



Review

Biodiesel synthesis using natural solid catalyst derived from biomass waste – A review



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ABSTRACT

Biodiesel serves as an ideal candidate for alternative fuel as it is made from renewable source with lower pollutant emission. However, current biodiesel production has several issues such as unrecoverable catalyst, expensive separation stage and high wastewater generation due to the use of homogeneous catalyst. Currently, there are several pathways to produce biodiesel without the problems stated above such as supercritical condition transesterification and enzymatic catalyst. However, the economic feasibility for both methods serve as a major hindrance due to extremely high pressure and pressure, expensive synthetic cost of enzyme, which lead to higher operation cost. At the present, heterogeneous catalyst is the alternative, especially heterogeneous catalyst derived from natural resources such as waste biomass are currently being extensively researched with promising results. Thus, this paper illustrates the comprehensive research of biodiesel synthesis and assesses the latest breakthroughs involved in the use of catalysts derived from waste biomass. Furthermore, an amalgam of experimental data obtained from similar literature has been thoroughly reviewed to provide a better framework to produce biodiesel. Apart from that, this study aims to alleviate problems associated with heterogeneous catalyst separation and enhance the economic viability of the industry, thus, sustaining the environment while meeting energy demands.

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Introduction

Biodiesel has become an increasingly prevalent alternative medium for biofuels following the repercussions from the exponential depletion of fossil fuels and the several environmental issues that surface with its use [1]. The prime factor of the globalization of biodiesel is its suitability with currently available diesel engines without the need for mechanical modifications. Contrary to fossil-based diesel, biodiesel also offers biodegradability and non-toxicity [2]. Furthermore, McCormick et al. [3] reported that biodiesel is free of aromatic groups and possesses significantly low sulfur content when compared to that of ultra-low sulfur diesel (ULSD). The value is specifically reported to be 5 ppm lower in sulfur content [4]. Greenhouse gas emissions which encompasses hydrocarbons, CO, CO₂, SO₂ and dust are less in the combustion of biodiesel when compared to that of fossil diesel [5]. The various techniques of biodiesel synthesis include dilution, thermal cracking (pyrolysis), micro-emulsification, supercritical process, microwaves technique, ultrasonic reactor, and lipase-assisted enzymatic method [6]. That aside, the transesterification method reigns in terms of popularity among others in commercial plants that produce biodiesel. This method is carried out by the reaction of oils, which may comprise of animal fats, vegetable oils, used cooking oils or algae oil, with alcohols of low molecular weight, which is typically methanol or ethanol. Transesterification is a catalyzed reaction that utilizes three main groups of catalysts, namely acid or base heterogeneous catalysts, acid or base homogeneous catalysts as well as enzymatic catalysts. According to Narowska et al. [7], the most common catalyst adopted in the commercialized synthesis of biodiesel is the homogeneous base catalyst.

However, this existing method of producing biodiesel on an industrial scale is faced with challenges such as the difficulty of separating the products formed and the use of irrecoverable homogeneous base catalysts. Carbon derived heterogeneous catalyst are viewed as a promising candidate to replace homogeneous catalyst. For these reasons, biodiesel production has been linked to high separation and purification costs as well as significant wastewater and waste generation due to the irrecoverable catalysts used [8]. In turn, the wastewater produced poses as a health threat to marine life and humans as it possesses chemical components that are harmful towards life [9]. The use of acid homogeneous catalyst also faces similar problems as it possesses corrosive properties and requires harsh reaction condition. Other types of catalyst face problems in initial stages of development such as high initial synthesis cost or high operating cost.

On the other hand, the persistent problem in agricultural industry on the disposal of waste biomass ensues. Carbon derived heterogeneous catalysts are viewed as promising candidates to replace homogeneous catalysts in industrialized biodiesel production as it has shown good reusability, comparable catalytic activity, high surface area and decent thermal stability [10]. Carbons functionalised with various groups of sulfonic acids, alkoxides, alkali metals, transition metals and enzymes to improve the heterogeneous catalytic activity in the transesterification of oil feedstock to biodiesel. Waste biomass from the agricultural industry can be used to derive carbon-based catalyst. In Malaysia, 1.2 million tons of agricultural waste is estimated to be disposed of at landfills every year [11]. Therefore, development of effective methods to utilize the waste biomass such as these could serve to be a way to reduce the land occupied by landfills by reducing the agricultural waste.

Among the various methods for improving the characteristics of a catalyst is the integration of magnetic properties in carbon nanomaterials. This technique supplies a substance with flexibility to be utilized in several domains which encompasses adsorption, active compound immobilization, CO₂ capturing, super capacitance and catalysis. Nonetheless, the most constructive advantage of magnetizing carbon nanomaterials is the simplicity of its separation process merely by applying a magnetic field [12]. In the field of catalysis, this is particularly beneficial for the separation of a solid catalyst in a liquid medium. That said, this review paper offers an extensive insight to various types of natural catalysts used for the synthesis of biodiesel. A brief introduction on biodiesel is given together with its assorted methods of production, followed by the shift in focus onto the catalyzed transesterification method. Apart from that, catalysts derived from biomass waste and their characteristics are being extensively discussed in this review paper. This paper also offers a succinct kinetic study of catalyzed transesterification reactions in hopes to comprehend and further develop the application of natural catalysts in biodiesel production.

General background of biodiesel

Biodiesel is the most promising solution to overcome the various arising matters attributed to fossil fuel consumption, especially considering the renewable nature of biodiesel as it is derived using renewable feedstock such as crops, biomass and even algae. It also possesses similar characteristics to those of diesel and hence, allowing it to be applied in diesel engines without the need for engine modifications. Aside from that,

biodiesel is sulfur-free, emits less smoke, hydrocarbons (HC), carbon monoxide (CO), as well as particulate matters (PM) while possessing higher cetane number and flashpoint than conventional fossil-based diesel [13]. Besides, the fact that they contain a higher concentration of free oxygen, as high as 10–11% by weight, than petrol diesel allows for a complete combustion reaction and in turn, encourages the reduction of harmful emissions [14]. These can all be achieved without compromising the initial design of the engine while persisting or even improving engine efficiency. Its biodegradability and lubricity are also worth noting as a sustainable resource for diesel fuels in the future [15]. Furthermore, waste biomass such as waste animal fat or cooking oil and factory effluents high in oily sludge content can be used as feedstock for the biodiesel production. This helps to reduce the overall cost of production while addressing the ever-rising issues of waste disposal in the world.

Oil feedstock

Biodiesel possesses physicochemical attributes similar to that of diesel derived from fossil fuels and thus, can be directly applied in a diesel engine without the need of mechanical alteration [16]. This biomass-derived diesel can be categorised under four generations based on the raw material used for production. The first-generation biofuel consists of commercially produced fuels yielded from edible natural sources, for example, corn, canola, wheat and sunflower [17]. Second generation fuels are also industrially synthesised in this era and they utilise inedible lignocellulose biomass as feedstock. Examples of these lignocellulose materials are straw, forest residues and bagasse. Biofuels categorized under the third generation are those produced using marine biomass and algal feedstock. Commercial synthesis has yet to be achieved as its metabolic production and separation operations are still subjected under research and development [18]. Finally, fourth generation biofuels are fuels produced via genetically modified algae or cyanobacteria from synthetic biology technologies. Although this technology is still in its pioneering stage, it possesses insurmountable potential for the shift of energy generation from fossil-based resources to renewable sources [19].

First-generation biofuel makes up of more than 95% of biodiesel today [20]. This means that edible sources, which may otherwise be used for food, are being used to produce automotive fuels. Due to this controversy, the further expansion of biodiesel production is presumed to cause a hike in oil prices because both automotive and food industries would be competing for the same resources and place the market of supply and demand at an imbalance [21]. Nevertheless, edible oils are currently the cheapest option for biodiesel production when compared with the use of non-edible or algal biomass. The extra processes required to manufacture biodiesel will increase the final cost of the product to be on similar pars as that manufactured from edible oils but with extra steps involved. On the other hand, algal-based biodiesel is expensive, unstable and has a tendency to degrade especially at elevated temperatures [22]. Table 1 depicts the oil sources suitable for biodiesel production. However, the free fatty acid (FFA) content in the oil feedstock is a crucial factor to determine the process of biodiesel production. For FFA content >0.5 wt%, an acid pre-esterification step may be needed to reduce the amount of FFA which will hinder transesterification reaction if left untreated [23]. Table 2 shows the FFA content in some typical oil feedstock for biodiesel production.

Method of synthesizing biodiesel

There are different processes which can be used to synthesize biodiesel, for example, thermal cracking, non-catalytic

Table 1
Oil feedstock for biodiesel synthesis [24].

Edible oils	Non-edible oil	Other sources
Canola oil	Eucalyptus oil	Microalgae
Castor oil	Jatropha oil	Animal fats
Coconut oil	Karanja (Pongamia oil)	Beef tallow
Cottonseed oil	Linseed	Chicken fat
Mustard oil	Mahua oil	Chlorella protothecoides microalgae
Palm oil	Neem	Fish oil
Rapeseed oil	Polanga	Poultry fat
Soybean oil	Rubber seed	<i>Spirulina platensis</i> algae
Sunflower oil	Yellow oleander	Waste cooking oil

supercritical process and the most conventional way is transesterification process [26].

Thermal cracking

Thermal cracking or in another term called, pyrolysis is expressed as the process of converting one substance into another form using heat with or without the assistance of a catalyst. This process comprises of heating in the absence of air or oxygen and breakage of chemical bonds to produce smaller size molecules. The pyrolysis of specifically vegetable oil, to yield biofuels has been researched and discovered to produce alkanes, alkenes, alkadienes, aromatics and carboxylic acids in different quantities. The cost of equipment for thermal cracking is high for ordinary production of biodiesel especially in developing countries. As for disadvantages, the removal of oxygen throughout the thermal cracking process, eliminates environmental advantages of consuming an oxygenated fuel. To note another disadvantage of thermal cracking is the requirement of distinct distillation equipment for the separation process of the numerous fractions. Parawira [27] stated that the product obtained is known to be similar to gasoline that contains sulphur which deems it to be less eco-friendly. Pyrolytic chemistry is not easy to distinguish because of the variation of reaction path and the multiplicity of reaction products that may be attained from the occurring reaction. The first pyrolysis of vegetable oil was carried out in an effort to produce petroleum from vegetable.

Non-catalytic supercritical process

Non-catalytic supercritical transesterification process provides high conversion and reaction rate which results in large yield in a limited time scope. Easier separation and purification techniques are involved as catalyst is absent. Supercritical biodiesel production is not influenced by the presence of FFA and water content which are in oils or fats. Pre-treatment measures that are done to limit the water content in oils are not required. Moreover, the operating temperature and pressure of supercritical reaction typically varies in the range of 200–400 °C and 10–25 MPa, respectively. The temperature and pressure conditions must be set at above the critical values of alcohol to increase solubility in oils [28]. A few examples of transesterification in supercritical methanol are shown in Table 3. It can be observed that the operating temperatures and pressures of the reaction are greater than the critical temperature (T_c) and pressure (P_c) of methanol which are 239 °C and 8.09 MPa, respectively [29]. These operating conditions spend large amount of energy, thus making biodiesel production economically implausible and limiting it from striding into industrial level.

Transesterification

The usual way to produce biodiesel is using the conventional transesterification method, which means to generate a catalysed chemical reaction comprising of vegetable oil and alcohol to produce methyl esters (biodiesel) and glycerine (soap). The reaction needs a catalyst, normally a strong base, like potassium

Table 2
Free fatty acid content in different oil feedstock [25].

Oil feedstock	FFA content (wt%)	Oil feedstock	FFA content (wt%)
Rapeseed oil	3	Crude rice bran oil	15–60
Soybean oil	1	Yellow grease	5–20
Jatropha curcas oil	4–10	Karanja oil	7–8
Animal fats	2–50	Inedible tallow	2–35
Brown grease	30–100	Coconut oil	5
Waste cooking oil	2–7	Crude tall oil	20–60
Corn oil	9	Trade return margarine	<1
Microalgal oil	4.5–9	Acidulated soapstocks	50–60
High acid oils	>98	Sunflower oil	3.5
Deodorizer distillate	90	Crude palm oil	4.5

Table 3
Supercritical transesterification reaction.

Oil feedstock	Reaction Conditions					Ref.
	Temperature (°C)	Pressure (MPa)	Time (h)	Methanol to oil molar ratio	Yield (%)	
Waste vegetable oil	271.1	23.1	0.34	33:8:1	Y = 95.27	[30]
Refined and used palm olein oil	400	15	0.333	12:1	C = 99	[26]
Krating oil	260	16	0.167	40:1	Y = 90.4	[31]
Jatropha oil	320	15	0.0833	40:1	Y = 84.6	[31]
Karanja oil	300	26	1.5	43:1	Y = 81.15	[32]
Jatropha oil	325	35	1.5	42:1	C = 100	[33]
					Y = 99.5	

and sodium hydroxide or sodium methylate [34] or sulfuric acid based transesterification processes. Following that, acid catalysts are too time consuming to be realistic for the conversion of triglycerides to biodiesel; nevertheless, acid catalysts are applicable at converting free fatty acids, FFAs to biodiesel. Hence, an acid-catalysed pre-treatment measure to convert the FFAs to methyl esters, then an alkali-catalysed step to convert the triglycerides would offer an efficient method to convert high FFAs to methyl ester [35]. Transesterification process benefits in the reduction of viscosity of the oil [34]. Catalysts are usually used to further enhance the reaction rate and the yield. Due to the reversibility, excessive alcohol is normally implemented to alter the equilibrium to the products side. Specifically, methanol is used as alcohol as its low cost benefit. Methanol can rapidly react with oil feedstock [36]. The triglycerides are used to react with an appropriate alcohol in the presence of a catalyst under a constant temperature for a given duration of time. Fig. 1 below represents the transesterification

process of a biodiesel production, where R_1 , R_2 , and R_3 represent long-chain of fatty acid [37].

Homogeneous base catalysed transesterification. The most common method employed in commercial biodiesel production is homogeneous base catalyzed biodiesel process. The chosen oil feedstock (waste cooking oil, refining cooking oil etc.) is reacted with a suitable alcohol such as methanol to undergo transesterification under the presence of homogeneous catalyst. The types of common homogeneous catalyst used includes sodium hydroxide or sodium methylate with the former being the most common due to its economic benefit, i.e. lower cost [23]. A block flow diagram of the homogeneous base catalyzed biodiesel process is shown in Fig. 2.

As indicated by Fig. 2, several filtration and purification stage are required in this kind of process. These separation stages are needed due to the formation of soap induced by the side reaction catalyzed by alkaline catalyst. Alkaline catalyst will react with FFA

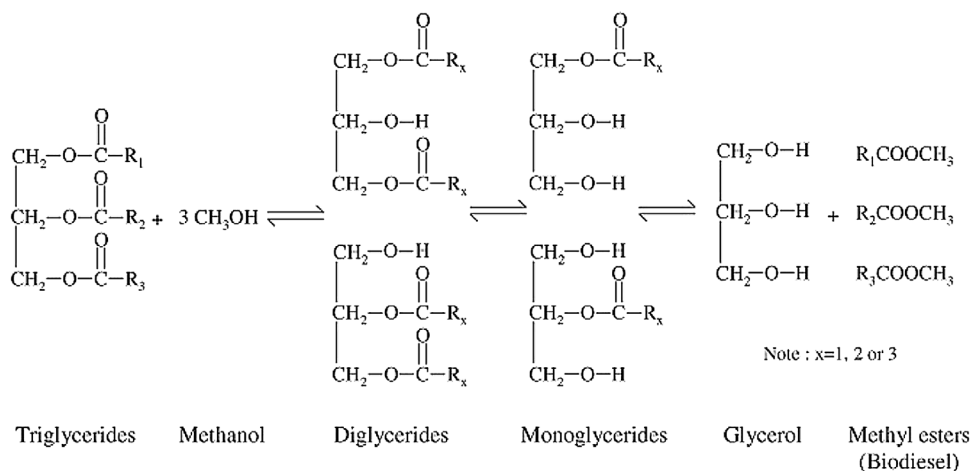


Fig. 1. Mechanism of triglyceride with methanol to produce fatty acid methyl ester and glycerine [38].

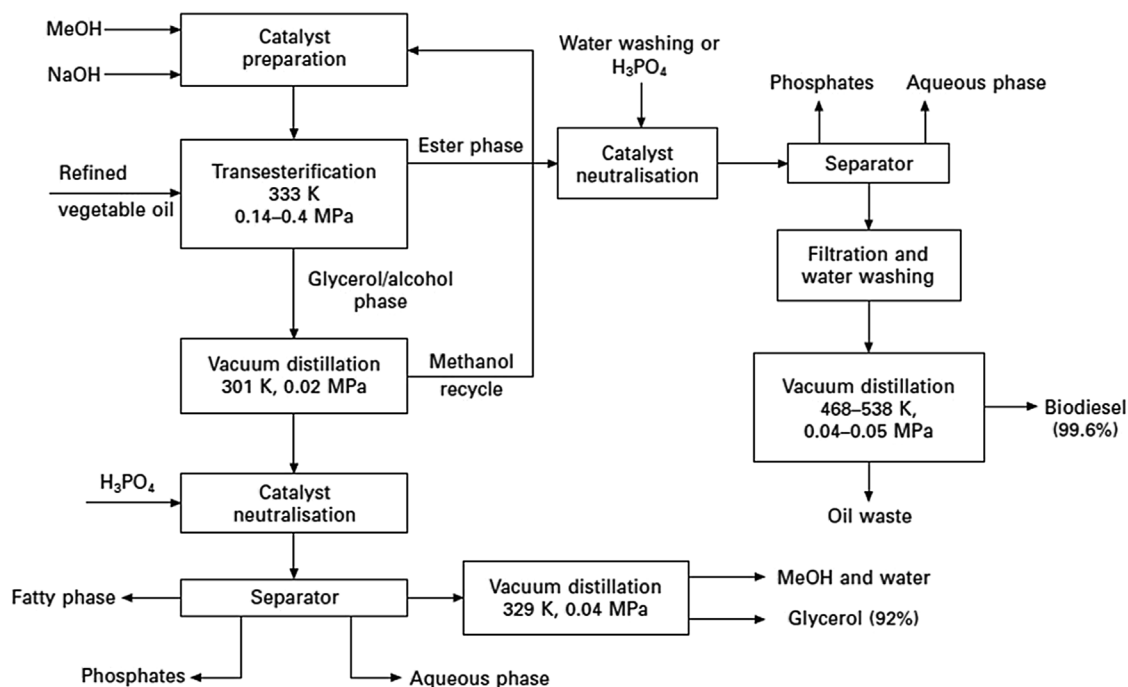


Fig. 2. Block flow diagram for the transesterification process in the presence of a base catalyst [23].

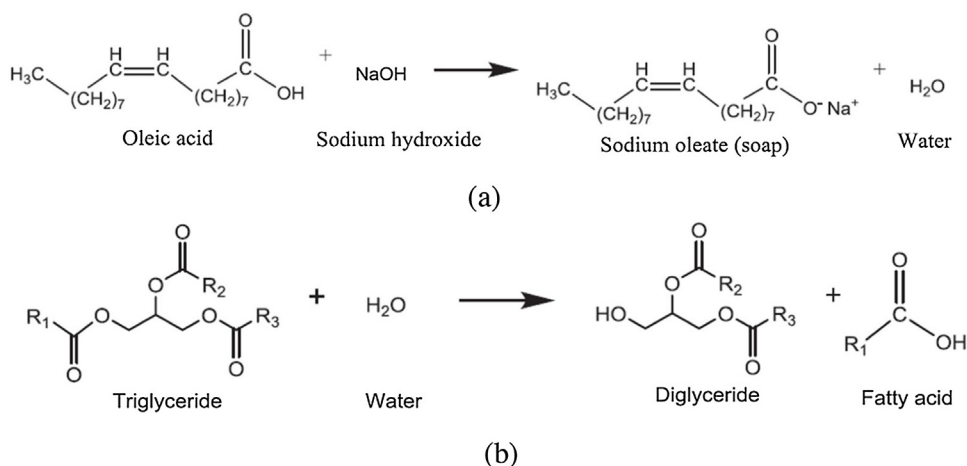


Fig. 3. (a) Saponification reaction between oleic acid and sodium hydroxide (b) Hydrolysis reaction of triglyceride [39].

to produce soap, which is an unwanted product. The reaction equation is shown in Fig. 3. As a further discussion to this matter, homogeneous alkaline catalyst is also susceptible to water due to the hydrolysis of triglycerides. Fig. 3 below shows the reaction equation and the resulting free acid will undergo saponification reaction with the alkaline catalyst to produce more soap. Therefore, the formation of soap and the removal of it is one of the major drawbacks of this type of catalyst.

Homogeneous acid catalysed transesterification. Acid catalysed biodiesel production process is not as ubiquitous as its base counterpart due to the harsher reaction condition requirement and significantly longer reaction time required to achieve desired yield. Other than that, acid catalysed biodiesel process demands harsh reaction condition at high reaction temperature, high methanol to oil ratio and can cause environmental issue due to the highly corrosive nature of the catalyst [39]. Thus, acid catalysed biodiesel

process is often employed before base catalysed process to remove FFA content in the oil feedstock to reduce the formation of soap, normally referred as pre-esterification. An acid-catalysed reaction is typically used as the pre-esterification process to decrease the FFA content of an oil feedstock to an extent of less than 1% before the usual base-catalysed transesterification process [23]. The capability of such reduction in FFA content extends the potentiality of utilizing low-grade feedstocks, which can be obtained at a low cost that may include yellow grease with FFA content at a range of 9–20 wt%. Fig. 4 below portrays a block flow diagram that simplifies the acid-catalysed pre-esterification process. The process demonstrates that several stages of alcohol recovery and recycle are essential as this process requires alcohol of high volumes in excess [23].

Enzymatic catalysed transesterification. The concept of enzymatic catalyst such as lipase being used to catalyze biodiesel production

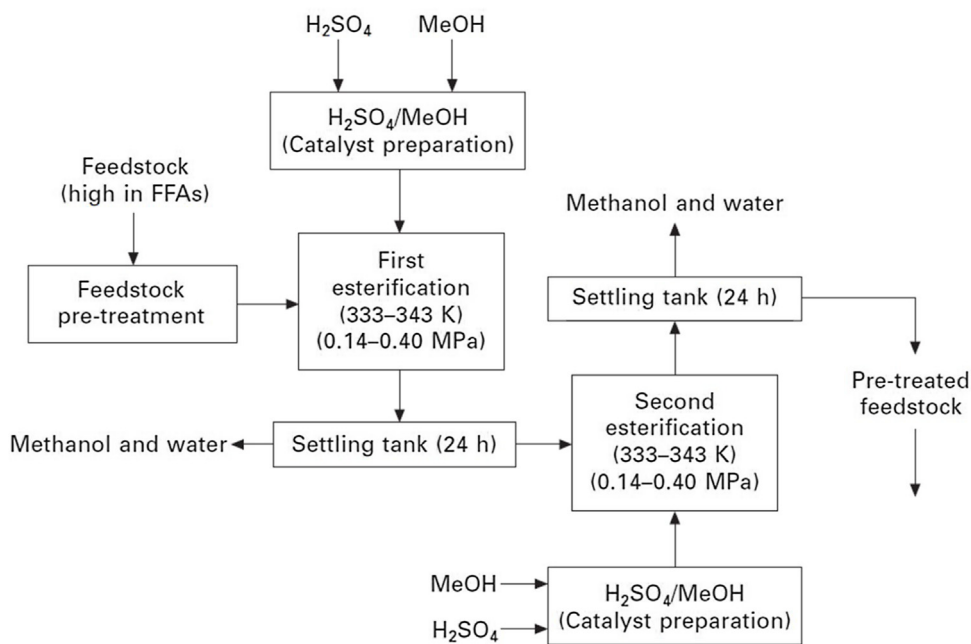


Fig. 4. Block flow diagram for the pre-esterification process in the presence of an acid catalyst [23].

was proposed two decades ago. However, its actual performance and feasibility are only being explored extensively in recent times due to the trend of developing new types of catalyst for biodiesel production. Lipase is a highly complex chains of amino acids that demonstrates both acidity and basicity owing to its unique composition of amino acids, possessing both $-\text{COOH}$ and $-\text{NH}_2$ groups simultaneously. It is a water soluble enzyme under the class of hydrolases (enzyme specifically catalyzes hydrolysis reaction) present in living organism. Lipase allows the splitting of ester bonds in triglycerides when water content in media is low and consequently, promote ester formation in environments with low water content [40]. The major advantage of using enzymatic catalyst is that it only requires mild reaction condition with atmospheric pressure, neutral pH and ambient temperature. Other than that, the production of specific product is made possible with the stereospecificity nature of enzyme.

On the other hand, enzymatic catalyst is free from the problem of soap formation that has plagued homogeneous base catalyst. Therefore, the separation/purification stage is not needed when enzymatic catalyst is used, thus reducing the operating cost and wastewater generation. Moreover, the catalytic activity of lipase is not affected by the presence of water, in contrary to homogeneous acid catalyzed reaction [41]. That said, the main hindrance preventing enzymatic catalyst from going into commercial scale production is the high synthesis cost due to the difficulty of isolating the enzyme from the microorganism that produces them. The other reason is that enzyme is easily denatured and only possesses high catalytic activity under highly specific condition. Narrow spans of operating conditions such as temperature and pH

are crucial in maintaining the performance of this catalyst as they are known to denature outside the optimum range. Apart from that, methanol, which has been the primarily used alcohol feedstock thus far, is poisonous towards most varieties of lipases [40]. Impurities that may be present in the oil feedstock used, like phospholipids, will also jeopardize the performance of the enzymatic catalyst due to poisoning [40]. Therefore, the use of enzymatic in commercial biodiesel production is still under development to overcome critical problems stated above. Table 4 summarized the biodiesel production with enzymatic catalysts and Table 5 tabulated the advantages and disadvantages of different types of catalyst.

Optimization of reaction condition

To optimize the reaction condition, one typically needs a large set of result to adequately cover the input space. For example, the parameters that affects the result of biodiesel yield includes methanol to oil ratio, temperature, catalyst loading, reaction time and stirring rate with fixed type of catalyst and oil feedstock. The effects of these parameters are further discussed below.

Effect of methanol to oil ratio

As transesterification is a reversible reaction, simply reacting 1 mol of methanol with 1 mol of oil feedstock will not produce 1 mol of biodiesel due to the reversible nature of the reaction. Therefore, higher methanol to oil ratio favours the forward reaction and thus provides higher yield at equilibrium. However, excess amount of alcohol may hinder the catalysis with excess amount of alcohol

Table 4
Transesterification reaction with enzymatic catalysts.

Catalyst	Feedstock	Reaction Conditions				Yield (%)	References
		Temperature (°C)	Time (h)	Methanol to oil molar ratio	Enzyme (wt.%)		
Eversa transform (L)	Castor oil	35	8	6:1	5	94.2	[42]
Candida rugosa lipase (I)	Tallow kernel oil	40	24	4:1	10	95.4	[43]
Candida antarctica lipase B	Waste tallow	–	0.333	4:1	6	85.6	[44]
Callera Trans L	Rapeseed oils	35	24	4.5:1	0.5	95.3	[45]

Table 5
Advantages and disadvantages of different types of catalyst [40].

Catalyst	Advantages	Disadvantages
Homogeneous base catalyst	Existing technology with validated results Cheap High yield of biodiesel at mild operating conditions High rate of reaction Low alcohol-to-oil ratio Relatively low investment cost	Demands refined and pre-treated oil or fat which is expensive Demanding feedstock quality (low moisture content, less than 0.5 wt % FFA) Non-recyclable catalyst High purification cost (formation of soap) Requires equipment made of stainless steel
Homogeneous acid catalyst	Insensitive to FFA content in the oil and low cost allowed Promotes the formation of long-chained or branched esters Short reaction times with FFA, no soap formation Simultaneous esterification/transesterification	Much slower reaction rates compared to alkaline catalyst Corrosion-resistant materials required Unfavourable reaction condition Non-reusable catalyst Inhibited by water
Enzymatic catalyst	High stereo-, regio- and chemo-selectivity Products formed are of high purity By-products are not formed Mild reaction conditions (low pressure, temperature and alcohol-to-oil ratio) Able to product long or branched esters Simple product recovery, no wastewater treatment needed	Expensive catalyst synthesis route Long reaction time Influenced by the presence of impurities (e.g. phospholipids) Narrow operating condition (strict range of temperature and pH) Longer processing time Low yield
Heterogeneous base catalyst	Higher rate of reaction than acid catalyst Mild reaction conditions Easy separation catalyst from liquid mixture Possibility to reuse and regenerate	Tend to absorb moist from the atmosphere Sensitive to FFA content in the oil Soap formation due to high FFA Catalyst leaching
Heterogeneous acid catalyst	Insensitive to FFA content in the oil Simultaneous esterification/transesterification Easy separation catalyst from liquid mixture Possibility to reuse and regenerate	Higher operating conditions (temperature, time, alcohol:oil ratio) Catalyst leaching
Non-catalytic supercritical	Simpler purification Simpler separation Generates good quality by product, glycerin No catalyst involvement	Extreme operating conditions (high temperature and pressure) Intensive energy requirement High alcohol: oil ratio Lower yield than conventional transesterification

adsorbed onto the catalyst active sites and inhibiting the reaction [46]. For example, from the work of Buasri et al. [47], methanol to oil ratio of 9:1 was found to be the optimal ratio for biodiesel yield at 96%. However, methanol to oil ratio higher than that resulted in lower overall biodiesel yield as too much excess methanol will interfere with the separation of glycerine and in turn inhibits the reaction [48].

Effect of catalyst loading

High amount of catalyst may favour the completion of the reaction and result in higher biodiesel yield in shorter reaction time, but excessive catalyst amount will increase the viscosity of the blend and thus decreases the surface contact between the catalyst active sites and reactants [49]. For example, from the work of Buasri et al. [47], catalyst loading of 10 wt% was found to be the optimum loading for biodiesel yield at 96%. Catalyst loading lower than 10 wt% will have lower overall yield due to insufficient active sites for reactants to react whilst loading higher than 10 wt% will have unfavourable mass transfer limitation inhibiting the reaction.

Effect of reaction temperature

Reaction temperature is an important parameter for all sorts of reaction let alone transesterification. Higher temperature allows more active movement for particle and more collision between particles resulting in higher reaction rate. However, maintaining high temperature requires large heat duty and incurs high operating cost. For example, from the work of Buasri et al. [47], reaction temperature of 65 °C was found to be the optimal temperature for biodiesel yield at 96%. Temperature lower than that will result in significant decrease in biodiesel yield as expected and reaction higher than 65 °C will also decrease the biodiesel yield as the boiling point of methanol is 70 °C. Approaching 70 °C will result in the boiling of methanol and thus interfere with the mass transfer properties.

Effect of reaction time

Reaction time is an important parameter to allow the reactants to undergo reaction and be converted to product. However, study from Buasri et al. [47] shows that reaction time exceeding the optimal value may result in reverse reaction occurring in the reaction medium, decreasing in overall biodiesel yield. For example, from the work of Buasri et al. [47], reaction time of 4 h was found to be the optimal value for biodiesel yield at 96%. Whilst longer reaction time has negative effect on overall yield when compared to shorter reaction time (insufficient time to complete the conversion), overall yield showed slight decrease when the reaction time is longer than 4 h. They deduced that the reaction might be reversible when product concentration is high, favouring the reverse reaction.

Effect of stirring

The stirring intensity also known as stirring speed of the reaction during the reaction is a very important parameter. Stirring intensity contributes a significant effect on the biodiesel yield as it triggers the reaction when the effective contact area between the two involved reactants that without stirring would just be in contact through the interface between two liquid phases. Stirring aids, the increase in reaction rate homogenizing the reactants to become single phase and elevates the biodiesel yield [50]. It has been reported that by increasing the stirring intensity from 150 rpm to 450 rpm, there is a prominent increase in biodiesel yield from 55.80% to 75.10% that remains constant throughout continuous stirring at the same intensity. At 450 rpm, a maximum yield of 75.10% was successfully achieved for a reaction time of 50 min.

Biomass waste catalysts

Catalysts are an essential integration to the biodiesel synthesis pathway as they function to increase the rate of conversion of

triglycerides to become FAME by offering a different course of reaction that requires a lower supply of activation energy. They can be classified under three major categories which are: homogeneous and heterogeneous catalysts as well as biocatalysts, whereas the two formers can be further broken down into two categories of acid and base catalysts [51]. Homogeneous base catalysts provide the most efficient pathway in transesterification reactions and are used in most industrial applications. However, this higher rate of reaction is achieved at the expense of the ease of product separation in large-scale operations [52]. Homogeneous catalysts are hard to be recovered and this poses as a challenge for their reusability. Adding to this, the production cost of biodiesel also surges from the numeral steps of washing and purification of the final product to meet standard requirements. Moreover, large volumes of water and mandatory treatment of the resulting wastewater generated from the purification process contribute to the overall cost of production as well [10]. Fig. 5 shows the flowchart of biodiesel synthesis via the base-catalysed transesterification method.

As mentioned earlier, the application of the transesterification reaction in the presence of a base catalyst to produce biodiesel persists as the most widely used technique, with most archetypal catalysts falling under the homogeneous category. Examples of frequently used base catalysts are CH_3ONa , KOH and NaOH . While these catalysts offer several benefits such as relatively high rates of reaction, gentle reactions and low cost, there are some disadvantages that are worth noting [7]. Shahbazi et al. [53] denotes that one of such disadvantages include the occurrence of saponification reaction which forms soaps as a result of the simultaneous presence of FFA and a base. Thus, the final biodiesel yield is severely decreased and an increased demand in base catalyst is observed as there are low possibilities of recovery or reusability of

the catalyst. Additionally, the separation of product proves difficult and cost-consuming as the esters tend to dissolve in the glycerol produced, forming an emulsion of ester-glycerol [54]. Therefore, it can be deduced that the pertinence of the base catalyst in the reaction is limited to high-purity feedstock containing minimal percentage of FFA and even water because it promotes the formation of FFA by hydrolysis. The method of washing with warm or acidified water is a typically adopted in industries to purify the biodiesel yielded. Consequently, a large amount of wastewater is generated which requires further purification and treatment. These factors will contribute to the high cost attributed to the manufacture of biodiesel.

The issues tied to the employment of base catalysts in transesterification reactions of biodiesel production can be countered with the alternative technique using esterification of FFA using acid catalysts. Acid catalysts are added to the alcohol during the pre-treatment of FFA that is of subpar quality to generate fatty acid alkyl esters (FAAE) [54]. The popular base-catalysed reaction step usually follows to promote further ester formation because of the slow process of acid-catalysed reaction. Hydrochloric, sulfonic and sulphuric acid are common examples of these acid catalysts [55]. Despite its capabilities to assist in the biodiesel synthesis reaction by transesterification, acid catalysts offer a significantly low rate of reaction that may take up to 24 h for the completion of oil to biodiesel conversion [56]. Regardless of that, the vitality of acid-catalysed esterification reaction prevails as an effective method to produce biodiesel when using non-edible oils or feedstocks that contain high levels of FFA such as industrial effluents, used cooking oil and poultry fat.

Aside from chemical catalysis as described before, biocatalysis is also gaining worldwide recognition in the biodiesel industry. This term refers to the use of biological enzymes that are naturally

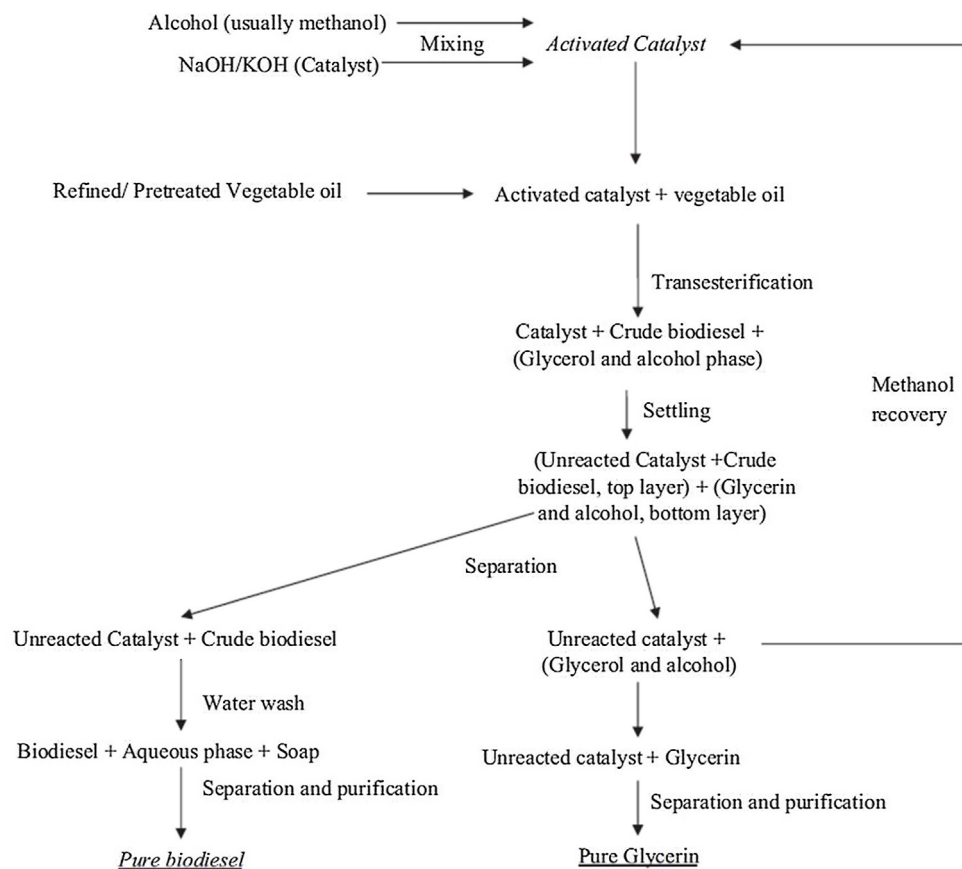


Fig. 5. Flowchart of biodiesel production via the transesterification method using homogeneous base-catalysts [10].

produced in living organisms as catalysts to increase the reaction rates of a process [57]. This catalyst is categorised under the group of heterogeneous catalysts. A prime example of a biocatalyst applied in the process of biodiesel synthesis is lipase which is applied to catalyse the hydrolysis and transesterification reactions under gentle conditions [58]. Contrary to transesterification processes that utilise base catalysts, the use of biocatalysts sustains the final amount of biodiesel obtained at the end of the reaction even when water is present as saponification will not occur. Apart from the presence of water in the reaction, Kulkarni and Dalai [59] also reported the insensitivity of enzymes towards FFA. Additionally, the reusability of enzymes was found to be relatively high which potentially reduce production cost. Unfortunately, the cost of manufacturing enzymes that far outweigh its benefits and the crucially slow process of biodiesel production renders it commercially unviable on industrial-scale applications at present day [52].

With all the inconveniences that come with homogeneous catalysts, heterogeneous catalysts have unquestionably taken some of the limelight throughout the decade as observed from the many studies that have recently surfaced on the production of this catalyst for the transesterification process. Unlike that of homogeneous catalysts, heterogeneous catalysts possess characteristics that allow for easier separation from the mixture of reaction and provide comparatively high reusability [7]. They are also cheap, less corrosive, non-toxic and highly stable even when subjected under high temperatures. Fig. 7 below illustrates the flow of the biodiesel synthesis process in the presence of heterogeneous catalysts. Numerous materials, natural and synthetic alike, have been the topic of study to be converted to heterogeneous catalysts for increased efficiency in biodiesel derivation from triglycerides [60]. Once again, they are differentiated into two categories: heterogeneous base and acidic catalysts. Heterogeneous base catalysts may include oxides of Mg, Ca, Na or K and basic zeolites while that of acidic properties include acidic ion exchange resins, sulphated zirconia and acid zeolites [61]. Fig. 6 displays the reaction mechanism of CaO heterogeneous catalyst to produce biodiesel.

Biomass waste solid catalyst

Recently, biomass-derived heterogeneous catalysts have been a popular topic of research in this field due to their potentiality to aid in production cost reduction and biodegradability. Biomass refers to the plant- and animal-sourced organic material that can be used

for energy generation by direct use or further enhancements. Apart from cost reduction, the exploitation of biomass for catalyst manufacture also provides a plausible answer to the biomass waste disposal issue that deteriorates with the ever-increasing rate of waste generation as a result of agricultural and other human activities [62]. The most common alkali heterogeneous catalyst are metal oxides such as calcium oxide (CaO), magnesium oxide (MgO) and strontium oxide (SrO). According to Zabeti et al. [63], CaO is the most suitable catalyst out of all metal oxide due to its low solubility in methanol and the highest alkalinity among all other alkaline earth metal oxides. In a research conducted by Kouzu et al. [64], a biodiesel yield of 93% was attained by reacting edible soybean oil and methanol under temperature of 64.7 °C, methanol to oil ratio of 12:1 for 1 h using CaO catalyst synthesized from the calcination of pulverized limestone (CaCO₃) at 900 °C for 1.5 h. On the other hand, a FAME yield of only 20% is achieved by using MgO as catalyst with same feedstock under similar reaction condition [65]. This validates that CaO is the superior catalyst over other alkaline earth metal oxides.

On the other side of the coin, acid heterogeneous catalyst has a lower catalytic activity when compared to basic heterogeneous catalyst. That said, the flexibility to catalyse esterification and transesterification simultaneously and thus eliminates sensitivity to FFA content still serves as one of the reasons to use the acid catalyst over base catalyst. Other than that, acid heterogeneous catalyst is less corrosive and toxic when compared to homogeneous catalyst. However, its lesser catalytic activity also means slower reaction rates. The occurrence of unwanted side reactions is also among its disadvantages. The most common types of acid heterogeneous catalyst are zirconium dioxide (ZrO₂), titanium dioxide (TiO₂), tin dioxide (SnO₂) and sulfonic ion-exchange resins such as Amberlyst-15, Amberlyst-35 and Nafion-NR50. Metal oxides needs to be impregnated with sulfuric acid to increase its surface acidity for it to show appreciable catalytic activity [66]. From a study conducted by Jitputti et al. [67], biodiesel production using palm kernel oil and crude coconut oil catalysed by impregnated ZrO₂ have yield of 90.3% and 86.3% respectively. Without impregnation however, the yields drop to 64.5% and 49.3% respectively. Sulfonic ion-exchange resin is an excellent catalyst for oil feedstock containing high FFA content as it demonstrates great catalytic activity for esterification. However, the shortcomings of this catalyst include low catalytic activity for transesterification, unsatisfactory thermal stability (unstable >140 °C) and requires high reaction temperature (150–200 °C). Moreover, it requires very high methanol to oil ratio. From the study conducted by Vicente

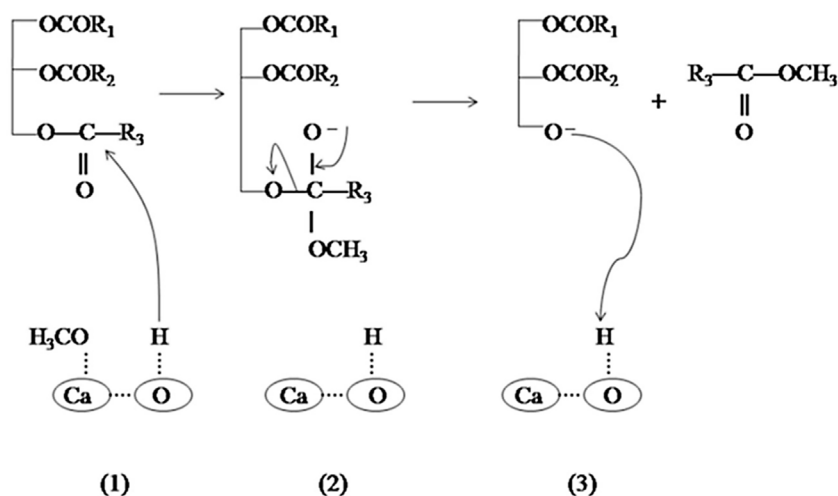


Fig. 6. Mechanism of CaO heterogeneous catalyst to produce biodiesel [10].

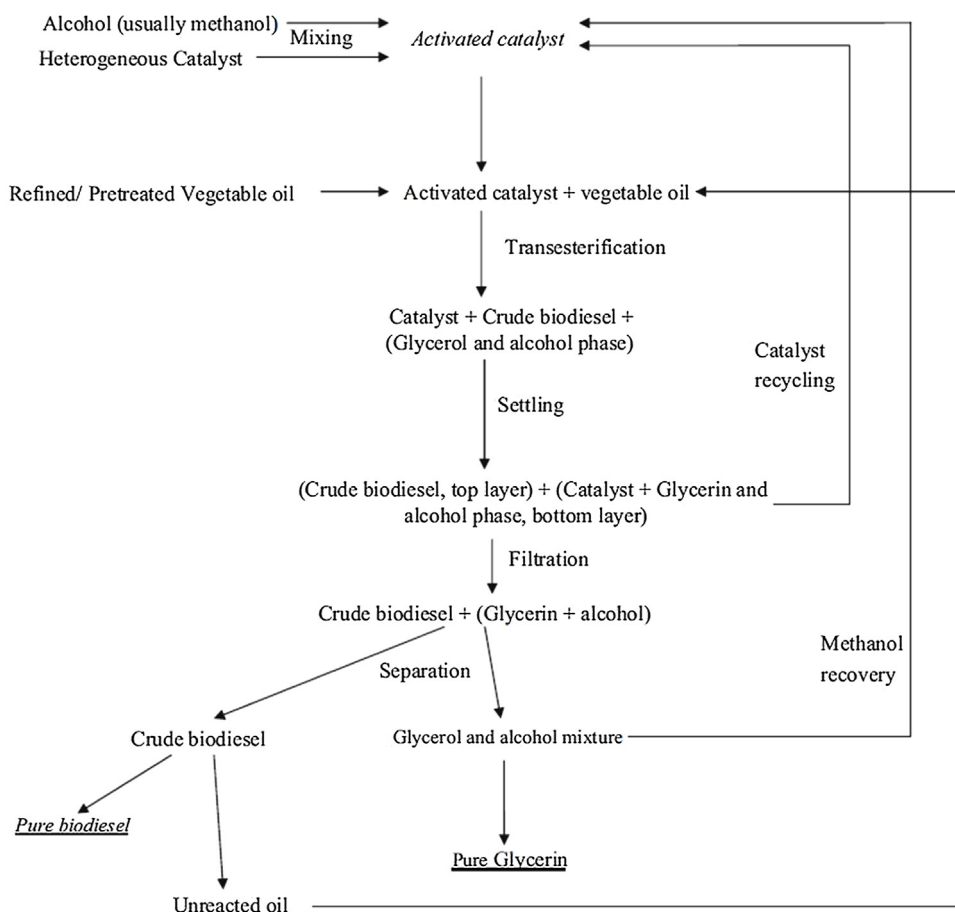


Fig. 7. Flowchart of biodiesel synthesis using heterogeneous catalyst [10].

et al. [68], refined sunflower oil and methanol catalyzed by Amberlyst-15 only resulted in 0.7% of yield at atmospheric pressure, 6:1 methanol to oil ratio for a duration of 8 h. However, Reis et al. [69] achieved biodiesel yield of 80% under similar condition but changing methanol to oil ratio to 100:1.

Other than typical commercialized metal oxide catalyst, the potential of catalyst derived from renewable sources are also being intensively studied by researchers. Industrial waste derived catalysts such as lime mud, red mud and slag, biological source derived catalysts such as shells and animal bones are all potential renewable sources of catalyst.

Lime mud is one of the wastes generated from construction industry. It is mainly composed of calcium carbonate (CaCO_3) with traceable amount of magnesium carbonate (MgCO_3). It has the potential to be a base catalyst because CaCO_3 will decompose to become CaO via calcination under elevated temperatures. Li et al. [70] calcined lime mud at 800°C and was able to obtain CaO as shown by XRD analysis. With reaction condition of 15:1 methanol to oil ratio, catalyst loading of 6 wt% and reaction temperature of 64°C for 3 h, a 94.4% yield was obtained for transesterification between peanut oil and methanol. This type of catalyst showed similar reactivity with comparable yield after 5 cycles. Red mud, the waste produced in the aluminum industry during the refinement of bauxite (aluminum ore) is a mixture of calcium, iron, silica and aluminum. The calcination of red mud at 200°C for 5 h rendered it the highest activity achievable [71]. A biodiesel yield of 94% for transesterification between soybean oil and methanol under condition of 24:1 methanol to oil ratio, 4 wt% catalyst loading and reaction temperature of 65°C for 3 h. The

catalyst showed significant decreased in activity as the subsequent run resulted in low yield (<20%) [71].

The other source of catalyst is dolomite rocks. It is a natural source of calcium which is available in bulk and thus its low cost. MgCO_3 and CaCO_3 are present in dolomite rocks in large amount which means that the formation of CaO is plausible for calcination at high temperature. Ngamcharussrivichai et al. [72] calcined dolomite rocks at 800°C for 2 h and subsequently used it to catalyze transesterification between refined palm kernel oil and methanol at 15:1 methanol to oil ratio, 10 wt% catalyst loading and reaction temperature of 60°C for 3 h. The resulting biodiesel yield was 99.9%. However, the activity of catalyst dropped significantly after the 5th cycle, resulting in only 20% yield. The reusability of the catalyst was improved by modifying the reaction condition to 30:1 methanol to oil ratio, 6 wt% catalyst loading with the same reaction temperature and time. With this set of reaction condition, biodiesel yield over 80% was attained even after 10th cycle [73].

Shells are one of the more commonly researched biological source derived catalyst as it is a rich source of CaCO_3 which can be decomposed into CaO , which is catalytic active when calcinated at elevated temperature [74]. The shell of freshwater mussel was calcinated by Hu et al. [75] at 900°C for 4 h followed by impregnation in deionized water and activation at 600°C for 3 h. The shell demonstrates large surface area ($23.2\text{m}^2/\text{g}$) and great activity with over 90% biodiesel yield using Chinese tallow oil and methanol under condition of 12:1 methanol to oil ratio, 5 wt% catalyst loading and reaction temperature of 70°C for 1.5 h. The reusability of the catalyst looks promising as only 10–15% decrease was noticed after 12th cycle. Quail eggshell calcinated at $>800^\circ\text{C}$

for 2 h whilst treated with 0.005 M HCl solution exhibited high catalytic activity, giving biodiesel yield over 98% for transesterification between palm oil and methanol at reaction condition of 12:1 methanol to oil ratio, 1 wt% catalyst loading and reaction temperature of 65 °C for 2 h [76]. Oyster shell is also a rich source of calcium of which the calcium content can be accessed through thermal pre-treatment.

Nakatani et al. [77] calcined oyster shell at >700 °C for 3 h and the catalyst is then used to catalyze transesterification between soybean oil and methanol with reaction conditions of 6:1 methanol to oil ratio, 25 wt% catalyst loading, reaction temperature of 65 °C for 5 h. The resulting biodiesel yield was 98.4%. Chakraborty et al. [78] obtained active β -Ca₃(PO₄)₂ catalyst through calcination of waste Rohu fish (*Labeo rohita*) scale at 900 °C for 2 h. The catalyst possesses high surface area (39m²/g) and uniform distribution of porous surface over the catalyst. It catalyzed transesterification reaction involving methanol and soybean oil at condition of 6.27:1 methanol to oil ratio, 1.01 wt% catalyst loading, reaction temperature of 70 °C for 5 h. The percentage of conversion was 97.73% and the catalyst remain its activity after six consecutive runs.

Animal bones from the meat industry mainly comprises of hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂) can also be used to catalyze transesterification after thermal treatment. Chen et al. [79] calcined waste pig bones at 600 °C for 4 h to transform it into HAP. The HAP is then used as a carrier to support K₂CO₃ for 30 wt%. The catalyst achieved biodiesel yield of 90% using refined palm oil and methanol under reaction conditions of 9:1 methanol to oil ratio, 8 wt% catalyst loading, reaction temperature of 65 °C for 1.5 h. The catalyst maintained its activity after 8th cycle (>90% yield).

Similar method has been done by Ghanei et al. [81] but they used waste sheep bone instead of pig bones and impregnated Ca(NO₃)₂ into it. The catalyst achieved biodiesel yield of 95.15% using canola oil and methanol under condition of 12:1 methanol to oil ratio, 5 wt% catalyst loading and reaction temperature of 60 °C for 5 h. The reusability of this catalyst is also promising as it only showed a slight decrease in activity after 4th cycle. Chakraborty et al. [81] calcinated turkey bone at 909.4 °C for 4 h to obtain BTCP (biological tri-calcium phosphate) to be utilized as catalyst for the transesterification reaction between methanol and Indian mustard oil without impregnating another compound. The optimal condition of 9.90:1 methanol to oil ratio, 4.97 wt% catalyst loading and

Table 6
Summary of waste biomass heterogeneous catalyst.

Raw material	Catalyst and preparation method	Reaction conditions					Yield (%)	Reusability	Ref.
		Oil feedstock	Temperature (°C)	Alcohol to oil molar ratio	Reaction time (h)	Catalyst loading (wt%)			
Lime stone (CaCO ₃)	Lime stone is calcinated at 900 °C for 1.5 h under helium gas flow to obtain CaO	Soybean oil	64.7	12:1	1.0	/	93.00	Maintained >80% yield after 3 consecutive runs	[64]
Lime mud	Lime mud is calcined at 800 °C to obtain CaO	Refined peanut oil	64	15:1	3.0	6	94.40	Maintained similar yield after 5 runs	[70]
Red mud	Red mud is calcined at 200 °C for 5 h to obtain CaO	Soybean oil	65	24:1	3.0	4	94.00	Low yield (<20%) resulted in 2nd run	[71]
Dolomite rock	Dolomite rock is calcined at 600 and 700 °C, then Ca(NO ₃) ₂ precipitation and calcined at 800 °C	Palm kernel oil	60	15:1	3.0	10	99.90	Maintained >95% yield for 3 runs	[72]
Dolomite rock	Dolomite rock is calcined at 800 °C	Palm kernel oil	60	30:1	3.0	6	98.00	Maintained >80% yield after 10 runs	[73]
Chicken eggshell	Chicken eggshell is calcined at 800 °C for 4 h	Palm olein oil	60	12:1	2.0	10	94.10	/	[74]
Golden apple snail shell	Golden apple snail shell is calcined at 800 °C for 4 h	Palm olein oil	60	15:1	2.0	10	93.20	/	[74]
Meretrix venus shell	Meretrix venus shell is calcined at 800 °C for 4 h	Palm olein oil	60	15:1	2.0	10	92.3	/	[74]
Freshwater mussel shell	Freshwater mussel shell is calcined at 900 °C followed by impregnation in deionized water and activation at 600 °C for 3 h	Chinese tallow oil	70	12:1	1.5	5	90.00	Yield only decreased by 10-15% after 12 consecutive run	[75]
Quail eggshell	Quail eggshell is calcined at 800 °C for 2 h whilst treated with 0.005 M HCl to obtain CaO	Palm oil	65	12:1	2.0	1	98.00	/	[76]
Oyster shell	Oyster shell is calcined at 700 °C for 3 h to obtain CaO	Soybean oil	65	6:1	5.0	25	98.40	/	[77]
Rohu fish (<i>Labeo rohita</i>) scale	Rohu fish scale is calcined at 900 °C for 2 h to obtain β -Ca ₃ (PO ₄) ₂	Soybean oil	70	6.27:1	5.0	1.01	97.73	Maintained similar yield after 6 consecutive runs	[78]
Pig bones	Pig bones is calcined at 600 °C for 4 h to obtain HAP. The HAP is then used as a carrier to support K ₂ CO ₃ at 30 wt%.	Refined palm oil	65	9:1	1.5	8	>90.00	Maintained >90% yield after 8 consecutive run	[79]
Sheep bones	Sheep bone is calcined at 600 °C for 8 h to obtain HAP. HAP is then used as a carrier to support Ca(NO ₃) ₂	Canola oil	60	12:1	5.0	5	95.15	Maintained similar yield after 4 consecutive runs	[80]
Turkey bones	Turkey bones is calcined at 909.4 °C for 4 h to obtain biological tri-calcium phosphate (BTCP)	Indian mustard oil	70	9.9:1	3.0	4.97	91.22	Maintained similar yield after 5 consecutive runs	[81]

reaction temperature of 70 °C for 3 h resulted in biodiesel yield of 91.22%. The reusability of the catalyst was promising as it showed identical activity after 5 consecutive runs. The summary of catalyst discussed above is listed in Table 6. Given that most of the biodiesel fuel obtained from these researches in Table 6 fulfilled the fuel specifications ASTM D6751 and/or EN14214 standards [70,72,73,75,77,78].

To sum up, homogeneous catalyst is significantly inferior in several ways when compared to traditional heterogeneous catalyst. Firstly, homogeneous catalyst is harder to separate from the product and side product, ester and glycerine respectively when compared to heterogeneous catalyst, which is the biggest drawback of homogeneous catalyst. Besides, heterogeneous catalysts display superior reusability when compared to homogeneous catalysts [10]. Despite the advantages that heterogeneous catalysts have to offer, they also possess several disadvantages that impedes their commercial use, for example, the low surface area of the catalyst. Apart from that, heterogeneous base catalysts are easily disabled in the presence of water [2] while heterogeneous acid catalysts may cause contamination of the biodiesel product as a result of the active components leaching into the product [82].

Various factories and mills generate a huge amount of excessive waste every year. Among these industries, agriculture, bakeries, fertilizer industries, paper and pulp mills provide major contribution to waste generation. Although solid catalysts derived from waste biomass requires pretreatment, especially by washing and heat treatment, these utilities are considered cheap. Waste materials can be found everywhere and modification towards this material can be performed. Therefore, the complete utilization of waste biomass has potential for further development to be employed in continuous biodiesel generation under heterogeneous catalysis conditions and to reduce the safety and health risks brought on by landfills. Thus, various catalyst supports have been developed from biomass in efforts to minimize these drawbacks [62]. Other renewable sources of catalyst such as industrial waste derived catalyst and biological derived catalyst are also being looked into by numerous researchers. Table 6 below summarizes various types of heterogeneous catalyst with their respective preparation method, reaction condition, yield and its reusability.

Biochar-based heterogeneous base catalyst

Homogeneous base catalyst demonstrates high catalytic activity in biodiesel production despite their difficulties in separation of product and side product. Thus, strong base catalyst impregnated on supporting material such as biochar derived from biomass are being researched by numerous researchers. Such catalyst possesses several desirable characteristics such as being easily accessible, environmentally friendly and cost effective [62]. Fig. 8 shows the production pathway for various biomass-derived alkali catalyst.

Buasri et al. [84] conducted an analysis on the catalytic properties of activated carbon derived from the seed kernel shell of *Jatropha curcas* supported by KOH. The *Jatropha curcas* seed kernel shell was impregnated with H₃PO₄ for 24 h with impregnation ratio of 1.7:1 and then calcinated at 500 °C for 24 h under nitrogen atmosphere. The resulting activated carbon was then impregnated with KOH by soaking it in 0.4 g/ml KOH solution for 24 h. The reaction was carried out in a 250 mm bed height packed bed reactor and 60 °C temperature, 20:1 methanol to oil ratio and 2 h residence time. The resulting biodiesel yield was 87%. The packed catalyst bed showed minimal catalytic activity lost after 5 runs with each run having >80% yield.

Dhawane et al. [85] used similar approach as Buasri et al. [84] by swapping out *Jatropha curcas* seed kernel shell with Flamboyant pods. The resulting biodiesel yield was slightly higher at 89.81% with optimal reaction condition as followed: catalyst loading of 3.5 wt%, methanol to oil ratio of 15:1, reaction temperature of 55 °C and reaction time of 1 h using *Hevea brasiliensis* oil. Meanwhile, Baroutian et al. [86] studied the performance of KOH catalyst supported on palm shell activated carbon. KOH is impregnated into activated carbon derived from palm shell and subsequently used to catalyze transesterification under reaction condition + as followed; catalyst loading of 30.3 wt%, methanol to oil ratio of 24:1 and reaction time of 1 h, achieving overall yield of 98.03%. The fuel physiochemical properties of the biodiesel met the standard specifications of ASTM D6751.

Furthermore, another technique of deriving both the catalyst support and active compound from two different carbon biomass

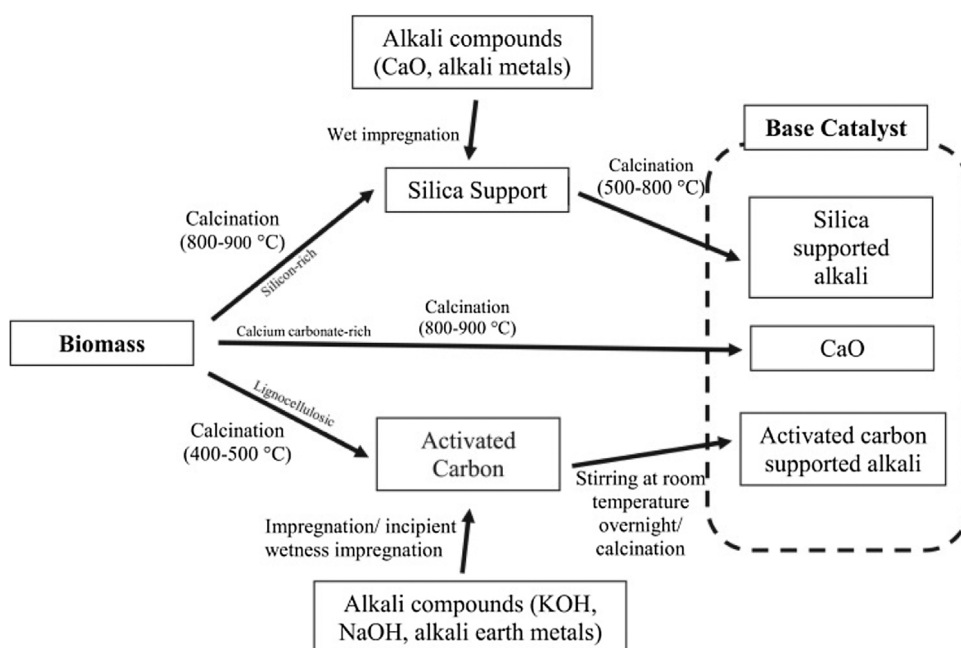


Fig. 8. Production pathway for various biomass-derived alkali catalyst [62].

each was reported by Chen et al. [87]. They had subjected dried rice husk to calcination under various temperatures (400 °C, 600 °C and 800 °C) for a residence time of 4 h. The resulting rice husk ash was used as the catalyst support. Meanwhile, dried chicken eggshell was calcined under 400 °C at a residence time of 4 h to be converted to CaO to be used as the active compound. The rice husk ash was then impregnated with the CaO through method of wet impregnation before being subjected to calcination once again under different temperatures (600 °C, 800 °C and 1000 °C) to synthesize the heterogeneous base catalyst. Its basicity, which is crucial in determining the catalytic performance of the catalyst, was obtained at a peak of 8.5 mmol/g. The biodiesel product yield was 91.5% when reaction conditions were at a methanol to oil ratio of 9:1 with a catalyst loading of 7 wt% under 65 °C for 4 h.

Next, Hindryawati et al. [88] conducted a study on the results obtainable from rice husk silica derived from rice husk ash. According to Mekhemer et al. [89], it served great potential in becoming a catalyst support due to superior active site dispersion among amorphous silica. To synthesize rice husk silica, the rice husk ash must first be loaded with sodium silicate, potassium silicate and lithium silicate. Prior to loading, the rice husk ash was washed using diluted HCl for the removal of residues of metal impurities and minerals. The carbon-based support was then impregnated with the basic metal catalyst through the wet impregnation technique before being calcinated to form the desired basic metal silicate catalyst. The resulting catalyst yielded biodiesel between a range of 96.5% and 98.2% under reaction conditions of 9:1 methanol to oil ratio at 65 °C for 1 h with 3 wt% catalyst loading.

Hadiyanto et al. [90] researched a novel method to synthesis catalyst by impregnating two different active components – namely NaOH and CaO onto the carbon support. The novelty of this study is that it combined both homogeneous and heterogeneous catalyst that is normally used separately. This approach achieved biodiesel yield of 95.12% with reaction condition as followed: catalyst loading of 7.5 wt%, methanol to oil weight ratio of 2:1, reaction temperature of 65 °C and reaction time of 3 h. Boro et al. [91] investigated the effect of doping on the catalytic performance of supported catalyst. They found that doping has positive effect on both basicity of the catalyst and reducing the leaching of active component Ca^{2+} . For example, *Turbonilla striatula* shell derived activated carbon impregnated with Ba doped CaO achieved highest biodiesel yield of >98% with reaction condition as followed: 1 wt% Ba doping, catalyst loading of 1 wt%, methanol to oil ratio of 6:1, reaction temperature of 65 °C and reaction time of 3 h. However, this particular doped catalyst showed poor reusability due to deposition of product on the catalyst and leaching of active sites.

Biochar-based heterogeneous acid catalyst

The two standard methods of impregnating acidic active compounds onto carbon-based supports are by hydrocarbon

reduction and by direct arylation or sulfonation with the latter being the more sought-after method [62]. It can be achieved by an elementary sulfonation pathway that applies heat treatment on the supporting materials and sulfonating agents which may include fuming sulfuric acid [92], concentrated H_2SO_4 [93], 4-benzenediazonium sulfonate (4-BDS) [94] or *p*-toluenesulfonic acid (PTSA) [95].

Several kinds of biomass can undergo direct sulfonation. They consist of *Jatropha curcas* kernel seed, bamboo, coconut shell, *C. inophyllum* seed cake, coconut meal residue, coffee residue and more [62]. Nonetheless, the most noteworthy biomass that may be used is the sugarcane bagasse and oil palm trunk as demonstrated by Ezebor et al. [93]. Maximum biodiesel yield is obtained by subjecting both biomass to pyrolysis for 4 h at 400 °C and subsequently direct sulfonated with concentrated H_2SO_4 at 150 °C for 4 h. The synthesized catalyst obtained maximum biodiesel yield of 95.67% and 88.18% for oil palm trunk and sugarcane bagasse respectively under reaction condition as followed: catalyst loading of 9 wt%, ethanol to oil ratio of 18:1 and reaction time of 5 h.

Ngaosuwan et al. [96] studied the effect of sulfonation temperature and sulfonation time on the outcome of direct sulfonation by analyzing the characteristics of catalyst produced. From the research, they concluded that weak acid sulfonating agent and strong acid sulfonating agent behaves differently to temperature. Strong acid sulfonating agent such as $-\text{SO}_3\text{H}$ are attached less onto the carbon support when subjected to high temperature while weak acid sulfonating agent shows the exact opposite behavior. However, they found that balanced proportion of strong acid agent and weak acid agent attached onto the support are crucial to achieve better biodiesel conversion due to balanced proportion of strong and weak acid promotes better dispersion of active sites resulting in better catalytic activity [97]. The studies conducted by Zhou et al. [98] inferred that the attachment of $-\text{SO}_3\text{H}$ groups onto carbon materials occurs optimally under a sulfonation temperature between 100 °C and 105 °C.

On the other hand, Ezebor et al. [99] had investigated the time of sulfonation on the catalytic performance of those produced from sugarcane bagasse and oil palm trunk. Both biomasses were directly sulfonated at 150 °C for different periods (2, 4, 6, 8 and 10 h). The results demonstrated a surge in both the yield of biodiesel and total density of acid throughout 2–6 h and a constant after 6 h. Similar results were obtained in the study carried out by Zhou et al. [98] to analyze the effect of sulfonating catalyst derived from bamboo at a temperature of 105 °C between 1 to 5 h. However, a contrasting outcome on the maximum yield of biodiesel of 98.4% was achieved at a sulfonation time of only 2 h with a dormant trend that follows past the 2-h mark. That aside, it can be observed that the former catalyst derived by Ezebor et al. [99] only required a low temperature of 65 °C to compensate for its elongated sulfonation period as compared to the latter derived by Zhou et al. [98] that needed 90 °C. Due to the hazardous nature of sulfonating agents that are required in the direct sulfonation method, the method of

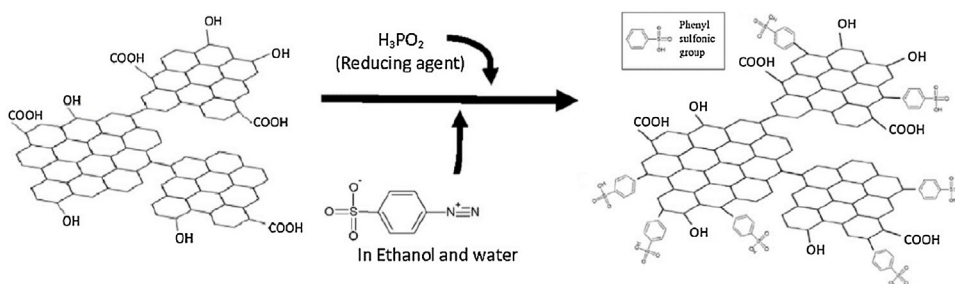


Fig. 9. Solid acid catalyst production using the reduction pathway via Arylation of 4-BDS [62].

reduction of carbon-based catalysts is more opted for in recent years [62]. The reduction pathway is depicted in Fig. 9 below.

The idea of arylation or reduction of hydrocarbon first started Liu et al. [94] investigated the potential of acid heterogeneous catalyst synthesized by grafting active component through reduction of 4-benzenediazonium sulfonate (4-BDS) under the presence of H_3PO_2 . This method circumvented the need to use highly corrosive sulfonating agent such as concentrated sulfuric acid by grafting sulfonic acid of aryl radicals produced from the reduction of 4-BDS onto the carbon support with strong covalent bond. Konwar et al. [83] used activated carbon derived from de-oiled waste cake of *P. Pinata* to undergo sulfonation with 4-BDS. The activated carbon was first pre-soaked with 50% (v/v) phosphoric acid and subsequently sulfonated with 4-BDS under the presence of H_3PO_2 . The synthesized catalyst has acid density of 0.84 mmol/g and obtained 95% biodiesel yield with oleic acid

under the reaction condition as followed: catalyst loading of 3 wt%, methanol to oil ratio of 20:1, reaction temperature of 64 °C and reaction time of 10 h.

Moreover, Konwar et al. [83] proceeded to obtain a comparison between the catalytic behavior of catalysts produced using both methods of arylation using 4-BDS and direct sulfonation. As stated earlier, weak acid groups like $-COOH$ groups are liberated via direct sulfonation with H_2SO_4 . In contrast, sulfonic groups, namely $-PhSO_3$, are created instead with the arylation method using 4-BDS. The implication of having a bulkier group is that the arylated catalyst has lower specific surface area and pore size when compared to the direct sulfonated catalyst. This can be ascribed to the formation of $-SO_3$ on the direct sulfonated catalyst. Thus, the catalyst arylated with 4-BDS obtained higher biodiesel yield of 90% when used to catalyze esterification between methanol and oleic acid while the direct sulfonated catalyst only obtained 50%. Other

Table 7
Summary of carbon-supported heterogeneous catalyst.

Basic/ acidic	Raw material	Catalyst and preparation method	Reaction conditions					Yield (%)	Reusability	Ref.
			Oil feedstock	Temperature (°C)	Alcohol to oil molar ratio	Reaction time (h)	Catalyst loading (wt%)			
Acidic	Oil palm trunk, H_2SO_4	Oil palm trunk subjected to pyrolysis at 400 °C for 4 h then undergo direct sulfonation with H_2SO_4 for 4 h at 150 °C	Palmitic acid	/	18:1	5.0	9.0	88.18	10.5–12.5% yield lost after six cycle	[93]
Acidic	Sugarcane bagasse, H_2SO_4	Sugarcane bagasse subjected to pyrolysis at 400 °C for 4 h then undergo direct sulfonation with H_2SO_4 for 4 h at 150 °C	Palmitic acid	/	18:1	5.0	9.0	95.67	10.5–12.5% yield lost after six cycle	[93]
Acidic	<i>P. Pinata</i> deoiled waste cake, 4-BDS, H_3PO_2	The waste cake is first soaked with phosphoric acid (50% v/v) then activated at 500 °C. Sulfonation of catalyst is completed through the reduction of 4-BDS to graft $-SO_3$ group onto the carbon support in the presence of H_3PO_2	Oleic acid	64	20:1	10	3	97.00	/	[83]
Basic	<i>Jatropha curcas</i> seed kernel shell, KOH	The <i>Jatropha curcas</i> seed kernel shell is impregnated with H_3PO_4 for 24 h with impregnation ratio of 1.7:1 and then calcinated at 500 °C for 24 h under nitrogen atmosphere. The resulting activated carbon is then impregnated with KOH by soaking it in 0.4 g/ml KOH solution for 24 h.	Waste frying oil (0.96% FFA)	60	20:1	2.0	(Others: Catalyst bed height: 250 mm)	87.00	Maintained >80% yield after 5 consecutive runs	[84]
Basic	Flamboyant pods	The flamboyant pods are carbonised at 500 °C for 1 h followed by steam activation at 350 °C for 1.5 h. The resulting activated carbon is impregnated with KOH by soaking it in 0.67 g/ml KOH solution for 24 h	Refined <i>Hevea brasiliensis</i> oil	55	15:1	1.0	3.5	89.81	1.4–1.8% yield lost after three cycle	[85]
Basic	Rice husk ash, egg shell	The eggshell is calcined at 800 °C for 4 h to obtain CaO. The rice husk is calcined at 800 °C for 4 h. 30 wt% of CaO obtained from calcination of eggshell is loaded to calcinated rice husk and then activated at 800 °C for 4 h.	Refined palm oil	65	9:1	4.0	7.0	91.50	Maintained >80% yield after 8 consecutive runs	[87]
Basic	Rice husk ash, alkali metal and silica	The rice husk ash is suspended in water along with alkali metal and silica (2:1 molar ratio) and then calcined at 500 °C for 2 h	Used cooking oil (1.77% FFA)	65	9:1	1.0	3.0	98.20	Maintained >87% yield after 3 consecutive runs	[88]
Basic	Palm shell activated carbon	Activated carbon derived from palm shell-based blended with the 0.5 g/ml KOH solution and agitated at 180 rpm, 25 °C for 24 h	Refined palm oil	64.1	24:1	1.0	30.3	98.03	/	[86]
Basic	Green mussels shell	Green mussels' shell is crushed and then calcined at 900 °C for 3 h to obtain CaO. 7.5 wt% of CaO was mixed with activated carbon along with 30% (w/w) NaOH overnight and then calcined at 500 °C for 5 h	Refined palm oil	65	2:1 (weight)	3.0	7.5	95.12	/	[90]
Basic	Ba doped CaO derived from <i>T striatula</i> shell	<i>T striatula</i> shell is calcined at 900 °C, doped with barium chloride and recalined at 900 °C	Waste cooking oil	65	6:1	3.0	1.0	98	Maintained >80% in 3 runs	[91]
Acidic	Biochar	Biochar activation method with KOH followed by carbonization at 675 °C. Sulfonation using fuming sulfuric acid for 15 h at 150 °C	Canola oil and oleic acid	150	10:1	3.0	24	48.1	Slight decrease yield (8%)	[92]

than that, the reusability of arylated catalyst is also superior when compared to direct sulfonated catalyst as the latter catalyst is prone to leaching of $-\text{SO}_3\text{H}$ group. A summary on both acidic and basic carbon supported heterogeneous catalyst is list in Table 7.

Magnetized biochar catalyst

Magnetized carbon catalyst has gained traction from researchers recently due to the difficulty of separating heterogeneous catalyst from the product. The incorporation of magnetic properties onto the carbon derived catalyst allows the catalyst to be separated from other media using magnetic fields. Thus, the expensive stage of separation via filtration or centrifugation will no longer be needed in the biodiesel production. The common methods to synthesise magnetized carbon derived catalyst are pre/postcoating pyrolysis and chemical co-precipitation. The recovery rate of magnetic catalyst is 1.7 times higher than that of non-magnetic catalyst due to its easier separation process. Other than that, particle size analysis showed that the surface area of magnetized porous carbon is higher than the non-magnetized one as the iron compound helps to release the volatile components during the decomposition in the pyrolysis and activation process [100]. A summary of the various magnetized biochar catalysts corresponding to their optimum conditions for transesterification reaction has been compiled under Table 8. Given that most of the obtained biodiesel from these researches in Table 7 and 8 met the EN 14214 and ASTM D 6751 standard specifications for biodiesel fuel [84,85,87,90,92].

Catalyst characteristics

General characteristics

There are a few tests that are done frequently on the catalyst and biomass precursor to identify their physical characteristics, namely TGA, XRD, BET surface area analysis, SEM, CO_2 -TPD and FT-IR. Thermogravimetric analysis (TGA) is often used to determine the calcination temperature of biomass precursor by identifying the compound loss during the heating at different temperature. For example, in the calcination of obtuse horn shell conducted by Lee et al. [103], they found out that small weight loss is experienced in the temperature range of 170–413 °C and they deduced that the weight lost is due to the loosely held water present in the sample. The sample then experienced significant weight lost in the temperature ranging from 558 °C to 857 °C. They verified that the weight lost is due to the decomposition of calcium carbonate into calcium oxide by matching the stoichiometric weight loss, which is 44%. The calcination temperature is then decided to be 800 °C for the obtuse horn shell sample.

Powder X-ray diffraction (XRD) is often used to identify the phase identity. For example, the obtuse horn shell sample (Lee et al.) [103] in the sample above is subjected to XRD analysis after the calcination to determine the phase identity. The sample calcinated shows strong peaks at $2\theta = 23.0^\circ, 29.3^\circ, 43.2^\circ, 48.5^\circ$ and $32.2^\circ, 37.3^\circ, 53.9^\circ$, which corresponds to calcium carbonate and

calcium oxide respectively. This shows that some of the calcium carbonate are not fully decomposed during the calcination process. Hence, the calcination temperature is raised to 800 °C and the results only shows strong peaks at $2\theta = 32.2^\circ, 37.3^\circ$ and 53.9° , which verifies that all calcium carbonate has been decomposed into calcium oxide, which is the catalytic active component in the catalyst. FT-IR serves similar purpose as the XRD, as it is able to identify the stretching vibration of certain bond and thus identify the presence of certain compound. For example, in study conducted by Sharma et al. [104], wood ash is calcined at elevated temperature alongside CaCO_3 to obtain carbon supported CaO. The resulting FT-IR spectrum for catalyst calcined at 500 °C contained characteristic bands 1797, 1432, 874 and 712cm^{-1} , which indicates the presence of CO_3^{2-} , PO_4^{3-} , $\text{Si}-\text{O}-\text{Si}$ and CaO, showing that the CaCO_3 is not fully decomposed. The FT-IR spectrum for catalyst calcined at 1200 °C shows characteristic bands of 3643cm^{-1} , which indicates the presence of CaO and the bands corresponding to CaCO_3 is not present in the FT-IR spectrum for catalyst calcined at this temperature.

The morphology of the catalyst is distinguished using SEM. For example, the SEM micrographs of undoped ZnO and Cobalt doped ZnO shows that the difference in surface morphology between the two and visualise why one has higher surface area over the other. BET surface area is identified by using the nitrogen adsorption-desorption isotherm using the Brunauer–Emmett–Teller (BET) technique. CO_2 -TPD is used to identify the distribution of basic sites densities of the catalyst by determining the amount of CO_2 desorbed from the catalyst. The implication of BET surface area and basicity of catalyst is further discussed in the section below.

BET surface area and basicity of catalyst

BET surface area's effect on catalyst's catalytic activity was investigated in a study conducted by Piker et al. [105]. It was found that BET surface area has significant effect on biodiesel yield under similar condition. Commercial CaO ($1\text{m}^2/\text{g}$ BET surface area) and eggshell derived CaO ($1.8\text{m}^2/\text{g}$ BET surface area) has biodiesel yield of 2% and 98% after stirred reaction for 12 h and 11 h respectively. Piker et al. [105] deduced that larger surface area provided more catalytic active basic sites for transesterification to take place, and thus the higher conversion rate.

From a study conducted by Chen et al. [87], different proportion of CaO is mixed with rice husk pyrolyzed at different temperature and activated at different temperature. Table 9 below shows the BET surface area (m^2/g), total basicity (mmol/g) and their respective biodiesel yield under same reaction condition for each catalyst with different treatment method. With the information extracted from Table 9 it can be deduced that the pyrolysis temperature is highly associated with the BET surface area of catalyst, the higher the pyrolysis temperature the higher the surface area.

One thing to note is that catalyst loading does affect the BET surface area as a 50% CaO loading will have a detrimental effect on the surface area as it decreases from $11.75\text{m}^2/\text{g}$ (30% CaO loading) to $3.18\text{m}^2/\text{g}$. This can be attributed to the overloading of CaO on the porous surface, filling up the porous volume thus decreasing the

Table 8

Summary of optimum conditions needed for biodiesel production using various magnetic biomass-derived catalysts.

Biomass	Type of catalyst	Reaction conditions					Yield (%)	Ref.
		Oil feedstock	Alcohol to oil molar ratio	Catalyst loading (wt%)	Reaction time (h)	Temperature (°C)		
Bamboo	Magnetic base catalyst	Soybean oil	9:1	65	1.7	65	98.1	[62]
Sawdust	Magnetic carbon acid catalyst	Acetic acid	1:5	34.5	–	88	93	[71]
Cotton	Magnetic heteropolyacid catalyst	P. chinensis oil	10:1	15	1.3	60	93.1	[101]
Glucose	Magnetic carbon acid catalyst	Jatropha oil	24:1	10	10	200	90.5	[102]

Table 9
Properties of various biomass after pyrolysis/activation.

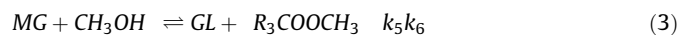
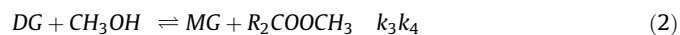
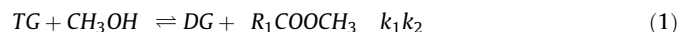
Biomass	Pyrolysis temperature (°C)	Pyrolysis time (h)	BET surface area (m ² /g)	Activation temperature (°C)	Activation time (h)	BET surface area after activation (m ² /g)	pH	Ref.
EFB	350	2	11.76	–	–	–	8.31	[106]
	500	2	15.42	–	–	–	9.89	
	600	2	28.20	–	–	–	10.29	
Rice Husk	350	2	32.70	–	–	–	6.66	
	500	2	230.91	–	–	–	7.99	
	600	2	261.72	–	–	–	8.88	
PKS	500	0.5	34.00	900	3	807	–	[107]

overall surface area [87]. For basicity, both catalyst loading percentage and pyrolysis temperature/activation temperature seemed to have shown direct proportional relationship towards total basicity. However, the basicity reduced when the activation temperature is increased to 1000 °C, dropping from 7.6 mmol/g (600 °C activation temperature) to 5.1 mmol/g with the same catalyst loading and pyrolysis temperature.

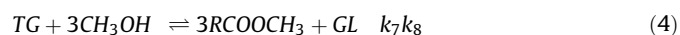
The catalysts are denoted as $xRHA_y - T$, where x is CaO loading (wt%), y being pyrolysis temperature and T being activation temperature. The biodiesel yield seemed to have shown strong relationship with BET surface area and total basicity of the catalyst. For 30% RHA₄₀₀₋₈₀₀ catalyst, the biodiesel yield: 56.2% is the lowest among all of the catalyst, while its BET surface area and total basicity is also lowest among all other catalyst, which are 2.23 m²/g and 0.4 mmol/g respectively while 30% RHA₈₀₀₋₈₀₀ showed highest biodiesel yield of 91.5% with highest BET surface area of 11.75 m²/g and basicity of 8.5 mmol/g. The results have been tabulated in Table 10 and this validates with the statement above that high BET surface area and total basicity corresponds to higher biodiesel yield.

Kinetic studies

There is a total of three subsequent reactions that produces intermediate formations in the transesterification process. Triglyceride (TG) when reacted with methanol will produce diglycerides (DG), then this product will continue to react with methanol and yield monoglycerides (MG) that at the end react with methanol to produce methyl ester and glycerine as described in Eqs. (1)–(3) [108]. The stepwise reactions:



The overall reaction:



Basically, a higher molar ratio of alcohol to oil compared to the stoichiometric amount is needed for the commencement and speeding up of the transesterification. In this reaction, alcohol will be produced excessively. Frequently, researchers presumed that conversion of intermediates i.e. diglyceride and monoglyceride to methyl ester takes place fast. So, typical kinetic studies on the transesterification of vegetable oils are subject of the overall reaction. The common form of the resulting set of differential equations describing the stepwise reactions elaborated in the transesterification process are showed as per following:

$$-\frac{d[TG]}{dt} = k_1[TG][A] - k_2[DG][E] \quad (5)$$

$$-\frac{d[DG]}{dt} = k_3[DG][A] - k_4[MG][E] - k_1[TG][A] + k_2[DG][E] \quad (6)$$

$$-\frac{d[MG]}{dt} = k_5[MG][A] - k_6[GL][E] - k_3[DG][A] + k_4[MG][E] \quad (7)$$

$$-\frac{d[E]}{dt} = k_1[TG][A] - k_2[DG][E] + k_3[DG][A] - k_4[MG][E] + k_5[MG][A] - k_6[GL][E] \quad (8)$$

where $[]$ denotes to the concentration of the related species and A, E and GL indicates alcohol, ester and glycerine, correspondingly. The reaction kinetic constant, k_{1-6} are predicted based on the data obtained from experimental plot. The number of parameters is compacted to three equilibrium constants, k_1, k_2 and k_3 which described as:

$$K_1 = \frac{k_1}{k_2}, \quad K_2 = \frac{k_3}{k_4}, \quad K_3 = \frac{k_5}{k_6} \quad (9)$$

The rate law is the result of the rate of a reaction correlated to the concentrations of the reactants and products that is portrayed as below:

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (10)$$

Table 10
Textural properties of CaO embedded rice husk catalyst [87].

Sample	BET surface area (m ² /g)	Total basicity (mmol/g)	Biodiesel yield (%)
30% RHA ₄₀₀₋₈₀₀	2.23	0.4	56.2
30% RHA ₆₀₀₋₈₀₀	5.27	2.4	74.2
30% RHA ₈₀₀₋₈₀₀	11.75	8.5	91.5
20% RHA ₈₀₀₋₈₀₀	10.54	6.7	78.8
50% RHA ₈₀₀₋₈₀₀	3.18	8.2	80.9
30% RHA ₈₀₀₋₆₀₀	14.28	7.6	87.2
30% RHA ₈₀₀₋₁₀₀₀	1.29	5.1	74.0

E_a represents the activation energy for the reaction, and A is used to represent a constant which is the pre exponential factor. Due to the dependence on temperature, it must be maintained at a constant value so as to measure the value of k that is accurate. To include activation energies into kinetic studies, rate constants are to be obtained at a series of temperatures.

First order kinetic model

As to establish the kinetics of the reaction, the effect of the reaction temperature and time will be studied. The catalyst is assumed to be utilized in satisfactory amount with subject to oil in order to shift the reaction equilibrium near the development of fatty acid methyl esters. Therefore, the reverse reaction could be overlooked and variation in concentration of the catalyst throughout the duration of reaction must be neglected [109]. The transesterification is assumed to be single reaction, the rate law of the reaction for forward reaction can be conveyed by:

$$-r_A = \frac{-d[TG]}{dt} = k_1 \times [TG] \times [ROH]^3 \quad (11)$$

The concentration of triglycerides and methanol is $[TG]$ and $[ROH]$ respectively and k_1 is the equilibrium rate constant. This complete first reaction is following a second order reaction rate law. Nevertheless, when the molar ratio of methanol to oil is high, the increment in methanol does not affect the reaction order and it acts as a first order reaction [110]. Thus, when the reaction follows pseudo-first order kinetics, the rate equation can be portrayed as:

$$-r_A = \frac{-d[TG]}{dt} = k \times [TG] \quad (12)$$

where k is modified rate constant and $k = k_1 \times [ROH]^3$. The initial triglyceride concentration was assumed to be $[TG_0]$ at time $t=0$, and at time t it falls $[TG_t]$. The integration of the equation above with the assumptions results in the following equation:

$$\ln [TG_0] - n [TG_t] = k.t \quad (13)$$

From mass balance:

$$X_{FAME} = 1 - \frac{[TG]}{[TG_0]} \quad (14)$$

Or

$$[TG] = [TG_0](1 - X_{FAME}) \quad (15)$$

After integration and rearrangement, the following gives,

$$-\ln(1 - X_{FAME}) = k.t \quad (16)$$

The consistency of the reaction with the pseudo-first order kinetic model can be verified by charting a graph of $Y(t) = -\ln(1 - X_{FAME})$ against t . Whereas, when tabulating $\ln k$ versus $1/T$, the gradient and intercept of the line gives the value of E_a/R and A , individually.

Reversible second order kinetic model

Eq. (1) is a reversible second order model as presented in Eq. (4), the overall transesterification reaction. Each mole of vegetable oil that undergoes transesterification forms three moles of methyl ester and a single mole of glycerine. Substitution of these corresponds into Eq. (17) and can be developed to Eq. (18). Besides, Eq. (19) can be used to attain the conversion of palm oil (X_{FAME}). The integration of this equation produces Eq. (20) where $M = \frac{[A_0]}{[TG_0]}$, TG_0 and A_0 are the initial concentrations of vegetable oil and methanol, respectively. The equilibrium constant, $K = \frac{k_8}{k_7}$ and Δ

can be defined from the integrated Eqs. (21) and (22) [111]

$$-\frac{d[TG]}{dt} = k_7[TG][A] - k_8[DG][E] \quad (17)$$

$$-\frac{d[X_{FAME}]}{dt} = k_7[TG_0] \left[(1 - X_{FAME})(M - 3X_{FAME}) - 3K.X_{FAME}^2 \right] \quad (18)$$

$$X_{FAME} = 1 - \frac{[TG]}{[TG_0]} \quad (19)$$

$$\frac{1}{2[TG_0]\sqrt{\Delta}} \ln \frac{6(1-K)X_{FAME} - (M+3) - \sqrt{\Delta}}{6(1-K)X_{FAME} - (M+3) + \sqrt{\Delta}} = K_1 t + C \quad (20)$$

$$K = \frac{(1 - x_{A_e})(M - 3x_{A_e})}{3x_{A_e}^2} \quad (21)$$

$$\Delta = (M+3)^2 - 12M(1-K) \quad (22)$$

The consistency of the reaction with reversible second order kinetic model was verified by tabulating $Y(t)$ against t . $Y(t)$ was determined based on the left side of Eq. (20), whereas the integration constant, C was equivalent to the intercept of the drawn line.

Irreversible second order kinetic model

The reaction intermediates are assumed to disappear rapidly into methyl esters enabling the kinetic model of the reaction to be simplified to Eq. (23). This equation will be developed to Eq. (24) which will then be integrated to Eq. (25). Consistency of the reaction kinetics with irreversible second order kinetic model is verified via plotting $Y(t) = \frac{1}{[TG_0](M-3)} \ln \frac{(M-3X_{FAME})}{(1-X_{FAME})}$ against t .

$$-r_A = \frac{-d[TG]}{dt} = K_1 \times [TG][A] \quad (23)$$

$$\frac{dX_{FAME}}{dt} = k_7[TG_0](1 - X_{FAME})(M - X_{FAME}) \quad (24)$$

$$\frac{1}{[TG_0](M-3)} \ln \frac{(M-3X_{FAME})}{(1-X_{FAME})} = -k_7 t + C \quad (25)$$

Kinetic model development

The kinetics of the transesterification reaction by heterogeneous catalysis is yet to be fully comprehended as it is broadly used for homogeneous catalysis. Research works are majorly focused on heterogeneous catalysis in the basis of the synthesis and implementation of catalysts, while research work regarding kinetic modelling is limited. Amid these, the attention has been on the application of tiny solid particles to achieve reaction optimum conditions based on the intrinsic kinetics and natural occurrence of both external and intraparticle mass transfer are insignificant. Therefore, heterogeneous vegetable oil transesterification is mostly found to obey a pseudo-first-order rate law. Like Kaur and Ali [112], have carried out a study of methanolysis and ethanolysis of *Jatropha curcas* L. oil with the presence of catalyst, 15-Zr/CaO-700. This study has concluded that both reactions

exhibited a pseudo-first-order rate law. The unimportance of the transport affects was validated by the Koros-Nowak test. Lukić et al. [38] have found the transesterification of sunflower oil catalysed by ZnO–alumina/silica-supported catalyst showed a first-order reversible rate law.

Noureddini and Zhu [113] have accomplished studies on the kinetics of base-catalysed transesterification of soybean oil at 6:1 molar ratio of methanol to oil. The reaction of the study was a pseudo first-order kinetics aided with experimental results at a larger molar excess of alcohol, while a second-order kinetics fitted

Table 11
Summary on kinetic modelling of heterogeneous transesterification.

Oil source and catalyst	Reaction conditions	Kinetic model: rate constant (k) and activation energy (E_a)	Ref.
<i>Jatropha Curcas L.</i> oil Catalyst: Zr/CaO	Molar ratio 30:1 methanol:oil Temperature: 200 °C Pressure: 37 bar Reaction time: 4 h Catalyst ZnO Al/Si ratio 3/1 Calcination 600 °C, 12 h Catalyst ZnO Al/Si ratio 1/0 Calcination 600 °C, 12 h Catalyst ZnO Al/Si ratio 1/0 Calcination 300 °C, 12 h	Kinetic model: Pseudo-first order $E_a = 29.8 \text{ kJ mol}^{-1}$; $k = 0.062 \text{ min}^{-1}$ $E_a = 42.5 \text{ kJ mol}^{-1}$; $k = 0.0123 \text{ min}^{-1}$	[112]
Sunflower oil Catalyst: ZnO/alumina-silica, 2 wt %	Temperature: 60 °C Agitation speed: 900 rpm Molar ratio 6:1, methanol:oil Agitation speed: 900 rpm Molar ratio 6:1, methanol:oil Agitation speed: 300 rpm Molar ratio 10:1, methanol:oil	Kinetic model: First-order, k model irreversible (for catalyst with lower activity) k_1, k_{-1} model reversible $k = 0.0138 \text{ min}^{-1}$; $k_1 = 0.0190 \text{ min}^{-1}$ $k_{-1} = 0.00140 \text{ min}^{-1}$ $k = 0.0027 \text{ min}^{-1}$; $k_1 = 0.0054 \text{ min}^{-1}$ $k_{-1} = 0.00170 \text{ min}^{-1}$ $k = 0.0036 \text{ min}^{-1}$; $k_1 = 0.0059 \text{ min}^{-1}$ $k_{-1} = 0.00082 \text{ min}^{-1}$ $k = 0.0064 \text{ min}^{-1}$; $k_1 = 0.0068 \text{ min}^{-1}$ $k_{-1} = 0.00014 \text{ min}^{-1}$	[38]
Refined palm oil Catalyst: NaOH	molar ratio of methanol to oil 6:1, temperature 60 °C, NaOH atmospheric pressure was studied. Molar ratio of methanol to oil, 6:1 NaOH concentration 1 wt% of oil, mixing intensity N_{Re} 2000 and at atmospheric pressure.	Kinetic model: Second order $k_1 = 1.057 \times 10^{-2} \text{ L/mol.s}$ $k_2 = 0.000 \text{ L/mol.s}$ $k_3 = 1.184 \times 10^{-1} \text{ L/mol.s}$ $k_4 = 8.187 \times 10^{-2} \text{ L/mol.s}$ $k_5 = 1.310 \times 10^{-1} \text{ L/mol.s}$ $k_6 = 2.011 \times 10^{-3} \text{ L/mol.s}$	[114]
<i>Jatropha</i> oil Catalyst: NaOH	temperatures (35–65 °C) temperatures (35–65 °C) agitation speeds (600–900 rpm) and temperatures (35–65 °C) using sodium hydroxide as a catalyst. The methanol to oil molar ratio of 6:1 was used and catalyst loading was 0.5% weight of oil. Molar ratio of methanol to oil, 6:1 NaOH concentration 0.5 wt% of oil Agitation speeds: 600–900 rpm Temperatures: 35–65 °C	Kinetic model: Second order $k_1 = 0.103 \text{ L/mol.s}$ $k_2 = 0.031 \text{ L/mol.s}$ $k_3 = 0.063 \text{ L/mol.s}$ $k_4 = 0.010 \text{ L/mol.s}$ $k_5 = 0.016 \text{ L/mol.s}$ $k_6 = 0.175 \text{ L/mol.s}$	[111]
Soybean oil Catalyst: Amberlyst A26-OH basic ion-exchange resin	Molar ratio of methanol to oil, 10:1 with 5% oleic acid and without acid Agitation speed: 550 rpm Temperature: 50 °C	Kinetic model: Eley-Rideal $k = 7.48 \times 10^{-4} \text{ h}^{-1}$ without FFA $k = 1.94 \text{ h}^{-1}$ with FFA	[115]
Canola oil Catalyst: KOH	Tubular reactor: 0.2–1.2 wt% per oil based on KOH concentration Temperatures: 30–65 °C Time: 1 h Flow rate: 2–12 mL/min	Kinetic model: Nonlinear regression Distribution coefficients and exponents being: $C_1 = 8.67$ $C_2 = 0$ (concurrent flow), $\alpha = 0.543$ $\beta = 0$ (concurrent flow) $\gamma = 0.269$ Reaction rate constant varies according to different conditions	[116]
Canola, palm, peanut, soybean and sunflower oil Alcohol: Methanol, ethanol, isopropanol, butanol and tert-butanol Catalyst: KOH and NaOH	Batch reactor: 6:1 molar ratio of alcohol to vegetable oil 0.8 g catalyst per 100 g of oil Reaction time: 30 min. (canola, peanut, soybean, and sunflower oil); 40 min. (palm oil) Temperatures: 40–60 °C Impeller speed: 400 rpm	Kinetic model: Activation energies and pre-exponential factors via nonlinear regression (Levenberg–Marquardt algorithm), model was solved using Runge–Kutta method Reaction rate constant and activation energy vary according to different conditions	[117]
Canola oil Catalyst: KOH	Batch reactor: 3–8:1 molar ratio of methanol to canola oil 0.2–1.2 g catalyst per 100 g of oil Reaction time: 25–75 min Temperatures: 30–70 °C Impeller speed: 100–600 rpm	Kinetic model: Nonlinear regression (Levenberg–Marquardt algorithm), model was solved using Runge–Kutta method Activation energies: Forward reaction = 47–61 kJ/mol Backward reaction = 31–49 kJ/mol Pre-exponential factors/activation energies: Triglyceride = $3-8 \times 10^7 \text{ m}^6 \text{ kmol}^{-2} \text{ min}^{-1}/47-61 \text{ kJ mol}^{-1}$ Diglyceride = $1-7 \times 10^8 \text{ m}^6 \text{ kmol}^{-2} \text{ min}^{-1}/50-61 \text{ kJ mol}^{-1}$ Monoglyceride = $1-9 \times 10^8 \text{ m}^6 \text{ kmol}^{-2} \text{ min}^{-1}/55-57 \text{ kJ mol}^{-1}$	[118]
Rapeseed and waste sunflower oil Catalyst: KOH	6:1 molar ratio of methanol-to-oil 1.0 wt% catalyst concentration Rotational speed: 500 rpm Temperatures: 40, 50 °C	Kinetic model: Nonlinear regression (Levenberg–Marquardt algorithm), model was solved using fourth-order Runge–Kutta method Mass-transfer coefficients = $0.2-1.2 \times 10^{-5} \text{ m min}^{-1}$ Activation energies: Waste sunflower oil: Forward reaction = 93 kJ/mol Backward reaction = 48 kJ/mol Rapeseed oil: Forward reaction = 47 kJ/mol Backward reaction = 36 kJ/mol	[119]

with experimental results at 6:1 molar ratio of alcohol to oil. As for the end scenario, an inclusion of shunt mechanism was not needed. Darnoko et al. [108] have studied the kinetics of base-catalysed transesterification of palm oil at 6:1 molar ratio of methanol to oil. The kinetics results emerged as a pseudo second order.

Nevertheless, a second order mechanism is known to be more suitable and reliable compared to a pseudo second order mechanism for forecasting a conversion yield at any reaction time. By using a pseudo second order mechanism, there is a need for an initial concentration of all reactants (triglycerides, diglycerides and monoglycerides); commonly, these concentrations are recognized confide to the respective condition. There is no dispute on the initial concentration of triglycerides, but the highest concentrations of diglycerides and monoglycerides must be provided. The reaction must be extended for a minute to determine these concentrations. Nevertheless, a pseudo second-order mechanism is unable to predict a real time biodiesel yield, which is contrasting the advantage of the second-order mechanism [114].

Moreover, complex kinetic studies, which involve a pilot scale system, are briefly reviewed in Table 11. The complex kinetic studies are much relevant to describe the actual mechanisms and pathways of heterogeneous catalysis to produce biodiesel in large amounts. This is important to employ the heterogeneous catalyst in biodiesel industry and promote the continuous production of biodiesel [116–119]. Several kinetic modellings work of heterogeneous transesterification are compiled in Table 11.

Conclusions

In the present work, an extensive insight has been offered on the various possibilities and opportunities of biodiesel implementation on a commercialized scale in the years to come. Current environmental issues caused by the consumption of fossil fuel has prompted the urge to search for alternative fuel option. Biodiesel serves as an ideal candidate as it is a renewable alternative to petroleum-based diesel fuel with lower pollutant emission in comparison to traditional diesel derived from fossil. However, current biodiesel production faces several issues such as unrecoverable catalyst, expensive separation stage and high wastewater generation which are mainly attributed to the utilization of homogeneous catalysts. Thus, the need to develop a new catalyst or a new technology to tackle the problems above are needed. Hence, the development of heterogeneous catalyst and reactor technologies, such as batch, semi-batch/semi-continuous, or continuous process modes shall be looked upon. A continuous packed bed reactor can be considered as it can eliminate the catalyst recycling process. Other than traditional commercial heterogeneous catalyst such as CaO, heterogeneous catalyst derived from renewable sources such as industrial waste (lime mud, red mud etc.) and food waste (pig bones, mussel shells etc.) are also being researched extensively. Modification to such catalyst such as magnetizing the catalyst to allow easy separation are also being discovered. Through the review of various types of catalyst, it can be deduced that the most important characteristics of the catalyst is basicity and BET surface area. Higher surface area allows better access of reactant to the catalytic active sites while higher basicity provides higher catalyst activity to result in higher overall biodiesel yield.

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