Chapter 1

Introduction

1.1 Introduction

Today, worldwide energy demand and consumption have tremendously and continuously increased due to the population surge, rapid industrialization and expansion of metropolitan areas (Yin et al., 2020). Energy is essentially required for industrial operations, transportation, electricity production, operating agricultural machinery and other domestic appliances. The fast-tracking of energy consumption has led the world towards an energy crisis, resulting in a direct hike in the price of fuels, electricity, goods and commodities. The energy crisis has a negative impact on individuals, businesses, the environment and the economies of the entire globe. For instance, the rise in transportation costs is the most visible problem caused by the elevation of fuel prices, which has directly risen the price of goods and services. This inflation leads to a loss or reduction in the buying capacity of consumers. Moreover, the energy crisis impacts on industrial and agricultural production, the cost of construction and company profit margins, which in turn can lead to higher unemployment and poverty rates (Farghali et al., 2023).

According to a statistical review of world energy (2020), the global energy consumption from the sources, viz. oil (31.2 %), coal (27.2 %), natural gas (24.7 %), nuclear (4.3 %), hydro (6.9 %) and other renewables (5.7 %) was known as recorded (BP, 2021). Although renewable energy sources like solar, wind and hydropower are rapidly growing to meet some portion of energy demand, out of the total primary sources of energy, 80-88 % of the energy supply is contributed by fossil fuel sources (Betiku et al., 2017; Thangaraj et al., 2019). As fossil fuels are non-renewable sources of energy, they require millions of years to generate and are consumed much faster than they are formed. In such circumstances, over-reliance on fossil fuels might run out of their reserves causing an energy shortage in the near future. Utilization and burning of fossil fuels have been emitting pollutants such as CO_2, CO, SO_x, NO_x, unburned hydrocarbons and particulate matters (Muhammad et al., 2018). Between 2007 and 2020, it was estimated that about 4.1 million metric tonnes of CO_2 were released into the earth's atmosphere and 98 % of those emissions originated from transportation. These emissions have drastically increased greenhouse gases causing global warming (Ewunie et al., 2021). Moreover, burning coal in coal-fired power stations releases nitrogen oxide and sulfur oxide gases that contribute to the degradation of ozone layer. The release of such harmful gases also contributes to the formation of acid rain (Muhammad et al., 2018). Therefore, to sort out as well as alleviate the negative factors associated with environmental issues and the energy crisis, scientific communities are challenged to explore alternative fuels and their resources with great enthusiasm. Researchers are dedicated to finding a viable alternative energy source, which is the transition to clean energy, sustainability, environmental friendliness and renewability that can substitute fossil fuels (Changmai et al., 2020b; Changmai et al., 2021). Nowadays, known renewable energy sources like hydropower, solar, wind, geothermal and biofuels including bioethanol, biodiesel and biogas from biomass, are being developed for energy supply to eliminate greenhouse gas emissions (Esan et al., 2021; Awogbenni et al., 2021). Although renewable energy sources have numerous and excellent advantages, they also have some disadvantages, such as their limited availability in specific regions, low efficiency, high initial costs and high maintenance costs (Faruque et al., 2020; Osman et al., 2022). Specifically, renewable energy sources like solar, hydropower and wind are only producing electricity and cannot equally meet the demand for oil in the transportation sector or any other field associated with petrodiesel engines (Khan et al., 2021b). Notably, global energy consumption from hydropower and other renewable sources recorded a total of 12.6 % only in 2020 (BP, 2021). Thus, much more renewable energy exploration and production is a crucial need of the hour to fulfil the acute issue of energy demand. In this context, scientific communities are focusing on the production of more renewable energy from biomass. Currently, biodiesel is the best type of biofuel and is popularly known for its excellent characteristics like carbon neutrality, sulfur free, non-toxicity, renewability, sustainability, biodegradability, portability, environmental benefits and being easily manufactured (Barua et al., 2014; Singh et al., 2020b; Miyuranga et al., 2023; Neupane et al., 2023). Biodiesel fuel has advantages over petrodiesel, such as a high cetane number, low viscosity, better lubricity, a high flash point and higher combustion efficiency (Changmai et al., 2020b; Abdullah et al., 2017). Therefore, considering these characteristics of biodiesel, it has the potential to mitigate and resolve the energy crisis, health and environmental issues. In this regard, researchers are emphasizing the development of technologies for the production and utilization of biodiesel.

1.2 Biodiesel background

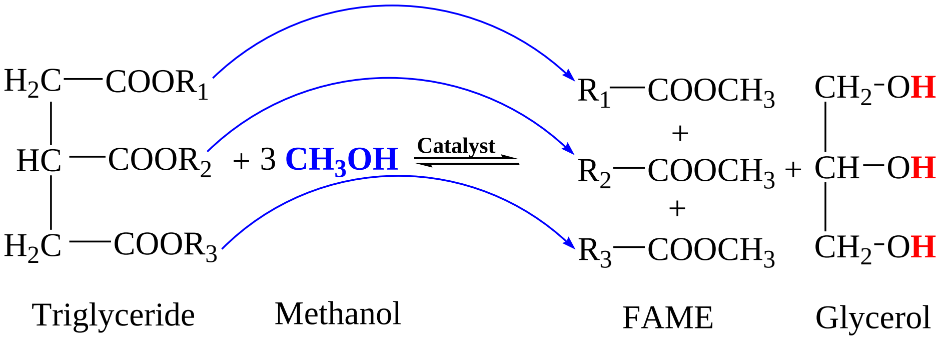
In the beginning of 1900, vegetable oil was used in place of diesel as a fuel, leading to the invention of the term "biodiesel" in 1988. A diesel engine was invented by Dr. Rudolf Diesel, and the roots of what became known as "biodiesel" can be traced back to these engines (Songstad et al., 2009). In 1900, Dr. Rudolf's engine was first demonstrated at the World

Exhibition in Paris, which ran on 100 % peanut oil. In 1911, Dr. Rudolf said “The diesel engine can be fed with vegetable oils and would help considerably in the development of agriculture of the countries which use it”. In 1912, he stated, **“**The use of vegetable oils for engine fuels may seem insignificant today. But such oils may become in course of time as important as petroleum and the coal tar products of the present time**”** (Owolabi et al., 2012). In 1940, buses in France and Belgium were powered by vegetable oil methyl and ethyl esters. Since World War II, studies have been conducted on the usage and development of vegetable oil as a biofuel (Narasimharao et al., 2007). Vegetable oil has been used since World War II from time to time (Nye et al., 1983). The first international conference on plant and vegetable oils used for fuel was held in Fargo, North Dakota, in August 1982 to propose more effective ways and to address the production of biofuel and its use issues (Demirbas et al., 2003). This conference discussed a wide range of issues, including how to handle seeds, how to extract and process seeds into oil, how the use of vegetable oil fuel affects the lifespan and performance of engines, how to produce fuel, the key parameters, and the cost of fuel generation (Ambat et al., 2018). Vegetable oil is a possible alternative energy source that may be used as a fuel for diesel engines, but using it directly has a number of drawbacks, such as reduced volatility, higher viscosity, engine knocking, carbon deposits on the engine and its pistons, gumming from oxidation, corrosion from the acid composition, polymerization and poor combustion, which leads to engine wear and worse efficiency in cold weather. These facts led to subsequent investigations focusing on other vegetable oil derivatives (Ambat et al., 2018; Yusuf et al., 2011). In this context, the four basic processes such as blending by preheating, microemulsification, pyrolysis or thermal cracking and transesterification are applied to transform animal oils or fats and vegetable oils into biodiesel (Rezania et al., 2019).

Biodiesel is an alkyl ester of long chain fatty acids that is obtained from vegetable oils or animal fats. It is a form of renewable fuel that can be used as an alternative to fossil fuels (Gashaw et al., 2015; Talha and Sulaiman, 2016). A variety of convertible feedstock oils are investigated by researchers and can be categorized as animal fats, non-edible vegetable oils, edible vegetable oils, microbial, algae, waste and recycled oils as well as mixed oils (Rahman et al., 2021; Brahma et al., 2022). The application of edible vegetable oils is considered a first-generation feedstock. A wide array of first-generation feedstocks such as mustard, palm, coconut, olive, walnut, rice bran, soybean, sunflower, canola, corn, rapeseed oil, etc. are examined for the production of biodiesel (Singh et al., 2020b; Pikula et al., 2020; Abdullah et al., 2017; Bashir et al., 2022; Oladipo et al., 2020). Although such crops are readily available and have a comparatively simple conversion process, the main disadvantage of using first generation feedstock is the risk of food supply shortages, which increase the cost of food products. The production of biodiesel from first-generation feedstock is also complicated due to its high cost and limited cultivation areas. Thus, for the production of biodiesel, scientific communities are switching to non-edible vegetable oils that are referred to as second-generation feedstock (Singh et al., 2020a). Some of the examples of second-generation feedstocks are jatropha, jojoba, mahua, tobacco seed, safflower, bitter almond oil, *Calophyllum inophyllum*, sandbox seed, karanja, rubber seed, neem, yellow oleander, moringa, coffee ground, passion seed, hone oil, etc (Veluru et al., 2022; Mofijur et al., 2020; Singh et al., 2020b; Pikula et al., 2020; Bashir et al., 2022; Rahman 2021; Oladipo et al., 2020). Using these feedstocks, we can avoid the limitations of first-generation feedstocks and solve the debate over whether a food product is a fuel (Pikula et al., 2020). Biodiesel is also derived from animal tallow, poultry fat, chicken fat, fish oil, waste cooking oil (WCO), etc. as well as from microalgal lipids such as *Dunaliellasalina* algae, *Chlorella vulgaris* algae, etc. which are considered third-generation feedstock (Singh et al., 2020a; Brahma et al., 2022; Oladipo et al., 2020). Despite the fact that third-generation feedstock has advantages such as not requiring agricultural lands, generating more oil and reducing the impact on the food supply, it also has drawbacks. For example, it is expensive to extract oil from algal biomass, and its use on an industrial scale is limited. WCO contains a high concentration of free fatty acid (FFA), which negatively influences the production of biodiesel. Animal fat derived biodiesel has a low pour point due to its FFA, and low oxidative stability due to the absence of natural antioxidants (Pikula et al., 2020). Besides that, researchers are modifying and investigating the fourth-generation biodiesel feedstock, which includes photobiological solar biodiesel, synthetic cells, electro-biofuels, etc (Singh et al., 2020b; Bashir et al., 2022). Researchers are also investigating the application of genetically modified microorganisms and techniques for the improvement of lipid yield to enhance oil extraction from microalgal biomass (Pikula et al., 2020). Although the fourth-generation feedstock offers significant advantages, it also possesses an environmental and health risk, including the release of toxic algae strains into the environment (Abdullah et al., 2019). While the biodiesel production from the fourth-generation feedstock is in the early stages of development, it could surpass the drawbacks of other generations of feedstock in the future (Pikula et al., 2020). Considering the current circumstances, non-edible vegetable feedstock is the most practical source of feedstock for the production of biodiesel due to its cost-effectiveness and environmental safety (Atabani et al., 2013; Ashraful et al., 2014).

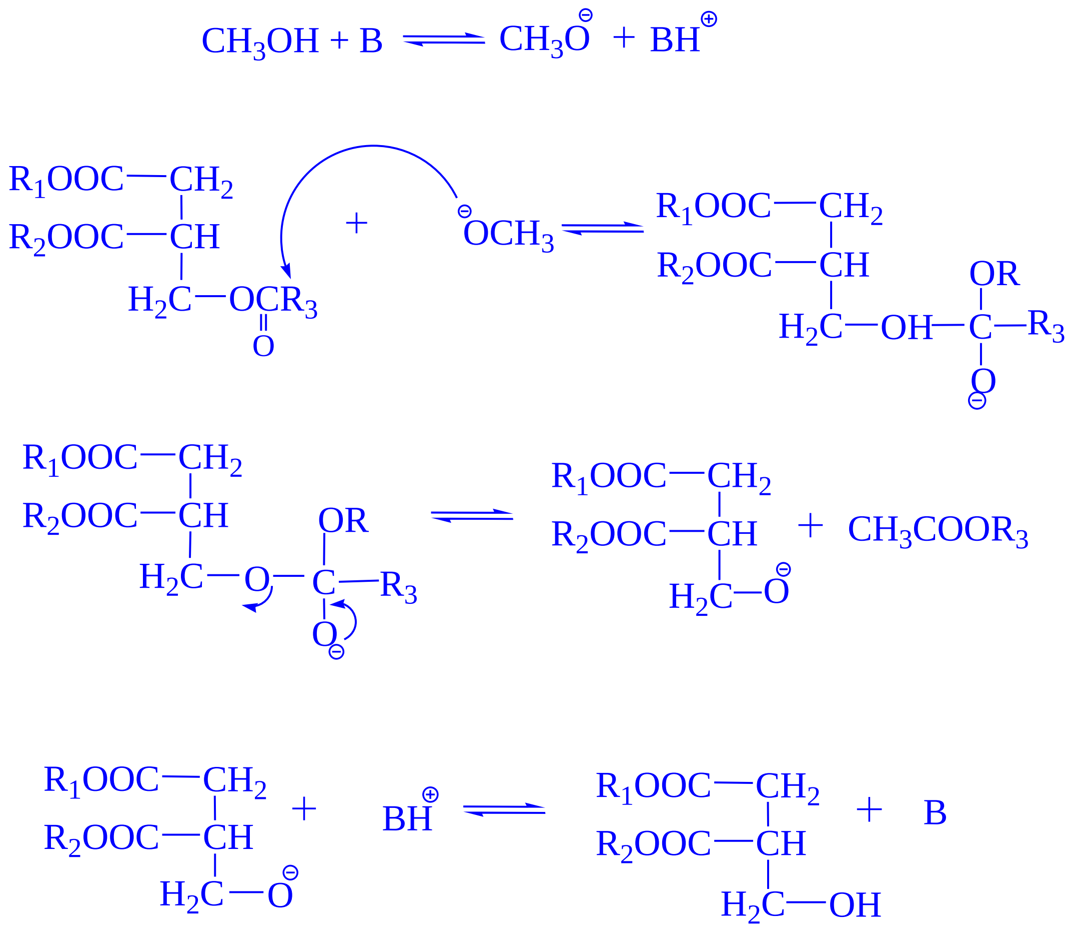
1.3 Transesterification reaction in the synthesis of biodiesel

Among the methods of biodiesel production, transesterification is considered a convenient technology and a simple procedure (Rezania et al., 2019; Bhuiya et al., 2020; Wang et al., 2023). The transesterification process can be noncatalytic, enzyme-based, and catalytic. Non-catalytic transesterification requires higher temperatures and pressures due to supercritical conditions, whereas it is not an economically viable option (Oloyede et al., 2023). Therefore, the most convenient way to produce biodiesel is through catalytic transesterification. Biodiesel production via the catalytic transesterification process involves a chemical reaction between triglycerides of vegetable or animal oils or micro-algal lipids and a typical alcohol most often ethanol or methanol, by employing an acid or base catalyst to produce fatty acid alkyl ester, i.e., biodiesel, along with the byproduct glycerol. This transesterification reaction is also referred to as alcoholysis (Ramadhas et al., 2004; Changmai et al., 2020b). The general reaction of triglyceride with methanol is shown in **Scheme 1.1**.



Scheme 1.1. Transesterification of triglyceride with methanol (Schuchardt et al., 1998; Bhuiya et al., 2016).

The base catalyzed transesterification reaction mechanism of triglycerides is illustrated in **Scheme 1.2**. The reaction mechanism has three stages, the first of which involves the interaction of the base with the alcohol, which produces an alkoxide and a protonated catalyst (Bhuiya et al., 2016). A tetrahedral intermediate is generated by the nucleophilic attack of the alkoxide on the triglyceride's carbonyl group, which in turn forms the alkyl ester and the corresponding anion of the diglyceride. Once deprotonated, the catalyst then interacts with a second molecule of alcohol to initiate a second catalytic cycle. By the same mechanism, diglycerides and monoglycerides are transformed into alkyl esters and glycerol (Schuchardt et al., 1998; Koh et al., 2011; Bhuiya et al., 2016; Changmai et al., 2020b).



Scheme 1.2. Alkali-catalyzed transesterification reaction mechanism (Schuchardt et al., 1998; Koh et al., 2011; Bhuiya et al., 2016; Changmai et al., 2020b).

Transesterification is a reversible reaction. So, excess alcohol is employed to shift the equilibrium in favor of the product (Gashaw et al., 2015). Despite the fact that stoichiometrically, 1 mole of triglyceride and 3 moles of alcohol are required to produce 3 moles of fatty acid alkyl ester and 1 mole of glycerol. Whereas excess alcohol is employed to maximize the yield of the fatty acid alkyl ester within a short duration (Mathiyazhagan et al., 2011; Salaheldeen et al., 2021). However, more excessive use of alcohol not only reduces biodiesel yield but also raises the expense of alcohol recovery (Mathiyazhagan et al., 2011). The alcohol used in the transesterification reaction is an important reactant since it assists in the conversion of triglycerides into biodiesel. The types of alcohol that can be used include methanol, ethanol, butanol, propanol, isopropanol, etc. Among these alcohols, methanol is the most commonly utilized alcohol because it has the shortest chain, reacts fast, readily dissolves and is less expensive (Gashaw et al., 2015; Oloyede et al., 2023; Abdullah et al., 2017; Demisu, 2021). When methanol or ethanol are employed, the product is known as fatty acid methyl ester

(FAME) or fatty acid ethyl ester (FAEE) which refers to biodiesel (Oloyede et al., 2023). The important parameters that influence the transesterification reaction and the biodiesel yield include the reaction temperature, mixing intensity, a molar ratio of alcohol to oil taken for reaction, concentration of a catalyst employed and the quality of the chosen feedstock such as their FFA and water content (Mandari and Devrai, 2022; Gashaw et al., 2015). Besides that, the type of catalyst used in the transesterification reaction is also one of the factors that influences the reaction rate and yield of biodiesel (Fatta et al., 2020; Talha and Sulaiman, 2016).

1.4 Catalysts used in the synthesis of biodiesel

The types of catalysts used in the production of biodiesel can be categorized as mentioned in **Fig. 1.1**. The catalysts used for the production of biodiesel are primarily acids, alkalies and enzymes (Talha and Sulaiman, 2016; Veluru et al., 2022). The utilization of homogeneous acid catalysts like H_2SO_4 (Zhang et al., 2008), HCl (Sagiroglu et al., 2011), $C_2HF_3O_2$ (Miao et al., 2009), etc. provides advantages such as being non-reactive to moisture and avoiding soap formation. However, it is also not suitable since it is non-recyclable, corrosive in nature, requires a high reaction temperature and pressure, necessitates a high amount of alcohol, and cannot be accelerated to complete the reaction faster (Talha and Sulaiman, 2016). Homogeneous bases such as KOH (Karmee et al., 2005; Refaat et al., 2008; Yusup and Khan, 2010), $NaOCH_3$ (Chen et al., 2012; Rashid et al., 2009), NaOH (Uzun et al., 2012; Ilham and Zakaria, 2009), etc. can be employed in transesterification reactions, which reflect the advantages of faster kinetics and higher activity. But such a homogeneous base also showed some limitations for feedstocks with high FFA, it is non-recyclable, the utilized catalysts become more difficult to separate from the product mixture causing a large volume of water waste (Oladipo et al., 2020). For the production of biodiesel via transesterification, the known and applicable enzyme catalysts are like lipase (Jayaraman et al., 2020), lipase immobilized on bio-support beads (Kumar et al., 2019), etc. The employment of such enzyme catalyst has a very slow rate of reaction, preparation of enzyme catalyst is expensive and they may get deactivated because they are very sensitive to alcohol (Talha and Sulaiman, 2016). Examples of heterogeneous acid catalysts are SnO_2/SiO_2 (Xie et al., 2012), WO_3/SnO_2 (Xie et al., 2013), $WO_3/AlPO_4$ (Xie and Yang, 2012), etc. Heterogeneous acid catalysts also have drawbacks because their utilization requires high reaction temperatures and pressures, consumes a larger quantity of alcohol and oil, most of the acid heterogeneous catalysts possess low catalytic activity, and is expensive too (Changmai et al., 2020b).

In the recent past, heterogeneous alkali catalysts derived from various different sources have been utilized and the tested experiments reported better performance than heterogeneous acid, homogeneous acid or base and enzyme catalysts. Heterogeneous alkali catalysts are more effective, can be recycled more than once, can avoid soap formation, better quality biodiesel is transformed in mild reaction conditions and the entire process is environmentally beneficial (Basumatary et al., 2018; Liu et al., 2008b; Reddy et al., 2007; Teng et al., 2009; Li and Rudolph, 2008). However, some of the heterogeneous alkali catalysts derived from the chemical sources such as KF-Eu_2O_3 (Sun et al., 2008), KF/Al_2O_3 (Bo et al., 2007), KF/ZnO (Hameed et al., 2009), Cs-Na_2ZrO_3 (Torres-Rodríguez et al., 2016), calcium methoxide (Liu et al., 2008b), Al_2O_3-supported metal oxides (Benjapornkulaphong et al., 2009), Ca-based metal oxides (Kawashima et al., 2008), K_2CO_3/CaO (Sahu et al., 2017), K_2CO_3-MgO (Liang et al., 2009), zirconia supported tungsten oxide (Ramu et al., 2004), KOH-Nd_2O_3 (Li et al., 2011), KF/γ-Al_2O_3 (Teng et al., 2009), etc. have drawbacks that include soap formation, saponification, active site of catalyst leaching, slower rate of reaction, only appropriate for lower FFA feedstock, and costly to synthesize such catalyst (Changmai et al., 2020b). A number of studies have reported that the CaO based catalysts derived from biomasses have produced good results for the synthesis of biodiesel (Talha and Sulaiman, 2016). Examples of such types of catalysts are snail shell (Laskar et al., 2018), oyster shell (Nakatani et al., 2009), shrimp shell (Yang et al., 2009), eggshell (Wei et al., 2009), mussel shell (Hu et al., 2011), crab shell (Boey et al., 2009), cockle shell (Boey et al., 2011), biont shell (Xie et al., 2009), chicken eggshells (Sharma et al., 2010), clamshell (Nair et al., 2012), chicken bone (Suwannasom et al., 2016), animal bones (Obadiah et al., 2012), etc. Although CaO based catalysts are very basic, non-toxic, insoluble in alcohol, inexpensive, and widely accessible, they are also sensitive to FFA (above 2 %) contents in the feedstock, where they produce undesired byproducts such as saponification and lose their effectiveness due to excessive leaching (Marinković et al., 2017; Mazaheri et al., 2021; Changmai et al., 2020b). In order to resolve the inherent problem of CaO based catalysts, they are incorporated with other chemical compounds. Some of the combined catalysts are CaO/Na-ZSM-5 (Shankar et al., 2017), K^+/CaO (Gupta et al., 2017), Na-C/CaO (Kumar et al., 2016), C/CaO/NaOH (Hadiyanto et al., 2017), Mo-Zr/CaO (Mansir et al., 2018), CaO/Fe_2O_3 (Shi et al., 2017), Li/CaO (Boro et al., 2014), etc. However, these catalysts drive up the price of producing biodiesel since the preparation of such catalysts requires extra steps like impregnation, drying and re-calcination at a certain temperature, as well as mixing with costly chemicals. In light of this, the researcher's attention has been drawn towards the derivation of an advantageous heterogeneous base catalyst with excellent catalytic activity from agricultural waste using a simple and straight forward approach (Basumatary et al., 2018).

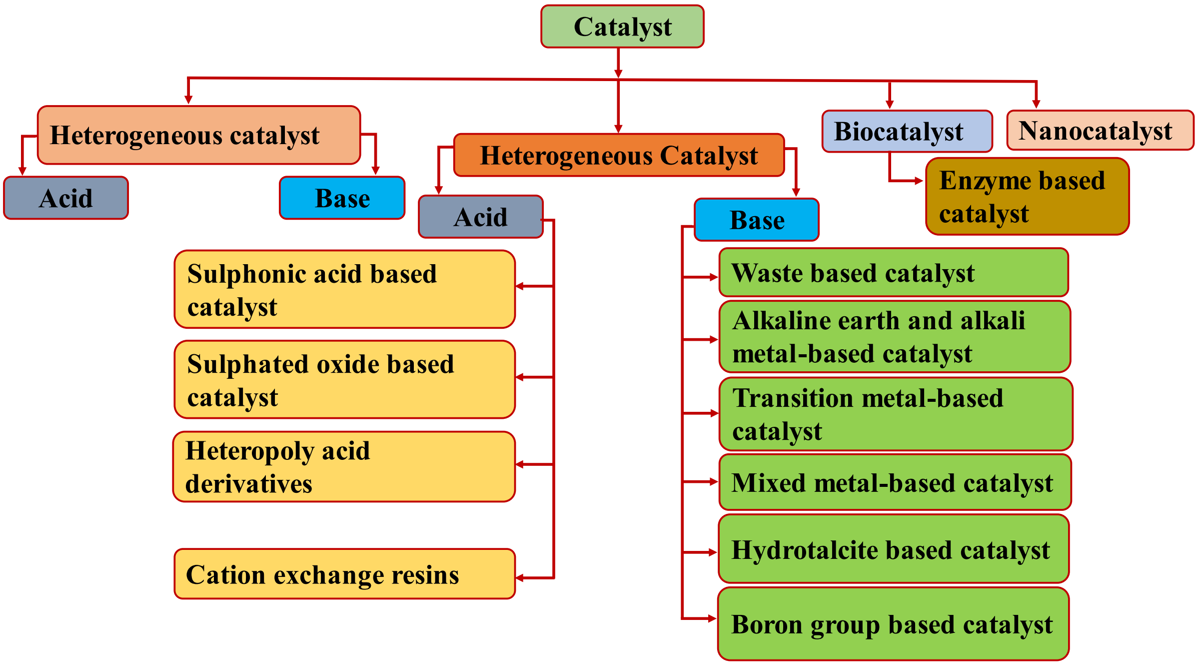


Fig. 1.1. Types of the catalysts applicable for the production of biodiesel (Fattah et al., 2020; Chouhan and Sarma, 2011; Changmai et al., 2020b).

In recent years, the use of heterogeneous base catalysts made from agro-waste materials have aroused scientific curiosity in research for the production of biodiesel. Heterogeneous base catalysts derived from agro-waste material have many advantages over other catalysts, including abundance, derived from renewable resources, cost effectiveness, ease of separation from biodiesel and glycerol, recyclable, non-toxicity, ease of handling and use, environmental friendliness, simpler synthesis process, and suitability for use in large scale industrial production (Basumatary et al., 2018). There are several agro-waste heterogeneous catalysts derived from *Tectona grandis* leaves (Gohain et al., 2020b), *Carica papaya* peel (Etim et al., 2021), *Musa* 'Gross Michel' peel (Betiku et al., 2016), wood (*Acacia nilotica*) stem (Sharma et al., 2012), bamboo leaf (Fatimah et al., 2019), *Musa acuminata* peel (Pathak et al., 2018), *Sesamum indicum* (Nath et al., 2020), cocoa pod husk (Betiku et a., 2017), rice husk (Chen et al., 2015), *Carica papaya* stem (Gohain et al., 2020a), *Musa paradisiacal* peel (Betiku and Ajala, 2014), *Heteropanax fragrans* (Basumatary et al., 2021a), *Musa balbisiana* Colla (Gohain et al., 2017), peanut husk (Dai et al., 2014), tucumã peels (Mendonça et al., 2019b), *Musa acuminate* peduncle (Balajii and Niju, 2019), kola nut pod husk (Betiku et al., 2019), cupuaçu (Mendonça et al,. 2019a), orange peel (Changmai et al., 2020a), coconut husk (Vadery et al., 2014), *Lemna perpusilla* (Chouhan and Sarma, 2013), etc. There are still many agro-waste resources from which heterogeneous solid catalysts can be derived and investigated for the faster conversion of biodiesel.

1.5 Literature review

1.5.1 Agro-waste derived catalysts and their chemical composition

Numerous agricultural wastes can be found on the earth, primarily originating from agricultural plants. The agricultural wastes mainly produced after harvesting are referred to as field residues, which include seed pods, stalks, leaf stems, etc. The residues of a process are the material left over after it has been converted into another valuable resource. Examples of process residues include stalk shell peels, stems, husks, roots, bagasse, and leaf straw (Sadh et al., 2018). It has been estimated that the world's total land biomass reserves are around 1.8 trillion tons, it is adequate to derive the catalysts and other materials (Tursi, 2019). Globally, a number of researchers have begun to work on developing green catalysts from various agricultural waste streams in order to achieve more efficient production methods and other ecological advantages for the production of biodiesel. It is advantageous to derive a catalyst from agricultural waste because reusing such agro-waste reduces waste management and environmental issues (Khan et al., 2021a). In the literature, many catalyst preparation techniques are described. In order to derive a heterogeneous solid catalyst from agricultural waste, first its residues are reported to be collected and then the material is washed in water to remove any dirt, sand, or other undesirable pollutants that may have attached to it. In the second step, materials are allowed to dry. Some of the research included drying in a hot air oven or outside in the sun (Olatundun et al., 2020; Eldiehy et al., 2022; Etim et al., 2021). The different steps included in the preparation of catalyst in different ways are described in **Fig. 1.2.** Olatundun et al. (2020) burned cocoa pod husk-plantain peel after drying and turned it into ashes and followed by calcination at 700 °C for 4 h and then ground it into a fine powder that was further characterized and applied in transesterification. Laskar et al. (2022) utilized the *Musa acuminate* flower petal just after it burned into ashes without calcination. Eldiehy et al., 2022 also prepared a solid base catalyst from sweet potato leaves. Their steps of preparation after drying in a hot air oven were followed by direct grinding of the material, which was then calcinated at 900 °C for 3 h.

Basumatary et al. (2021) reported a catalyst, calcined at 550 °C–850 °C, and an uncalcined catalyst derived from *Heteropanax fragrans* and further investigated them by employing in the transesterification reaction. According to their work, the uncalcined catalyst has less activity than the catalyst calcined at 550 ºC whereas increasing the calcination temperature to 850 °C decreased activity of the catalyst. The reported reason for the decrease in catalytic activity with increasing the calcination temperature beyond 550 ºC is that the concentration of metal carbonate decreases. Consequently, this leads to a decrease in the basicity of the catalysts. Several works investigated the elemental composition of prepared heterogeneous base catalysts from agro-wastes material which are illustrated in **Table 1.1.** Depending on the materials and method of catalyst preparation, different catalysts exhibit different compositions of elements. From the literature as described in **Table 1.1**, it can be disclosed that the catalysts prepared from agro-waste material are mainly composed of Na, K, C, O, Ca, Mg, Al, Si, P, Cl, Fe, Mn, Zn, Sr, etc. All of the agro-based catalysts may not contain all the metals mentioned above, and the composition percentage varies depending on the variety of materials. Basically, the reported compounds found in the agro-based catalysts are metal oxides and carbonates, which are the chief components that play a role in increasing the basicity of the catalysts and enhancing their catalytic activity. For instance, Pathak et al., 2018 found 70.06 % of potassium (K) and other materials along with Ca (9.54 %), Mg (1.78 %), Si (4.56 %), P (7.55 %), Cl (3.23 %), Fe (1.79 %) and O (1.03 %) in the burnt *Musa acuminate* peel catalyst. Similarly, Balajii and Niju (2019) reported K (42.23 %), Ca (1.70 %), Mg (1.39 %), Si (1.54 %), P (1.91 %) and O (50.54 %) in the catalyst derived from *Musa acuminata* peduncle. The literature review on the elemental composition of agro-based catalysts revealed that most of the catalysts have potassium as a dominant element. Such as Laskar et al. (2022) reported 45.44 % of K in burnt *Musa acuminate* flower petal catalyst, Falowo et al. (2022) obtained 45.16 % of K in ripe-unripe plantain ash, Daimary et al. (2022b) detected 36.54 % of K in potato peel and in the same manner, Nath et al. (2023) also reported K (51.93 %) as a prime element in *M. champa* peduncle. In the agro-based catalysts mentioned in **Table1.1**, some of the authors did not show the composition % of carbon or oxygen elements, which is very important for the formation of metal carbonates and oxides. Agro-based catalysts vary in composition depending on the sort of sources they are generated from, but they are often recognised by the presence of metal oxides and carbonates which may include K_2CO_3, K_2O, KCl, $CaCO_3$, CaO, SiO_2, Fe_2O_3, Al_2O_3, P_2O_5, and MgO (Abdullah et al., 2017; Khan et al., 2021a; Balakrishnan et al., 2011; Basumatary et al., 2018). The presence of metal carbonate and oxides in the catalyst contributes to raising the basicity of catalysts, making them more efficient. Possibly, the catalysts with higher concentrations of potassium existed in the form of K_2O and K_2CO_3 claimed to have excellent catalytic activity (Basumatary et al., 2018; Changmai et al., 2020b).

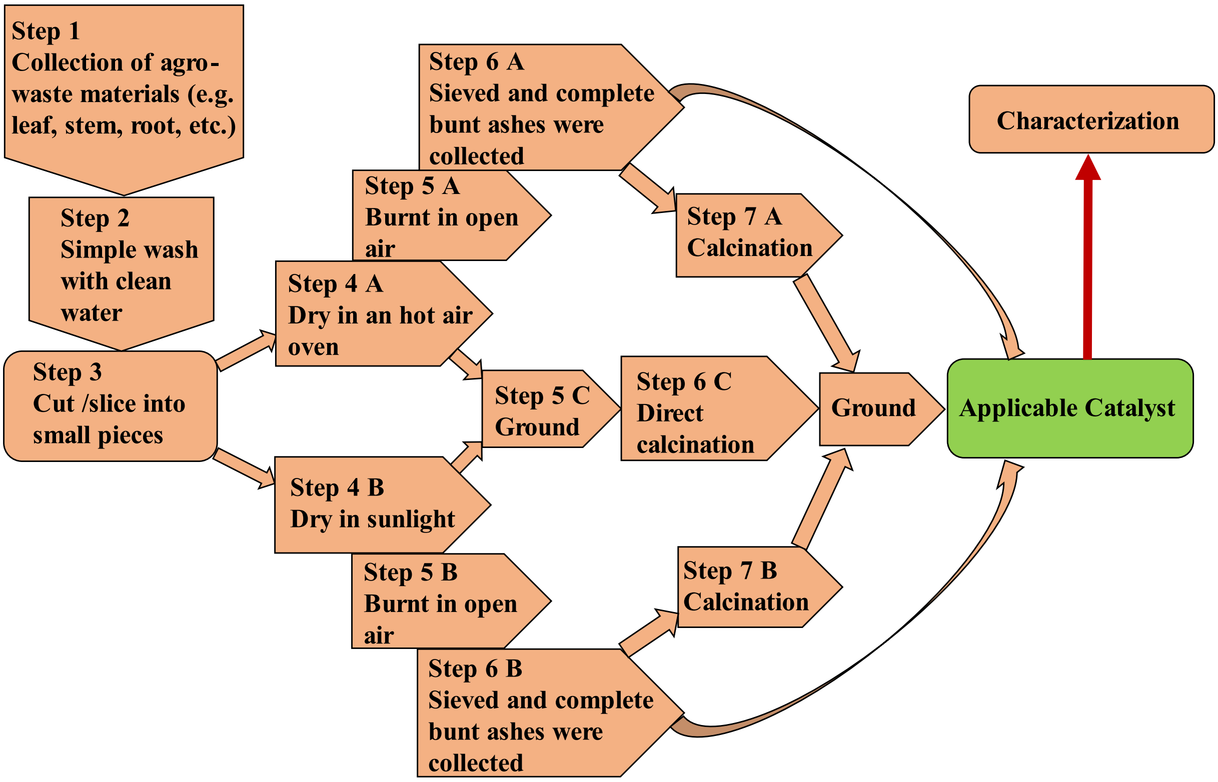


Fig. 1.2. Flow chart of different steps involved in catalysts preparation from agro-wastes.

Table 1.1: Composition of various solid base catalysts derived from waste biomasses.

Source of catalyst	**Calcination condition**	**Composition (%)**														**References**
		Na	**K**	**Ca**	**Mg**	**Al**	**Si**	**P**	**Cl**	**Fe**	**Mn**	**Zn**	**Sr**	**C**	**O**	
Musa acuminate peel	Burnt	-	70.06	9.54	1.78	-	4.56	7.55	3.23	1.79	-	-	-	-	1.03	Pathak et al. (2018)
Musa acuminata peduncle	700 °C, 4 h	–	42.23	1.70	1.39	–	1.54	1.91	–	–	–	–	–	–	50.54	Balajii and Niju (2019)
Musa spp peduncle	700 °C, 4 h	–	52.04	5.27	5.71	–	–	–	–	–	–	–	–	–	36.99	Balajii and Niju (2020)
Musa balbisiana peel	700 °C, 4 h	10.41	41.37	36.08	12.02	–	–	–	–	–	–	–	–	–	–	Gohain et al. (2017)
Carica papaya stem	700 °C, 4 h	14.78	56.71	21.08	4.41	–	3.02	–	–	–	–	–	–	–	–	Gohain et al., (2020a)
Musa acuminate flower petal ash	Burnt	-	45.44	2.4	3.05	-	1.95	2.03	-	-	-	-	-	1.9	41.84	Laskar et al. (2022)

Wheat straw	Burnt	-	7.7	1.5	1.1	-	18.2	-	1.3	-	-	-	-	41.4	28.9	Veličković et al. (2021)
Sweet potato leaves	900 ºC, 3 h	0.70	65.45	18.02	4.63	0.94	3.54	-	4.12	0.88	-	-	-	-	-	Eldiehy et al. (2022)
Waste Mangifera indica peel	Burnt	0.25	43.89	9.44	3.67	-	2.61	4.21	-	0.46	-	-	0.55	2.38	32.54	Laskar et al. (2020)
Ripe-unripe plantain ash	500 ºC, 4 h	-	45.16	-	3.61	-	3.87	-	-	-	-	-	-	12.02	35.34	Falowo et al. (2022)
Cocoa pod husk-plantain peel	700 ºC, 4 h	0.00	51.94	0.00	2.05	0.00	1.01	1.04	2.77	0.00	-	-	-	-	40.93	Olatundun et al. (2020)
Kola nut pod husk	500 ºC, 4 h	-	47.14	7.59	5.32	-	0.00	2.31	4.41	-	-	-	-	-	31.07	Betiku et al. (2019)
Theobroma grandiflorum seed	800 ºC, 4 h	1.52	54.76	3.61	17.57	-	-	18.80	-	-	-	-	-	-	-	Mendonça et al. (2019a)
Tectona grandis leaves	700 ºC, 4 h	1.67	53.25	30.28	4.77	-	10.03	-	-	-	-	-	-	-	-	Gohain et al. (2020b)

Coconut husk ash	350 °C, 3 h	2.92	42.9	-	1.21	-	3.25	-	43.57	-	-	-	-	1.29	4.44	Vadery et al. (2014)
Potato peel	700 °C, 3 h	1.85	36.54	2.71	2.02	-	3.06	-	1.24	1.30	0.45	0.10	-	9.18	41.55	Daimary et al. (2022b)
Passion fruit peel	400 °C, 4 h	-	44.4	-	-	-	-	-	16.6	-	-	-	-	7.9	-	Tarigan et al. (2022)
M. champa peduncle	550 °C, 2 h	-	51.93	4.72	1.83	-	3.60	1.53	3.52	-	-	-	-	2.48	30.38	Nath et al. (2023)
M. champa peduncle	Burnt ash	-	31.88	2.65	0.70	-	4.36	-	0.71	-	-	-	-	14.90	44.81	Nath et al. (2023)
Sesamum indicum	550 °C, 2 h	1.42	29.64	33.80	9.68	–	11.32	–	–	1.70	0.80	0.54	11.09	–	–	Nath et al. (2020)
Carica papaya peel	700 °C, 4 h	0.82	36.74	3.64	1.16	-	0.71	4.22	10.3	-	-	-	-	-	44.1	Etim et al., (2021)
Musa paradisiacal peel	700 °C, 4 h	–	51.02	–	1.15	0.29	2.51	1.84	6.27	–	–	–	–	–	36.43	Etim et al. (2018)
Pawpaw peel	600 °C, 4 h	0.00	23.89	2.86	1.00	-	0.00	3.04	0.87	0.00	-	-	-	29.16	36.72	Oladipo et al. (2020)

Musa acuminata peduncle	Uncalcined	–	25.63	–	0.97	–	0.56	0.78	–	–	–	–	–	–	72.06	Balajii and Niju (2019)
Brassica nigra	550 ºC, 2 h	0.94	56.13	26.04	2.86	–	5.37	–	–	1.26	0.05	1.63	5.72	–	–	Nath et al. (2019)
Moringa leaves	500 ºC, 2 h	–	9.87	10.09	5.92	–	–	1.19	–	–	–	–	–	12.19	59.57	Aleman-Ramirez et al. (2021)
Lemna perpusilla Torrey	550 ºC, 2 h	0.53	11.32	–	–	–	82.51	–	–	–	–	–	–	5.10	–	Chouhan and Sarma (2013)
Poovan banana pseudostem	700 ºC, 4 h	0.4	20.2	7.4	4.52	0.25	3.79	1.91	8.99	0.51	–	–	–	–	–	Niju et al. (2021)
Citrus sinensis peel	Burnt	-	8.95	5.01	1.30	-	-	-	-	27.54	-	-	-	-	37.20	Changmai et al. (2021)
Heteropanax fragrans	550 ºC, 2 h	-	19.05	5.13	0.86	0.44	8.51	0.64	1.92	-	-	-	-	16.71	46.74	Basumatary et al. (2021a)
Camphor leaf	800 ºC, 2 h	0.23	1.22	12.05	1.82	2.70	–	–	–	–	–	–	–	–	–	Li et al. (2018)

Acacia nilotica stem	800 ºC, 3 h	5.7	5.7	17.8	4.5	1.2	21.5	0.5	–	–	–	–	–	–	–	Sharma et al. (2012)
Musa balbisiana underground stem	550 ºC, 2 h	0.61 (Na_2O)	25.09 (K_2O)	10.44 (CaO)	10.04 (MgO)	4.07 (Al_2O_3)	35.92 (SiO_2)	4.47 (P_2O_5)	–	1.88 (Fe_2O_3)	–	–	1.89 (SrO)	–	–	Sarma et al. (2014)
Acacia nilotica stem	500 ºC, 3 h	0.6	6.7	13.3	2.7	8.3	15.7	0.80	–	–	–	–	–	–	–	Sharma et al. (2012)

1.5.2 Catalysts derived from agro-waste materials for biodiesel synthesis

Numerous important factors have been investigated in order to maximize the advantages of agricultural waste-derived catalysts, including the various types of agricultural waste sources, catalyst manufacturing processes, surface area, particle shape, particle size, catalytic basicity, active site density, and reusability. The alcohol to oil molar ratio, catalyst amount, temperature, and reaction time must all be limited during optimization to get the maximum biodiesel percentage (Khan et al., 2021a). The performance of various catalysts and the output of the significant parameters in the production of biodiesel from the different scientific works reported in the literature are summarized in **Table 1.2**. Laskar et al. (2022) investigated the development of a heterogeneous catalyst from *Musa acuminata* flower petals. The dried petal was burned in the air and ground into a fine powder to prepare the catalyst. According to the catalyst's characterization, chiefly K_2O (60.23 %) was present and it is the main component of catalytic activity. The catalyst's BET surface area was reported to be 79.33 m^2 g^{-1}, demonstrated catalytic activity with 99.99 % conversion in 221 min at the optimal reaction conditions of 5.63 wt. % catalyst loading and 6.24:1 MTOMR at 28 °C. Their catalyst has a maximum reusability of four runs, achieving 82 % conversion of WCO to biodiesel. They claimed that the catalyst's poor performance might be due to the leaching of active sites and also caused by the absorption of moisture, CO_2, oil on its surface, contaminants, glycerol and ester after repeated usage. A solid base catalyst derived from sweet potato leaves was utilized by Eldiehy et al. (2022) in the transesterification reaction to transform *Scenedesmus obliquus* and WCO into biodiesel. The catalyst was prepared by calcination at 600-900 °C for 3 h. Under optimum reaction conditions (ORC's), a high biodiesel conversion from *Scenedesmus obliquus* oil and WCO was recorded at 99.50 % and 98.0 % respectively. They reported that potassium (65.45 wt. %) is present in the catalyst as a dominant element in the form of oxides and carbonates with a high basic strength of $9.8 < H \leq 12.2$. The catalyst was found to be reusable up to the fifth reaction cycle with biodiesel conversion of 85.40 % under ORC's.

Daimary et al. (2022a) studied the preparation and application of a heterogeneous base catalyst from *Musa acuminata* peel for the conversion of WCO which was pretreated with H_2SO_4 (1 wt. % of oil). The conversion of 98.0 % was attained in 120 min under ideal reaction conditions, which was loaded with 1.5 wt. % of catalyst and set reaction temperature at 60 °C and added methanol to oil molar ratio (MTOMR) was of 9:1. On the fifth cycle of the reusability tests, conversion efficiency was 92.0 %. Daimary et al. (2022b) also prepared a catalyst from potato peel through pyrolysis process and obtained biochar was again calcined at 700 °C for 3 h. They also reported that their synthesized catalyst revealed high catalytic activity due to high potassium content (36.54 %) in oxide and carbonate form. The maximum oil conversion (97.50 %) was obtained in 120 min using the optimized parameters that is reaction temperature at 60 °C, MTOMR of 9:1 and catalyst loading of 3 wt. %. They performed catalyst reusability tests up to the fifth cycle where it was reported that 89 % of WCO was converted to biodiesel. Chen et al. (2015) prepared the catalyst from rice husk calcined at different temperatures (600 °C to 1000 °C) for 4 h. They reported that calcination of the catalyst source at high temperatures would affect the surface area and basicity of it. Based on catalyst preparation, they found that the catalyst calcinated at 800 °C has a high crystalline phase composition of CaO and Ca_2SiO_4 including high alkaline, basicity and surface area, which leads to high catalytic activity obtaining the highest yield of 95.1 % of biodiesel in 240 min under ORC's. They have reported 8 times reuse of their catalysts with the biodiesel yield exceeding 80 %.

Laskar et al. (2020) studied the application of the heterogeneous base catalyst derived from waste mango peel (*Mangifera indica*). Their catalyst was made by just burning in the open air until it turned into powdered ashes. Their catalyst has a quite large surface area of 123.34 m^2 g^{-1}. They also noted the basic strength of $15 < H\_ < 18.4$ obtained by Hammett indicator test. They have investigated the use of the catalyst load from 4 wt. % to 7 wt. % in room temperature through transesterification reaction. They have obtained the optimum ratio of methanol to oil at only 6:1 and a catalyst load of 6 wt. %, from which the achievement of biodiesel yield was 98 % in the reaction time of 240 min. Moreover, they reported that the reduced activation energy of 47.82 kJ mol^{-1} was found with 6 wt. % of catalyst as opposed to 5 wt. % (61.3 kJ/mol^{-1}) and 7 wt. % (55.98 kJ mol^{-1}). The catalyst decreased its activity after the fifth cycle, they have claimed that the reason for the low yield of 59 % was the leaching of active K and Ca elements. Similarly, the synthesized catalyst from *Tectona grandis* leaves by Gohain et al. (2020b) has a large surface area of 116.833 m^2 g^{-1}, which was employed in the transesterification reaction at room temperature. They have reported 100 % conversion of WCO to biodiesel in 180 min using 2.5 wt. % catalyst and 6:1 MTOMR. Their catalyst can also be reused and has been shown to reuse up to 5 cycles with decreased biodiesel yield. Olatundun et al. (2020) prepared a heterogeneous base catalyst by mixing the two variety of agro-waste materials namely cocoa pod husk and plantain peel. The cocoa pod husk and plantain peel were individually burned to ash, combined in an equal amount, and calcined at various temperatures (300-1000 °C. They reported that a sample calcinated at 500 °C showed a high concentration of two main active species K (50.95 %) and Ca (2.30 %) and considered as an ideal calcination temperature. They have investigated the production of biodiesel in the two steps, i.e., initially by esterification and then transesterification process. Their work reported the reduction of acid value of honne oil from 35.5 to 1.68 ± 0.57 g KOH/g oil. According to the reports, the pretreated oil was transesterified using their catalyst, which yielded 98.98 % of biodiesel under ORCs in 150 min of reaction time.

Sarma et al. (2014) prepared a catalyst from *Musa balbisiana* Colla underground stem (MBCUS) and applied it for the production of biodiesel from *Jatropha curcas* L. oil (JCO) which has high FFA. The ash obtained by burning in an open-air atmosphere was calcinated at 550 °C and they reported that it contains carbon (0.14 %) at 550 °C, volatile matter (7.45 %) at 350 °C and moisture (91.34 %) at 105 °C. They detected SiO_2 (36 %) and K_2O (25 %) as prime component in MBCUS catalyst. The research examined the use of MBCUS catalysts in a high pressure–high temperature (HT) reactor via transesterification reaction and demonstrated 98.0 % of biodiesel production at HT (275 °C) and internal pressure (4.2 MPa) with 9:1 ratio of alcohol to oil in 60 min of reaction time. Their work reported that the high FFA containing in JCO can be used for biodiesel production in a single batch by avoiding the process of two step transesterification. The use of a heterogeneous base catalyst was also studied by Barros et al. (2020) derived from waste pineapple leaves. Their study illustrated the fast conversion of soybean oil into biodiesel of 98 % in 30 min under the reaction parameters of a high MTOMR of 40:1, 4 wt. % of catalyst load and the reaction temperature at 60 °C via tranesterification process. They have examined the reuse of the catalyst up to four times, achieving conversions above 85 %. Nath et al. (2023) also utilized *Musa champa* peduncle as a heterogeneous base catalyst in transesterification reaction for the production of biodiesel in short period of reaction time. They have considered 550 °C as an ideal calcination temperature. The ORCs were 12:1 MTOMR, 7 wt. % catalyst, at the reaction temperature of 65 °C where a high % of biodiesel (98.23 %) was obtained in a very short period of time i.e. 6 min. In their work, highest percentage of potassium (51.93 wt. %) was reported in the form of oxide and carbonates. They reported that the catalyst has micro-mesoporous structure and follows pseudo-first order kinetic model. Miladinović et al. (2020) prepared a heterogeneous base catalyst from walnut shell catalyst by burning it to biochar and calcinating it at 800 °C. According to reports, the produced catalyst had a surface area of 8.8 $m^2 g^{-1}$ and mainly consisted of K (26.29 %), Ca (11.62 %), and Mg (6.77 %). They obtained a maximum biodiesel yield of 98 % in minimum reaction time of 10 min by employing 5 wt. % of catalyst in the transesterification reaction at 60 °C and by using methanol and sunflower oil in a ratio of 12:1. They reported that such excellent catalytic activity is due to its alkali in nature of the metal oxides (dominantly CaO and K_2O). They regenerated the catalyst which was recalcinated at 800 °C and reused for fourth times. Their study also explained that while increasing catalyst loading and MTOMR, the reaction rate increased, which shortened the reaction times to achieve the highest biodiesel yields.

Moreover, in literature there are several works of utilization of agro-waste heterogeneous base catalysts including birch bark (Uprety et al., 2016), ginger leaves (John et al., 2021), *Tamarindus indica* fruit shell ash (Nabora et al., 2019), *Musa paradisiacal* peels (Betiku and Ajala, 2014) and *Musa balbasiana* peel (Gohain et al., 2017) were reported to transform variety of oils into biodiesel with satisfactory yield % only, catalyst loading from the range of 1.6-5 wt. % with mild ratio of methanol to oil and the reaction temperature at 60 °C. Additionally, some agro-wastes based catalysts such as *Musa spp* “Pisang Awak” (Balajii and Niju, 2020), cocoa pod husk (Betiku et al., 2017), kola nut pod husk (Betiku et al., 2019), *Brassica nigra* (Nath et al., 2019), *Sesamum indicum* (Nath et al., 2020) and poovan banana pseudostem (Niju et al., 2021) were employed at 65 °C for the production of biodiesel revealing high percentage of biodiesel yield % in short period of reaction time. The effectiveness of a few additional catalysts made from agricultural waste are summarized in **Table 1.2**. Overall, the literature review of the agro-waste catalysts illustrated that such types of catalysts have the tendency to produce biodiesel in the most convenient process. The application of such catalysts is noted as environmentally benign, non-toxic and cost-effective since they are easily prepared, materials are abundant and they are recyclable a number of times (Basumatary et al., 2018; Olatundun et al., 2020; Veličković et al., 2021).

Table 1.2: Comparisons of the catalysis of transesterification reaction by various catalysts from waste biomasses in the production of biodiesel from diverse oil feedstocks.

Biodiesel feedstock	**Catalyst source (Ash)**	**Surface area ($m^2\ g^{-1}$)**	**Parameters**				**Biodiesel, Y or C (%)**	**Recyclability**		**References**
			Catalyst (wt. %)	**MTOMR**	**Temp (°C)**	**Time (min)**		**No. of cycle**	**Biodiesel, Y or C (%)**	
WCO	*Musa acuminata* flower petal	79.33	5.63	6.24:1	28	221	99.99 (C)	4	82 (Y)	Laskar et al. (2022)
Scenedesmus obliquus oil	Sweet potato leaves	2.81	7	15:1	60	90	99.50 (C)	5	85.40 (C)	Eldiehy et al. (2022)
WCO	Sweet potato leaves	2.81	5	9:1	60	120	98.0 (C)	5	85.40 (C)	Eldiehy et al. (2022)
WCO	*Musa acuminata* peel	12	1.5	9:1	60	120	98 (C)	5	50.60 (C)	Daimary et al. (2022a)
WCO	Potato peel	23.5	3	9:1	60	120	97.5 (C)	5	89 (C)	Daimary et al. (2022b)
Soybean oil	*Mangifera indica* peel	123.34	6	6:1	RT	240	98 (Y)	5	59 (Y)	Laskar et al. (2020)
WCO	*Carica papaya* stem	78.6	2	9:1	60	180	95.23 (C)	5	>85 (C)	Gohain et al. (2020a)

Honne oil	Cocoa pod husk-plantain peel	18.86	4.5	15:1	65	150	98.98 (Y)	3	-	Olatundun et al. (2020)
Jatropha oil	MBUS	38.7	5	9:1	275	60	98 (Y)	3	-	Sarma et al. (2014)
Soybean oil	Pineapple leaves	-	4	40:1	60	30	>98 (C)	4	>85 (C)	Barros et al. (2020)
Jatropha oil	*Musa champa peduncle*	8.57	7	12:1	65	6	98.23 (Y)	3	90.03 (Y)	Nath et al. (2023)
Sunflower oil	Walnut shell	8.8	5	12:1	60	10	98 (Y)	4	-	Miladinović et al. (2020)
Palm oil	Birch bark	-	3	12:1	60	180	88.06 (Y)	-	-	Uprety et al. (2016)
Yellow oleander oil	MB trunk	1.4	20	20:1	32	180	96 (Y)	2	91 (C)	Deka and Basumatary (2011)
Sunflower oil	Wheat straw	98.5	11.6	18.3 :1	60.3	124	98.6 (Y)	3	-	Veličković et al. (2021)
Palm oil	Passion fruit peel	-	7	15:1	RT	30	95.4 (Y)	5	63 (Y)	Tarigan et al. (2022)
WCO	Ripe-unripe plantain ash	1.10	0.5	6:1	45	45	97.96	5	-	Falowo et al. (2022)

Sunflower oil	Ginger leaves	0.834	1.6	6:1	60	90	90.13 (Y)	-	-	John et al. (2021)
Parinari curatellifolia seed oil	*Tamarindus indica* fruit shell ash	378	5	9:1	60	120	96.2 (Y)	4	74.2 (Y)	Nabora et al. (2019)
WCO	*Tectona grandis* leaves	116.833	2.5	6:1	RT	180	100 (C)	5	>70 (C)	Gohain et al. (2020b)
Ceiba pentandra oil	*Musa spp* “Pisang Awak”	-	1.978	9.20:1	65	60	98.69 (Y)	-	-	Balajii and Niju (2019)
Soybean oil	*Theobroma grandiflorum* seed	-	10	10:1	80	480	98.36 (C)	2	98 (C)	Mendonça et al. (2019a)
Azadirachta indica oil	Cocoa pod husk	2.76	0.65	0.73 (v/v)	65	57	99.3 (Y)	-	-	Betiku et al. (2017)
Kariya Seed Oil	Kola nut pod husk	5.2199	3	6:1	65	75	98.67 (Y)	4	96.28 (Y)	Betiku et al. (2019)
Yellow oleander oil	*Musa paradisiacal* peels	–	3	0.3 (v/v)	60	90	95.25 (Y)	-	-	Betiku and Ajala (2014)
Jatropha oil	*Lemna perpusilla*	9.6	5	9:1	65	300	89.43 (Y)	3	-	Chouhan and Sarma (2013)
Mesua ferrea oil	MBUS	38.7	5	9:1	275	60	95 (C)	3	-	Aslam et al. (2014)

Bauhinia monandra oil	Banana peel	4.4	2.75	7.6	65	69	98.5 (C)	-	-	Betiku et al. (2016)
WCO	MB peel	14.0	2	6:1	60	180	100 (C)	5	50 (C)	Gohain et al. (2017)
Soybean oil	MA peel	1.4	0.7	6:1	32	240	98.95 (C)	4	52.16 (C)	Pathak et al. (2018)
Ceiba pentandra oil	MA peduncle	45.9	2.68	11.46:1	65	106	98.73 (C)	3	>90 (C)	Balajii and Niju (2020)
Palm oil	Banana peel	4.4	4	3:2.4	65	65	99 (Y)	-	-	Odude et al. (2019)
Yellow oleander oil	*Brassica nigra*	7.3	7	12:1	65	25	97.78 (Y)	3	96 (Y)	Nath et al. (2019)
Jatropha oil	*Brassica nigra*	7.3	7	12:1	65	30	98.26 (Y)	3	96 (Y)	Nath et al. (2019)
Soybean oil	*Brassica nigra*	7.3	7	12:1	65	25	98.79 (Y)	3	96 (Y)	Nath et al. (2019)
Soybean oil	Tucumã peels	1.0	1	15:1	80	240	97.3 (C)	5	60 (C)	Mendonça et al. (2019b)
Sunflower oil	*Sesamum indicum*	3.6	7	12:1	65	40	98.9 (Y)	3	94.2 (Y)	Nath et al. (2020)

Moringa oleifera oil	Pawpaw peel	3.6	3.5	9:1	35	40	96.43 (Y)	4	90.10 (Y)	Oladipo et al. (2020)
Soybean oil	Orange peel ash	605.60	7	6:1	RT	420	98 (C)	5	85 (C)	Changmai et al. (2020a)
Madhuca indica oil	Poovan banana pseudostem	4.58	5.9	14.9:1	65	178	97.97 (C)	3	>90 (C)	Niju et al. (2021)
Soybean oil	*Moringa oleifera* leaves	–	6	6:1	65	120	86.7 (Y)	3	53.11 (Y)	Aleman-Ramirez et al. (2021)
Used vegetable oil	*Carica papaya* peel	–	3.5	12:1	65	60	97.5 (Y)	3	88.5 (Y)	Etim et al. (2021)
Jatropha curcas oil	Coconut husk ash	-	5	12:1	45	60	99.77 (Y)	-	-	Vadery et al. (2014)
Jatropha oil	*Heteropanax fragrans*	27.50	7	12:1	65	65	97.75 (Y)	3	90.22 (Y)	Basumatary et al. (2021)
Calophyllum inophyllum oil	Residual ash from sugarcane leaves	–	5	19:1	64	180	97 (Y)	10	<80 (Y)	Arumugam and Sankaranarayanan (2020)

MTOMR–methanol to oil molar ratio; wt–weight; min–minute; Temp–temperature; C–conversion; Y–yield; MBUS–*Musa balbisiana* underground stem; MB–*Musa balbisiana*; MA–*Musa acuminata*; WCO-Waste cooking oil.

1.5.3 Fuel properties of biodiesel

The fuel properties of produced biodiesel from variety of feedstock must meet the quality requirements set by international regulations in order to perform engines without any problems. The quality of biodiesel can be characterized by measuring many parameters or examining in different units including its density at 15 ºC (g/cm), viscosity (40 ºC, $mm^2 s^{-1}$), cetane number, acid value (mg of KOH/g), iodine value (g I_2 /100 g), calorific value (MJ/kg), saponification value **(**mg KOH/g), American petroleum index**,** diesel index**,** flash point (ºC), cloud point (ºC), pour point (ºC), cold filter plugging point (ºC), etc. Moreover, the physicochemical properties of synthesized biodiesel are affected by the quantity of fatty acid composition in the source feedstock, degree of saturation as well as the length and branching of the fatty acid chain. Besides that, the quality of biodiesel is strongly influenced by the production methods, reaction operating conditions and type of catalyst employed. In addition, contamination of feedstock's unreacted glycerides and non-fatty acids fraction may affect the quality of biodiesel (Reddy et al., 2018). The fuel properties of the biodiesel synthesized by using the agro-waste based heterogeneous catalysts from different feedstocks are shown in **Table 1.3**. Their work illustrated that the biodiesel produced through the transesterification reaction and catalyzed by an agro-waste based heterogeneous catalyst has reduced density and viscosity and is well comparable with petro-diesel. Most of the stated cetane numbers for biodiesel shown in **Table 1.3** are greater than those for petro-diesel and above the minimal requirements of international standards. The biodiesel produced in their research appears to have good fuel quality indicating no ignition delay and improved cold start specifications (Benni et al., 2021). The flash point values of the biodiesel specified in **Table 1.3** are higher than those of petro-diesel, which means it is suitable for storage, handling and transport. In fact, the flash point varies in inverse proportion to the volatile nature of the fuel (Silitonga et al., 2013). The calorific values of biodiesel cited in **Table 1.3** are above the minimum limits prescribed by EN–14214 standard reflecting that biodiesel generates an energy acceptable for a good fuel. Overall, it is evident from the stated fuel characteristics shown in **Table 1.3** that the biodiesel produced using the transesterification method and catalysts made from agricultural waste satisfy the requirements of ASTM D6751 and EN-14214 standards.

Table 1.3: The fuel properties of synthesized biodiesel using agro-waste based heterogeneous catalysts and comparison with petro-diesel /International standard.

Biodiesel Feedstocks/Petro-diesel/International standards	**Properties**													**References**
	Density (15 °C, g/cm³)	**KV (40 °C, mm²/s)**	**CN**	**CI**	**PP (°C)**	**FP (°C)**	**CP (°C)**	**AV (mg of KOH/g)**	**IV (g I_2 /100 g)**	**DI**	**SV (mg KOH/ g)**	**CV (MJ/kg)**	**API**	
WCO	0.88	3.90	52	-	-6	148	-4	0.25	-	-	-	39.80	-	Daimary et al. (2022b)
JCO	0.875	5.7	48.6	-	+3	110	-	4.000	119.0	-	-	39.25	-	Sarma et al. (2014)
JCO	0.891	6.800	-	-	-	108	-	0	-	-	-	37.100	-	Chouhan and Sarma (2013)
JCO	0.875	4.75	48.3	-	-6	112	-	4.6	74.5	-	-	38.35	-	Kumar et al. (2016)
JCO	-	4.07	-	-	-	-	-	0	109	-	-	-	-	Vadery et al. (2014)
Soybean oil	0.86	5.88	51	-	-0.2	146	2	-	-	-	-	38.2	-	Changmai et al. (2020a)

Scenedesmus obliquus oil	0.870	31	-	-	-1	-	5	0.96	-	-	-	-	-	Eldiehy et al. (2022)
WCO	0.85	4.15	58	-	-9	148	-5	0.07	-	-	-	39.32	-	Gohain et al. (2020b)
WCO	0.865	5.37	52	-	-2	-	0	0.52	-	-	-	-	-	Laskar et al. (2022)
Sunflower oil	0.8669	3.69	-	-	-	-	-	0.1	110	-	-	-	-	Veličković et al. (2021)
WCO	0.860	3.2	52	-	-3	145	-2	0.10	-	-	-	40	--	Daimary et al. (2022a)
Yellow oleander oil	0.875	4.33	61.5	62.9	+3	75	+12	0.057	69.9	-	-	44.986	-	Deka and Basumatary (2011)
Honne seed oil	870.19	5.98	55.1126	-	-	-	-	0.45	76.14	-	-	39.66	-	Olatundun et al. (2020)
Moringa Oil	0.877 (25 ºC)	4.95	63.05	-	+12	-	+18	0.224	-	-	-	40.70	-	Oladipo et al. (2020)
Palm oil	-	4.7	44.4	-	-3	300	+12	0.5	24.7	47.78	-	-	30.51	Odude et al. (2019)

Yellow oleander oil	0.816	3.92	234.58	-	-	-	-	0.508	73.20	311.918	26.648	47.312	23.484	Adepoju et al. (2018)
WCO	0.89	3.12	55	-	-9	145	-4	0.08	-	-	-	40.20	-	Gohain et al. (2017)
Yellow oleander oil	0.887	6.0	123.25	-	+1	-	+8	0.46	90.23	157.29	-	-	28.03	Betiku and Ajala (2014)
Petro-diesel	0.820-0.845	2-4.5	51.0	-	-	52-96	-	-	-	-	-	43.1	-	Sarma et al. (2014); Kumar et al. (2016)
ASTM–D6751 standard	–	1.9−6.0	47 (min)	–	-	93 (min)	-	0.50 (max)	NS	331.0	-	NS	36.95	-
EN–14214 standard	0.86−0.90	3.5−5.0	51 (min)	–	-	120 (min)	-	0.50 (max)	120 (max)	-	-	35 (min)	-	-

WCO- Waste cooking oil; JCO- *Jatropha curcas* oil; PP–Pour point; KV– Kinematic viscosity; SV– Saponification value; FP–Flash point; CP–Cloud point; AV–Acid value; IV–Iodine value; CV–Calorific value; DI– Diesel index; API– American petroleum index; min–minimum, max–maximum.

1.6 Significance and scope of the present research work

The present study has the scope to challenge the issues associated with the employment of homogeneous base or acid catalyst for the production of biodiesel. Although homogeneous alkali catalysts, such as NaOH, KOH, etc., are frequently employed in the synthesis of industrial biodiesel because of their quick reaction rate, these catalysts are difficult to remove from the product and cannot be recycled, which raises the cost of manufacturing. Furthermore, homogenous alkali catalysts do not work well with feedstock that contains high of FFA and are not environmentally friendly. Therefore, researchers are still exploring a catalyst which can be easily prepared, abundant and cheap, possesses high catalytic activity, environmentally friendly and recyclability. Recently, there have been many reports on heterogeneous base catalysts for the production of biodiesel derived from biomasses. Among the biomass sources of the catalyst, the use of heterogeneous base catalysts derived from agro-waste is more beneficial because they are readily available, easily derivable and the usage of such catalysts reduces the waste dumping. Besides that, such catalysts do not produce any harmful byproducts, do not mix with biodiesel, and are easily recoverable and reusable. Employment of heterogeneous base catalysts derived from agro-waste can reduce the overall production cost of biodiesel on an industrial scale.

Considering environmental constraints, cost-effectiveness and the problems associated with the usage of homogeneous acid or base catalysts, the present study targeted the search for a heterogeneous alkali catalyst with high activity. In this work, it is the opportunity to be the first candidate to investigate the preparation and utilization of catalyst derived from agricultural post-harvested materials viz. *Musa paradisiaca*, *Musa champa*, sugarcane bagasse and Bharatmoni banana (*Musa* AAA) plants. The post-harvest banana wastes are replenished with potassium element which will help in enhancing the activity of the catalyst. The Bodo community of Assam in India use different section of post-harvest banana plants and other agricultural post- harvest material for the preparation of *Khardwi.* The term *Khardwi* is a word in the Bodo language which has been used as food additive for preparing many traditional cuisines. *Khardwi* is made from the water extract of banana ash, which is highly alkaline in nature. This high alkaline property of the material could be developed into an effective catalyst for the production of biodiesel. In this context, the application of post-harvest materials for catalyst preparation could provide an opportunity for cost-effective and environmentally benign biodiesel production. Moreover, investigation of the employment of heterogeneous base catalysts from such materials rich in potassium and highly basic could have distinct characteristics with high catalytic activity and would be more beneficial because of their renewability and degradability.

1.7 Objectives of the current work

The aim of the present study is to search the potential catalyst which is both cost-effective as well as eco-friendly apart from exhibiting high catalytic activity in biodiesel production. Following are the objectives of the present research.

(a) To collect the post-harvest plants or agro-wastes for catalyst preparation.
(b) Transesterification of non-edible oil to biodiesel using the catalyst and reusability study of the catalyst.
(c) The produced biodiesel will be analyzed using FT-IR, GC-MS, ^{1}H NMR and ^{13}C NMR.
(d) Determination of fuel properties of the biodiesel.