). i. The life span of the catalyst is long (Atadashi *et al.*, 2013) j. The reaction happened at mild reaction	e. The catalyst is poisonous during exposure to ambient air (Lam *et al.*, 2010). f. The basicity property causes the sensitivity towards the free fatty acids content to be high (Lam *et al.*, 2010). g. There is a limitation in diffusion (Leung *et al.*, 2010) h. The transesterification process will require more molar ratio of methanol to oil (Leung *et al.*, 2010)

which eventually minimizes the
energy utilization (Lam *et al.*, 2010).

2.5 Heterogeneous catalyst from biomass

Agricultural waste has gotten a lot of attention lately, because of its remarkable merits resulting from its abundant sources and inexpensive cost. Eggshells, duck shells, rice, banana peels, husks, and other environmentally friendly heterogeneous catalysts from agricultural waste have been used to produce biodiesel (Nasrollahzadeh *et al.*,2017), (Xiulian *et al.*, 2016), (Roschat *et al.*, 2017). Notably, bananas were the most consumed tropical fruit, and their by-product (banana peel) was widely used; the use of banana peel was gaining popularity (Matharu *et al*., 2016). The banana peel was successfully employed as a substrate for the manufacture of extracellular laccase by Osma *et al*. Banana peel was also used by M. Lopez-Garcia et al. (López-García *et al.*, 2013) to chelate Cr (VI) from an aqueous solution.

Calcium or potassium oxide has been identified as the most reliable heterogeneous basic catalyst in biodiesel synthesis in various studies (Teo *et al.*, 2017). Calcium or potassium oxide can be found in a variety of agricultural wastes, like banana peels, eggshells. This can be utilized as a heterogeneous catalyst in the manufacture of biodiesel from several types of oil feedstocks and alcohol (Marwan *et al.*, 2016).

Miscellaneous catalysts, including both heterogeneous and homogeneous catalysts, were utilized to obtain high catalytic activity to effectively use biodiesel (Rui *et al.*, 2015). Unfortunately, a strong base (NaOH, KOH, $NaOCH_3$) and strong acid (such as sulfuric acid, p-toluenesulfonic acid, etc.) were utilized as catalysts in the classic transesterification reaction to make biodiesel. In addition, several efforts have been made to develop new low-cost and effective catalysts to enhance biodiesel production. Cao, K_2O, hydrotalcite, basic ion exchange resin, and other heterogeneous solid catalysts are beneficial for biodiesel synthesis because of their reusability, which makes them more environmentally friendly, and they also make product separation easier (Lee *et al.*, 2015).

The most explored basic materials as solid catalysts for transesterification processes are listed in Table 3.

Table 3: Basic Solid Catalyst Used in Biodiesel Production

Catalyst	Feedstock	Temp.	Time	Methanol/Oil	Catalyst Amount	Biodiesel Yield	Reference
CaO from eggshells	Palm oil	65°C	2 h	12:1	1.5 wt%	98%	Cho *et al*; 2010
CaO	Sunflower oil	80°C	5.5 h	6:1	1 wt%	91%	Verziu *et al*; 2011
KNO_3 /CaO	Rapeseed oil	65°C	3 h	6:1	1 wt%	98%	Martínez *et al.*, 2010
CaO/Al_2O_3	Palm oil	64.29°C	5 h	12.14:1	5.97 wt%	98.64%	Zabeti et al., 2010
CaO/Fe_3O_4	Jatropha curcas oil	70°C	1.3 h	15:1	2 wt%	95%	Encinar *et al.*, 2010
Li/MgO	Soybean oil	60°C	2 h	12:1	9 wt%	93.9%	Wen *et al.*, 2010
KOH/MgO	Mutton fat	65°C	0.3 h	22:1	4 wt%	98%	Mutreja *et al.*, 2011
Dolomite	Palm kernel oil	60°C	3 h	30:1	6 wt%	98%	Ngamcharussrivichai *et al.*, 2010
Dolomite	Canola oil	67.5°C	3 h	6:1	3 wt%	91.78%	Ilgen, 2011
CaMgO and CaZnO	Jatropha curcas oil	65°C	6 h	15:1	4 wt%	80%	Taufiq-Yap *et al.*, 2011
KF/Ca-Al hydrotalcite	Palm oil	65°C	5 h	12:1	5 wt%	97.98%	Gao *et al.*, 2010
Mg-Al hydrotalcite	Soybean oil	230°C	1 h	13:5	5 wt%	90%	Silva *et al.*, 2010
Mg-Al hydrotalcite	Jatropha oil	45°C	1.5 h	4:1	1 wt%	95.2%	Deng *et al.*, 2011
CaO/mesoporous silica	Soybean oil	60°C	8 h	16:1	5 wt%	95.2%	Samart *et al.*, 2010
Sodium silicate	Soybean oil	60°C	1 h	7.5:1	3 wt%	100%	Guo *et al.*, 2010

III. BIODIESEL PRODUCTION AND OPTIMIZATION FROM MICROALGAE USING HETEROGENEOUS CATALYST.

In terms of conversion efficiency, reaction parameters, energy consumption, and reusability, Guldhe *et al*. (2017) compared tungstated zirconia (WO_3/ZrO_2) as a heterogeneous acid catalyst to sulphuric acid as a homogeneous chemical catalyst and immobilized *Pseudomonas fluorescence* lipase as an enzyme catalyst for the conversion of *S. obliquus* lipids a specie from the algae family. Tungstated zirconia catalyst achieved maximum biodiesel conversion of 94.58% at $100^{O}C$ temperature, 12:1 methanol to oil molar ratio, and 15% catalyst quantity based on oil weight in 3 h, according to their findings. Tungstated zirconia processed biodiesel at a similar rate as a homogeneous catalyst and a higher rate than an enzyme catalyst. According to their findings, the time required for heterogeneous catalysts was the shortest, however, the energy consumption was the highest of the catalysts tested. The physicochemical characteristics of biodiesel produced by tungstated zirconia catalyzed conversion of *S. obliquus* lipids met ASTM and EN specifications. The reaction conditions for heterogeneous acid-catalyzed conversion were optimized using three-level three factorial Box-Behnken response surface methodology (RSM) experimental design of Minitab statistical software (Guldhe *et al*., 2017).

From the research of Arul *et al.*, (2019) using methanol as an acyl acceptor, they used a nanocomposite consisting of Mn-ZnO capped with Polyethylene Glycol (PEG) as a heterogeneous catalyst for the transesterification of oil derived from *Nannochloropsis oculata* a marine eukaryotic unicellular phytoplankton into biodiesel. Sonication and a biphasic solvent technique were used to extract lipids from microalgae. By using the Response Surface Method, the process parameters for heterogeneous catalysis of *N. oculata* to biodiesel were improved and determined to be an oil to methanol molar ratio of 1:15, catalyst loading of 3.5 wt.%, and reaction temperature of 60°C for 4 h.

The yield of biodiesel obtained from *N. oculata* species using Mn-ZnO nanocomposite capped with PEG was 87.5% (Vinoth Arul Raj *et al*., 2019).

Due to the increased interest in transesterification, Azcan *et al.*, (2013) studied the reaction activity utilizing a heterogeneous base catalyst, KOH/Al_2O_3. Time, oil to methanol molar ratio, and catalyst amount were increased to 35 min, 1:12, and 3wt.%, respectively, due to the slow reaction rate of heterogeneously catalyzed reactions. At these temperatures, biodiesel conversion was determined to be 97.79%.

Akubude *et al*., (2019) reviewed the challenges involved in microalgae production, as well as the economic applications of microalgae, such as fuel production, food supplement extraction, and CO_2 capture for biorefineries that produce bio-methane, biohydrogen, bioethanol, and other byproducts. The use of nanocatalysis in biodiesel production was also examined, with comparative issues in different types of catalysts such as homogeneous, heterogeneous, and enzymatic catalysts being discussed.

Galadima *et al.* (2015) gave an overview of the transesterification reaction employing heterogeneous catalysts made of oxides, zeolites, and their derivatives. Solid acid and solid base catalysts are possibly cheaper and may be recovered, regenerated, and reused after the transesterification process, according to their findings. If properly built, they showed extremely little sensitivity to free fatty acids in the feed and so create high purity biodiesel with qualities that meet international requirements. They did, however, recommended that the actual reaction mechanisms and methods for optimizing triglyceride esters conversion with several of these catalysts be thoroughly explored.

Çakırca *et al*., (2018) examined the influence of reaction time, methanol to oil ratio, and catalyst amount on biodiesel yield using dolomite as an affordable and environmentally friendly catalyst, and found high catalytic activity compared to typical homogeneous catalysts in biodiesel production. 90% of microalgae oil was converted to biodiesel utilizing these materials. These findings suggest that at mild reaction conditions, high-efficiency biodiesel synthesis can be maintained using cleaner and less expensive raw materials.

Niharika *et al.* (2016) used an acid-catalyzed transesterification technique to make biodiesel from microalgae. They compared the biodiesel's characteristics to those of fossil diesel. Biodiesel produced from microalgae was shown to be the best resource for future generations base on the minimal competition between food and fuels.

In the biodiesel synthesis from Spirulina oil, a filamentous cyanobacterium, a mixed metal oxide (barium–calcium–zinc) was utilized as a heterogeneous catalyst on Spirulina platensis, optimization research was conducted on numerous reaction parameters such as temperature, duration, molar ratio, and catalyst weight. At optimal conditions of 2.5wt% catalyst, 1:18 molar ratio (methanol/oil), and 65°C temperature for 120 min, the highest fatty acid methyl esters conversion was found to be 98.94% (Singh *et al.*, 2019).

Hindarso, (2018) investigated a mathematical model that described the kinetics of microalgae oil transesterification utilizing CaO as a heterogeneous catalyst. Three sequential forward and reverse first-order and second-order transesterification reactions were assumed to occur in the model. The 3% catalyst had a better yield than the 1 wt.% catalyst, while the molar ratio of microalgae oil to methanol remained steady at 1:6. The best reaction conditions were achieved with a reaction time of 5 min, microwave power of 400 W, and a CaO catalyst concentration of 3 wt.%, yielding a maximum biodiesel yield of 93.23%.

To circumvent the drawbacks of homogeneous catalysts currently utilized in industrial facilities, (Carrero et al., 2011) evaluated the potential of microalga lipids as a feedstock in biodiesel production employing hierarchical zeolites as heterogeneous catalysts. Because it provided a secondary porosity in the range of micro-mesopores while keeping the acid characteristics of the Beta zeolite, hierarchical Beta zeolite demonstrated substantial activity in the microalga oil reaction with methanol. According to their findings, biodiesel yield increased as the temperature rose from 85^{O}C to 115^{O}C Carrero *et al*., (2011).

Deka & Basumatary, 2011 developed a novel catalyst from the trunk of *Musa balbisiana Colla* (a banana plant type), which they used to convert Thevetia peruviana seed oil to biodiesel. They converted 96% of the oil to biodiesel using a 20 wt.% catalyst and a 3 h reaction time at 32^{o}C. The catalyst can be made from the waste of banana plants that have been harvested and functions as a heterogeneous catalyst. It was discovered that the catalyst efficiency decreased with each recycling (Deka & Basumatary, 2011).

Boro *et al*., (2011) synthesized a solid oxide catalyst from Turbonilla striatula waste shells and used it as a renewable heterogeneous catalyst for the conversion of mustard oil to biodiesel. During the preparation of the catalyst from the shells, the calcination temperature ranged from 600 to 900 C for 4 h, and solid CaO formed at 800^{o}C. The transesterification of mustard oil using a 3 wt% catalyst and a 9:1 methanol to oil ratio for 6 h reaction time at 65^{o}C temperature yielded 93.3% biodiesel.

Wei *et al*., (2009) developed a cost-effective solid catalyst from waste eggshells. They calcined the catalyst at 1000^{o}C and used it to make biodiesel from soybean oil, with good catalytic results. The transesterification of soybean oil was carried out at 65°C for 3 h using a 9:1 methanol to oil molar ratio, 3 wt% catalysts. During the transesterification process, more than 95% biodiesel was produced. The eggshell catalyst was applied repeatedly and showed no appreciable loss of catalytic activity until cycle 13.

Fan *et al*., (2019) synthesized an economical, effective, and well dispersed K_2O-KCl alkaline catalyst from banana peel and used it for the transesterification of soybean oil into biodiesel. The synthesized catalyst from banana peel showed excellent catalytic activity under the optimized conditions of 1.5 wt% catalyst amount, 15:1 methanol to soybean oil, 1 h. reaction time at 65^{o}C, and resulted in a 95.1% biodiesel yield. Also, from the characterization of the calcined banana peel using XRD, K_2O and KCl are the main active catalysts.

IV. SUMMARY

Several investigations on heterogeneous catalysts were carried out based on the review, to find solutions to the issues associated with the use of homogeneous catalysts to synthesize biodiesel. As a result, many heterogeneous catalysts derived from agricultural waste have been investigated, with many of them demonstrating strong catalytic activity.

Microalgae have sparked a lot of interest as a contemporary research topic for biodiesel production since they have the potential to generate enough fuel to meet world demand *(*Banerjee *et al*., 2019). Furthermore, because of their high oil content, rapid growth rate, ability to grow even in saline water, the potentiality of microalgae to minimize competition for land used for other traditional crops, as well as food and fuel issues, Through CO_2 bio fixation, they can reduce greenhouse gas emissions.

V. CONCLUSION

This paper provides a detailed assessment of prior research on the production of biodiesel from second and third-generation biodiesel feedstocks using various heterogeneous catalysts obtained from agricultural waste. A concerted effort has been made to include all the significant contributions while also highlighting the most relevant literature for researching biodiesel feedstocks. The following are the findings of the current literature review.

1. Biodiesel is a viable alternative transportation fuel with qualities such as renewability, biodegradability, nontoxicity, and environmental benefits.
2. Biodiesel can be made from a variety of fatty acid-containing feedstocks, including animal fats, edible oils, non-edible oils, waste cooking oils, etc.
3. Microalgae can be considered as an ideal feedstock for biodiesel production because of their high oil content, rapid growth rate, ability to grow even in saline water, the potentiality to minimize competition for land used for other traditional crops, as well as food and fuel issues, Through CO_2 bio fixation, they can reduce greenhouse gas emissions.
4. Biodiesel can be made in several ways. Transesterification, on the other hand, is the most prevalent process for producing it. The goal of this method is to use an acid or base catalyst in the presence of alcohol to lower the viscosity of oil or fat.
5. During the transesterification of various oils for biodiesel synthesis, heterogeneous catalysts proved to be effective. Furthermore, heterogeneous catalysts may provide a solution to the problems associated with the use of homogeneous catalysts in the production of biodiesel.

6. The molar ratio of alcohol, reaction temperature, reaction time, mixing intensity, presence of water, and catalyst concentration all have a significant impact on biodiesel production.

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