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Exploring the Role of Different Types of Catalysts to Enhancing Biodiesel Production from Waste Cooking Oil – A Review

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Abstract: *Biodiesel from waste cooking oil (WCO) is an eco-friendly and cost-effective alternative to fossil fuels. This review focuses on catalytic reactions in biodiesel production, especially transesterification using various homogeneous and heterogeneous catalysts. The growing demand for sustainable energy, particularly in Asia, has increased interest in biodiesel. Transesterification converting triglycerides into fatty acid alkyl esters (biodiesel) using acid or base catalysts is the most common method. Sodium hydroxide (NaOH) and potassium hydroxide (KOH) are widely used but generate waste and require specific feedstock. Heterogeneous catalysts are preferred for their reusability and ability to process feedstock with high free fatty acid (FFA) content. Waste cooking oil is highlighted as a low-cost, sustainable feedstock that supports India's biodiesel blending goals. Despite its benefits, biodiesel production still faces challenges like catalyst selection, feedstock variability, and costs. This paper reviews recent catalytic advances and explores future directions for improving efficiency and sustainability.*

Key Words: *Waste cooking oil (WCO); Biodiesel; Transesterification; homogeneous catalysis; heterogeneous catalysts.*

1. INTRODUCTION:

Biodiesel, an alternative to fossil fuels is Composed from renewable Organic Matters like vegetable oil & animal fats. It is Biodegradable, Environmentally Friendly, Nontoxic, has low emissions [1]. According to the report of International Energy Agency, In Asia Energy need will raise by 76% by 2030 [2]. There are four Methods use for Conversion of Oil & Fats in Biodiesel such as Blending, Micro emulsions, Pyrolysis & Transesterification. Among all these methods Transesterification is widely accepted because it lowers the viscosity of oil [3]. India's transport sector uses about 132 MKL of diesel, contributing 6.7% to GDP, while 81% of crude is imported. The government's 5% biodiesel blending goal could save ₹10,000 crore by using waste cooking oil as a viable feedstock [4]. Waste cooking oil (WCO) is more affordable and accessible than edible oils, making it a preferred feedstock for many biodiesel producers. The Ukraine-Russia conflict has further raised biodiesel costs due to raw material scarcity and price hikes [5].

Biodiesel can assist in decrease reliance on fossil fuels, together with alternative energy sources including solar, wind, hydroelectric, and nuclear power [6-8]. Transesterification can be done using homogeneous or heterogeneous catalysts. However, conventional homogeneous catalysts have limitations like feedstock sensitivity, soap formation, and poor recovery, leading to lower yields and higher costs [9]. This review explores various catalysts for biodiesel production from WCO, their process and concentration, reaction mechanisms, recent advancements, and key production challenges.

2. LITERATURE REVIEW:

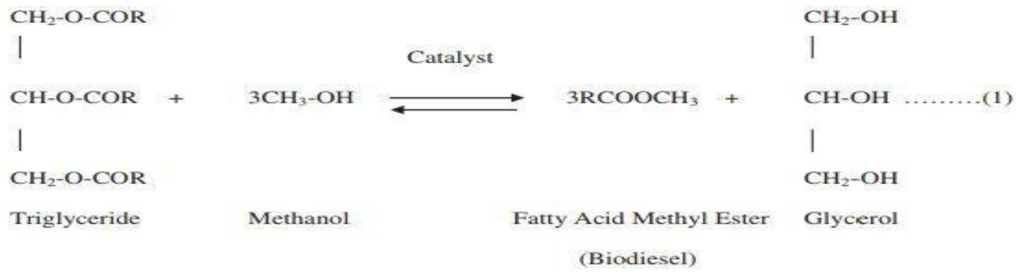
2.1 Waste cooking oil

For Biodiesel production appropriate alternative can be a Waste Cooking Oil (WCO) which is the Oil that left after the deep frying process.A published report says that around 1.65 crore tons of WCO are produced annually [10]. In India Biodiesel is Made using oil extracted from non- edible Feed stock because of the shortage and high importation of edible oil [11]. There is a Difference between Characteristics of WCO and Fresh oil due to the chemical reactions that happens during frying. In terms of density, acid value, iodine value and kinematic viscosity, WCO have equal quantities to make

Biodiesel and complete the quality need [12]. An Online food delivery business (Zomato) in India started the collection of WCO from restaurants.The Indian Government set a goal of collection of about 5MT of WCO per year for 5% biodiesel blending with diesel fuel by 2030. To meet this target Zomato is working on this government criterion [13]. Compare to Vegetable oil, the price of WCO is two to three times more affordable and it also decreases the expense of waste product removal and treatment [14].

2.2 Transesterification

Transesterification or Alcoholysis is the traditional process for Production of Biodiesel, in which the Triglycerides are reacted with alcohols (typically methanol), to generate fatty acid alkyl esters [typically fatty acid methyl esters (FAME)] in the presence of a catalyst, either homogeneous or heterogeneous, which is acting as a reaction promoter [15]. The transesterification Reaction is a method of transforming oils and fatty acids into alkyl esters, commonly Known as biodiesel. In the process of Transesterification alcohol (methanol or ethanol) and triglycerides interact with each other to produce methyl or ethyl ester of fatty acids and glycerol. Methanol is more affordable than ethanol for this reason many countries make alkyl ester as methyl ester [16].



Transesterification Reaction Eq (1) [17]

The reaction, as represented in Eq. (1), is reversible, so excess alcohol is employed to drive the equilibrium toward the product side. The surplus alcohol enhances the transesterification process and removes products from the catalyst surface, thereby regenerating the catalytic sites [18]. Transesterification process requires acidic catalysts (sulfuric acid, hydrochloric acid) or basic catalyst (sodium hydroxide, potassium hydroxide), because Non Catalytic Transesterification Reaction is too delayed and Not energy-efficient. As alcohol dissolves only slightly in oil, the catalyst boosts its solubility, consequently accelerating the reaction [19].

2.3 Catalyst

Biodiesel synthesis through transesterification can be facilitated using alkali, acid, or enzyme catalysts.When compared with enzyme catalyzed process acid and alkali Transesterification processes demand shorter reaction time and inexpensive [20-21]. KOH is Homogenous Catalyst having a advantage of low cost, easy availability, and high catalytic efficiency[22].

Calcium oxide is one of the best researched heterogeneous catalysts as it has higher basicity, lower price, lower solubility, is non-corrosive, inexpensive, lower solubility, non corrosive, eco-friendly lower solubility and More accessible than homogeneous catalysts [23].

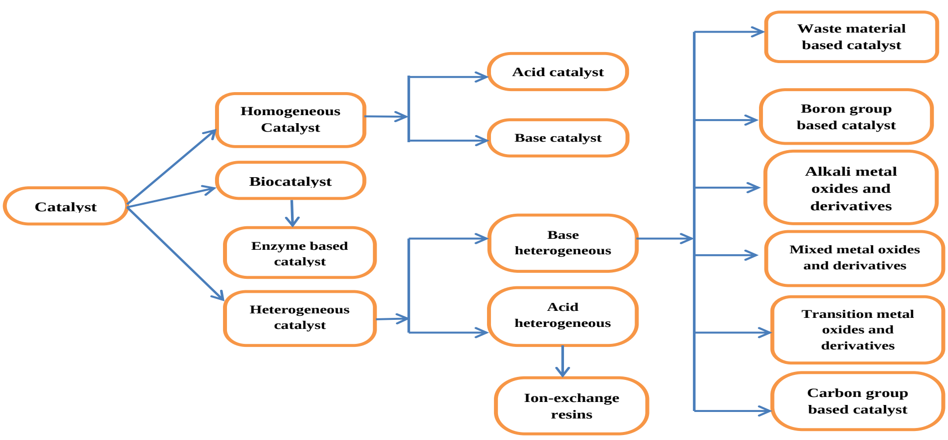


Figure 1. Classification of Different Types of Catalysts. [24]

2.3.1 Homogenous Catalyst

Homogeneous catalysts exhibit superior activity in transesterifying fats to biodiesel, leading to high production and high reaction rates [25]. Traditionally, Biodiesel Produced from different types of Oil with application of Homogeneous catalysts. Homogenous Catalyst is easy-to-use and Biodiesel yield is achieved in less time so it is widely used Catalyst for industrial Biodiesel Production.Homogeneous catalysts, which are typically in liquid or gaseous form, and reactants exist in the same phase [26,27]. These catalysts are categorized into two types: acidic catalysts and alkaline catalysts [28]. Most commonly used Homogeneous catalysts for Biodiesel Production are Sodium hydroxide (NaOH) or potassium hydroxide (KOH). despite this some researchers suggest that only Low FFA content feedstocks is appropriate for homogeneous base catalysts. If the FFA content exceeds 6 wt%, the base catalyst method becomes inappropriate for biodiesel production. Therefore, some researchers suggest that the FFA content should be below 2 wt% [29-32].

2.3.1(a) Homogenous acid catalyst

Acidic Homogeneous catalysts examples are phosphoric acid, hydrochloric acid, sulfuric acid or organic sulfuric acid [33,34] as compared to alkaline homogeneous catalysts. This acid catalyst needs more time and higher temperature to complete the conversion. The liquid acid-catalyzed Transesterification method is not as widely used in commercial applications as its base-catalyzed counterpart. Compared to base Catalyst, the acid-catalyzed reaction is approximately 4000 times slower [35].

Daniyan et al [36] performed Conversion of frying oil through Transesterification considering that Free Fatty Acid (FFA) presence in the frying oil has not influenced by the Catalytic activity of utilized acid catalyst like hydrochloric acid. For the removal of trapped water molecules The frying oil has been first preheated to gain temperature 120°C and then enabled to cool down at 60°C. Hydrochloric acid mixed with the Methanol at a concentration of 0.8 to 1.8% of the weight of oil, after that the mixture has been carefully poured into the frying oil in the molar ratio of 8:1 and stirred at 200 rpm for 8 hours. After that the mixture was subsequently poured into a separating funnel and left to settle for 24 hours, after which the lighter biodiesel at the top layer was collected.

2.3.1(b) Homogeneous Base Catalysts

Homogeneous base catalysts are generally used for triglyceride transesterification. Potassium methoxide, sodium methoxide, carbonates, sodium hydroxide, and barium hydroxide are the some examples of Metal based oxide [37]. High conversion percentage, faster reaction rate and moderate reaction conditions can be achieved, When Transesterification Reaction done using alkaline Catalysts including sodium and potassium hydroxide (NaOH and KOH, respectively[38]. however drawbacks are non reuse of Catalysts and seperation and purification of products is still exist [39]. Fadhil and Ali [40] investigated on same topic where Catalyst used for reaction is KOH for trans-esterification of Heckel fish oil, and 97% of biodiesel yield was recorded at 32 °C reaction temperature, 60 min reaction time, 6:1 methanol to oil ratio and 5.5 wt% catalyst loading. Still some problems delay the biodiesel yield like formation of soap, impurities present in low-grade feedstocks and other unwanted emulsions as a result of presence of FFA content (> 1%).

2.3.2 Heterogeneous Catalysts

Borges and Díaz [41] performed experiment using potassium-loaded pumice material (K-Pumice) as the heterogeneous catalyst in the sunflower oil and waste oil transesterification reaction for biodiesel production, using a packed-bed catalytic reactor in a recirculation system. Navajas et al.[42] suggested the expend of alumina (Al_2O_3) as a catalyst support Effectively support the active elements and improve the surface characteristics of the resulting catalyst, Consequently preventing diffusion constraints during the reaction [43].

2.3.2(a) Heterogeneous Solid acid catalysts

Solid acid Heterogeneous Catalyst are powerful for biodiesel Production from lipids with high FFA content [44]. Transesterification method of Zanthoxylum bungeanum seed oil using Sulphuric acid Catalyst along with methanol improved >94% in 12h [45].Transesterification method of Zanthoxylum bungeanum seed oil using Tin tetrachloride ($SnCl_4$) along with methanol achieved > 96% in ideal reaction conditions [46].

2.3.2(b) Heterogeneous Base Catalyst

Alkaline earth metal oxides, mixed metal oxides and supported alkali metal are most common studied heterogeneous base catalyst employed in the biodiesel production. [47]. CaO is Solid Base catalyst, and it is praising because it is Environmental friendly material which boosts longer catalyst life, high activity and optimal reaction conditions [48]. Liu et al.[49] reviewed the transesterification of oil using CaO as a Heterogeneous catalyst and Accomplished 95% conversion of the oil to the ester utilizing a methanol to oil molar ratio of 12:01, CaO content is 8% in relation to the oil mass and a 3 hour reaction time. Viola et al.[50] performed the same reaction and reached 93% of conversion with 80 min of reaction time using CaO as the catalyst at a reaction temperature of 65 C using 5% of catalyst in relation to oil (m/m). The authors used a methanol to oil molar ratio of the 6:1.

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2.3.3.Enzyme Catalyst

Over the past few years, Enzyme Catalyst have gain attention in the debate of Biodiesel production. The employment of enzymatic biocatalysts in biodiesel production is a unique approach in contrast to traditional chemical processes. Enzymatic transesterification aligns with the principles of green chemistry, By reducing waste generation during biodiesel production, helping to minimize environmental impacts[51]. Lipases (triacylglycerol acylhydrolases, EC 3.1.1.3) are widespread enzymes present in animals, plants, fungi, and bacteria. They catalyze the hydrolysis of triglycerides into free fatty acids (FFA) and glycerol at the water–lipid interface. In addition to hydrolysis, lipases can catalyze esterification, interesterification, alcoholysis, acidolysis, and aminolysis reactions [52].

Table 1. Different types of Homogeneous Acid Catalyst used for Biodiesel Production.

Catalyst	Oil	Molar Ratio	Catalyst Dosage (wt%)	Reaction Temperature (°C)	Reaction Time	yield %	References
H_2SO_4	WCO Esterification	12:1	5%wt;	60 ◦C	3 h	95.4	[53]
Orthophosp -horic acid H_3PO_4	Calophyllum inophyllum L.	9:1	0.8%wt;	60 ◦C	1.25 h	97.14	[54]
HCl	Waste Coconut Oil Esterification	10:1	3%wt;	80 ◦C	1 h	90.45	[55]
$C_2HF_3O_2$	Soybean oil	20:1	2 M	120 ◦C	5 h	98.4	[56]

Table 2. Different types of Homogeneous Base Catalyst used for Biodiesel Production

Catalyst Type	Oil	Molar Ratio	Catalyst Dosage (wt%)	Reaction Temperature (°C)	Reaction Time	yield %	References
CH_3ONa	WCO	9:1	0.75%wt	65 ◦C	0.13 h	97.10%	[57]
NaOH	WCO	9.4:1	5%wt	62.4 ◦C	0.017 h	99.70%	[58]
KOH	WCO	6:1	1.2wt%	65 ◦C	1 h	93.20%	[59]
Sodium methoxide ($NaOCH_3$)	Sesamum indicum L. seed oil,	6:1	0.75%wt	50◦C	0.5 h	87.80%	[60]

Tables 1 and Table 2, represent the different Acid and Base homogeneous catalysts with their Optimal reaction conditions, different feedstock oil and Their respective Yield. By comparing Both Acid and Base Homogeneous Catalyst, it shows that Homogeneous basic catalyst enables the production of biodiesel at moderate temperatures (∼60 ◦C). The methanol:oil ratio (M:O) is also to be decreased under basic catalysis. The Homogeneous Base Catalysts give Higher yield in Lower Reaction time. It is not only cost-effective but also provide several significant advantages, including being cost-effective and requiring low-energy consumption. These benefits contribute to a substantial reduction in operational costs and environmental impact.

Table 3. Different types of Heterogeneous Acid Catalyst used for Biodiesel Production

Catalyst Type	Oil	Molar Ratio	Catalyst Dosage (wt%)	Reaction Temperature (°C)	Reaction time	yield %	References
Sulfated zirconia	Neem oil,	9:1	1%wt	65◦C	2 h	95%	[61]
Carbon-based solid acid catalyst	Waste vegetable oil,	16.8:1	0.25%wt	220◦C	4.5 h	94.80%	[62]
RS-SO_3H	WCO	18:1	5%wt	70 ◦C	1 h	90.38%	[63]

$MgFx(OH)_2-x$	WCO	6:1	5%wt	150 ◦C	5 h	75.29%	[64]
$C-SO_3H$	Oleic acid	21:1	8%wt	80 ◦C	1 h	96.77%	[65]

Table 4. Different types of Heterogeneous Base Catalyst used for Biodiesel Production

Catalyst Type	Oil	Molar Ratio	Catalyst Dosage (wt%)	Reaction Temperature (°C)	Reaction Time	yield %	References
CaO	WCO	9:1	2%wt	80 ◦C	0.17 h	98.70%	[66]
MgO	WCO	24:1	2%wt	65 ◦C	1 h	93.30%	[67]
SrO	WCO	9:1	3%wt	65 ◦C	0.07 h	93%	[68]
KOH /limestone	WCO	12.26:1	5.36%wt	65 ◦C	0.97 h	97.15%	[69]

Tables 3 and Table 4, Demonstrate the different Acid and Base heterogeneous catalysts with their Optimal reaction conditions, different feedstock oil and Their respective Yield. By comparing Both Acid and Base Heterogeneous Catalyst, it shows that Heterogeneous basic catalyst enables the production of biodiesel at moderate temperatures (∼65 ◦C).The Homogeneous Base Catalysts give Higher yield in Lower Reaction time. The methanol:oil ratio (M:O) is also to be approximately same in basic catalysis and Reaction time is Low when Feedstock is WCO is used.

Table 5. Different types of Enzyme Catalyst used for Biodiesel Production

Catalyst Type	Oil	Molar Ratio	Catalyst Dosage (wt%)	Reaction Temperature (°C)	Reaction time	yield %	References
Immobilized lipase on crystalline PVA	Soybean oil	6:1	4%wt	37°C	72 min	66.30%	[70]
Lipase	WCO	4:1	-	52.1°C	-	83.31%	[71]
Pseudonomas cepacia	Jatropha	4:1	5%wt	8 ◦C	0.97 h	1.0%	[72]
Candida sp. Lipase	WCO	-	1%wt	40 ◦C	12 h	80%	[73]

3. Research gap and future perspective

More research is required in the field for discovering optimizing catalyst that can improve the transesterification process, making it more efficient and scalable for industrial applications. There is lack of detailed exploration into specifically genetic modification that can significantly improve oil yields and reduce Free Fatty Acid (FFA) content in oil. The long-term environmental impacts on large-scale biodiesel production using these methods are not fully addressed. Also there is lack of research on how to scale-up the described technologies from laboratory settings to commercial scale biodiesel production.

4. Conclusion

Among methods like blending, pyrolysis, and thermal cracking, transesterification is the most effective for biodiesel production. Waste cooking oil (WCO) is an ideal feedstock due to its low cost, reduced emissions, lower carbon footprint, and minimized waste disposal issues. Catalysts used in biodiesel production are mainly chemical (acid/base) or biological (enzymes). Homogeneous base catalysts like NaOH and KOH offer high yields at moderate temperatures, making them energy-efficient. In contrast, acid catalysts require higher temperatures and longer reaction times. Heterogeneous base catalysts (e.g., CaO, MgO, SrO) are also effective, offering fast reactions with low catalyst doses and easier recovery. Enzyme-based catalysts work under mild conditions and prevent soap formation but are costly and non-reusable. Overall, base catalysts—both homogeneous and heterogeneous—are preferred for efficient, high-yield biodiesel production.

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