# Chapter 1

## Introduction

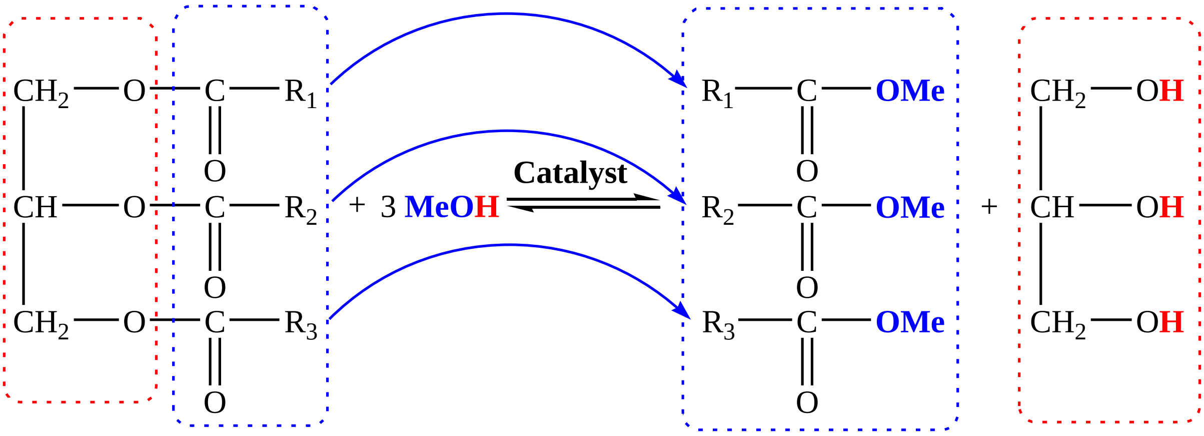
### 1.1 Biodiesel: An overview

Global energy demand is being astonishingly increasing with the growth of population as well as expansion in urbanisation along with industrialization and transportation. Besides electricity, fuel is the most significant energy source to run the modern-day society and fossil fuels are accomplishing the major energy demand [1]. Out of total global energy consumption, 81% is associated with fuel and the 90% of the need is being satisfied by fossil resources [1,2]. Amongst the total worldwide energy consumption, 54% is being spent in the transport sector which is increasing at an average rate of 1.1% yearly and by 2050, the total energy consumption of the world is estimated to rise by triggering 57% [3]. To mitigate the increasing energy demand, fossil fuels are being utilized in massive amount which leads to the depletion of the petroleum reservoirs in a high rate of $10^5$ times of its natural creation, escalating a situation of energy crisis for the near future [1,4]. The present shrinking rate of petroleum resources projected that these may exhaust by 2050 which may create a situation of perilous energy emergency [1,5]. Furthermore, the combustion of fossil fuels leads to the emission of greenhouse gases which is contributing a lot to environmental pollution. Accordingly, the mankind is pushing own self to an environmental threat with increasing global warming [1,4]. To combat with the present dwindling situation of energy sources and environmental worries, emphasis on the development of alternative renewable and environmentally benign energy sources for utilization is being intensified from the last two decades [6].

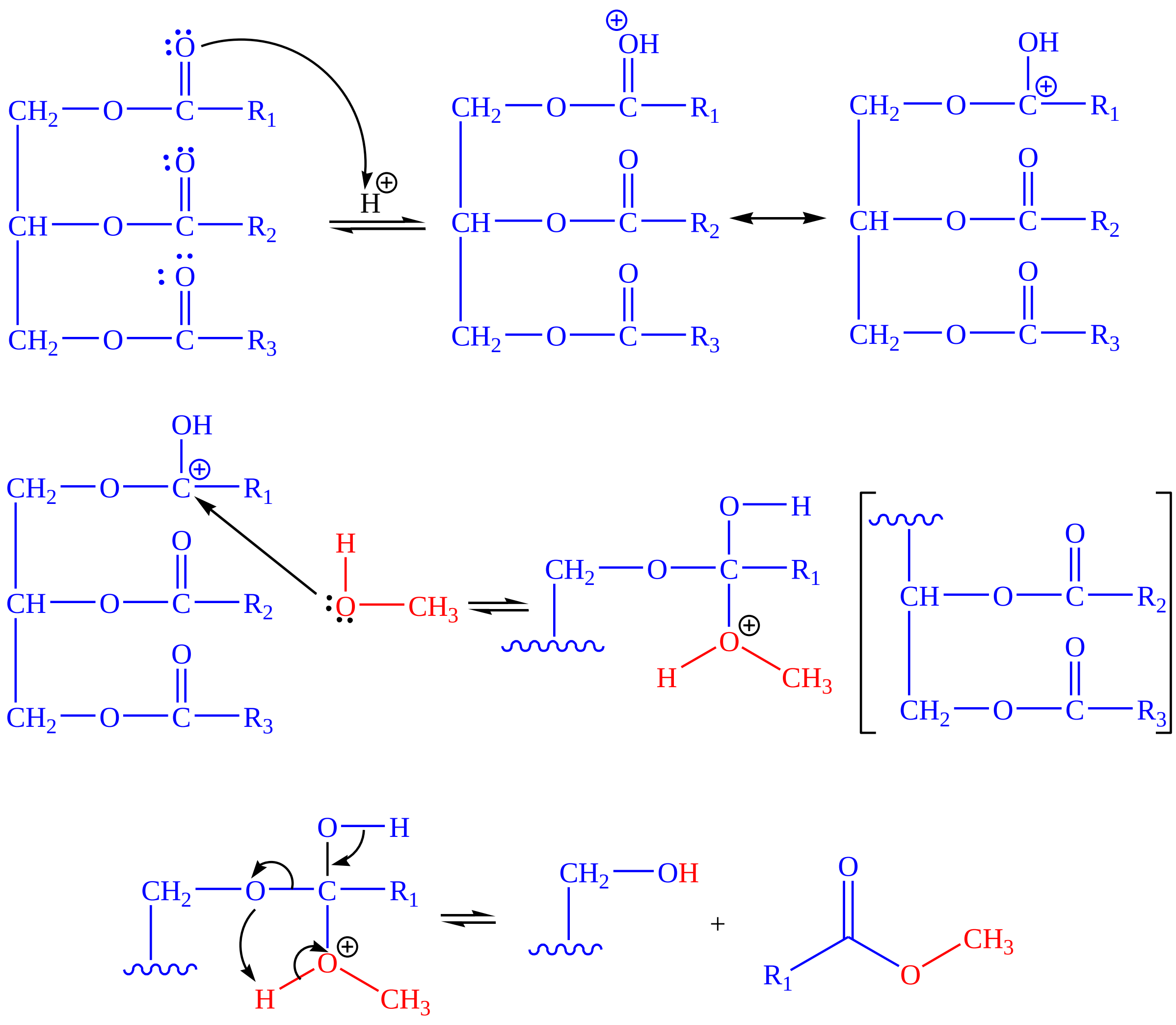
There are diverse renewable energy resources such as solar, wind, hydro, tidal, geothermal and biomass, and except biomass, all are being utilised in the generation of electricity rather than fuel. These resources can hardly overcome the contemporary and impending major energy demand of fuel. Therefore, urgent need of an alternate energy source to combat the scarcity of petrodiesel is a burning issue. In this context, conversion of biomass to energy particularly to biofuel is a persuading field of sustainable alternate energy for the future. Biofuels such as biodiesel, bioethanol and biogas have emerged as the potential renewable fuels that can supplant the conventional fossil fuels [7,8]. To alleviate the fuel demand of transport and allied sectors, a renewable green fuel which can directly be used in diesel engine or by blending with petrodiesel is of high priority. From the last two decades, biodiesel prepared from various renewable natural resources is gaining global attention as an environmentally friendly and sustainable alternative since it is biodegradable, non-toxic, carbon-neutral, and renewable [8]. The chemical composition, and flow and combustion properties of biodiesel are also similar to those of diesel and thus can be effectively used by blending with diesel in diesel-engine directly or with slight modification of the engine to provide similar engine performance [9,10]. Biodiesel is advantageous over conventional fossil fuel as it possesses high cetane number, high flash point, low viscosity, and good lubricity. It contains no sulphur and aromatics and thus, resulting in the increase of engine durability as well as reduces the emission of particulate matters, CO, $CO_2$ and $NO_x$ [7,11,12]. In addition to that, biodiesel has lower ignition delay time and high combustion efficiency which is preferable for good engine life [13]. Thus, the combustion of biodiesel significantly will reduce the adverse effect on the environment and can succeed the present high energy demand at least to some extent as well as can be a sustainable alternative fuel for the future. Sustainable development in the field of alternate energy is dependent on the availability of feedstocks as well as their environment-friendly behaviour along with cost-effectiveness. A variety of oil feedstocks were investigated for the synthesis of biodiesel. Depending on the types and sources, biodiesel feedstocks are specified as the first generation, second generation, third generation and fourth generation feedstocks. The first-generation biodiesel feedstocks are edible oils such as rapeseed, soybean, palm, sunflower, peanut, safflower, corn, rice bran, coconut, hazelnut, olive, castor, mustard, milkweed seed, linseed, walnut, cotton seed, etc. [14–16]. These feedstocks inherently compete with food, and accordingly their usage as biodiesel feedstock is hotly debated [14]. The second-generation feedstocks are non-edible oils such as *Jatropha curcas*, *Thevetia peruviana*, *Pongamia glabra*, *Nicotiana tabacum*, *Crotalaria retusa*, *Simarouba glauca*, *Xanthium spinosum*, *Croton tiglium*, rubber tree, neem, *Madhuca indica*, *Calophyllum inophyllum*, etc. [15–18]. These feedstocks overcome the limitations of first-generation biodiesel as these are generated from non-edible sources, diminishing the food versus fuel debates [19]. The third-generation feedstocks are waste oils/fats from cooking oils, restaurant grease, beef tallow, animal fats, pork lard, chicken fat, poultry fat, etc. as well as algae/microalgae such as *Chlorella* sp., *Chlorella vulgaris*, *Botryococcus braunii*, *Dunaliella salina*, etc. [15,19,20]. The third-generation feedstock, microalgae, is not economically competitive compared to first- and second-generation feedstocks due to low lipid yield and very high production cost as well as expensive oil extraction process [15,19,21]. Third generation feedstock from waste oils needs to be processed before biodiesel production resulting the addition of supplementary cost in the overall production process [22]. The fourth-generation feedstocks are genetically modified microalgae, macroalgae and cyanobacteria such as *Chlamydomonas reinhardtii* sp., *Phaeodactylum tricornutum* sp., *Thalassiosira pseudonana* sp., etc. [15,16,19–21,23]. The fourth-generation biodiesel feedstocks possess very high initial investment and is yet in the infancy stage of development [15,23]. Genetically modified microalgae, the fourth-generation biodiesel feedstock, can overcome the limitation of low lipid yield of third generation feedstock by increasing the lipid yield to 35% [19]. The major disadvantage of fourth generation biodiesel feedstock is the high risk of leaking of genetically modified organism to the environment that may lead to ecological disruption [21,24]. However, the energy efficiency of first-generation biodiesel is comparatively higher than other generations [19]. In view of environmental issues, the integration of some or all four generation of biodiesel feedstocks for commercial production seems to be viable [16]. However, to mitigate the potential environmental risk factors, research and development on genetically modified microalgae, as well as advancement of low-cost harvesting technique may overcome the difficulties of fourth generation biodiesel feedstocks. And concerning the present scenario, currently the second-generation biodiesel feedstock may provide economic pathway for cost-effective biodiesel production.

## 1.2 Catalysts in biodiesel synthesis

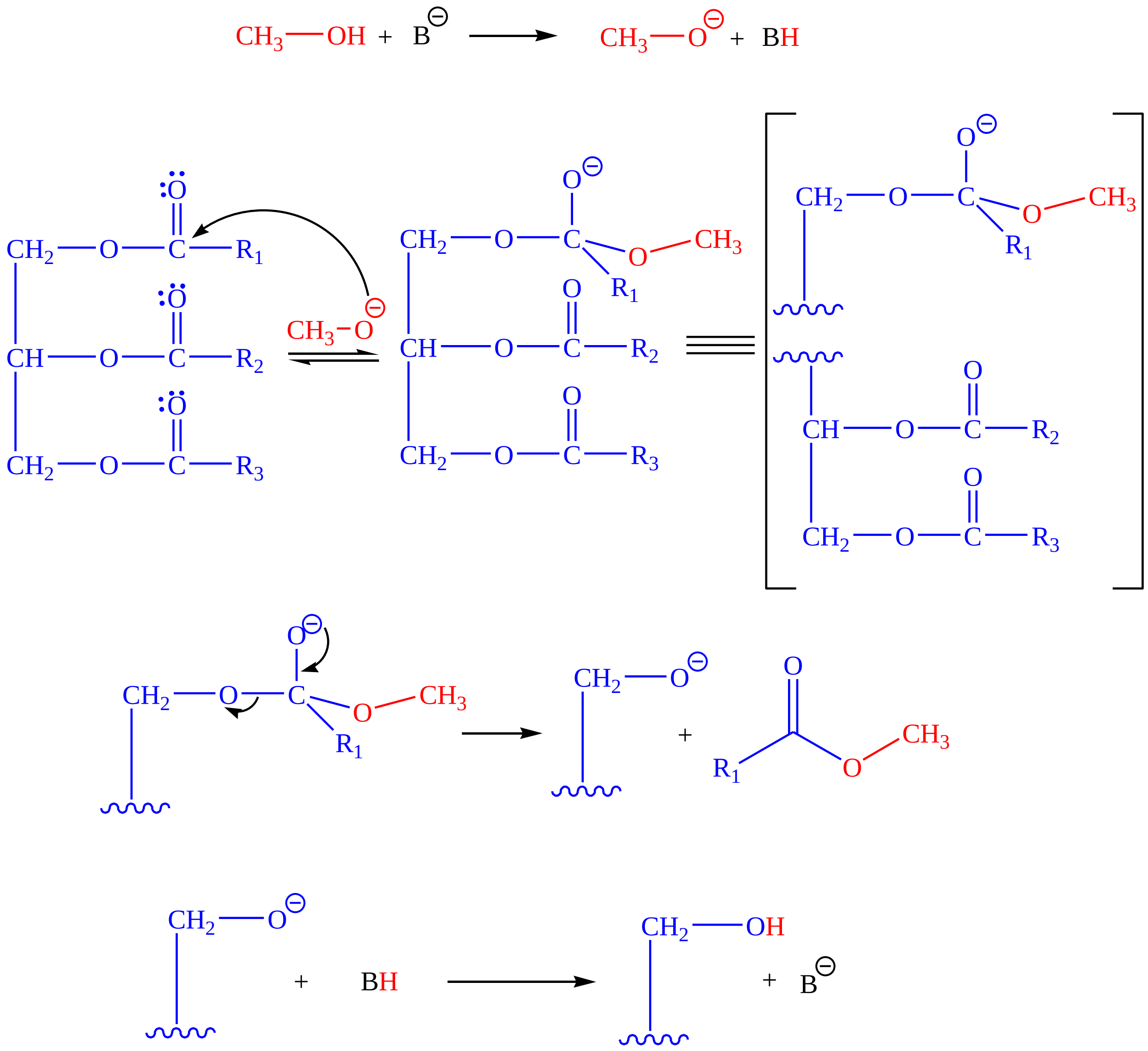
Biodiesel is prepared from vegetable oils via a number of ways of which four different approaches have been reported and these are dilution, pyrolysis or thermal cracking, micro-emulsion, and transesterification [25,26]. Transesterification which is also known as alcoholysis is one of the easiest and most effective methods for the production of biodiesel where the triglycerides present in oils and fats react with alcohol in the presence of a catalyst resulting fatty acid esters, and glycerol as side-products (**Scheme 1.1**) [27–29]. Biodiesel is produced mostly by catalytic transesterification of fats or oils with lower alcohols such as methanol, ethanol, propanol, butanol, etc., of which methanol is most widely used due to its advantageous properties [3,28,30–33]. A variety of catalysts such as acid, base and enzyme are being reported for the production of biodiesel [34,35]. **Scheme 1.2** is showing the acid catalysed reaction mechanism of transesterification, revealing the conversion of triglyceride to diglyceride, diglyceride to monoglyceride and finally monoglyceride to glycerol yielding one molecule of fatty acid methyl esters (FAME) in each step [34–36]. Sulphuric acid ($H_2SO_4$), sulphonic acid ($H_2SO_3$), hydrochloric acid (HCl), ferric sulphate ($Fe_2(SO_4)_3$), phosphoric acid ($H_3PO_4$), organic sulphonic acids, etc., are some of the homogeneous acid catalysts used in the transesterification of oil [37,38]. However, homogeneous acid catalysts have drawbacks like they are corrosive, require high pressure and temperature, and need long reaction time, and accordingly, the process is economically confronting to be considered as efficient in biodiesel production [39–42]. Though homogeneous base (sodium hydroxide, potassium hydroxide, sodium methoxide, etc.) catalysed reaction (mechanism shown in **Scheme 1.3**) requires milder conditions and converts biodiesel in a shorter time with high conversion, the soap formation and difficulty in the separation of catalyst from the product mixture causing to the generation of wastewater are the major drawbacks of the process [32,43,44]. Hence, this process can be considered not feasible for economical production of biodiesel [7]. Similarly, enzyme catalysed transesterification, in spite of its environmental friendliness and mild reaction conditions, faces economic issues due to high-cost of enzyme [39,45].



**Scheme 1.1**: Transesterification of oil or fat to biodiesel.



**Scheme 1.2**: Homogeneous acid catalysed transesterification of vegetable oil to biodiesel (FAME).



**Scheme 1.3**: Homogeneous base catalysed transesterification of vegetable oil to biodiesel (FAME).

The heterogeneous base catalysts are performing encouragingly good in biodiesel production and gaining worldwide attention due to their various advantages over homogeneous and enzyme catalysts. These catalysts could produce good quality product in mild conditions with better efficacy, be recycled several times easily and does not produce soap during reaction, and hence, the entire process is eco-friendly [30,46–49]. Heterogeneous solid bases such as oxides and mixed oxides of metals are reported with higher catalytic activity [50,51]. Recently, heterogeneous solid catalysts prepared from various chemical sources are testified with good performance in terms of biodiesel conversion and yield. Some of these catalysts are SrO [52], CaO [53,54], KF/$Al_2O_3$ [55], Na/$SiO_2$ [56], KF/g-$Al_2O_3$ [57], KF/ZnO [58], KF-$Eu_2O_3$ [59], KOH-$Nd_2O_3$ [60], $K_2CO_3$-MgO [61], $K_2CO_3$/CaO [62], Cs-$Na_2ZrO_3$ [63], KF/g-$Al_2O_3$ [48],

$Na_2MoO_4$ [64], vanadyl phosphate [65], calcium methoxide [66], sulfated zirconia [67], zirconia supported tungsten oxide [68], F/hydrotalcite [69], KF/Ca-Mg-Al hydrotalcite [70], calcium ethoxide [49], copper vanadium phosphate [71], MgO [72], $Al_2O_3$-supported metal oxides [73], Ca-based metal oxides [74], etc. However, all these catalysts are still not favourable in terms of economical point of view as their preparation steps are more complex such as chemical incorporation followed by calcination, etc., which increases the cost of catalyst resulting in an increase of biodiesel production cost [75,76]. In addition to that, as these catalysts are derived from non-renewable sources, they pose disposal problems and also, they are not environmentally friendly [7].

Biodiesel production using several CaO-based solid catalysts from various biomass sources have also been reported by many researchers with satisfactory yield. These biomass sources are shrimp shell [77], mussel shell [78], crab shell [79, 80], eggshell [81, 82], *Labeo rohita* scale [83], cockle shell [84], biont shell [85], ostrich eggshell [86], *Turbonilla striatula* shell [87], snail shell [88], clamshell [89], chicken eggshells [90], chicken bone [91], oyster shell [92], animal bones [93], etc. However, these CaO-based catalysts, in spite of their roles in the reaction, also possess major drawbacks due to the poisoning of their active sites and storage problems [50, 94]. Accordingly, to overcome such problems, CaO based catalysts are incorporated with other chemicals and these loaded catalysts are $K^+$/CaO [75], Li/CaO [95], CaO/Na-ZSM-5 [96], CaO/$Fe_2O_3$ [76], C/CaO/NaOH [97], Na-C/CaO [98], Mo-Zr/CaO [99], etc. These solid catalysts are reported with promising results in terms of yield and conversion of biodiesel. In such cases, the modification of the catalyst is done for stabilization, i.e., the calcined CaO catalysts derived from biomass sources are mixed with the desired chemicals by various methods like wet impregnation, homogenization with aqueous solution etc. followed by drying and re-calcination at a particular temperature [75, 76, 95, 96]. These additional steps along with costly chemicals necessitated in the preparation of such incorporated catalyst increases the cost of catalyst resulting in to the increase of biodiesel production cost. Thus, development of a stable heterogeneous catalyst from natural sources possessing minimal production cost along with green, environment-friendly as well as superior catalytic activity has become a challenge in the biorefinery sector for large scale production of biodiesel.

In recent years, plant ash-based heterogeneous catalysts obtained from various waste plants and other agricultural by-products are drawing increasing attention among the researchers as the promising green catalysts for the synthesis of biodiesel. Application of such catalysts can overcome the aforementioned problems associated with other catalysts. The ash from waste plants is mainly composed of alkali, alkaline earth and other metal oxides and carbonates which exhibit significant efficacy in catalysis with good recyclability. Further, they do not possess storage and disposal problems. Therefore, various waste plant-based catalysts in the synthesis of biodiesel are mainly getting more focus for the rigorous research and development. Recently reported such heterogeneous catalysts in biodiesel synthesis from plant-based sources are tucumã peels [12], coconut husk [100], sugarcane bagasse [101–104], banana peel [105, 106], plantain fruit peel [107], *Musa acuminata* peel [108], *Musa balbisiana* peel [109], *Musa balbisiana* trunk [11], *Musa balbisiana* underground stem [110, 111], *Musa paradisiacal* peel [112], rice husk [113], *Lemna perpusilla* [114], cocoa pod husk [115], wheat husk [116], corncob [117], cotton stalk [118, 119], etc. In all of these mentioned reports, the agricultural waste-plant based heterogeneous catalysts showed promising potential in converting oil into biodiesel. In addition to such reported catalysts with good catalytic efficacy there is still a need to extensively search the potential raw materials which is not only cost-free but should also be easily available and can serve effectively for application purposes at a large scale in a cost-effective and eco-friendly synthesis of biodiesel.

## 1.3 Literature review

### 1.3.1 Preparation of plant-based heterogeneous catalyst for biodiesel synthesis

Plant-based resources, being renewable, inexpensive and abundantly available in nature, can play a potential role in supplementing energy and bio-based chemicals [120]. The use of biomass instead of petroleum in the production of chemicals and fuels contributes lesser pollution with no net $CO_2$ output to the environment as well as results in biodegradable and sustainable products [121]. The current global scenario shows that the total biomass production exceeded to 1.8 trillion tons, which can be an enormous source of chemicals and energy for the world [122, 123]. The agricultural sector is the major producer of plant-based wastes worldwide followed by forest biomass waste [124]. The current scenario estimated that there are 140000 million tons of biomass waste generated from the agricultural sector globally per year with an increasing rate of 5-10% annually [125–129]. Reutilization of these wastes is an environmentally safe and cost-effective process of waste management and conversion of waste to wealth. Proper and optimal utilization of these waste by-products is one of the major challenges for human society nowadays. Plant waste biomasses are composed of starch, cellulose, lignocellulose, hemicellulose, lignin and oil, which are being utilized as feedstocks in the production of biofuel, platform chemicals and various other value-added products [123, 124, 130, 131]. Applications of waste plant-based biofertilizers in the plantation of crops have been studied and reported with effective results [132, 133]. Plant-based wastes have been successfully employed as active materials and precursors for the synthesis of catalysts for various applications [51]. A flow chart showing various applications and value-added products [122,123,134] from waste plants is represented in **Fig. 1.1**.

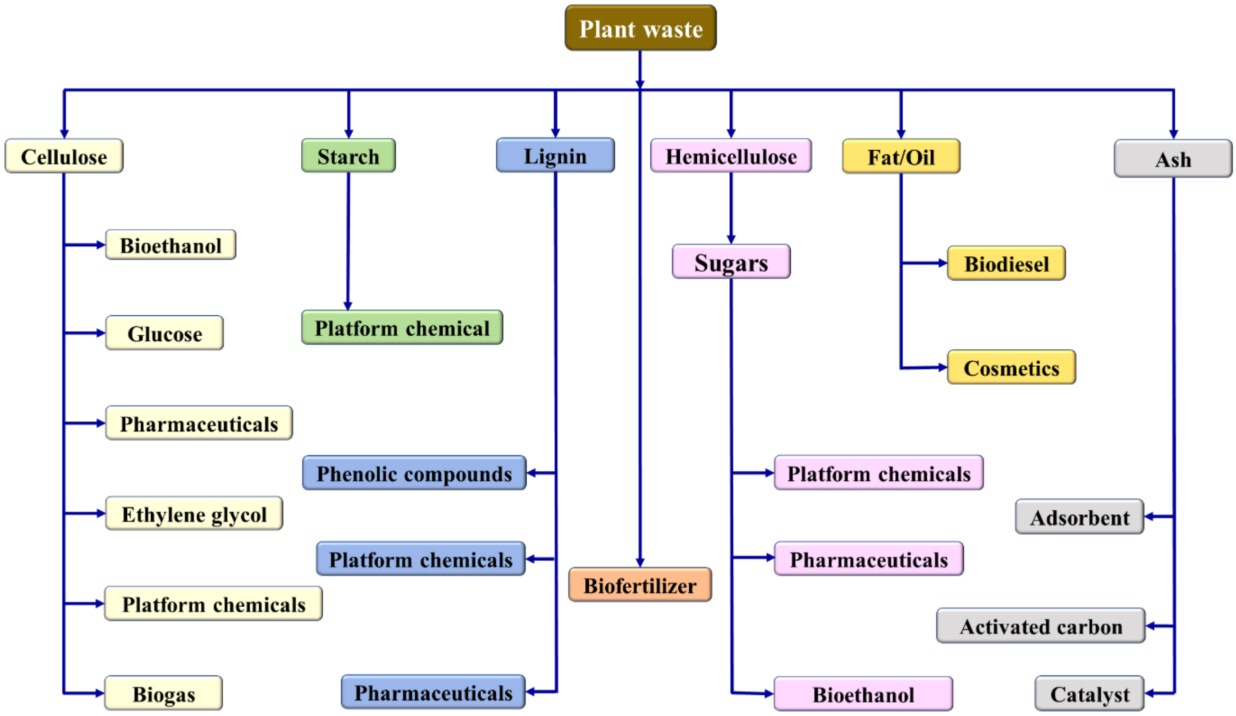


**Fig. 1.1**: Waste plant to sustainable value-added products.

In recent times, one of the most important applications of the plant-wastes is the preparation of solid base catalyst for biodiesel production. **Fig. 1.2** is showing how the catalyst is generally prepared from waste plants. The plant-based material is composed of organic compounds and various metals like Na, K, Ca, Mg and other elements [7]. The plant-based materials on combustion produces ashes that mainly consists of various metal carbonates and oxides [100,135]. The most common employed approach for the solid catalyst preparation from plant materials is the calcination process, and it is performed at temperatures ranging from 300–1200 $^{o}$C for 2–4 h. It is also reported that the calcination temperature plays a vital role in the composition and morphology development of the catalyst. The variation in alkalinity, porosity and accordingly, the catalytic activity of the calcined catalyst is significantly influenced by the calcination temperature [7,136]. In this regard, Gouran et al. [116] recently reported the preparation of catalyst from wheat bran ash and utilized in biodiesel production from waste cooking oil. Similarly, preparation of heterogeneous solid acid catalyst from corncob was investigated for transesterification of algal oil and stated good yield of biodiesel [117]. Sugarcane bagasse waste is also explored as an efficient precursor of the heterogeneous catalyst with good catalytic activity in biodiesel synthesis [101–104]. The cotton stalks generated as waste from cotton-producing farms are compatibly reported as a catalyst in transesterification as well as other reactions too [118,119]. Jute sticks obtained after removal of jute fibber remains as waste are also efficiently used in the preparation of activated carbon with the potential for being used as a catalyst along with other activities [137]. Plantation crops such as tea, coffee, coconut, etc. also generate huge waste which can also be utilized in the generation of catalysts for industrial application. Akbayrak et al. [138] reported the preparation of catalyst from tea waste and utilized the catalyst in the hydrolysis of ammonia borane. Elabadagama et al. [139] also prepared heterogeneous catalyst from tea waste and utilized in the esterification of free fatty acid to biodiesel. Waste coffee residues are successfully utilized in the preparation of catalysts and applied in various applications such as isomerisation of glucose to fructose, esterification, etc. [140,141]. Coconut coir is also reported in the preparation of heterogeneous catalysts for the preparation of biodiesel [100,142–144]. Betiku et al. [105], Etim et al. [145] and Falowo et al. [146] reported calcination temperature of 700 $^{o}$C for preparation of catalyst from *Musa* Gross Michel fruit, *Carica papaya* peels and elephant-ear tree pod husk, respectively. Chouhan and Sarma [114] and Sarma et al. [111] reported 550 $^{o}$C as calcination temperature for preparation of catalyst from *Lemna perpusilla* Torrey ash and *Musa balbisiana* stem ash respectively. Whereas John et al. [147] reported the calcination at 800 $^{o}$C for ginger leave in the preparation of the catalyst. Similarly, Fadara et al. [148] and Oladipo et al. [149] reported 400 and 600 $^{o}$C as the calcination temperature for the preparation of the catalyst. In addition to the fact that waste plant-derived catalysts are safe, environmentally benign, and cost-effective, they exhibit high catalytic activity in terms of conversion and selectivity. Studies were found utilizing water extracts of ashes from plant wastes as green and non-conventional solvents or catalysts in several reactions [150]. Because of the basic nature of the waste-plant derived catalysts, they have also been reported as the catalyst in various other reactions like Dakin reaction [151], Suzuki-Miyaura coupling reaction [152], Henry reaction [153], peptide bond formation reaction [154] as well as in *ipso*-hydroxylation reaction [150]. Considering the facts, waste plant residues from the agricultural sector can be investigated as precursors of catalysts for biodiesel production as well as other relevant industrial applications.

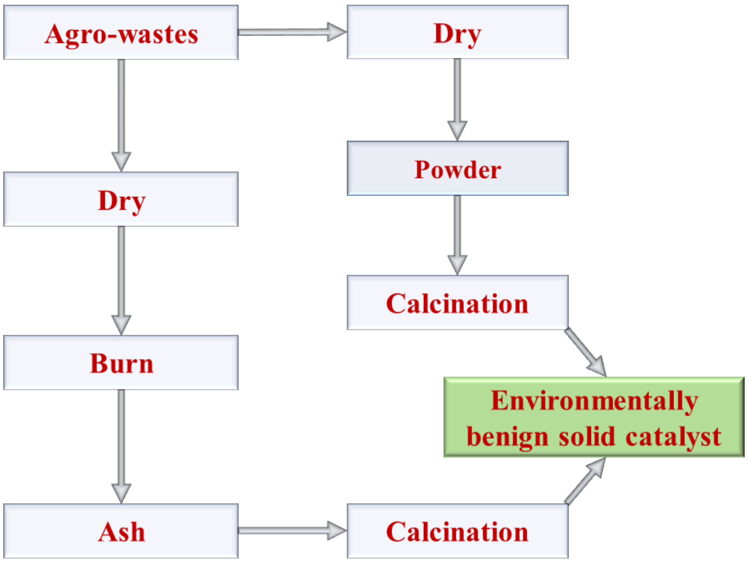


**Fig. 1.2**: Preparation of heterogeneous catalysts from waste plants [129].

### 1.3.2 Composition of solid catalyst obtained from plant materials

Complete combustion of any plant part resulted to ash material and is composed of inorganic components. Depending on the type of sources, the composition of such materials varies and are generally found to consists of oxides and carbonates of metals such as $K_2O$, $K_2CO_3$, KCl, CaO, $SiO_2$, MgO, $Fe_2O_3$, $P_2O_5$, $Al_2O_3$, etc. [7,51,134,155]. The literature disclosed that these materials possessed highly basic character [111,135,150,152], and exhibited good catalytic efficacy in biodiesel production [12,111,115]. Thus, the presence of higher percentage of carbonate and oxide of potassium in the catalyst is accountable for making it alkaline, resulting in high catalytic efficiency in biodiesel synthesis. The chemical/elemental compositions of various waste plant derived heterogeneous catalysts reported in biodiesel synthesis are listed in **Table 1.1**, and reveals that most of the catalysts prepared from waste plant sources possess higher percentage of K compared to other metals. The highest potassium content of 99.73% was reported by Betiku et al. [105], where the presence of oxygen and carbon was not reported. Eldiehy et al. [156] reported 65.45% of potassium content in sweet potato generated catalyst, where the presence of oxygen and carbon is also not reported. Comparable potassium content for catalysts generated from *Musa paradisical* peel (54.73%) [112], *Musa paradisical* peel (51.02%) [107], *Tectona grandis* leaves (53.25%) [157] and cocoa pod husk + plantain peel (51.94%) [158] was observed from **Table 1.1**. Li et al. [159] reported very low potassium content of 1.12% in camphor tree leave derived catalyst. Good percentage of oxygen and carbon along with potassium in the catalysts supports the presence of oxide and carbonates of potassium, which are stated to play the key role in the activity of the catalyst in transesterification of vegetable oil to biodiesel.

**Table 1.1:** Chemical/elemental composition of catalyst derived from agricultural waste plants

| **Source of catalyst (Ash)** | **Calcination with time** | **Composition (%)** | | | | | | | | | | | | | **References** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | **Na** | **K** | **Ca** | **Mg** | **Mn** | **Fe** | **Zn** | **Al** | **P** | **Si** | **Cl** | **C** | **O** | |
| *Acacia nilotica* tree stem | 500$^{o}$C, 3 h | 0.6 | 6.7 | 13.3 | 2.7 | - | - | - | 8.3 | 0.80 | 15.7 | - | - | - | [136] |
| *Acacia nilotica* tree stem | 800$^{o}$C, 3 h | 5.7 | 5.7 | 17.8 | 4.5 | - | - | - | 1.2 | 0.5 | 21.5 | - | - | - | [136] |
| *Lemna perpusilla* Torrey | 550$^{o}$C, 2 h | 0.53 | 11.32 | - | - | - | - | - | - | - | 82.51 | 1.10 | 5.10 | - | [114] |
| *Musa balbisiana* underground stem | 550$^{o}$C, 2 h | 0.61 | 25.09 | 10.44 | 10.04 | - | 1.88 | - | 4.07 | 4.47 | 35.92 | - | - | - | [111] |
| *Musa paradisiacal* peels | 500$^{o}$C, 3.5 h | - | 54.73 | 1.13 | - | 0.05 | 0.04 | 0.01 | 3.42 | 1.99 | 33.01 | 4.89 | - | - | [112] |
| Banana (*Musa* Gross Michel) peels | 700$^{o}$C, 4 h | 0.19 | 99.73 | 0.03 | 0.03 | 0.01 | 0.01 | 0.004 | - | - | - | - | - | - | [105] |
| *Musa balbisiana* peels | 700$^{o}$C, 4 h | 10.41 | 41.37 | 36.08 | 12.02 | - | - | - | - | - | - | - | - | - | [109] |
| Cocoa pod husk | 700$^{o}$C, 4 h | - | 59.2 | - | 3.0 | - | - | - | - | 0.8 | 0.3 | - | - | 36.2 | [115] |
| *Musa paradisiacal* peels | 700$^{o}$C, 4 h | - | 51.02 | - | 1.15 | - | - | - | 0.29 | 1.84 | 2.51 | 6.27 | - | 36.43 | [107] |
| Camphor tree leaf | 800$^{o}$C, 2 h | 0.23 | 1.22 | 12.05 | 1.82 | - | - | - | 2.70 | - | - | - | | - | [159] |

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Orange peel | Burnt | - | 14.67 | 7.34 | 2.02 | - | - | - | - | 1.57 | - | - | 32.50 | 40.86 | [160] |
| *Tectona grandis* leaves | 700 $^{o}$C, 4 h | 1.67 | 53.25 | 30.28 | 4.77 | - | - | - | - | - | 10.03 | - | - | - | [157] |
| *Carica papaya* peel | 700 $^{o}$C, 3 h | 0.82 | 30.74 | 3.64 | 1.16 | - | - | - | - | 4.22 | 0.71 | 10.3 | - | 44.1 | [145] |
| *Carica papaya* peel | 600 $^{o}$C, 4 h | 0.0 | 23.89 | 2.86 | 1.00 | - | 0.0 | - | - | 3.04 | 0.0 | 0.87 | 29.16 | 36.72 | [149] |
| Moringa leaves | 500 $^{o}$C, 2 h | - | 9.87 | 10.09 | 5.92 | - | - | - | - | 1.19 | - | - | 13.19 | 59.57 | [161] |
| Cocoa pod husk + plantain peel | 700 $^{o}$C, 4 h | 0.0 | 51.94 | 0.0 | 2.05 | - | 0.0 | - | - | 1.04 | 1.01 | 2.77 | - | 40.93 | [158] |
| *Mangifera indica* peel | Burnt | 0.25 | 43.89 | 9.44 | 3.07 | - | 0.46 | - | - | 4.21 | 2.61 | - | 2.38 | 32.54 | [162] |
| Wheat straw | Burnt | - | 7.7 | 1.5 | 1.1 | - | - | - | - | - | 18.2 | 1.3 | 41.4 | 28.9 | [163] |
| *Carica papaya* trunk | 400 $^{o}$C, 4 h | 0.63 | 23.85 | 15.40 | 1.78 | - | - | - | - | 2.85 | 0.0 | 1.18 | - | 51.34 | [148] |
| *Musa paradisiaca* peel | 700 $^{o}$C, 4 h | - | 20.95 | - | - | - | - | - | - | - | - | 8.06 | 49.48 | 10.98 | [164] |
| *Musa acuminate* flower petal | Burnt | - | 45.44 | 2.4 | 3.05 | - | - | - | - | 2.03 | 1.95 | - | 1.9 | 41.84 | [165] |
| Plantain peels | 500 $^{o}$C, 4 h | - | 45.16 | - | 3.61 | - | - | - | - | - | - | - | | 35.34 | [166] |
| Hazelnut shell | 800 $^{o}$C, 2 h | - | 26.29 | 11.62 | 6.77 | - | - | - | - | 6.10 | - | - | - | - | [167] |
| Potato peel | 700 $^{o}$C, 3 h | 1.85 | 36.54 | 2.71 | 2.02 | 0.45 | 1.30 | 0.10 | - | - | 3.06 | 1.24 | 9.18 | 41.55 | [168] |
| Sweet potato leaves | 900 $^{o}$C, 3 h | 0.70 | 65.45 | 18.02 | 4.63 | - | 0.88 | - | 0.94 | - | 3.54 | 4.12 | - | - | [156] |

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Musa paradisiacal* peel | 550 $^{o}$C, 2 h | - | 29.25 | 4.01 | 1.08 | - | - | - | - | 1.06 | 3.81 | 3.01 | 24.02 | 33.34 | [169] |
| *Musa paradisiacal* trunk | 550 $^{o}$C, 2 h | - | 36.31 | 2.21 | 3.08 | - | 0.59 | - | 0.63 | 1.12 | 2.84 | 2.13 | 13.22 | 37.87 | [169] |
| *Musa paradisiacal* rhizome | 550 $^{o}$C, 2 h | - | 30.06 | 3.06 | 0.69 | - | - | - | - | 1.00 | 1.67 | 1.83 | 18.43 | 43.27 | [169] |
| Sugarcane bagasse | 550 $^{o}$C, 2 h | 0.60 | 12.07 | 2.43 | 1.12 | - | 0.25 | - | 0.24 | 2.14 | 24.11 | - | 5.89 | 50.22 | [104] |

### 1.3.3 Waste plant derived heterogeneous base catalyst in biodiesel synthesis

In recent times, plant wastes from post-harvested agricultural products are extensively investigated for sustainable development of value-added products and processes, and one of the potential applications is the utilization of the waste plants as precursors for heterogeneous base catalysts in biodiesel production, which are attracting increasing attention around the worldwide. Waste plant derived catalysts are easily available, simple to prepare, easy to handle, biodegradable, less toxic, more environmentally friendly, and cost-effective. The performances of heterogeneous catalysts derived from several waste agricultural products in biodiesel synthesis from different feedstocks are summarized in **Table 1.2**. These reported catalysts are *Musa balbisiana* stem [111], *Musa balbisiana* underground stem [110], *Musa balbisiana* peel [109], *Musa balbisiana* trunk [11], *Musa paradisiacal* peel [112], *Musa paradisiacal* fruit peels [107], ripe banana (*Musa* 'Gross Michel') fruits peels [105], banana peel (CBPA) and cocoa pod husk (CCPHA) [106], flamboyant pods [170], *Lemna perpusilla* Torrey [114], *Acacia nilotica* tree stem [136], cocoa pod husk [115], Birch bark [171], coconut husk [100], etc.

Recently, Jitjamnong et al. [172] studied the effect of calcination temperature on heterogenous base catalysts derived from desert banana peel. They prepared the catalyst by drying the banana peel in an oven followed by calcination at different temperatures ranging from 550–650 $^{o}$C. The 600 $^{o}$C calcined catalyst showed high percentage of K, Ca, Mg and P and exhibited the highest catalytic activity. The transesterification was carried out by microwave irradiation with soybean oil and the 99.3 % of FAME yield was reported in 2 min with optimum reaction conditions of 1 wt.% of catalyst loading, and 12:1 MTOR (methanol to oil ratio). The reusability study showed good reusability up to the fourth run with 80.7% of yield. Changmai et al. [160] investigated the catalytic performance of heterogeneous catalyst derived from orange peel in the transesterification of soybean oil to biodiesel. The EDX analysis of the catalyst showed increase of potassium content from 0.18% to 14.67% from dried orange peel to orange peel ash. A good surface area of 605.60 $m^2 g^{-1}$ with mesoporous structure was obtained for orange peel ash. They reported 98% of conversion under optimum conditions of 7 wt.% of catalyst load, 6:1 MTOR in a reaction time of 7 h. The catalyst was successfully reused up to fifth cycle with a biodiesel conversion of 85%. *Tamarindus indica* fruit shell ash was investigated as heterogeneous catalyst for biodiesel synthesis from *Parinari curatellifolia* oil by Nabora et al. [173]. The oven dried shell is calcined at 800 $^{o}$C to prepared the catalyst. The catalyst showed high basicity with a surface area of 378 $m^2 g^{-1}$. At optimum conditions of 5 wt.% catalyst loading, 9:1 MTOR, and at 60 $^{o}$C of reaction temperature, a good biodiesel yield of 96.2% was reported in a reaction time of 120 min. The catalyst reusability showed

74% of yield at fourth run of reaction. Miladinović et al. [174] reported the catalytic activity of walnut shell ash in the sunflower oil methanolysis for biodiesel production. They prepared the catalyst by combustion of the dried shell followed by calcination at 800 $^{o}$C for 2 h. The optimum reaction conditions were reported to be 5 wt.% of catalyst loading, 12:1 MTOR and 60 $^{o}$C of reaction temperature yielding 98% of biodiesel in a reaction time of 10 min. The regeneration of catalytic activity was done by recalcination at 800 $^{o}$C for 2 h and reused up to fourth run. Gohain et al. [157] prepared heterogeneous catalyst form *Tectona grandis* leaves and applied in waste cooking oil biodiesel production. Catalyst preparation was done by calcination of the dried leaves at 700 $^{o}$C for 4 h. 100% conversion of oil to biodiesel was reported in 180 min with 2.5 wt.% of catalyst loading and 6:1 MTOR at room temperature.

Oladipto et al. [149] investigated the activity of heterogenous catalyst prepared from *Carica papaya* peel in moringa oil methanolysis. The catalyst preparation was done by calcination of the air burnt peels at 200–1000 $^{o}$C and 600 $^{o}$C is reported as the best temperature resulting highest percentage of active components. The Taguchi orthogonal array approach was applied to identify the optimum conditions and reported to be 3.5 wt.% of catalyst loading, 9:1 MTOR and 35 $^{o}$C of reaction temperature resulting biodiesel yield of 96.43% in 40 min. Oladipto et al. [175] also investigated the catalytic activity of heterogeneous catalyst derived from kola nut pod husk for transesterification of rubber oil to biodiesel. The optimum reaction conditions reported was 3.5 wt.% of catalyst loading, 6:1 MTOR and 65 $^{o}$C of reaction temperature. A biodiesel yield of 96.97% was obtained in 75 min. Aleman-Ramirez et al. [161] prepared heterogeneous catalyst from moringa leaves and utilized in the biodiesel production from soybean oil. Inorganic components of dolomite, calcite and $K_2Ca(CO_3)_2$ were the composition of the catalyst after calcination. The reported optimum reaction conditions were 6 wt.% of catalyst loading, and 6:1 MTOR at 65 $^{o}$C that yielded 86.7% of biodiesel in 120 min. Olatundun et al. [158] reported blending of cocoa pod husk and plantain peel for preparation of heterogeneous catalyst for biodiesel production. They prepared the catalyst by separately burning the cocoa pod husk and plantain peel to ash, mixed in equal amount and calcined at different temperatures (300–1000 $^{o}$C). The key active components K and Ca were found to be the highest on calcination at 500 $^{o}$C and considered it as optimum. The best reported operating conditions resulting the highest biodiesel yield of 98.98% were 4.5 wt.% of catalyst loading, and 15:1 MTOR at 65 $^{o}$C in a reaction time of 150 min. John et al. [147] investigated the transesterification of soybean oil using heterogeneous catalyst derived from waste ginger leaves. They prepared catalysts from the oven dried leaves following three different methods, viz. (i) calcination at 800 $^{o}$C for 2 h, (ii) potassium hydroxide activation and (iii) sodium hydroxide extraction. The optimum conditions for transesterification were reported to be 1.6 wt.% of catalyst load, and 6:1 MTOR at room temperature with 200 rpm. A biodiesel yield of 90.13% in a reaction time of 90 min was reported for calcined ginger leaves catalyst. Waste *Mangifera indica* peel was investigated as catalyst source by Laskar et al. [162] in the soybean oil biodiesel production. The surface area of the prepared catalyst was reported as 123.34 $m^2$ $g^{-1}$. The characterization of the catalyst showed the presence of 59.14% of potassium and reported that $K_2O$ played the vital role in the catalytic activity. The optimum reaction conditions reported were 6 wt.% of catalyst, and 6:1 MTOR at room temperature (28 $^oC$) resulting biodiesel yield of 98% in a reaction time of 240 min. Similarly, Barros et al. [176] investigated the catalytic activity of heterogeneous catalyst derived from pineapple leaves in the soybean oil biodiesel synthesis. The catalyst was prepared by calcination of the oven dried leaves at 600 $^oC$ for 2 h and then at 900 $^oC$ for 30 min. 4 wt.% of catalyst loading with 40:1 MTOR at 60 $^oC$ were reported as optimum conditions with 98.2% of biodiesel yield in 30 min. The catalyst was reused up to fourth run of reaction with 85% of biodiesel yield.

Veličković et al. [163] investigated the catalyst prepared from wheat straw ash in sunflower oil biodiesel production. The catalyst was prepared by burning the dried straw in open air. The BET surface area of wheat straw ash catalyst was reported to be 98.5 $m^2g^{-1}$. A good biodiesel yield of 98% was obtained in 124 min at the optimum reaction condition of 11.6 wt.% of catalyst loading and 18.3:1 MTOR at 60.3 $^oC$ of reaction temperature. Very sharp decrease of biodiesel yields gradually to 37%, 12% and 3% on second, third and fourth run of reactions respectively were noticed. Mares et al. [177] studied the biodiesel production from soybean oil using heterogeneous catalyst prepared from Acai seed ash by calcination at 500–900 $^oC$ of which 800 $^oC$ for 4 h resulted the best performance. The optimum reaction conditions for synthesis of biodiesel were 12 wt.% of catalyst loading, and 18:1 MTOR at 100 $^oC$ that yielded 98.5% of biodiesel at a reaction time of 60 min. The catalyst characterization portrayed the presence of oxides and carbonates of potassium and calcium as the key active component. The reusability study showed 80% biodiesel yield at fourth reaction cycle. Catalyst prepared from poovan banana pseudostem was studied by Niju et al. [178] for biodiesel synthesis from *Madhuca indica* oil. They prepared the catalyst by drying the pseudostem followed by calcination at 700 $^oC$ for 4 h. The surface area of the catalyst was 4.850 $m^2g^{-1}$. Response surface methodology was employed to optimize the conditions and a biodiesel yield of 98.8% was achieved in 178.1 min using 5 wt.% of catalyst loading, 14.9:1 MTOR and 65 $^oC$ of reaction temperature. Gouran et al. [116] reported the heterogeneous catalyst from wheat bran ash for biodiesel synthesis from waste cooking oil. Biodiesel yield of 93.6% was reported using 11.66

wt.% of catalyst loading, and 1.46:1 MTOR at 54.6 °C during 114.21 min. Basumatary et al. [169] reported heterogeneous base catalyst from *Musa paradisiaca* peel, trunk and rhizome for the synthesis of *Jatropha curcas* oil biodiesel. Characterization of the catalyst revealed the surface areas of 4.1, 6.4 and 7.0 $m^2$ $g^{-1}$ and high potassium content of 36.31, 30.06 and 29.25% in peel, trunk and rhizome catalysts, respectively. *Musa paradisiaca* trunk with highest pH and basicity than peel and rhizome showed the highest catalytic activity exhibiting the turnover frequency of 68.24 $min^{-1}$. The optimum reaction conditions reported were 5 wt.% of catalyst loading, 9:1 MTOR and 65 °C of reaction temperature resulting 97.65% of biodiesel yield in a short duration of 9 min. Basumatary et al. [104] also investigated sugarcane-bagasse derived heterogeneous catalyst for jatropha biodiesel synthesis. The catalyst was prepared by calcination at 550 °C for 2 h. Catalyst characterization showed the presence of 12.07% of potassium. Low potassium revealed lower catalytic activity at optimum reaction conditions of 10 wt.% of catalyst, 9:1 MTOR and 65 °C of reaction temperature that yielded 92.84% of biodiesel in 285 min with a TOF of 6.59 $h^{-1}$. Laskar et al. [165] also studied the preparation of heterogeneous catalyst from *Musa acuminata* flower petal for biodiesel production from waste cooking oil. The catalyst preparation was done by open air burning of the dried petal. The characterization of the catalyst showed the presence of highly basic $K_2O$ (60.23%) which was responsible of catalytic activity. The BET surface area of the catalyst was reported to be 79.33 $m^2$ $g^{-1}$ showing good catalytic activity with 99.99% conversion at the optimum reaction conditions of 5.63 wt.% of catalyst loading, 6.24:1 MTOR and 4 h of reaction time at room temperature.

Falowo et al. [166] reported the biodiesel production using catalyst from ripe and unripe plantain peels mixture prepared by calcination of dried peels at 500 °C. The optimum reaction conditions were found to be 0.5 wt.% of catalyst, 6:1 MTOR and 45 °C of reaction temperature with corresponding biodiesel yield of 97.96%. K content of 45.16% was revealed from catalyst characterization along with a low surface area of 1.10 $m^2$ $g^{-1}$. Falowo et al. [179] also studied the preparation of heterogeneous catalyst from cocoa, kola nut and fluted pumpkin waste and utilized in the transesterification of yellow oleander and rubber oil blend to biodiesel. The catalytic activity was reported due to high percentage of potassium (48.4%). The oil blend was first esterified and then transesterified with optimum catalyst loading of 1.5 wt.%, 9:1 MTOR at 65 °C reaction temperature resulting 95.02% biodiesel in 40 min. Similarly, Adepoju et al. [180] prepared heterogeneous catalyst from three agro waste peels mixture viz. *Cucurbita pepo*, *Musa acuminate* and *Citrullus lanatus* and utilized in the transesterification of vegetable oil blend of *Luffa cylindrical* oil, *Datura stramonium* oil, *and Lagenaria siceraria* oil. The characterization of the catalyst showed high percentage of CaO (75.65%) in the mixture compared to individual *Cucurbita pepo* (62.83%), *Musa acuminate* (65.50%) and *Citrullus lanatus* (58.67%) calcined catalyst. The mixture catalyst resulted the highest biodiesel yield of 97.20% compared to *Cucurbita pepo* (83.50%), *Musa acuminate* (88.75%) and *Citrullus lanatus* (80.32%) catalysts. The reported optimum reaction conditions were 3.53 wt.% of catalyst loading, 9:1 MTOR, 90 $^{o}$C of reaction temperature and 80 min of reaction time. *Musa acuminata* peel was also utilized in the preparation of heterogeneous catalyst by Daimary et al. [181] and applied for soybean waste cooking oil biodiesel production. The reported optimum conditions were 1.5 wt.% of catalyst, and 9:1 MTOR at 60 $^{o}$C that resulted the biodiesel yield of 98.0% in 120 min. Daimary et al. [168] also reported the preparation of heterogeneous catalyst from potato peel for transesterification of waste cooking oil biodiesel production. The catalyst was found to be rich in K, Ca, Mg, Na, and Si showing good catalytic activity at optimum reaction conditions of 3 wt.% of catalyst loading, and 9:1 MTOR at 60 $^{o}$C temperature resulting the biodiesel yield of 97.50%. Similarly, sweet potato leaves were reported as catalyst source by Eldiehy et al. [156] for *Scenedesmus obliquus* oil as well as waste cooking oil biodiesel production. The optimum reaction conditions for *Scenedesmus obliquus* oil were found to be 7 wt.% of catalyst loading, and 15:1 MTOR at 60 $^{o}$C of reaction temperature yielding 99.50% of biodiesel in 90 min. In case of waste cooking oil, 5 wt.% of catalyst loading and 9:1 MTOR at 60 $^{o}$C produced 98.0% of biodiesel in 120 min. Miladinović et al. [167] investigated the catalytic activity of heterogeneous catalyst prepared from hazelnut shell ash in the transesterification of used cooking oil. They prepared the catalyst by burning the shell to biochar followed by calcination at 800 $^{o}$C. The EDX analysis of the calcined catalyst revealed the presence of K (26.29 %), Ca (11.62 %), and Mg (6.77 %) as abundant elements responsible for catalytic activity. The highest biodiesel yield of 98% was achieved at catalyst loading of 5 wt.%, and MTOR of 12:1 at 60 $^{o}$C in a reaction time of 10 min. Sitepu et al. [182] reported the successful utilization of heterogeneous catalyst from palm bunch in the homogenizer-intensified biodiesel production from palm oil. With MTOR of 15:1, rotational speed of 4000 rpm and 18 wt.% of catalyst in a reaction time of 10 min, the highest biodiesel yield of 98.9% was achieved. They also stated that this method could save 6-98% of electricity and 67-87% of reaction time. In addition to the utilization of agricultural waste plant ashes as catalysts, thermal power plant fly ash [183], coal fly ash [184,185] tars and alkali ashes [186] have also been reported as catalysts for biodiesel synthesis.

**Table 1.2**: Performances of agricultural waste plant based heterogeneous catalysts in biodiesel synthesis from various oil feedstocks

| **Biodiesel feedstock** | **Source of catalyst (Ash)** | **Surface area $(m^2\,g^{-1})$** | **Parameters** | | | | **Biodiesel, Y or C (%)** | **References** |
|---|---|---|---|---|---|---|---|---|
| | | | **Catalyst load (wt.%)** | **MTOR** | **Temp $(^{o}C)$** | **Time (min)** | | |
| Jatropha oil | Coconut husk | – | 5 | 12:1 | 45 | 60 | 99.77 (Y) | [100] |
| *Thevetia peruviana* oil | *Musa balbisiana* Colla trunk | 1.487 | 20 | 20:1 | 32 | 180 | 96 (Y) | [11] |
| *Jatropha curcas* oil | *Acacia nilotica* tree stem | 3.72 | 5 | 12:1 | 65 | 180 | 98 (C) | [136] |
| *Jatropha curcas* oil | *Lemna perpusilla* Torrey | 9.622 | 5 | 9:1 | 65 | 300 | 89.43 (C) | [114] |
| *Jatropha curcas* oil | *Musa balbisiana* underground stem | 38.71 | 5 | 9:1 | 275 | 60 | 98 (C) | [111] |
| *Mesua ferrea* oil | *Musa balbisiana* underground stem | 38.71 | 5 | 9:1 | 275 | 60 | 95 (C) | [110] |
| *Thevetia peruviana* oil | *Musa paradisiacal* peels | – | 3 | 10:3 | 60 | 90 | 95.25 (Y) | [112] |
| *Bauhinia monandra* oil | Banana (*Musa* Gross Michel) peels | 4.442 | 2.75 | 7.6:1 | 65 | 69.02 | 98.5 (Y) | [105] |
| Palm oil | Birch bark | - | 3 | 12:1 | 60 | 180 | 69.7 (C) | [171] |
| Waste cooking oil | *Musa balbisiana* peels | 10.176 | 2 | 6:1 | 60 | 180 | 100 (C) | [109] |
| *Azadirachta indica* oil | Cocoa pod husk | 2.76 | 0.65 | 3:2.2 | 65 | 57 | 99.3 (Y) | [115] |
| *Azadirachta indica* oil | *Musa paradisiacal* peels | 18.80 | 0.65 | 3:2.2 | 65 | 57 | 99.3 (Y) | [107] |
| Palm kernel oil | Banana fruit peels | - | 4 | 3:2.4 | 65 | 65 | 99.5 (Y) | [106] |
| Palm kernel oil | Cocoa pod husk | - | 4 | 3:2.4 | 65 | 65 | 99.3 (Y) | [106] |
| Soybean oil | *Musa sapientum* Linn peel | - | 1 | 12:1 | MW | 2 | 99.3 (Y) | [172] |
| Soybean | Orange peel | 605.60 | 7 | 6:1 | RT | 420 | 98 (C) | [160] |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| *Parinari curatellifolia* oil | *Tamarindus indica* fruit peel | 378 | 5 | 9:1 | 60 | 120 | 96.2 (Y) | [173] |
| Sunflower oil | Walnut shell | 8.8 | 5 | 12:1 | 60 | 10 | 98 (Y) | [187] |
| Waste cooking oil | *Tectona grandis* leaves | 116.833 | 2.5 | 6:1 | RT | 180 | 100 (C) | [157] |
| *Moringa oleifera* oil | *Carica papaya* peel | 3.6042 | 3.5 | 9:1 | 35 | 40 | 96.43 (Y) | [149] |
| Soybean oil | Moringa leaves | - | 6 | 6:1 | 65 | 120 | 86.7 (Y) | [161] |
| Honne oil | Cocoa pod husk + plantain peel | 18.86 | 4.5 | 15:1 | 65 | 150 | 98.98 (Y) | [158] |
| Sunflower oil | Ginger leaves | 0.834 | 1.6 | 6:1 | 60 | 90 | 90.13 (Y) | [147] |
| Palm oil | Spent coffee | - | 4.94 | 6.68:1 | 65 | 82.42 | 97.08 (Y) | [188] |
| Soybean oil | *Mangifera indica* peel | 123.34 | 6 | 6:1 | 28 | 240 | 98 (Y) | [162] |
| Refined soybean oil | Pineapple leaves | - | 4 | 40:1 | 60 | 30 | 98 (C) | [176] |
| Palm oil | *Musa sapientum* peel | - | 4 | 15:1 | 65 | 120 | 99.16 (Y) | [189] |
| *Hevea brasiliensis* oil | Kola nut pod husk | - | 3.5 | 6:1 | 65 | 75 | 96.77 (Y) | [175] |
| Sunflower oil | Wheat straw | 98.5 | 11.6 | 18.3:1 | 60.3 | 124 | 98.6 (Y) | [163] |
| Soybean oil | Acai seed | - | 12 | 18:1 | 100 | 60 | 98.5 (Y) | [177] |
| Waste cooking oil | Sugarcane bagasse | 20.78 | 5 | 15:1 | 60 | 15 | 92.12 (Y) | [190] |
| *Madhuca indica* oil | Banana pseudostem | 4.58 | 5.9 | 14.9:1 | 60 | 178.1 | 98.8 (C) | [178] |
| Waste cooking oil | Wheat bran | - | 11.66 | 1.46:1 | 54.6 | 114.21 | 93.6 (Y) | [116] |
| Jatropha oil | *Musa paradisiacal* peel | 4.1 | 5 | 9:1 | 65 | 12 | 97.56 (Y) | [169] |
| Jatropha oil | *Musa paradisiacal* trunk | 6.4 | 5 | 9:1 | 65 | 9 | 97.65 (Y) | [169] |
| Jatropha oil | *Musa paradisiacal* rhizome | 7.0 | 5 | 9:1 | 65 | 14 | 95.67 (Y) | [169] |
| Jatropha oil | Sugarcane bagasse | 7.66 | 10 | 9:1 | 65 | 285 | 92.84 (Y) | [104] |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Waste cooking oil | *Musa acuminata* flower petal | 79.33 | 5.63 | 6.24:1 | 28 | 221 | 99.99 (C) | [165] |
| Waste cooking oil | Plantain peel | 1.10 | 0.5 | 6:1 | 45 | 45 | 97.96 (Y) | [166] |
| Yellow oleander + rubber oil | Cocoa + kola nut + pumpkin | 17.266 | 1.5 | 9:1 | 55 | 40 | 95.02 (Y) | [179] |
| *Luffa cylindrical, Datura stramonium, and Lagenaria siceraria* oils | *Musa acuminate* and *Citrullus lanatus* peels | - | 3.53 | 9:1 | 90 | 80 | 96.63 (Y) | [180] |
| Waste cooking oil | Hazelnut shell | 4.9 | 5 | 12:1 | 60 | 10 | 98 (Y) | [167] |
| Waste cooking oil | Potato peel | 23.5 | 3 | 9:1 | 60 | 120 | 97.5 (C) | [168] |
| Waste cooking oil | *Musa acuminata* peel | 12 | 1.5 | 9:1 | 60 | 120 | 98 (C) | [181] |
| Microalgal oil | Sweet potato leaves | 2.81 | 7 | 15:1 | 60 | 90 | 99.5 (C) | [156] |
| Waste cooking oil | Sweet potato leaves | 2.81 | 5 | 9:1 | 60 | 120 | 98 (C) | [156] |
| Palm oil | Palm bunch | - | 18 | 15:1 | RT | 10 | 98.9 (C) | [182] |

MTOR–Methanol to oil ratio.; Temp–Temperature; min–minute; Y–Yield; C–Conversion.

### 1.3.4 Biodiesel properties

Transesterification of oil to biodiesel resulted in the decrease of density and viscosity with moderate increase of volatility of oil, which makes the properties of biodiesel similar to petro-diesel [10,31,191]. Density (15 °C, g cm$^{-3}$), kinematic viscosity (40 °C, mm$^{2}$ s$^{-1}$), cetane number, CFPP (°C), pour point (°C), flash point (°C), cloud point (°C), calorific value, etc., are some of the parameters to evaluate the quality of biodiesel. It is prerequisite that the properties of the produced biodiesel must meet the specification recommended by ASTM-D6751, EN-14214 and other standards before being used as the fuel. The properties of some biodiesel produced using the waste plants derived heterogeneous base catalysts from varied feedstocks are depicted in **Table 1.3**. This reveals that the properties of the produced biodiesel are within the range of international standards specified by ASTM-D6751 and EN-14214. The density and viscosity of the reported biodiesels are found well comparable with one another as well as are within the range of international standards except the value reported by Chouhan et al. [114] (6.80 mm$^{2}$ s$^{-1}$) for jatropha biodiesel. A worthy cetane number is desirable for a biodiesel to evaluate the ignition quality as a good fuel and higher value indicates higher combustion efficiency [192,193]. **Table 1.3** also reflects that the cetane number of the reported biodiesels are well above the minimum limit specified by ASTM-D6751 and EN-14214, which are signifying compatible efficiency of the biodiesels. The higher heating value (calorific value) of the reported biodiesel showed variation from higher to lower value which measures the energy content of the fuel indicating the amount of energy produced when the biodiesel burns completely [194]. It is reported that, with increase in alkyl chain length and molecular weight, the calorific value increases and with increasing degree of unsaturation it decreases [195,196]. Conclusively, the fuel properties of the produced biodiesel were found to meet the specification of international standards and waste plant derived heterogeneous base catalyst are efficient enough in producing quality biodiesels.

**Table 1.3:** Comparison of properties of biodiesel produced using various heterogeneous base catalysts derived from agro-wastes

| **Biodiesel feedstocks** | **Properties** | | | | | | | | | **References** |
|---|---|---|---|---|---|---|---|---|---|---|
| | **Density (15 $^{o}$C, g/cm$^{3}$)** | **Viscosity (40 $^{o}$C, mm$^{2}$/s)** | **Cetane Number** | **PP ($^{o}$C)** | **FP ($^{o}$C)** | **CP ($^{o}$C)** | **AV (mg of KOH/g)** | **IV (g $I_2$ /100 g)** | **CV (kJ/g)** | |
| *Thevetia peruviana* | 0.875 | 4.33 | 61.5 | +3 | +75 | +12 | 0.057 | 69.9 | 44.986 | [11] |
| *Jatropha curcas* | – | 4.07 | – | – | – | – | 0.00 | 109 | – | [100] |
| *Jatropha curcas* | 0.875 | 5.7 | 48.6 | +3 | 110 | – | 4.0 | 119.0 | 39.25 | [111] |
| *Mesua ferrea* | 0.890 | 5.525 | – | – | 113 | – | 1.8 | 113.2 | 35 | [110] |
| Waste cooking oil | 0.89 | 3.12 | 55 | −9 | 145 | −4 | 0.08 | – | 40.20 | [109] |
| *Thevetia peruviana* | 0.887 | 6.0 | 123 | +1 | 196 | +8 | 0.46 | 90.23 | – | [112] |
| *Azadirachta indica* | 0.88 | 5.0 | 81 | 9 | 274 | 21 | 0.45 | 58.6 | 48.7 | [107] |
| *Bauhinia monandra* | 0.876 | 4.90 | 59.83 | +0 | 285 | +20 | 0.45 | 52.22 | 43.19 | [105] |
| Palm oil | 0.86 | 4.3 | 76.93 | −6 | 284 | +3 | 0.4 | 40.90 | – | [106] |
| *Jatropha curcas* | 0.891 | 6.80 | – | – | 108 | – | 0.00 | – | 37.100 | [114] |
| *Jatropha curcas* | – | 4.21 | 57.1 | – | 164 | – | 0.05 | – | – | [136] |
| *Azadirachta indica* | 0.887 | 5.3 | 83 | −10 | 262 | 23 | 0.5 | 58.96 | 45.88 | [115] |
| Palm kernel oil | 0.87 | 4.7 | 44.4 | −3 | 300 | +12 | 0.5 | 24.7 | – | [106] |
| *Jatropha curcas* | 0.875 | 4.75 | 48.3 | −6 | 112 | – | 4.6 | 74.5 | 38.35 | [197] |
| Soybean oil | 0.888 | 4.9 | 52 | +0 | 200 | – | – | 115.5 | – | [198] |
| ASTM–D6751 standard | – | 1.9−6.0 | 47 (min) | – | 130 (min) | – | 0.50 (max) | NS | – | - |
| EN–14214 standard | 0.86−0.90 | 3.5−5.0 | 51 (min) | – | 120 (min) | – | 0.50 (max) | 120 (max) | – | - |

PP–Pour point; FP–Flash point; CP–Cloud point; AV–Acid value; IV–Iodine value; CV–Calorific value; min–minimum, max–maximum.

## 1.4 Rationale of the present work

Cost-effective and environmentally friendly biodiesel production at industrial scale is still a challenge for implementing it as alternative green fuel to petro-diesel. Apart from the cost of feedstock, the biodiesel production cost is governed by the cost of catalyst and manufacturing process. As the use of homogenous catalyst is not considered environmentally friendly, utilization of waste biomass base heterogeneous catalyst is expected for the large-scale biodiesel production in terms of economical point of view. The waste plant derived heterogeneous catalysts are showing prominent efficiency as cost-effective and environmentally friendly along with good yield of biodiesel. Researchers are still investigating for more suitable catalyst sources from waste plant which may give high catalytic activity for transesterification in very short time as well as possesses good recyclability. A number of heterogeneous catalysts derived from waste plant sources are reported. In addition to such heterogeneous catalysts, there is a need to extensively search of the superior catalyst which is not only cost-free but should also be easily available that can be served for large scale application in a cost-effective and eco-friendly production of biodiesel.

In the present study, it was aimed to utilize the waste/post-harvest plants such as *Brassica nigra*, *Sesamum indicum*, *Heteropanax fragrans* and banana waste as the solid catalysts for biodiesel production. These post-harvest plants are used for the preparation of traditional food-additive by the local people of North East India. This food-additive is the water extract of ash which is highly alkaline (basic) and is being used to make several traditional curry items. Locally, this water extract is known as *Khardwi* or *Khar* and the people of the region use it as a medicine also for the recovery from gas related problems. In this context, it was presumed that the highly basic ash material from the mentioned post-harvest plants could be utilized as the effective heterogeneous base catalyst for biodiesel production. Hence, in this study, we are attracted to develop solid catalyst from the waste plants for the purpose of cost-effective and eco-friendly synthesis of biodiesel.

## 1.5 Objective of the present study

The present study was proposed with the following objectives in order to find out the ideal catalyst which is both cost-effective as well as eco-friendly apart from exhibiting the high catalytic activity for biodiesel synthesis.

(a) Preparation of heterogeneous catalysts from waste biomasses/plants.
(b) Biodiesel synthesis from oils using the prepared catalysts.
(c) Characterization of chemical composition of the produced biodiesel.
(d) Determination of fuel properties of the biodiesel.