

# Optimization of Sustainable Empty Fruit Bunches as Heterogeneous Catalysts in Biodiesel Production: A Study of Modifications and Performance

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## Abstract

The growing demand for renewable energy has increased the need for sustainable catalysts. These catalysts are crucial in biodiesel production as they enhance reaction rates and selectivity, thereby improving efficiency and reducing costs. Empty Fruit Bunches (EFB), a form of solid waste from the palm oil industry, are underutilized despite their potential as a valuable resource. This review explores the potential of EFB as a heterogeneous catalyst for biodiesel production. It leverages the high potassium content of EFB as a promising source of  $K_2O$ . Processing EFB at low combustion temperatures is essential to preserve potassium. This preservation enhances the catalytic performance. Various modifications have been investigated to further improve EFB's effectiveness. These include acid and base-impregnated catalysts, magnetic catalysts, and nano-catalysts. Biodiesel production using EFB catalysts has achieved a conversion rate of 99%. This demonstrates significant potential in supporting the circular bioeconomy. This approach not only transforms agricultural waste into valuable catalysts but also reduces environmental impact and adds economic value. However, challenges such as optimizing processing conditions, scaling up production, and ensuring consistent catalyst quality remain. Further research into more efficient and cost-effective processing methods is crucial for advancing the use of EFB catalysts in industrial applications.

**Keywords:** EFB, Catalyst, Biodiesel, Modification

## 1. Introduction

Energy is a key driver of economic growth and production activities worldwide, making the sustainability of the global economy highly dependent on the stability of energy supplies (Kopetz, 2013; S. Wang *et al.*, 2023). As population growth accelerates, energy demand continues to rise, placing increased pressure on global energy resources (Wackernagel *et al.*, 2021; Ahmad *et al.*, 2023). Currently, most energy needs are still met by fossil fuels, despite the fact that their combustion emits harmful pollutants and contributes to environmental degradation (Khan *et al.*, 2023). Carbon dioxide emissions resulting from fossil fuel use continue to rise and are identified as a major contributor to global warming (Rahman *et al.*, 2024). In 2020, global carbon dioxide emissions reached 30.6 gigatons (Gt) and are projected to increase by 50% by 2030 (International Energy Agency, 2021). Given the profound impact of fossil fuel use, the shift toward renewable energy and the development of sustainable energy resources is now a necessity.

Biomass is one of the renewable alternative energy sources with great potential for development (Reddy *et al.*, 2023). It serves as an alternative energy source due to its organic material content, allowing for its use as a sustainable energy resource (Ahmad *et al.*, 2023). Biomass can be processed into various types of fuels, such as bioethanol and biomethane (Garg, Sabouni and Ahmadipour, 2023). The utilization of biomass releases fewer harmful gases and can even help control emissions (Moreira *et al.*, 2023). Fuels derived from biomass present a more environmentally friendly alternative to fossil fuels (Awosusi *et al.*, 2022). Moreover, fuels from vegetable oils, such as biodiesel, are renewable and environmentally friendly; the abundant availability of raw materials positions biodiesel as a promising replacement for petroleum (Arita *et al.*, 2020).

Biodiesel, or fatty acid methyl ester (FAME), is a sustainable and clean energy source that offers advantages over fossil fuels (Mohammed *et al.*, 2023). It is produced by converting various oils and fats using methods such as transesterification, direct use and blending, microemulsion, and pyrolysis (Bhatia *et al.*, 2020; Ismaeel *et al.*, 2024). Among these methods, transesterification is the most commonly employed due to its high productivity and cost efficiency, producing biodiesel with properties similar to conventional diesel fuel (Athar and Zaidi, 2020; Karmakar, Lalthazuala Rokhum and Halder, 2022). In the transesterification process, biodiesel is generated by reacting raw materials containing triglycerides with alcohol. The efficiency of biodiesel production is influenced by several factors, including reaction time, stirring, temperature, solvent, molar ratio of oil to alcohol, and the presence of catalysts (Zahan and Kano, 2019).

Heterogeneous catalysts can be easily separated from the reaction mixture using mechanical separation methods, allowing for their reuse. The use of heterogeneous catalysts addresses challenges associated with enzymatic and homogeneous catalysts (Liku, Iskandar and Sulardjaka, 2021). Furthermore, heterogeneous catalysts are generally more environmentally friendly, less corrosive, and cost-effective compared to homogeneous catalysts (Ismaeel *et al.*, 2024). Heterogeneous catalysts play a significant role in biodiesel production by offering cost-effectiveness and environmental benefits, primarily by reducing purification steps in comparison to enzymatic and homogeneous catalyst (Kibar *et al.*, 2023). Research indicates that biodiesel yields obtained from heterogeneous catalysts are typically higher than those from homogeneous catalysts (Pasae *et al.*, 2020; Khan *et al.*, 2021).

Biomass-based heterogeneous catalysts derived from biomass waste materials, such as banana peels (Efeovbokhan, Omoleye and Kalu, 2016), oil palm empty fruit bunches, walnut shells, durian shells, and other bio-waste sources, present promising alternatives for biodiesel production (Yadav, Yadav and Ahmaruzzaman, 2023; Raising Rathod *et al.*, 2024). These biomass-based heterogeneous catalysts have demonstrated excellent catalytic activity, stability, recyclability, and reusability, providing a greener approach to biodiesel synthesis (Atadashi, Aroua and Aziz, 2011; Chouhan and Sarma, 2011; Ao *et al.*, 2023). This review will focus on catalysts derived from Empty Palm Kernel Bunches (EPB) used in the biodiesel production process. Various modifications aimed at improving catalyst performance, as well as the challenges associated with applying EPB catalysts in current and future biodiesel production, will also be discussed

## **2. Biodiesel and Production Process**

Biodiesel is defined as fatty acid methyl esters (FAME) produced from renewable sources (Parandi *et al.*, 2022). As a sustainable alternative to fossil fuels, biodiesel contributes significantly to energy security and environmental protection by reducing greenhouse gas emissions. Its importance lies in its ability to provide a cleaner energy source while supporting local economies. Chemically, biodiesel is an alkyl ester of fatty acids produced through a transesterification process involving oil or fat and an alcohol, such as methanol or ethanol. The main products of this process are methyl esters (biodiesel) and glycerol (Muhammad *et al.*, 2021). Renewable materials for biodiesel production primarily consist of vegetable oils and animal fats, which account for approximately 80% of production costs (El-Gharbawy *et al.*, 2021).

### **2.1. Raw Materials Sources**

Most biodiesel production utilizes vegetable oils, with over 95% sourced from these oils. Common feedstocks include soybean (Karmakar, Karmakar and Mukherjee, 2010), peanut (Silveira Junior *et al.*, 2016), rapeseed oil (Musil *et al.*, 2018), sunflower (Jalalmanesh *et al.*, 2021), palm oil (Ishfaq *et al.*, 2022), hazelnut oil (Bilgin and Gulum, 2018) and coconut oil (Lugo-Méndez *et al.*, 2021). However, the reliance on edible vegetable oils poses a threat to food availability, prompting a trend toward non-edible oils for biodiesel production. This shift not only addresses food security concerns but also encourages the exploration of alternative feedstocks that can be produced without compromising food supply.

Non-edible oils, such as pine oil (Vallinayagam *et al.*, 2014), rapeseed (Tanner *et al.*, 2023), jatropha (Maftuchah *et al.*, 2020), jojoba (Singh, Singh and Sharma, 2022), nyamplung oil (Hamid *et al.*, 2022), used cooking oil (Foroutan *et al.*, 2021), rubber seed oil (Ulfah *et al.*, 2018), rice bran oil (Taslim *et al.*, 2018), Jatropha oil (Yaakob *et al.*, 2012), crude palm oil distillate (Esan *et al.*, 2021), eggshell waste (Putra *et al.*, 2017) and microalgae (Zhang *et al.*, 2022) are increasingly popular due to their potential to reduce competition with food crops. Utilizing waste-derived feedstocks, such as crude palm oil distillate and used cooking oil, not only lowers production costs but also enhances waste management practices. This strategy supports a more sustainable biodiesel production cycle by transforming waste into valuable energy resources.

### **2.2. Role of Alcohol in Biodiesel Production**

Alcohol feedstocks also play a significant role in biodiesel production. Methanol and ethanol are the primary alcohols used in the transesterification process (Verma and Sharma, 2016). Additionally, short-chain alcohols, such as isopropanol (Redel *et al.*, 2021) and butanol (Likozar and Levec, 2014), have also been reported in biodiesel production. Methanol remains the most commonly used alcohol due to its wide availability, lower cost, and favorable reaction kinetics compared to other short-chain alcohols. This choice of alcohol

significantly influences the efficiency and economics of the biodiesel production process, ensuring that the final product is both cost-effective and environmentally friendly.

### 2.3. Transesterification Reaction

The biodiesel production process involves several steps: feedstock processing, transesterification, product separation, and purification. Initially, the feedstock is processed to extract pure oil or fat. These oils or fats are then reacted with alcohol in the presence of a catalyst through transesterification, converting them into methyl esters (biodiesel) and glycerol. After the reaction is complete, the products are separated and purified to yield biodiesel ready for use. Glycerol, a valuable by-product, can be utilized in various industrial applications.

Transesterification is the most widely used method for biodiesel production (Baskar *et al.*, 2019). This process converts triglycerides (TG) or free fatty acids (FFA) in oils into esters (biodiesel) and glycerol using alcohol. The ester bonds in triglycerides are broken and replaced by alkyl groups from alcohols. The presence of a catalyst is essential to ensure the reaction proceeds efficiently, leading to the formation of methyl esters (biodiesel) and glycerol as a by-product (Farouk *et al.*, 2024)

The transesterification process typically follows several stages (Alsultan *et al.*, 2021); (B. Wang *et al.*, 2023): (1) Alcohol Protonation which increases the likelihood of nucleophile attack by the alcohol on the ester, (2) nucleophile attack where the protonated alcohol attacks the carbon attacks the ester, forming a reactive complex called tetrahedral ion, (3) alkoxy group transfer from the alcohol replace the ester, forming methyl esters (biodiesel) and a new alcohol, and (4) Complex Breakdown: The intermediate complex breaks down, yielding methyl esters, new alcohol, and regenerated catalysts.

Several factors influence the efficiency and success of the transesterification reaction (Chozhavendhan *et al.*, 2020):

1. Type of Feedstock: the type of raw material has a different composition. The content contained in the raw material, especially the content of free fatty acids (FFA) and water, can affect the transesterification process. (Ismaeel *et al.*, 2024).
  - a. High Free Fatty Acid (FFA) levels can react with the catalyst, reducing both efficiency and reaction speed. Additionally, this can lead to soap formation, which complicates product separation and increases purification costs (Chanakaewsomboon *et al.*, 2020; Mandari and Devarai, 2022; Farouk *et al.*, 2024).
  - b. High water content can deactivate the catalyst and disrupt the reaction equilibrium, lowering biodiesel yield (Elgharbawy *et al.*, 2021) Water can affect catalyst activity and disrupt reaction equilibrium (Anantapinitwatna *et al.*, 2021).
2. Reagent Ratio: The molar ratio of feedstock, alcohol, and catalyst must be optimized to maximize conversion and yield. An improper ratio can lead to increased glycerol waste and reduced biodiesel quality (Coniwanti, Surliadji and Triandini, 2019).
3. Catalyst Type: Catalyst selection plays a significant role in the reaction rate and conversion efficiency. While basic catalysts are commonly used, acid catalysts such as sulfuric acid ( $H_2SO_4$ ) or hydrochloric acid (HCl) are also effective, especially for feedstocks with high FFA content (Maulidiyah *et al.*, 2022).
4. Temperature and Pressure Higher temperatures can accelerate the reaction but also raise the risk of by-product formation. Therefore, optimizing temperature and pressure conditions is crucial to balance reaction speed with product quality (Mandari and Devarai, 2022).
5. Reaction Time: Prolonging the reaction time may improve conversion rates but must be balanced to avoid inefficiencies. The optimal reaction time ensures high yields without compromising production efficiency (Okwundu, El-Shazly and Elkady, 2019)..

### 3. Catalyst in Transesterification Reaction

Catalysts play a crucial role in the transesterification process by accelerating the reaction and improving the conversion of triglycerides into biodiesel. Typically, acidic or basic catalysts are utilized in biodiesel production. The presence of a catalyst lowers the activation energy, thereby enhancing the reaction rate and increasing the overall yield of biodiesel (Hazrat *et al.*, 2024). Various catalysts have been studied to optimize biodiesel production, with the choice of catalyst depending on factors such as feedstock type, reaction conditions, and production costs (Kosuru *et al.*, 2024). Catalysts used in biodiesel production can be categorized into three main types: enzymatic, homogeneous, and heterogeneous catalysts.

#### 3.1. Enzymatic Catalyst

Enzymatic catalysts, which include free lipase, immobilized lipase on non-magnetic materials, and lipase immobilized on magnetic nanoparticles (MNPs), offer significant potential for high catalytic activity. These biocatalysts are biodegradable and environmentally friendly, making them attractive for sustainable processes. However, their industrial application is constrained by high costs, difficulties in enzyme recovery, and limited reusability. Furthermore, enzymatic catalysts are sensitive to high temperatures, which limits their feasibility for large-scale operations, despite their potential for high biodiesel yields (Kibar *et al.*, 2023).

#### 3.2. Homogeneous Catalyst

Homogeneous catalysts are extensively employed in biodiesel production due to their high conversion efficiency (B. Wang *et al.*, 2023). There are two types of homogeneous catalysts commonly used in transesterification reactions, namely acid catalysts and basic catalysts.

- a. Acid Catalysts: Common acid catalysts, such as sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and hydrochloric acid (HCl), facilitate the transesterification process by increasing proton availability, which promotes nucleophilic attacks by alcohols (Puagsang *et al.*, 2021; Maulidiyah *et al.*, 2022).
- b. Base Catalysts: Sodium hydroxide (NaOH) and potassium hydroxide (KOH) are the most commonly used base catalysts, particularly in large-scale biodiesel production. These catalysts activate oils or fats by forming alkoxide ions that react with esters to produce biodiesel and glycerol. Base catalysts tend to be more cost-effective and efficient than acid catalysts, especially for commercial biodiesel production (Muhammad *et al.*, 2021).

#### 3.3. Heterogeneous Catalyst

While homogeneous catalysts are effective, they present challenges such as difficulty in separating the catalyst from the reaction mixture, leading to increased purification costs. Heterogeneous catalysts address these challenges by allowing easy separation from the reaction mixture, enabling reuse, and reducing overall production costs (Mohiddin *et al.*, 2021). Additionally, heterogeneous catalysts are generally more environmentally friendly, less corrosive, and more sustainable. They eliminate the need for extensive purification steps and offer significant recyclability advantages (Ismaeel *et al.*, 2024).

Heterogeneous catalysts are catalysts that can be easily separated from the reaction mixture using mechanical separation so that they can be reused. Heterogeneous catalysts play an important role in biodiesel production as they offer cost effectiveness and provide environmental benefits by reducing purification steps compared to enzymatic catalysts and homogeneous catalysts. (Kibar *et al.*, 2023). Research has shown that heterogeneous catalysts can produce higher biodiesel yields compared to their homogeneous counterparts (Pasae *et al.*, 2020; Khan *et al.*, 2021). Various heterogeneous catalysts containing metal oxides, mixed oxides, hydrotalcites, carbon-based catalysts and zeolites are examples of heterogeneous catalysts used in biodiesel production. Biomass-based heterogeneous catalysts derived from biomass waste materials such as banana peels (Efeovbokhan, Omoleye and Kalu, 2016) walnut shells, durian shells, and other bio-waste sources are also promising alternatives for

biodiesel production (Yadav, Yadav and Ahmaruzzaman, 2023; Raising Rathod *et al.*, 2024). Biomass-based heterogeneous catalysts have shown excellent catalytic activity, stability, recyclability and reusability, and offer a greener approach to biodiesel synthesis (Atadashi, Aroua and Aziz, 2011; Chouhan and Sarma, 2011; Ao *et al.*, 2023).

#### **4. Empty Palm Oil Bunches (EFB)**

Palm oil is a key plantation commodity that significantly contributes to economic activities due to its ability to produce vegetable oil, which is highly sought after by various industrial sectors. Its high resistance to oxidation and capability to dissolve otherwise insoluble chemicals make palm oil suitable for a wide range of applications, including cooking oil, industrial oil, and biodiesel fuel.

The palm oil industry generates substantial solid waste, predominantly in the form of lignocellulosic residues composed of approximately 45.95% cellulose, 22.84% hemicellulose, and 16.49% lignin (Machado *et al.*, 2022). Fresh fruit bunches from oil palms contain only 21% palm oil, with the remaining components consisting of 6-7% palm kernels, 14-15% fiber, 6-7% peels, and 23% empty palm fruit bunches. Among the biomass produced by the palm oil industry, palm kernel shell (PKS) is the most dominant waste. The empty fruit bunches (EFB), are generated during the sterilization of fruit in the threshing unit at the initial stage of crude palm oil (CPO) production. EFB has significant economic potential due to its abundant availability and low cost, offering the capability to produce a wide range of products, including energy, chemicals, and materials (Abdulrazik *et al.*, 2017).

EFB contains indigenous plant growth-promoting microorganisms that can enhance plant growth and nutrient availability, making it suitable as a biofertilizer in oil palm plantations (Truckell *et al.*, 2019). Moreover, EFB has potential applications in hydrogen gas production (Sivasangar *et al.*, 2015), biosyngas generation (Li and Chen, 2018), briquette manufacturing (Mohamed Nazari and Idroas, 2019), and activated carbon production (Osman, Shamsuddin and Uemura, 2016). Additionally, it holds promise for the production of biochemical products such as levulinic acid and furfural (Gozan *et al.*, 2018), , serves as a biopolymer in arthritis treatments (Sazuan *et al.*, 2023) and functions as a heterogeneous catalyst in biodiesel production (Husin *et al.*, 2018).

##### **4.1. EFB as a Catalyst in Biodiesel Production**

One of the primary challenges in biodiesel production is identifying effective and environmentally friendly catalysts. EFB has gained attention as an alternative catalyst material due to its abundant availability and economic viability. Current estimates indicate that approximately 73.4% of EFB waste remains unutilized (R. D. P. Ananda *et al.*, 2023). The push for renewable resources and sustainable waste management encourages the conversion of EFB waste into economically valuable products (Laskar *et al.*, 2018). Research has demonstrated the potential of using oil palm empty fruit bunches as effective catalysts in biodiesel production, as the K<sub>2</sub>O content within the waste can serve as a potassium source in heterogeneous catalysts (Balajii and Niju, 2019).

##### **4.2. The Physical Characteristics of EFB**

The physical characteristics of TKKS are critical for optimizing its effectiveness as a heterogeneous catalyst for biodiesel production and other applications. TKKS has a complex fiber structure and high porosity, which influence its various physical properties. Proximate and ultimate analyses of TKKS indicate a moisture content of 9.34%, volatile matter of 71.20%, fixed carbon content of 14.76%, and ash content of 4.70%. The elemental composition consists of C (43.70%), H (6.37%), N (0.06%), and O (47.69%) (Erdiwansyah *et al.*, 2024; Gani *et al.*, 2024). Research by Komariah *et al.* (2024) revealed that the average particle size of TKKS ash ranged from 110 to 190 microns, with a surface area of 0.1294 mm<sup>2</sup>/g. The pore diameters measured during adsorption and desorption processes were 13.33

nm and 13.349 nm, respectively. The micropore volume during adsorption was  $7.67 \times 10^{-4}$  cc/g, decreasing to  $2.76 \times 10^{-4}$  cc/g during desorption. The specific surface area was recorded at 0.12942 m<sup>2</sup>/g during adsorption and 0.0412897 m<sup>2</sup>/g during desorption. The ash exhibited a crystalline structure, predominantly due to the presence of potassium (Komariah, Arita and Ananda, 2024). The combustion of palm biomass ash, especially TKKS, yields varying compositions and morphological structures. These variations are influenced by the combustion technique, process conditions, and the characteristics of the ash used for characterization. TKKS ash generally exhibits a more fused structure with fewer pores than TKKS charcoal, alongside a uniform distribution of potassium elements (Arfiana et al.). Calcination of TKKS ash promotes the development of a mesoporous structure in the catalyst, enhancing its surface area and porosity. Additionally, the calcination and activation process can prevent agglomeration and sintering, facilitating the formation of the desired porous structure in the catalyst (Lim et al., 2020).

**Table 1. Chemical composition, ultimate and proximate characteristics of EFB**  
(Anyaocha *et al.*, 2018); (Erdiwansyah *et al.*, 2024); (Obada *et al.*, 2023);  
(Chang, 2014); (R. A. Ananda *et al.*, 2023)

Parameters	Value of EFB	Ash
Humidity (mass %)	-	38,40
<b>Proximate Analysis</b>	-	% dry base mass
Volatile	67,59-83,86	66,10
Fixed Carbon	8,36 - 21,80	28,40
Moisture content	5,18 - 8,31	-
Ash	3,45 - 7,54	5,50
HHV (MJ/Kg dry)	-	14,8
<b>Ultimate Analysis</b>	-	% dry base mass
C	43,52 - 54,76	5,40
H	4,37-7,42	0,30
S	0,01 - 1,10	1,10
O	38,29 - 48,90	47,0
N	0,25 - 1,65	-
Ash Composition	-	% dry base mass
SiO <sub>2</sub>	-	12,12
Al O <sub>23</sub>	-	0,26
CaO	-	9,65
MgO	-	1,90
Na O <sub>2</sub>	-	0,09
K O <sub>2</sub>	-	55,48
SO <sub>2</sub>	-	1,66
Cl	-	6,84
P O <sub>24</sub>	-	3,58
Cellulose	13,75 - 59,70	-
Hemicellulose	12,79 - 22,10	-
Lignin	7,79 - 30,45	-

### 4.3. Chemical Characteristics of EFB

EFB contains chemical compounds that significantly influence its catalytic activity. The cellulose content in EFB is comparable to that of hardwood, but it has a lower lignin content,

ranging from 17% to 32%, and a relatively higher pentosan and hemicellulose content of approximately 29% (Indriati, Elyani and Dina, 2020). Kim et al. (2012) research shows that EFB contains 39.8 cellulose, 17.3 hemi cellulose and 28.8 lignin (Kim *et al.*, 2012). (Kim *et al.*, 2012). EFB also has a very high moisture content of up to 60% (Anyaocha *et al.*, 2018). Table 1 presents the chemical composition of TKKS and TKKS ash, indicating cellulose content ranging from 13.75% to 59.70%, lignin content from 7.79% to 30.45%, and hemicellulose from 12.79% to 22.10%. The proximate analysis shows volatile matter content ranging from 67.59% to 83.86% of dry fiber weight, fixed carbon content from 8.36% to 21.80%, moisture content between 5.18% and 8.31%, and ash content from 3.45% to 7.54%. The ultimate analysis reveals carbon content ranging from 43.52% to 54.76%, hydrogen content from 4.37% to 7.42%, oxygen from 38.29% to 48.90%, nitrogen from 0.25% to 1.65%, and sulfur from 0.01% to 1.10% (Chang, 2014). The proximate analysis of the ash indicates volatile matter content of 66.1% of dry fiber weight, fixed carbon of 28.40%, and ash content of 5.50%. The ultimate analysis highlights potassium as the main element in the combustion residue. Potassium is highly reactive and combines with oxygen to form potassium oxide, underscoring the potential of TKKS ash as a catalyst, as potassium oxide plays a crucial role in various catalytic reactions (Komariah, Arita and Ananda, 2024).

#### **4.4. Effect of Combustion Temperature on Ash Characteristics**

The combustion temperature is a critical factor that governs the physical and chemical characteristics of ash derived from Empty Fruit Bunches (EFB), directly influencing its catalytic properties (Zajac, Szyszlak-Barglowicz and Szczepanik, 2019). Understanding this effect is crucial for optimizing the use of EFB as an efficient and sustainable catalyst in biodiesel production and other industrial applications.

At lower combustion temperatures (below 500°C), EFB generally exhibits a more amorphous structure, resulting in a larger surface area. This increased surface area enhances catalytic activity by providing a greater contact area with reactants. However, combustion at excessively low temperatures may not effectively remove carbon residues, potentially hindering catalyst performance. Conversely, at higher temperatures (above 700°C), PKS ash tends to develop a more stable crystalline structure, which can reduce surface area due to the sintering process, where ash particles coalesce. While a stable crystalline structure can be advantageous for certain applications, the resulting reduction in surface area diminishes the effectiveness of the catalyst. Therefore, identifying appropriate combustion temperatures is essential for producing EFB ash with properties that favor catalytic performance (Husin *et al.*, 2018; Samadhi, Wulandari and Tirtabudi, 2020).

Variations in combustion temperature also impact particle size, surface area, and porosity (Intarachandra, Siriworakon and Sangmanee, 2019). At lower temperatures, the ash surface area is larger due to the formation of amorphous structures, which favors catalytic activity. However, as the temperature increases, the sintering process can lead to particle coalescence and a decrease in surface area. A reduction in surface area at high temperatures may limit the catalyst's ability to interact with reactants, potentially impacting reaction efficiency (Bernard *et al.*, 2021).

Moreover, variations in combustion temperature can lead to significant changes in the crystalline structure, surface area, particle size, and chemical composition of the ash, particularly in terms of metal oxides such as potassium oxide, which play a crucial role in catalytic reactions (Mabate *et al.*, 2023). Therefore, careful control of combustion temperatures is crucial for maximizing the catalytic potential of EFB ash in biodiesel production, warranting further research into optimal processing conditions. A thorough understanding of combustion temperature effects can lead to the development of more efficient catalytic processes in biodiesel production.



## 5. Modification of EFB for Catalytic Applications

Raw Oil Palm Empty Fruit Bunches (EFB) possess a robust lignocellulosic surface structure, making them suitable for various catalytic applications. In contrast, the surface of raw Palm Kernel Shells (PKS) is typically dense, featuring few cracks and fissures, which results in limited porosity. However, through calcination and activation processes, the surface structure of EFB can be transformed into a more porous form. This transformation promotes the formation of mesoporous structures, significantly enhancing its surface area (Al-Fatesh and Fakeeha, 2012). The increase in surface area directly contributes to improved catalytic efficiency and activity, positioning EFB as a promising candidate for various reactions, including biodiesel production through transesterification. To further enhance the catalytic characteristics of EFB, modifications such as activation with acids or bases and the development of nanocatalysts have been implemented. These modifications can improve acid-base strength, thermal stability, and reaction selectivity, thereby optimizing the catalyst's performance. The following section presents an overview of the various modifications applied to EFB, aimed at improving its efficiency as a catalyst in biodiesel production.

### 5.1. Thermal Modification

Empty Palm Oil Bunches (EFB) can be effectively utilized as catalysts by converting them into ash through thermal modification processes such as combustion and calcination. These processes alter the physical and chemical structures of EFB, resulting in ash that contains valuable metal oxides. The thermal treatment of EFB at medium temperatures primarily produces ash composed of inorganic compounds, with potassium being the main component (Okoye *et al.*, 2019). The potassium content in the ash from combustion typically ranges from 30% to 40% (Lim *et al.*, 2020). When exposed to oxygen, potassium readily reacts with oxygen atoms to form potassium oxide.

EFB ash has demonstrated significant potential as a catalyst in biodiesel production. The active  $K_2O$  group present in EFB ash reacts with methanol to form methoxide ions, which act as nucleophiles or active catalysts, facilitating the conversion of fats or oils into methyl esters (Rezki *et al.*, 2020). Studies indicate that EFB ash can effectively catalyze the esterification process (Ibrahim *et al.*, 2019; Wong *et al.*, 2020) (Ibrahim *et al.*, 2019) and pyrolysis (Zhou *et al.*, 2018).

Deli *et al.* (2023) investigated the use of PKS ash as a catalyst in biodiesel production using used cooking oil as the feedstock. The concentration of the EFB ash catalyst was varied from 1% to 5% of the cooking oil's weight, with a mole ratio of 1:6 (oil to methanol). The highest biodiesel yield, reaching 94%, was achieved with a 1% EFB ash concentration (Deli, Sihotang and Khairiah, 2023). Additional research by Komariah *et al.* (2024) explored the application of EFB ash in biodiesel production. The ash was produced through simple open burning and calcination, with a 100 mesh size obtained from combustion at temperatures between 500°C and 600°C, resulting in a high potassium content. The potassium was primarily present as oxides ( $K_2O$ ) and potassium carbonate ( $K_2CO_3$ ). The unique structure and large pore volume of the ash contribute to its catalytic properties. In their study, using a 16% (w/w) catalyst concentration and a methanol-to-oil ratio of 30%, along with reaction conditions of 65°C and a stirring speed of 450 rpm for one hour, Komariah *et al.* achieved a methyl ester yield of 98.9%. The effectiveness of EFB ash as a catalyst in biodiesel production was confirmed, with the resulting biodiesel meeting the standards set by ASTM D6751 and SNI 7182: 2015. This research underscores the potential of EFB ash as a sustainable and cost-effective catalyst in biodiesel production (Komariah, Arita and Ananda, 2024).

### 5.2. Modified Base Impregnation

Base modification aims to enhance the properties of catalysts by incorporating base compounds. The impregnation of Empty Palm Oil Bunches (EPB) with these bases seeks to create basic active sites on the catalyst surface. The potassium content in EPB ash serves as a heterogeneous base catalyst; however, the combustion and calcination of EPB at high temperatures can lead to a reduction in potassium content, which negatively impacts the catalyst's effectiveness. Therefore, impregnation methods can be employed to increase catalytic activity (Fitriana *et al.*, 2018). Potassium hydroxide (KOH) impregnation has been shown to significantly improve conversion rates in biodiesel production (Ali *et al.*, 2024).

By adding KOH to EPB ash, the potassium content can be enhanced, thereby improving the catalytic activity of the resulting catalyst. Research conducted by Yaakob *et al.* (2012) revealed that X-ray diffraction (XRD) analysis of EPB burned at 750°C demonstrated a decrease in peak intensity compared to EPB burned at 550°C. The addition of KOH through impregnation achieved a potassium content of 20% by weight and intensified the corresponding peaks in the XRD pattern, indicating the presence of potassium-containing compounds. In experiments utilizing the KOH-impregnated EPB catalyst at 65°C with an oil-to-methanol ratio of 15 and a catalyst concentration of 20% by weight, biodiesel conversion exceeded 98%. Notably, using a lower concentration of 15% by weight of KOH-doped EPB ash under similar conditions resulted in a remarkable conversion rate of over 99.45% in just 45 minutes. The biodiesel produced also met higher specifications than those established by the European biodiesel quality standard EN 14214. (Yaakob *et al.*, 2012). These findings highlight the potential of KOH-impregnated EPB ash as an effective and efficient catalyst in biodiesel production, offering significant advantages over unmodified EPB ash.

### 5.3. Sulfuric Acid Impregnation Modification

The modification of heterogeneous catalysts through the impregnation of substances can significantly enhance their catalytic activity and conversion rates in biodiesel production (Basumatary *et al.*, 2023). Specifically, the impregnation of Empty Palm Oil Bunch (EPB) catalysts with concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ) has been explored to improve their performance.

Wong (2020) developed an innovative and environmentally friendly catalyst derived from EPB-extracted activated carbon (AC) through direct sulfonation with concentrated sulfuric acid (Wong *et al.*, 2020). This study meticulously investigated the impact of synthesis variables—such as carbonization and sulfonation temperatures, as well as holding times—on the yield of fatty acid methyl esters (FAME) in the transesterification reaction of oleic acid and methyl acetate. The sulfonated activated carbon exhibited a high total acid density due to the presence of hydrophilic surface functional groups, including sulfonic, carboxyl, and phenolic groups. Under optimal conditions, with carbonization at 600 °C for 3 hours and sulfonation at 100 °C for 6 hours, the catalysts demonstrated excellent catalytic activity. These catalysts displayed an amorphous structure with a total acid density of 9.0 mmol NaOH g<sup>-1</sup>, benefiting from a well-developed porous structure in the carbon support. Scanning Electron Microscopy (SEM) analysis revealed morphological changes that increased the specific surface area from 0.54 to 1.03 m<sup>2</sup>/g after chemical activation, indicating enhanced porosity. X-ray Diffraction (XRD) analysis confirmed the amorphous nature of all samples, with both activated carbon and the catalyst showing the formation of stable carbonaceous materials. Fourier Transform Infrared (FTIR) spectroscopy indicated the presence of sulfonate groups on the catalysts, which serve as active sites. Additionally, Thermogravimetric Analysis (TGA) demonstrated good thermal stability below 200 °C, making these catalysts suitable for catalytic processes in biodiesel production.

Under optimal conditions, the solid acid catalyst derived from oil palm empty fruit bunch (OPEFB) achieved outstanding catalytic activity, yielding 50.5% methyl oleate at 100 °C after 8 hours. This was accomplished using a methyl acetate to oleic acid molar ratio of 50:1 and a catalyst dosage of 10% by weight. The hydrophilic functional groups in the catalyst not only prevent catalyst poisoning but also enhance the accessibility of reactants to the catalytic active sites, exhibiting excellent stability that allows for reuse over four cycles (Chen *et al.*, 2017).

Further research by Thushari and Babel (2014, 2017) demonstrated the effectiveness of concentrated H<sub>2</sub>SO<sub>4</sub>-impregnated palm empty bunch powder as a catalyst for biodiesel production. This catalyst featured a unique amorphous structure with a total acid density of 5.40 mmol g<sup>-1</sup>, a surface area of 5.5 m<sup>2</sup>/g, and a pore volume of 0.31 cm<sup>3</sup>/g. The study reported that utilizing 5% catalyst by weight, under reaction temperature conditions of 65-70 °C and a methanol-to-oil ratio of 14:1 over 14 hours, resulted in the highest biodiesel yield of 91%. The fuel properties of the produced biodiesel also met international standards for biodiesel (Thushari and Babel, 2017)..

#### **5.4. Impregnation Modification with H<sub>3</sub>PO<sub>4</sub>**

The utilization of Empty Palm Oil Bunch (EFB) as a heterogeneous catalyst in biodiesel production continues to grow, with an emphasis on improving catalyst efficiency and reliability through various modification processes. One effective approach is the impregnation of EFB ash with phosphoric acid (H<sub>3</sub>PO<sub>4</sub>), which aims to increase the specific surface area and pore volume. These factors play an important role in facilitating the diffusion of reactants into the catalyst and enhancing the activity of active sites during the transesterification reaction.

In a study conducted by Umeagukwu *et al.* (2023), the EFB ash was produced by burning 250 µm-sized EFB in a furnace for 4 hours at 800 °C, followed by an activation process using phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) in a 1:1 (g/ml) ratio (Umeagukwu, Onukwuli and Ude, 2023). This process effectively increased the pore volume to 0.606 cm<sup>3</sup>/g and the specific surface area to 1706.14 m<sup>2</sup>/g, significantly higher than the raw catalyst, which had a surface area of only 173.688 m<sup>2</sup>/g and a pore volume of 0.111 cm<sup>3</sup>/g. Activation with H<sub>3</sub>PO<sub>4</sub> breaks the molecular bonds on the catalyst's active sites, allowing reactants such as methanol and oil to diffuse faster and be absorbed more efficiently. This increase in porosity and surface area not only enhances the number of available active sites but also accelerates the transesterification process, resulting in higher biodiesel conversion rates.

FT-IR spectrum analysis of the activated catalyst showed the dominance of OH and SiO<sub>2</sub> functional groups, indicating the presence of silica as one of the main components of the catalyst. The presence of SiO<sub>2</sub> functional groups was further confirmed by changes in the physico-chemical structure of the EFB ash, as observed through Scanning Electron Microscopy (SEM) analysis, which demonstrated an increase in both the number and size of pores after acid activation. SEM images of the raw and activated catalysts revealed that the irregular pore structure transformed into a more defined and regular one, indicating an increased ability of the catalyst to adsorb reactants. Further X-ray Diffraction (XRD) studies revealed that the raw EFB ash catalyst contained several compounds such as graphite, silvite, marialite, davyne, cristobalite, and englishite, indicating the presence of alumina, alkali metals, alkaline earth metals, and silica. Acid activation with H<sub>3</sub>PO<sub>4</sub> altered the composition of the catalyst, resulting in a decrease in graphite content and the elimination of phosphorus, thus improving the selectivity of the catalyst towards the transesterification reaction.

The optimal process variables identified in this study were a temperature of 61.21 °C, a reaction time of 3.3 hours, a methanol-to-oil molar ratio of 10.3:1, a catalyst concentration of 3.16% by weight, and a stirring speed of 320.51 rpm. These conditions resulted in an optimal biodiesel conversion rate of 90.1%, indicating that the acid-activated EFB ash catalyst

possesses excellent catalytic activity in the transesterification reaction of African pear seed oil (APSO). The successful activation of EFB ash with  $\text{H}_3\text{PO}_4$  as a heterogeneous catalyst opens up opportunities for further applications in efficient and environmentally friendly biodiesel production. The increase in surface area, pore volume, and changes in the chemical structure of the catalyst significantly contributed to the improvement in performance, positioning it as one of the superior candidates for biodiesel production from vegetable oil sources.

### 5.5. BDS Impregnation Modification

Solid acid catalysts were produced from oil palm empty fruit bunch (EFB) biomass powder, which served as a carbon precursor and was subsequently sulfonated with 4-benzenediazonium sulfonate (4-BDS). This sulfonation method has been shown to provide superior stability and free fatty acid (FFA) conversion rates in the esterification reaction of palm fatty acid distillate (PFAD) for biodiesel production (Konwar *et al.*, 2015).

Research by Kam Huei *et al.* investigated the use of EFB as a carbon precursor for synthesizing activated carbon (AC), which was then sulfonated with 4-BDS for solid acid catalyst applications in biodiesel production. Initially, the EFB biomass was impregnated with 30% phosphoric acid at a weight ratio of 7:1 for 24 hours. This was followed by carbonization at temperatures ranging from 200 °C to 600 °C, yielding various types of activated carbon (AC200, AC300, AC400, AC500, AC600) with distinct physical and chemical properties (Kam Huei *et al.*, 2019). The results indicated that calcination at a lower temperature (200 °C) produced AC with a more pronounced porous structure and rough surface, enhancing the catalyst's effectiveness after the sulfonation process.

Scanning Electron Microscopy (SEM) analysis revealed a well-defined porous structure in AC calcined at lower temperatures. In contrast, higher calcination temperatures damaged the carbon structure, resulting in a looser AC that was less effective at attaching sulfonate groups. Fourier Transform Infrared (FTIR) analysis further supported these findings, confirming the successful attachment of sulfonate groups, with spectra showing S-O and  $\text{SO}_3\text{H}$  stretching, alongside indications of incomplete carbonization evidenced by the presence of C=C groups.

The sulfonation process using 4-BDS offers advantages over traditional methods that utilize sulfuric acid. Specifically, sulfonation with 4-BDS yields more stable results and minimizes corrosive effects, thereby enhancing the competitiveness of this process on an industrial scale. Additional SEM analysis showed that higher temperature treatments compromised the activated carbon structure, reducing its capacity to retain active sites and ultimately diminishing catalyst efficiency. Moreover, characterization through Thermogravimetric Analysis (TGA) and Energy Dispersive X-ray Spectroscopy (EDX) suggested that lower calcination temperatures are ideal for producing stable and effective activated carbon over the long term.

Catalyst testing for the esterification reaction was conducted using PFAD as the raw material. The catalytic activity tests demonstrated that the AC200 catalyst yielded the highest biodiesel output. Specifically, the sulfonated AC catalyst, using a sulfanilic acid to AC ratio of 15:1, achieved an impressive biodiesel yield of 73.14%. In a subsequent study, Lim *et al.* reported even better results, with a catalyst loading of 20% by weight producing a biodiesel yield of 98.1% (Lim *et al.*, 2020). These findings highlight the efficiency of the sulfonation method using 4-BDS, showcasing its capability to deliver significantly high yields in biodiesel production.

### 5.6. Oxidation and Sulfonation

The use of homogeneous acid catalysts in esterification reactions often encounters challenges related to the difficult separation from the reaction medium. Therefore, developing heterogeneous (solid) catalysts that can be easily separated is essential for streamlining the production process. Research by Ibrahim et al. (Ibrahim, Hidayat and Santoso, 2017) focused on modifying oil palm empty fruit bunches (EFB) through oxidation and sulfonation processes to introduce acidic groups that function as active sites in catalytic reactions.

The initial modification of EFB involved oxidation with sodium periodate at various temperatures and times to convert lignocellulose into aldehydes. The pretreated EFB was oxidized using sodium periodate at a ratio of 0.8 at temperatures of 40, 50, and 60 °C for 3, 6, 9, and 12 hours in a waterbath shaker (150 strokes/min) without light. The results indicated a significant effect of temperature and oxidation reaction time on the formation of carbonyl groups ( $p < 0.01$ ). Specifically, treatment at 50 °C for 9 hours yielded the highest carbonyl group content of  $98.34 \pm 1.52 \mu\text{mol/g-sample}$ . Notably, a two-stage oxidation process further increased carbonyl group content by 12.02% compared to the one-stage reaction. This finding aligns with previous studies demonstrating that optimal reaction conditions greatly enhance the formation of carbonyl groups, which are crucial for improving the reactivity of EFB as a catalyst.

Following oxidation, a sulfonation process was performed to produce sulfonated EFB. The oxidized EFB was treated to convert carbonyl groups into sulfonates based on the method described by Shet (1996). In this process, 6 g of oxidized EFB was mixed with 180 mL of a 2.5%  $\text{Na}_2\text{S}_2\text{O}_5$  solution in water, and the sulfonation reaction was conducted in a waterbath shaker for 3 hours at 45 °C. The results revealed that the conversion of carbonyl groups to sulfonates reached 27.97%, with a total sulfur content of  $6.30 \pm 0.29\%$ . Despite this conversion, the yield of the ethyl oleate esterification reaction remained low at  $29.12 \pm 5.15\%$ . These findings suggest that while the modification increased the acid content of EFB, other factors, such as the structure and physical properties of the resulting catalyst, may also influence reaction efficiency.

Analysis of the morphology and textural properties of the modified EFB showed that structural changes due to the modification process enhanced surface area and pore accessibility, significantly impacting catalytic activity. FTIR characterization demonstrated significant changes in the functional groups of EFB after the oxidation and sulfonation processes. The FTIR spectrum of oxidized EFB displayed an absorption band at  $1720 \text{ cm}^{-1}$ , indicating the presence of carbonyl groups ( $\text{C=O}$ ), while a band at  $1220 \text{ cm}^{-1}$  confirmed the presence of sulfonates ( $-\text{SO}_3^-$ ) after the sulfonation process. These results signify successful modification, increasing acidic group content, which contributes to catalytic activity.

Thermogravimetric analysis (TGA) indicated that the modified EFB exhibited better thermal stability than the original EFB. The oxidized and sulfonated EFB showed lower mass loss at high temperatures—10% at 200 °C—compared to the original EFB, which experienced 15% mass loss at the same temperature. These results demonstrate that the modification improved the thermal durability of the catalyst, a critical factor in the catalytic reaction process.

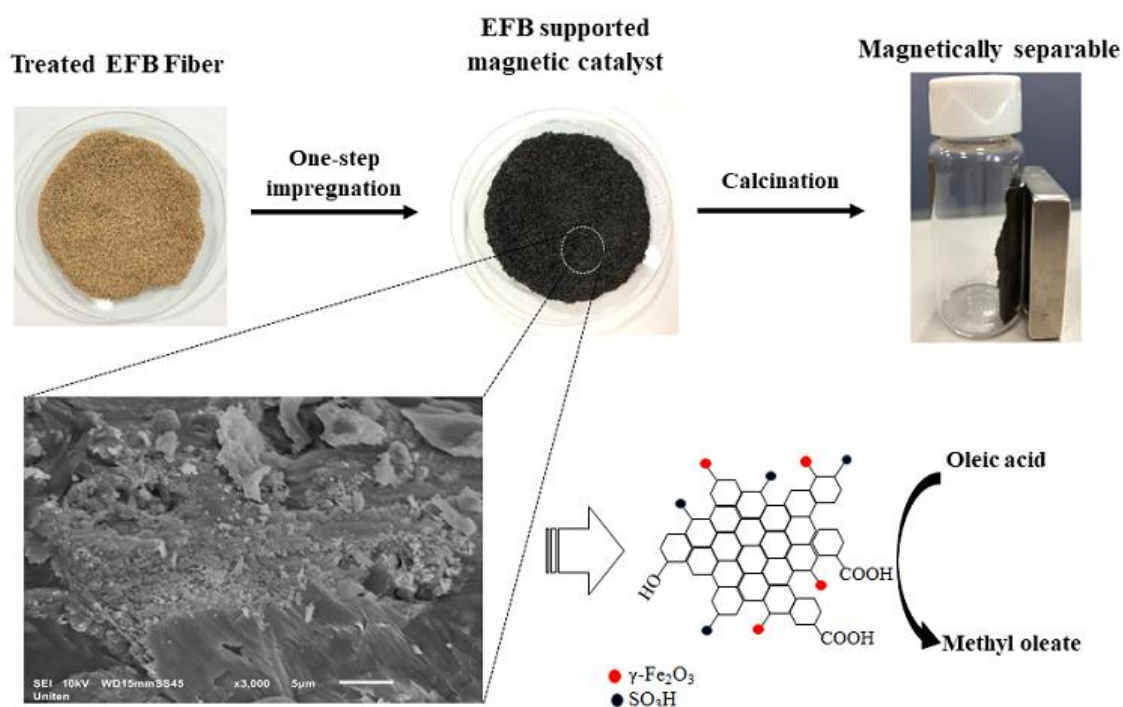
The findings from FTIR and TGA analyses align with previous studies indicating that biomass modification enhances thermal stability and alters chemical properties, thereby increasing its potential as a catalyst. Overall, this study confirms the potential of EFB as a sustainable resource for developing heterogeneous acid catalysts, facilitating more efficient and environmentally friendly biodiesel production. The oxidation and sulfonation modifications not only enhance acidic group content but also improve thermal stability. The characterization results suggest that modified EFB can compete with conventional catalysts in terms of activity and efficiency, opening avenues for further development in catalytic applications and renewable fuel production.

### 5.7. Magnetic Metal Modification

EFB presents significant potential for processing into heterogeneous catalysts through various modifications, including those discussed in the previous section. However, in addition to acid-base modifications, innovative approaches are being developed to maximize the effectiveness of EFB as a catalyst by introducing magnetic properties. Metal impregnation can impart magnetic characteristics to the catalyst, facilitating easier separation after the reaction. The development of EFB-based magnetic acid catalysts has shown considerable promise in enhancing the efficiency of biodiesel production processes.

EFB waste-based magnetic acid catalysts have the potential to replace existing solid catalysts, offering advantages such as cost-effectiveness and environmental friendliness in esterification processes for biofuel applications. Koguleshun et al. (2015) reported the preparation and characterization of a new catalyst derived from EFB (Koguleshun *et al.*, 2015). Characterization analysis indicated that the solid acid catalyst was successfully produced from EFB through direct impregnation with transition metal sulfide ( $\text{Fe}_2(\text{SO}_4)_3$ ). Experimental results demonstrated that this catalyst effectively converted free fatty acids into esters prior to the transesterification reaction for biodiesel production, achieving the highest catalytic activity with an esterification rate of 90.95%.

In another study, Krishnan et al. (2022) utilized a magnetic acid catalyst prepared by impregnating EFB fibers with a solution of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{Fe}_3(\text{SO}_4)_2$  at a chemical ratio of 1:2. This impregnation process resulted in an increased catalyst surface area of  $188.87 \text{ m}^2/\text{g}$  and total acidity of  $2.4 \text{ mmol/g}$ , with iron oxide identified in the form of  $\gamma\text{-Fe}_2\text{O}_3$ . The catalyst exhibited a magnetization value of  $24.97 \text{ emu/g}$ , allowing for easy separation using an external magnet after the reaction. Under optimal conditions—specifically, a 9% catalyst by weight, a reaction temperature of  $60^\circ\text{C}$ , a molar ratio of methanol to oleic acid of 12:1, and a reaction time of 2 hours—maximum conversion reached 94.91%. Notably, this catalyst can be reused up to five cycles without a significant decrease in activity (Krishnan, Pua and Tan, 2022).



Synthesis of Magnetic Catalysts  
Source (Krishnan, Pua and Tan, 2022)

### 5.8. EFB-Based Nanocatalysts for Biodiesel Production

Nanocatalysts have been the focus of intensive research to improve the efficiency of biodiesel production. Defined as catalyst materials with particle sizes on the nanometer scale (less than 100 nm), nanocatalysts possess a very large surface area compared to conventional catalysts, enhancing interaction between the catalyst and the substrate. This increased surface area contributes to heightened catalytic activity and reaction efficiency, particularly in chemical processes that require rapid reaction rates and high product selectivity.

EFB waste-based nanocatalysts show promising potential. Husin et al. (2018) conducted research to explore the use of EFB ash as a source of nanocatalysts (Husin *et al.*, 2018). In this study, the process began with burning the EFB to produce ash, which was then crushed and heated to yield particles in nanoparticle sizes smaller than 100 mesh. The K<sub>2</sub>O-rich EFB ash was subsequently calcined at 600 °C for 4 hours to increase the number of active sites available for reaction. The results indicated that the use of nanocatalysts derived from EFB ash at optimal conditions could convert palm oil into biodiesel with a maximum conversion of 97.90% at 600 °C for 3 hours with the addition of 1% catalyst. This success highlights the potential of EFB as a source of nanocatalysts in biodiesel production. Furthermore, the use of waste-based nanocatalysts supports the principles of sustainability and waste management, making EFB an attractive alternative catalyst in the biodiesel industry.

Building on this, research conducted by Abdullah et al. (2020) explored the use of palm oil waste for nanocatalyst synthesis through the development of bifunctional nanocatalysts (Abdullah *et al.*, 2020). The process involved carbonization at 700 °C and functionalization with K<sub>2</sub>CO<sub>3</sub> and Cu(NO<sub>3</sub>)<sub>2</sub> via wet impregnation. An important aspect of nanocatalysts is their physicochemical characterization, which can be performed using BET (Brunauer-Emmett-Teller) analysis. BET analysis is utilized to determine the specific surface area, pore volume, and pore size of the catalyst material. The BET analysis results of the EFB ash nanocatalyst showed a significant surface area, contributing to increased reaction efficiency. A higher surface area translates to more active sites available for reaction, thereby enhancing product conversion. Additionally, the large pore volume favors substrate diffusion into the catalyst structure, accelerating the reaction rate.

The BET analysis results for the bifunctional nanocatalysts also demonstrated promising outcomes. The resulting catalyst exhibited high thermal stability, with a BET surface area of 438.08 m<sup>2</sup>/g, pore volume of 0.367 cm<sup>3</sup>/g, and pore width of 3.8 nm. The combination of high basicity (8.866 mmol/g) and acidity (27.016 mmol/g) contributed to the success of the simultaneous transesterification-esterification reaction, allowing both reactions to occur in one stage, thereby reducing production time and cost. Under optimal conditions, a 4% loading of the bifunctional catalyst achieved 97.3% conversion of Free Fatty Acids (FFA) with a 95% biodiesel yield, utilizing a methanol-to-oil ratio of 12:1 at 80 °C for 4 hours. The catalyst also demonstrated reusability across five reaction cycles without a significant loss of catalytic activity, adding to its economic appeal.

Overall, nanocatalysts and bifunctional catalysts represent a significant step forward in developing more efficient and sustainable biodiesel production technologies. Further research in this area is expected to yield more optimized and environmentally friendly catalysts, supporting the transition toward renewable energy.

### 5.9. Challenges in Biodiesel Production Using EFB Heterogeneous Catalysts

The use of EFB as a heterogeneous catalyst in biodiesel production holds significant promise. However, several technical and operational challenges must be addressed to enable effective large-scale implementation.

### 1. Process Optimization

One of the primary challenges is optimizing process conditions, particularly the temperature parameters during the combustion of EFB. The high potassium ( $K_2O$ ) content in EFB is critical for its catalytic activity. However, at excessively high combustion temperatures, potassium may vaporize, thereby reducing the catalyst's overall effectiveness. Therefore, it is essential to find a balance between a combustion temperature that preserves potassium and one that produces a stable and efficient catalyst structure. This approach requires precise regulation of combustion operating conditions.

### 2. Quality Consistency

Maintaining consistent quality of EFB-based catalysts poses another challenge. The chemical composition of EFB varies naturally, influenced by geographical location, growing conditions, and the harvesting and pretreatment processes. Without standardization in these processes, ensuring consistent catalyst quality becomes difficult. Non-uniform raw materials can lead to varying catalyst performance, ultimately diminishing reliability in industrial applications.

### 3. Catalyst Modification

Catalyst modification requires careful consideration. Techniques such as acid and base treatment, metal impregnation, and enhancement via nanomaterial technology have been proposed to improve performance. However, these modifications often introduce complexity and increase production costs. For instance, the use of chemicals for acid or base modification entails additional expenses and may complicate safety and waste management. Thus, developing more cost-effective modification techniques while maintaining catalyst performance is a significant challenge.

### 4. Catalyst Durability

Catalyst durability is crucial for large-scale biodiesel production. Industrial processes necessitate catalysts that can maintain activity over multiple reaction cycles to keep operational costs efficient. EFB-based catalysts may degrade over time due to fouling, poisoning, or leaching of active components like potassium. Frequent catalyst replacement raises production costs, highlighting the need for further research to enhance stability, potentially through protective coatings or surface modifications.

### 5. Production Scalability

Scalability is another challenge. While quality control is more manageable at the laboratory scale due to smaller production volumes, scaling up complicates this process. Producing large quantities of EFB catalyst requires adequate infrastructure for efficient transportation, storage, and processing of raw materials. Integrating EFB catalysts into existing biodiesel production facilities necessitates technical adjustments in equipment and processes. Optimizing operational parameters such as temperature, reaction time, and feedstock ratios to accommodate the unique characteristics of EFB catalysts adds complexity to the transition from research to industrial application.

### 6. Environmental and Economic Considerations

Although the use of EFB for catalysis aligns with the principles of a circular economy, the environmental impact of the entire process must be considered. The thermal activation required to prepare the catalyst consumes energy, and the chemicals used in catalyst modification can generate waste needing special management. Moreover, economic factors are vital; catalysts that are effective but costly or technologically complex may not find widespread application in the cost-sensitive biodiesel industry. Consequently, thorough life cycle assessments and technical-economic evaluations are necessary to ensure EFB-based catalysts are environmentally sustainable and economically viable in the long run.



Overall, while EFB demonstrates great potential as a sustainable heterogeneous catalyst for biodiesel production, existing challenges highlight the need for further research to overcome technical and economic constraints. A systematic approach encompassing optimization of the production process, development of cost-effective modification techniques, and enhancement of catalyst durability and quality is essential for EFB to compete with conventional catalysts in the market.

#### **5.10. Conclusion**

In an effort to meet the increasing demand for renewable energy, this study demonstrates that EFB has significant potential as a heterogeneous catalyst in biodiesel production. As a solid waste from the palm oil industry, EFB can be optimally utilized due to its high potassium ( $K_2O$ ) content, which enhances catalytic performance. Processing EFB at low combustion temperatures is crucial for retaining potassium, thereby improving catalyst effectiveness. Various modifications, including acid and base impregnation, as well as the development of magnetic and nanocatalysts, have shown promising results in biodiesel conversion, achieving rates of up to 99%.

These findings highlight that EFB can not only transform agricultural waste into a valuable resource but also contribute to the circular economy by reducing environmental impacts and increasing economic value. However, challenges related to optimizing processing conditions, scaling production, and ensuring consistency in catalyst quality must be addressed. Future research focusing on more efficient and cost-effective processing methods is essential to enhance the industrial application of EFB catalysts.

An integrated approach will maximize the utilization of EFB, providing innovative solutions that improve biodiesel production efficiency while being environmentally friendly. Furthermore, EFB can support sustainable and economical biodiesel production, playing a vital role in reducing dependence on fossil energy sources. Continued research and development in this field are crucial for realizing the potential of EFB as a sustainable solution in the future energy industry.

## LITERATURE

- Abdullah, R. *et al.* (2020) 'Synthesis of bifunctional nanocatalyst from waste palm kernel shell and its application for biodiesel production', *RSC Advances*, 10, pp. 27183–27193. Available at: <https://doi.org/10.1039/D0RA04306K>.
- Abdulrazik, A. *et al.* (2017) 'Multi-products productions from Malaysian oil palm empty fruit bunch (EFB): Analyzing economic potentials from the optimal biomass supply chain', *Journal of Cleaner Production*, 168, pp. 131–148. Available at: <https://doi.org/https://doi.org/10.1016/j.jclepro.2017.08.088>.
- Ahmad, W. *et al.* (2023) 'Future prospects of biomass waste as renewable source of energy in Pakistan: A mini review', *Bioresource Technology Reports*, 24, p. 101658. Available at: <https://doi.org/https://doi.org/10.1016/j.biteb.2023.101658>.
- Al-Fatesh, A.S.A. and Fakeeha, A.H. (2012) 'Effects of calcination and activation temperature on dry reforming catalysts', *Journal of Saudi Chemical Society*, 16(1), pp. 55–61. Available at: <https://doi.org/https://doi.org/10.1016/j.jscs.2010.10.020>.
- Ali, J.S. *et al.* (2024) 'Alkali-impregnated blast furnace slag heterogeneous catalyst for biodiesel production', *Results in Engineering*, 22, p. 102082. Available at: <https://doi.org/https://doi.org/10.1016/j.rineng.2024.102082>.
- Alsultan, A.G. *et al.* (2021) 'A Short Review on Catalyst, Feedstock, Modernised Process, Current State and Challenges on Biodiesel Production', *Catalysts*. Available at: <https://doi.org/10.3390/catal11111261>.
- Ananda, R.. D.P. *et al.* (2023) 'Potensi dan karakteristik abu tandan kosong kelapa sawit sebagai katalis heterogen untuk produksi biodiesel', *Jurnal Teknik Kimia*, 29(1), pp. 36–45. Available at: <https://doi.org/10.36706/jtk.v29i1.1551>.
- Ananda, R.A. *et al.* (2023) 'Potensi dan karakteristik abu tandan kosong kelapa sawit sebagai katalis heterogen untuk produksi biodiesel', *Jurnal Teknik Kimia*, 29, pp. 36–45. Available at: <https://doi.org/10.36706/jtk.v29i1.1551>.
- Anantapinitwatna, A. *et al.* (2021) 'Water influence on the kinetics of transesterification using CaO catalyst to produce biodiesel', *Fuel*, 296, p. 120653. Available at: <https://doi.org/https://doi.org/10.1016/j.fuel.2021.120653>.
- Anyaocha, K.E. *et al.* (2018) 'Critical evaluation of oil palm fresh fruit bunch solid wastes as soil amendments: Prospects and challenges', *Resources, Conservation and Recycling*, 136, pp. 399–409. Available at: <https://doi.org/https://doi.org/10.1016/j.resconrec.2018.04.022>.
- Ao, S. *et al.* (2023) 'Microwave-assisted Sustainable Production of Biodiesel: A Comprehensive Review', *Current Microwave Chemistry*, 10(1), pp. 3–25. Available at: <https://doi.org/https://doi.org/10.2174/2213335610666230223100707>.
- Arita, S. *et al.* (2020) 'Pembuatan Biodiesel dari Limbah Cair Kelapa Sawit dengan Variasi Katalis Asam Sulfat pada Proses Esterifikasi', *Jurnal Teknik Kimia*, 26(1), pp. 1–11. Available at: <https://doi.org/https://doi.org/10.36706/jtk.v26i1.89>.
- Atadashi, I.M., Aroua, M.K. and Aziz, A.A. (2011) 'Biodiesel separation and purification: A review', *Renewable Energy*, 36(2), pp. 437–443. Available at: <https://doi.org/https://doi.org/10.1016/j.renene.2010.07.019>.
- Athar, M. and Zaidi, S. (2020) 'A review of the feedstocks, catalysts, and intensification techniques for sustainable biodiesel production', *Journal of Environmental Chemical Engineering*, 8(6), p. 104523. Available at: <https://doi.org/https://doi.org/10.1016/j.jece.2020.104523>.
- Awosusi, A.A. *et al.* (2022) 'The dynamic impact of biomass and natural resources on

ecological footprint in BRICS economies: A quantile regression evidence', *Energy Reports*, 8, pp. 1979–1994. Available at: <https://doi.org/https://doi.org/10.1016/j.egy.2022.01.022>.

Balajii, M. and Niju, S. (2019) 'A novel biobased heterogeneous catalyst derived from *Musa acuminata* peduncle for biodiesel production – Process optimization using central composite design', *Energy Conversion and Management*, 189, pp. 118–131. Available at: <https://doi.org/https://doi.org/10.1016/j.enconman.2019.03.085>.

Baskar, G. *et al.* (2019) '7 - Advances in bio-oil extraction from nonedible oil seeds and algal biomass', in K.B.T.-A. in E.-F. for a S.E. Azad (ed.) *Woodhead Publishing Series in Energy*. Woodhead Publishing, pp. 187–210. Available at: <https://doi.org/https://doi.org/10.1016/B978-0-08-102728-8.00007-3>.

Basumatary, S.F. *et al.* (2023) 'Advances in CaO-based catalysts for sustainable biodiesel synthesis', *Green Energy and Resources*, 1(3), p. 100032. Available at: <https://doi.org/https://doi.org/10.1016/j.gerr.2023.100032>.

Bernard, P. *et al.* (2021) 'Demonstration of the Influence of Specific Surface Area on Reaction Rate in Heterogeneous Catalysis', *Journal of Chemical Education*, 98(3), pp. 935–940. Available at: <https://doi.org/10.1021/acs.jchemed.0c01101>.

Bhatia, S.K. *et al.* (2020) 'Conversion of waste cooking oil into biodiesel using heterogenous catalyst derived from cork biochar', *Bioresource Technology*, 302, p. 122872. Available at: <https://doi.org/https://doi.org/10.1016/j.biortech.2020.122872>.

Bilgin, A. and Gulum, M. (2018) 'Effects of various transesterification parameters on the some fuel properties of hazelnut oil methyl ester', *Energy Procedia*, 147, pp. 54–62. Available at: <https://doi.org/https://doi.org/10.1016/j.egypro.2018.07.033>.

Chanakaewsomboon, I. *et al.* (2020) 'Investigation of saponification mechanisms in biodiesel production: Microscopic visualization of the effects of FFA, water and the amount of alkaline catalyst', *Journal of Environmental Chemical Engineering*, 8(2), p. 103538. Available at: <https://doi.org/https://doi.org/10.1016/j.jece.2019.103538>.

Chang, S.H. (2014) 'An overview of empty fruit bunch from oil palm as feedstock for bio-oil production', *Biomass and Bioenergy*, 62, pp. 174–181. Available at: <https://doi.org/https://doi.org/10.1016/j.biombioe.2014.01.002>.

Chen, S.S. *et al.* (2017) 'Valorization of biomass to hydroxymethylfurfural, levulinic acid, and fatty acid methyl ester by heterogeneous catalysts', *Chemical Engineering Journal*, 328, pp. 246–273. Available at: <https://doi.org/https://doi.org/10.1016/j.cej.2017.07.020>.

Chouhan, A.P.S. and Sarma, A.K. (2011) 'Modern heterogeneous catalysts for biodiesel production: A comprehensive review', *Renewable and Sustainable Energy Reviews*, 15(9), pp. 4378–4399. Available at: <https://doi.org/https://doi.org/10.1016/j.rser.2011.07.112>.

Chozhavendhan, S. *et al.* (2020) 'A review on influencing parameters of biodiesel production and purification processes', *Current Research in Green and Sustainable Chemistry*, 1–2, pp. 1–6. Available at: <https://doi.org/https://doi.org/10.1016/j.crgsc.2020.04.002>.

Coniwanti, P., Surliadji, L. and Triandini, D. (2019) 'The effects of catalysts type, molar ratio, and transesterification time in producing biodiesel from beef tallow', *IOP Conference Series: Materials Science and Engineering*, 620(1), p. 12019. Available at: <https://doi.org/10.1088/1757-899X/620/1/012019>.

Deli, nur A., Sihotang, A.J. and Khairiah, H. (2023) 'Produksi Biodiesel Dari Minyak Goreng Bekas Menggunakan Katalis Abu Tandan Kosong Sawit', *JUTIN: Jurnal Teknik Industri Terintegrasi*, 7(1), pp. 1–7.

Efeovbokhan, V., Omoleye, J. and Kalu, E. (2016) 'Extraction and Use of Potassium Hydroxide from Ripe Plantain Peels Ash for Biodiesel Production', *Journal of Biobased Materials and Bioenergy*, 10, pp. 1–9. Available at: <https://doi.org/10.1166/jbmb.2016.1567>.

El-Gharbawy, A. *et al.* (2021) 'A REVIEW ON BIODIESEL FEEDSTOCKS AND PRODUCTION TECHNOLOGIES', *Journal of the Chilean Chemical Society*, 66, p. 5098.

Available at: <https://doi.org/10.4067/S0717-97072021000105098>.

Elgharbawy, A.S. *et al.* (2021) 'Glycerolysis treatment to enhance biodiesel production from low-quality feedstocks', *Fuel*, 284, p. 118970. Available at: <https://doi.org/https://doi.org/10.1016/j.fuel.2020.118970>.

Erdiwansyah *et al.* (2024) 'Analysis study and experiments SEM-EDS of particles and porosity of empty fruit bunches', *Case Studies in Chemical and Environmental Engineering*, 9, p. 100773. Available at: <https://doi.org/https://doi.org/10.1016/j.cscee.2024.100773>.

Esan, A.O. *et al.* (2021) 'Synthesis of biodiesel from waste palm fatty acid distillate (PFAD) and dimethyl carbonate (DMC) via Taguchi optimisation method', *Biomass and Bioenergy*, 154, p. 106262. Available at: <https://doi.org/https://doi.org/10.1016/j.biombioe.2021.106262>.

Farouk, S.M. *et al.* (2024) 'Recent advances in transesterification for sustainable biodiesel production, challenges, and prospects: a comprehensive review', *Environmental Science and Pollution Research*, 31(9), pp. 12722–12747. Available at: <https://doi.org/10.1007/s11356-024-32027-4>.

Fitriana, N. *et al.* (2018) 'Synthesis of K<sub>2</sub>O/Zeolite catalysts by KOH impregnation for biodiesel production from waste frying oil', *IOP Conference Series: Materials Science and Engineering*, 334, p. 12011. Available at: <https://doi.org/10.1088/1757-899X/334/1/012011>.

Foroutan, R. *et al.* (2021) 'Biodiesel production from edible oils using algal biochar/CaO/K<sub>2</sub>CO<sub>3</sub> as a heterogeneous and recyclable catalyst', *Renewable Energy*, 168, pp. 1207–1216. Available at: <https://doi.org/https://doi.org/10.1016/j.renene.2020.12.094>.

Gani, A. *et al.* (2024) 'Analysis of chemical compounds and energy value for biocoke fuel by FTIR and TGA', *Case Studies in Chemical and Environmental Engineering*, 9, p. 100644. Available at: <https://doi.org/https://doi.org/10.1016/j.cscee.2024.100644>.

Garg, R., Sabouni, R. and Ahmadipour, M. (2023) 'From waste to fuel: Challenging aspects in sustainable biodiesel production from lignocellulosic biomass feedstocks and role of metal organic framework as innovative heterogeneous catalysts', *Industrial Crops and Products*, 206, p. 117554. Available at: <https://doi.org/https://doi.org/10.1016/j.indcrop.2023.117554>.

Gozan, M. *et al.* (2018) 'Evaluation of Separate and Simultaneous Kinetic Parameters for Levulinic Acid and Furfural Production from Pretreated Palm Oil Empty Fruit Bunches', *International Journal of Chemical Engineering*, 2018(1), p. 1920180. Available at: <https://doi.org/https://doi.org/10.1155/2018/1920180>.

Hamid, A. *et al.* (2022) 'Effect the Addition of Biodiesel from Nyamplung Oil (*Calophyllum Inophyllum*) on Performance and Emission Characteristics of Diesel Engines', *Jurnal Teknik Kimia dan Lingkungan*, 6, p. 120. Available at: <https://doi.org/10.33795/jtkl.v6i2.336>.

Hazrat, M.A. *et al.* (2024) 'Homogenous Alkaline Catalyst-Based Transesterification Process for Biodiesel Production From Sunflower oil: Optimization and Kinetic Model Development', in: Elsevier. Available at: <https://doi.org/https://doi.org/10.1016/B978-0-323-93940-9.00176-6>.

Husin, H. *et al.* (2018) 'Solid Catalyst Nanoparticles derived from Oil-Palm Empty Fruit Bunches (OP-EFB) as a Renewable Catalyst for Biodiesel Production', *IOP Conference Series: Materials Science and Engineering*, 358(1), p. 12008. Available at: <https://doi.org/10.1088/1757-899X/358/1/012008>.

Ibrahim, N.A. *et al.* (2019) 'Synthesis of carbonaceous solid acid magnetic catalyst from empty fruit bunch for esterification of palm fatty acid distillate (PFAD)', *Energy Conversion and Management*, 195, pp. 480–491. Available at: <https://doi.org/https://doi.org/10.1016/j.enconman.2019.05.022>.

Ibrahim, T.M., Hidayat, C. and Santoso, U. (2017) 'Oksidasi dan Sulfonasi Tandan Kosong Kelapa Sawit sebagai Katalis Asam Heterogen', *Jurnal Rekayasa Kimia & Lingkungan*, 12(2), pp. 77–86. Available at: <https://doi.org/10.23955/rkl.v12i2.7020>.

Indriati, L., Elyani, N. and Dina, S.F. (2020) 'Empty fruit bunches, potential fiber source for

Indonesian pulp and paper industry', *IOP Conference Series: Materials Science and Engineering*, 980(1), p. 12045. Available at: <https://doi.org/10.1088/1757-899X/980/1/012045>.

Intarachandra, N., Siriworakon, S. and Sangmanee, T. (2019) 'Preparation of oil palm empty fruit bunch based activated carbon for adsorption of dye from aqueous solution', *MATEC Web Conf.*, 268. Available at: <https://doi.org/10.1051/mateconf/201926806008>.

International Energy Agency (2021) 'Global Energy Review 2021'. Licence: CC BY 4.0.

Ishfaq, R. *et al.* (2022) 'Synthesis and Characterization of Metal Sulfates Loaded Palm Empty Fruit Bunch (PEFB) for Biodiesel Production', *Sains Malaysiana*, 51, pp. 519–532. Available at: <https://doi.org/10.17576/jsm-2022-5102-16>.

Ismaeel, H.K. *et al.* (2024) 'Strategies for biodiesel production with the role of reactor technologies: A comprehensive review', *Chemical Engineering and Processing - Process Intensification*, 200, p. 109767. Available at: <https://doi.org/https://doi.org/10.1016/j.cep.2024.109767>.

Jalalmanesh, S. *et al.* (2021) 'Biodiesel Production from Sunflower Oil Using KCO Impregnated Kaolin Novel Solid Base Catalyst', *Journal of the American Oil Chemists' Society*, 98(6), pp. 633–642. Available at: <https://doi.org/https://doi.org/10.1002/aocs.12486>.

Kam Huei, W. *et al.* (2019) 'Synthesis of Solid Catalyst from Palm Empty Fruit Bunch for Production of Biodiesel through Esterification', *IOP Conference Series: Earth and Environmental Science*, 268(1), p. 12081. Available at: <https://doi.org/10.1088/1755-1315/268/1/012081>.

Karmakar, A., Karmakar, S. and Mukherjee, S. (2010) 'Properties of various plants and animals feedstocks for biodiesel production', *Bioresource Technology*, 101(19), pp. 7201–7210. Available at: <https://doi.org/https://doi.org/10.1016/j.biortech.2010.04.079>.

Karmakar, B., Lalthazuala Rokhum, S. and Halder, G. (2022) 'Injecting superheated C1 and C3 alcohol supports towards non-catalytic semi-continuous conversion of Hevea brasiliensis oil into biodiesel', *Fuel*, 314, p. 122777. Available at: <https://doi.org/https://doi.org/10.1016/j.fuel.2021.122777>.

Khan, K. *et al.* (2021) 'Comprehensive Comparison of Hetero-Homogeneous Catalysts for Fatty Acid Methyl Ester Production from Non-Edible Jatropha curcas Oil', *Catalysts*, 11, p. 1420. Available at: <https://doi.org/10.3390/catal11121420>.

Kibar, M.E. *et al.* (2023) 'Assessment of Homogeneous and Heterogeneous Catalysts in Transesterification Reaction: A Mini Review', *ChemBioEng Reviews*, 10(4), pp. 412–422. Available at: <https://doi.org/https://doi.org/10.1002/cben.202200021>.

Kim, S. *et al.* (2012) 'Sequential acid-/alkali-pretreatment of empty palm fruit bunch fiber', *Bioresource Technology*, 109, pp. 229–233. Available at: <https://doi.org/https://doi.org/10.1016/j.biortech.2012.01.036>.

Koguleshun, S. *et al.* (2015) 'Synthesis of Oil Palm Empty Fruit Bunch (EFB) Derived Solid Acid Catalyst for Esterification of Waste Cooking Oils', *Sains Malaysiana*, 44, pp. 1573–1577.

Komariah, L.N., Arita, S. and Ananda, R.A.D.P. (2024) 'Effectiveness of empty fruit bunch ash as the catalyst for palm oil transesterification', *South African Journal of Chemical Engineering*, 50, pp. 65–74. Available at: <https://doi.org/https://doi.org/10.1016/j.sajce.2024.07.010>.

Konwar, L.J. *et al.* (2015) 'Towards carbon efficient biorefining: Multifunctional mesoporous solid acids obtained from biodiesel production wastes for biomass conversion', *Applied Catalysis B: Environmental*, 176–177, pp. 20–35. Available at: <https://doi.org/https://doi.org/10.1016/j.apcatb.2015.03.005>.

Kopetz, H. (2013) 'Build a biomass energy market', *Nature*, 494(7435), pp. 29–31. Available at: <https://doi.org/10.1038/494029a>.

Kosuru, S.M.Y. *et al.* (2024) 'A review on the biodiesel production: Selection of catalyst, Pre-treatment, Post treatment methods', *Green Technologies and Sustainability*, 2(1), p. 100061. Available at: <https://doi.org/https://doi.org/10.1016/j.grets.2023.100061>.

Krishnan, S.G., Pua, F.-L. and Tan, E.-S. (2022) 'Synthesis of Magnetic Catalyst Derived from Oil Palm Empty Fruit Bunch for Esterification of Oleic Acid: An Optimization Study', *Bulletin of Chemical Reaction Engineering & Catalysis*; 2022: *BCREC Volume 17 Issue 1 Year 2022 (March 2022)* DO - 10.9767/bcrec.17.1.12392.65-77 [Preprint]. Available at: <https://journal.bcrec.id/index.php/bcrec/article/view/12392>.

Laskar, I.B. *et al.* (2018) 'Waste snail shell derived heterogeneous catalyst for biodiesel production by the transesterification of soybean oil', *RSC Advances*, 8(36), pp. 20131–20142. Available at: <https://doi.org/10.1039/C8RA02397B>.

Li, Y.-H. and Chen, H.-H. (2018) 'Analysis of syngas production rate in empty fruit bunch steam gasification with varying control factors', *International Journal of Hydrogen Energy*, 43(2), pp. 667–675. Available at: <https://doi.org/https://doi.org/10.1016/j.ijhydene.2017.11.117>.

Likozar, B. and Levec, J. (2014) 'Transesterification of canola, palm, peanut, soybean and sunflower oil with methanol, ethanol, isopropanol, butanol and tert-butanol to biodiesel: Modelling of chemical equilibrium, reaction kinetics and mass transfer based on fatty acid composition', *Applied Energy*, 123, pp. 108–120. Available at: <https://doi.org/10.1016/j.apenergy.2014.02.046>.

Liku, E.H., Iskandar, N. and Sulardjaka (2021) 'Pengaruh Komposisi Binder Tanah Liat Terhadap Kekuatan Pelet Katalis Zeolit Alam', *Jurnal Teknik Mesin S-I*, 9(2), pp. 255–260.

Lim, S. *et al.* (2020) 'Biodiesel synthesis from oil palm empty fruit bunch biochar derived heterogeneous solid catalyst using 4-benzenediazonium sulfonate', *Journal of Hazardous Materials*, 390, p. 121532. Available at: <https://doi.org/https://doi.org/10.1016/j.jhazmat.2019.121532>.

Lugo-Méndez, H. *et al.* (2021) 'Synthesis of biodiesel from coconut oil and characterization of its blends', *Fuel*, 295, p. 120595. Available at: <https://doi.org/https://doi.org/10.1016/j.fuel.2021.120595>.

Mabate, T.P. *et al.* (2023) 'Metal oxides and their roles in heterogeneous catalysis: special emphasis on synthesis protocols, intrinsic properties, and their influence in transfer hydrogenation reactions', *SN Applied Sciences*, 5(7), p. 196. Available at: <https://doi.org/10.1007/s42452-023-05416-6>.

Machado, H. *et al.* (2022) 'Bio-Oil: The Next-Generation Source of Chemicals', *Reactions*, pp. 118–137. Available at: <https://doi.org/10.3390/reactions3010009>.

Maftuchah *et al.* (2020) 'Biodiesel generated from Jatropha (*Jatropha curcas* Linn.) seeds selected based on various genotypes crossbred', *Energy Reports*, 6, pp. 345–350. Available at: <https://doi.org/https://doi.org/10.1016/j.egyr.2020.11.160>.

Mandari, V. and Devarai, S.K. (2022) 'Biodiesel Production Using Homogeneous, Heterogeneous, and Enzyme Catalysts via Transesterification and Esterification Reactions: a Critical Review', *BioEnergy Research*, 15(2), pp. 935–961. Available at: <https://doi.org/10.1007/s12155-021-10333-w>.

Maulidiyah, M. *et al.* (2022) 'Biodiesel Production from Crude Palm Oil Using Sulfuric Acid and K<sub>2</sub>O Catalysts through a Two-Stage Reaction', *Biointerface Research in Applied Chemistry*, 12, pp. 3150–3160. Available at: <https://doi.org/10.33263/BRIAC123.31503160>.

Mohamed Nazari, M. and Idroas, M.Y. (2019) *PRODUCTION OF CARBONIZED BRIQUETTE MADE FROM EMPTY FRUIT BUNCH (EFB) BY CARBONIZATION TREATMENT*.

Mohammed, A.S. *et al.* (2023) 'A comprehensive review on the effect of ethers, antioxidants, and cetane improver additives on biodiesel-diesel blend in CI engine performance and

emission characteristics', *Journal of the Energy Institute*, 108, p. 101227. Available at: <https://doi.org/https://doi.org/10.1016/j.joei.2023.101227>.

Mohiddin, M.N. Bin *et al.* (2021) 'Evaluation on feedstock, technologies, catalyst and reactor for sustainable biodiesel production: A review', *Journal of Industrial and Engineering Chemistry*, 98, pp. 60–81. Available at: <https://doi.org/https://doi.org/10.1016/j.jiec.2021.03.036>.

Moreira, B.R. de A. *et al.* (2023) 'Biomass off-gassing: A mini-review and meta-analysis aspiring to inspire future research and innovation in solid biofuels for safety-sensitive and environmentally responsible residential and industrial applications', *Industrial Crops and Products*, 205, p. 117508. Available at: <https://doi.org/https://doi.org/10.1016/j.indcrop.2023.117508>.

Muhammad *et al.* (2021) 'Optimization of Esterification and Transesterification Processes for Biodiesel Production from Used Cooking Oil', *Journal of Research and Technology*, 7(2), pp. 207–216. Available at: <https://doi.org/10.55732/jrt.v7i2.432>.

Musil, M. *et al.* (2018) 'Butanolysis: Comparison of potassium hydroxide and potassium tert-butoxide as catalyst for biodiesel preparing from rapeseed oil', *Journal of Environmental Management*, 218, pp. 555–561. Available at: <https://doi.org/https://doi.org/10.1016/j.jenvman.2018.04.100>.

Obada, D.O. *et al.* (2023) 'Palm oil mill derived empty palm fruit bunches as a feed stock for renewable energy applications in Nigeria: A review', *Bioresource Technology Reports*, 24, p. 101666. Available at: <https://doi.org/https://doi.org/10.1016/j.biteb.2023.101666>.

Okoye, P.U. *et al.* (2019) 'Promotional effect of calcination temperature on structural evolution, basicity, and activity of oil palm empty fruit bunch derived catalyst for glycerol carbonate synthesis', *Energy Conversion and Management*, 179, pp. 192–200. Available at: <https://doi.org/https://doi.org/10.1016/j.enconman.2018.10.013>.

Okwundu, O.S., El-Shazly, A.H. and Elkady, M. (2019) 'Comparative effect of reaction time on biodiesel production from low free fatty acid beef tallow: a definition of product yield', *SN Applied Sciences*, 1(2), p. 140. Available at: <https://doi.org/10.1007/s42452-018-0145-1>.

Osman, N.B., Shamsuddin, N. and Uemura, Y. (2016) 'Activated Carbon of Oil Palm Empty Fruit Bunch (EFB); Core and Shaggy', *Procedia Engineering*, 148, pp. 758–764. Available at: <https://doi.org/https://doi.org/10.1016/j.proeng.2016.06.610>.

Parandi, E. *et al.* (2022) 'Biodiesel production from waste cooking oil using a novel biocatalyst of lipase enzyme immobilized magnetic nanocomposite', *Fuel*, 313, p. 123057. Available at: <https://doi.org/https://doi.org/10.1016/j.fuel.2021.123057>.

Pasae, Y. *et al.* (2020) 'The Contribution Of Heterogeneous And Homogeneous Catalysts Towards Biodiesel Quality', *Journal of Physics: Conference Series*, 1464(1), p. 12054. Available at: <https://doi.org/10.1088/1742-6596/1464/1/012054>.

Puagsang, N. *et al.* (2021) *Production of Biodiesel from Low-Grade Crude Palm Oil Using Hydrochloric Acid*, *EnvironmentAsia*. Available at: <https://doi.org/10.14456/ea.2021.3>.

Putra, M. *et al.* (2017) 'Potential waste from palm empty fruit bunches and eggshells as a heterogeneous catalyst for biodiesel production', *RSC Advances*, 7, pp. 55547–55554. Available at: <https://doi.org/10.1039/C7RA11031F>.

Raising Rathod, D. *et al.* (2024) 'Prospects of novel heterogeneous base catalysts and nanocatalysts in achieving sustainable biodiesel production', *International Journal of Green Energy*, 21(5), pp. 1017–1042. Available at: <https://doi.org/10.1080/15435075.2023.2228886>.

Reddy, K.V. *et al.* (2023) 'Chapter 23 - Biomass waste and feedstock as a source of renewable energy', in M.P.B.T.-G.A. to A.F. for a S.F. Shah (ed.). Elsevier, pp. 325–334. Available at: <https://doi.org/https://doi.org/10.1016/B978-0-12-824318-3.00033-3>.

Redel, M. *et al.* (2021) 'Influence of Short Carbon-Chain Alcohol (Ethanol and 1-

Propanol)/Diesel Fuel Blends over Diesel Engine Emissions’, *Energies*, 14, p. 1309. Available at: <https://doi.org/10.3390/en14051309>.

Rezki, B. *et al.* (2020) ‘Biodiesel production from rapeseed oil and low free fatty acid waste cooking oil using a cesium modified natural phosphate catalyst †’, *RSC Advances*, 10, pp. 41065–41077. Available at: <https://doi.org/10.1039/d0ra07711a>.

Samadhi, T.W., Wulandari, W. and Tirtabudi, K.R. (2020) ‘Oil palm empty fruit bunch ash valorization through potassium extraction’, *IOP Conference Series: Materials Science and Engineering*, 823(1), p. 12035. Available at: <https://doi.org/10.1088/1757-899X/823/1/012035>.

Sazuan, N.S.A. *et al.* (2023) ‘Synthesising injectable molecular self-curing polymer from monomer derived from lignocellulosic oil palm empty fruit bunch biomass: A review on treating Osteoarthritis’, *Arabian Journal of Chemistry*, 16(2), p. 104500. Available at: <https://doi.org/https://doi.org/10.1016/j.arabjc.2022.104500>.

Silveira Junior, E.G. *et al.* (2016) ‘Potential of Virginia-type peanut (*Arachis hypogaea* L.) as feedstock for biodiesel production’, *Industrial Crops and Products*, 89, pp. 448–454. Available at: <https://doi.org/https://doi.org/10.1016/j.indcrop.2016.04.050>.

Singh, N.K., Singh, Y. and Sharma, A. (2022) ‘Optimization of biodiesel synthesis from Jojoba oil via supercritical methanol: A response surface methodology approach coupled with genetic algorithm’, *Biomass and Bioenergy*, 156, p. 106332. Available at: <https://doi.org/https://doi.org/10.1016/j.biombioe.2021.106332>.

Sivasangar, S. *et al.* (2015) ‘Supercritical water gasification of empty fruit bunches from oil palm for hydrogen production’, *Fuel*, 143, pp. 563–569. Available at: <https://doi.org/https://doi.org/10.1016/j.fuel.2014.11.073>.

Tanner, A. *et al.* (2023) ‘Biodiesel Production Directly from Rapeseeds’, *Water*. Available at: <https://doi.org/10.3390/w15142595>.

Taslim, T. *et al.* (2018) ‘Biodiesel production from rice bran oil by transesterification using heterogeneous catalyst natural zeolite modified with K<sub>2</sub>CO<sub>3</sub>’, *IOP Conference Series: Materials Science and Engineering*, 309, p. 12107. Available at: <https://doi.org/10.1088/1757-899X/309/1/012107>.

Thushari, P.G.I. and Babel, S. (2017) ‘Biodiesel Production From Waste Palm Oil Using Palm Empty Fruit Bunch-Derived Novel Carbon Acid Catalyst’, *Journal of Energy Resources Technology*, 140(3). Available at: <https://doi.org/10.1115/1.4038380>.

Truckell, I.G. *et al.* (2019) ‘Soil and transport factors in potential distribution systems for biofertilisers derived from palm oil mill residues in Malaysia’, *Computers and Electronics in Agriculture*, 166, p. 105005. Available at: <https://doi.org/https://doi.org/10.1016/j.compag.2019.105005>.

Ulfah, M. *et al.* (2018) ‘Biodiesel production methods of rubber seed oil: a review’, *IOP Conference Series: Materials Science and Engineering*, 334(1), p. 12006. Available at: <https://doi.org/10.1088/1757-899X/334/1/012006>.

Umeagukwu, O.E., Onukwuli, D.O. and Ude, C.N. (2023) ‘Methanolysis of African pear seed oil catalyzed with acid activated empty palm fruit bunch ash: Optimization and sensitivity analysis’, *Cleaner Energy Systems*, 6, p. 100093. Available at: <https://doi.org/https://doi.org/10.1016/j.cles.2023.100093>.

Vallinayagam, R. *et al.* (2014) ‘Pine oil–biodiesel blends: A double biofuel strategy to completely eliminate the use of diesel in a diesel engine’, *Applied Energy*, 130, pp. 466–473. Available at: <https://doi.org/https://doi.org/10.1016/j.apenergy.2013.11.025>.

Verma, P. and Sharma, M.P. (2016) ‘Comparative analysis of effect of methanol and ethanol on Karanja biodiesel production and its optimisation’, *Fuel*, 180, pp. 164–174. Available at: <https://doi.org/https://doi.org/10.1016/j.fuel.2016.04.035>.

Wackernagel, M. *et al.* (2021) ‘The importance of resource security for poverty eradication’,



*Nature Sustainability*, 4(8), pp. 731–738. Available at: <https://doi.org/10.1038/s41893-021-00708-4>.

Wang, B. *et al.* (2023) ‘Enabling Catalysts for Biodiesel Production via Transesterification’, *Catalysts*. Available at: <https://doi.org/10.3390/catal13040740>.

Wang, S. *et al.* (2023) ‘Catalytic conversion network for lignocellulosic biomass valorization: a panoramic view’, *Industrial Chemistry & Materials*, 1(2), pp. 188–206. Available at: <https://doi.org/10.1039/D2IM00054G>.

Wong, W.-Y. *et al.* (2020) ‘Synthesis of renewable heterogeneous acid catalyst from oil palm empty fruit bunch for glycerol-free biodiesel production’, *Science of The Total Environment*, 727, p. 138534. Available at: <https://doi.org/https://doi.org/10.1016/j.scitotenv.2020.138534>.

Yaakob, Z. *et al.* (2012) ‘Utilization of palm empty fruit bunch for the production of biodiesel from *Jatropha curcas* oil’, *Bioresource Technology*, 104, pp. 695–700. Available at: <https://doi.org/https://doi.org/10.1016/j.biortech.2011.10.058>.

Yadav, N., Yadav, G. and Ahmaruzzaman, M. (2023) ‘Microwave-assisted biodiesel production using –SO<sub>3</sub>H functionalized heterogeneous catalyst derived from a lignin-rich biomass’, *Scientific Reports*, 13(1), p. 9074. Available at: <https://doi.org/10.1038/s41598-023-36380-1>.

Zahan, K.A. and Kano, M. (2019) ‘Technological Progress in Biodiesel Production: An Overview on Different Types of Reactors’, *Energy Procedia*, 156, pp. 452–457. Available at: <https://doi.org/https://doi.org/10.1016/j.egypro.2018.11.086>.

Zajac, G., Szyszlak-Barglowicz, J. and Szczepanik, M. (2019) ‘Influence of Biomass Incineration Temperature on the Content of Selected Heavy Metals in the Ash Used for Fertilizing Purposes’, *Applied Sciences*, 9, p. 1790. Available at: <https://doi.org/10.3390/app9091790>.

Zhang, S. *et al.* (2022) ‘A review on biodiesel production from microalgae: Influencing parameters and recent advanced technologies’, *Frontiers in Microbiology*, 13. Available at: <https://www.frontiersin.org/journals/microbiology/articles/10.3389/fmicb.2022.970028>.

Zhou, W. *et al.* (2018) ‘Study on catalytic properties of potassium carbonate during the process of sawdust pyrolysis’, *International Journal of Hydrogen Energy*, 43(30), pp. 13829–13841. Available at: <https://doi.org/https://doi.org/10.1016/j.ijhydene.2018.02.002>.