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Contemporary approaches towards augmentation of distinctive heterogeneous catalyst for sustainable biodiesel production

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Abstract

In recent times, demand for energy has significantly increased due to the depletion of fossil fuels and the fast-industrial revolution. This has created a wide space for the development of sustainable and renewable energy sources. Biodiesel has attained exceptional contemplation among other biofuels due to the use of renewable and low-cost resources. Selection of suitable catalyst plays a vital role in biodiesel production by a catalytic transesterification reaction. Compared to homogeneous catalysts, heterogeneous catalysts are most preferred as they have high selectivity and stability with increased biodiesel yield. Heterogeneous catalyst has made incredible development in biodiesel production under mild operating conditions and has less impact on the environment. Nanocatalysts are the effective heterogeneous catalyst, which has brought a tremendous revolution in biodiesel production in recent years. Thus, present review provides a comprehensive analysis of the use of heterogeneous catalyst, importance and challenges associated in biodiesel production.

Keywords: Renewable energy; Transesterification, Heterogeneous catalyst; Nanocatalyst; Biomass

Short title: Biodiesel Production

1. Introduction

The express industrialization and population have stimulated the scientists and industries to identify alternative fuels. Till now, fossil fuel is a major source for transportation which is a limited resource. The demand for fossil fuel automatically increases the fuel price and cause environmental impacts such as carbon dioxide emission, ozone depletion and global warming. The transportation sector is increasing fossil fuel demand more than 55% of the global demand. The balance 45% demand from industries. In 2040, the demand for global energy will be about 30% higher when compared to 2010. In 2020, the crude oil global demand was 101.6 million barrels per day (Sonnichsen, 2020). The main tenacity of the global economy lies in the development of the energy sector with the help of various modernistic approaches towards technology. The global extinction of conventional fossil fuels has led to the establishment of alternative fuels. The environmental issues that are connected with conventional fuels gave a spark towards the research of renewable energy (Mansir et al., 2017).

Biodiesel has created a huge demand in recent times due to the consistent increase in population size and technological advancements (Baskar and Aiswarya, 2016). Biodiesel is produced through transesterification process. The characteristics such as higher flash point, low sulfur concentration and high lubricating capacity make it an excellent fuel compared to others (Islam et al., 2014; Teo et al., 2015). Biodiesel is more quality than fossil diesel because of the chemical structure of fatty acid esters. It is having more oxidation stability, thermal stability and storage stability (Bhatia, 2014). The major challenges on the commercialization of biodiesel production lie in the selection of feedstock and catalyst for the chemical reaction. Although the use of low-grade feedstock reduces the cost of biodiesel, it hampers the productivity rate due to the use of the homogeneous catalytic system (Cho et al., 2012; Wen et al., 2010). The use of fresh vegetable oils tends to increase 80% of the production cost and simultaneously it makes the production as expensive as other processes. Sodium hydroxide is the most commonly used homogenous catalyst for biodiesel production (Halek and Kavousi-Rahim, 2018; Shameer and Nishath, 2018; Shalmashi and Khodadadi, 2019). High energy consumption during separation and purification process is the main detriment on using homogeneous catalytic system (Bhuiya et al., 2014). In order to overcome these issues, heterogeneous catalysts are considered for the efficient production of biodiesel even from low-grade feedstock (Alhassan et al., 2013; Sirisomboonchai et al., 2015). The use of biodiesel in developing countries is still in prime research because of three important factors such as the utilization of high purified vegetable oils, multiple steps involved during processing, purifying and the use of an expensive catalytic system (Canakci and Sanli, 2008; Zhang, 2003). In concern to the cost, various technologies such as reactive distillation and non-catalytic supercritical fluid technology were introduced for the acceleration of biodiesel production (Velez et al., 2012).

The transesterification reaction is catalyzed by three different types of a catalyst such as homogeneous, heterogeneous and enzyme catalyst. The use of heterogeneous catalyst has drawn wide attention owing to its properties such as reusability without loss of activity for several cycles (Baskar et al., 2018). The use of heterogeneous catalyst at industrial level helps in the improvement of sustainable reaction and mitigating the catastrophic consequences during the process. The other ideal properties of the catalyst are availability, durability and easy separation from the reaction mixture (Marchetti and Errazu, 2008). The foremost aim of inexpensive biodiesel production lies in reducing the dosage of catalyst and the reaction temperature involved during the process. Nanocatalysts are one of the heterogeneous catalysts widely used for biodiesel synthesis as they have a high surface area and selectivity (Baskar and Aiswarya, 2015a). The functionalized nanomaterials, Ionic liquids (ILs), carbon and inexpensive biomass are directly used as a catalyst for biodiesel production (Ambursa et al., 2016; Konwar et al., 2016).

The present review emphasizes the importance of heterogeneous nanocatalyst and its conventional type of material used in the transesterification reaction. This review also illustrates the modernistic approach towards heterogeneous catalyst and its significance in design. The cogent economic cost involved during the synthesis of catalyst and its utilization in the transesterification process is also elucidated in this paper. Furthermore, this paper also discusses the methods for catalyst synthesis and factors influencing the heterogeneous catalytic system.

2. Overview of biodiesel production process

The transformation of plant oils to biodiesel has similar properties to those of petroleum-derived fuels. The various methods employed to produce biodiesel include pyrolysis, transesterification and micro-emulsion techniques (Meher et al., 2013). Thermal cracking or pyrolysis is the process of producing hydrocarbon at elevated temperature (>350°C) by decarboxylation in the presence or absence of the catalyst. The thermal cracking of soybean oil using bauxite as catalyst was investigated at elevated temperatures ranging from 380-400°C. It was found that the hydrocarbons were produced with long-chain fatty acids along with various intermediates. Pyrolysis is a challenging process as selectivity of the desired product is undesirable (Kozliak et al., 2013; Prado and Antoniosi-Filho, 2009). Micro-emulsions, thermodynamically stable isotropic fluid is used for the production of hydrocarbons mixtures with the help of solvents such as ethanol and non-ionic surfactants. The properties of fuel were similar to that of diesel as the viscosity and density of micro-emulsions was reduced. Though this process is feasible for production, it involves multiple steps that add drawback during cost estimation (Qi et al., 2013). Transesterification or alcoholysis is the most preferred process for the production of biodiesel as they produce high-quality biodiesel. Transesterification, a reversible process requires 1 mole of triglycerides and 3 moles of excess alcohol to produce 3 moles of Fatty Acid Acyl Ester (FAAE) and 1 mole of glycerol (Marchetti et al., 2007).

Biodiesel is also produced by other methods such as reactive distillation, Insitu-transesterification, ultrasound-assisted transesterification and supercritical conditions. The alternate route for the production of biodiesel by either catalyzed or non-catalyzed reduces the cost yielding a high-quality product. The ultrasound-assisted transesterification process consumes less amount of energy than other processes. The cavitation created between oil and alcohol helps in effective mixing and also enhances the mass transfer rate (Salamatinia et al., 2010). Biodiesel yield of 95% was reported for ultrasound-assisted transesterification using sunflower oil as feedstock while the frequency 24 kHz was maintained at 60°C for 20 min. This process mainly utilizes solid catalyst and the stability of the catalyst was maintained as it operates only at low-frequency mode (Samuel and Dairo, 2012). *Insitu*-transesterification process directly converts the dried seeds to diesel with the help of alcohol that assisted in extraction and transesterification process (Marchetti et al., 2007). This process reduces the cost involved during the degumming process and conversion of biodiesel. Use of transesterification and distillation in the same column reduced the cost to a great extent. Separation and recycling were easier ensuring the high purity of the product with the help of flash evaporator and distillation column (Salamatinia et al., 2010). The other established method for the production of biodiesel is a supercritical method which eliminates the use of the catalytic system. This process limits the mass transfer limitations as the temperature and pressure ensure the mutual solubility of oil and methanol. The thermal degradation of the reactants and products are minimized by supplementary addition of liquid co-solvents. The non-catalyzed supercritical transesterification of sunflower oil was investigated at 325°C and reported with a yield of 84%. The main drawback of using this method were the high operating conditions and cost involved during the additions of co-solvents and gaseous substance (Samuel and Dairo, 2012).

The other advanced techniques listed for the production of biodiesel are conventional reflux method and autoclave reactor. The reflux method equipped with a round bottom flask with a condenser was employed for the production of biodiesel. The major setback with this method is the slow reaction rate. In case with autoclave reactor, the operation condition can be high as they monitored and controlled with the help of a computer. But this method has a major drawback as it consumes high electricity with regular maintenance which simultaneously increases the cost of production (Marchetti et al., 2007).

Hence, transesterification catalyzed by heterogeneous catalyst was explored by many researchers. Also, simultaneous esterification and transesterification process was highly practised for the biodiesel production. The schematic representation of biodiesel production by transesterification process is shown in (Fig. 1).

3. Mechanism of heterogeneous catalytic system

It is necessary to understand the mechanism of acid and base-catalyzed mechanism for the design of a suitable catalyst under controlled conditions. The basic concept of nucleophilic attack and protonation on the triglyceride molecule helps in selecting the acid and base catalyst for the transesterification process (Olivares-Carrillo and Quesada-Medina, 2011). In base-catalyzed reaction, the alkali molecule reacts with the OH group to form alkoxide (RO^-) and a protonated catalyst (BH^+). The nucleophilic alkoxide of the alcohol attacks the nucleophilic part of the carbonyl group of the triglyceride ($R\text{-}COO\text{-}CH_2$) to form a tetrahedral intermediate ($R\text{-}COO\text{-}CH_2\text{-}CH\text{-}CH_2\text{-}O^-$). This unstable intermediate reacts with an alcohol (R-COOH) and undergoes protonation (BH^+) to form fatty acid and diglyceride. On the other hand, acid-catalyzed nucleophilic attacks are noted in the alcohol group and protonation in the carbonyl group of the triglycerides. This attack helps in the formation of unstable intermediates which further cleaves to produce ester (Lokman et al., 2014).

In acid-catalyzed reaction, triglycerides were found to be adsorbed at the surface of the catalyst due to protonation in the carbonyl group. The acid-catalyzed reactions are based on two hypotheses, known as a single site and dual-site mechanism. The single-site mechanism (Eley-Rideal model) is based upon the absorption and protonation of carbonyl atom of triglyceride with alcohol, whereas in dual-site (Langmuir Hinshelwood model) both triglycerides and alcohol are absorbed in the catalyst surface. The acid-catalyzed reactions are mainly based on the type of carbon in alcohol (Singh and Singh, 2010).

4. Heterogeneous-nanocatalyst for the production of biodiesel

The heterogeneous catalyst acts in a dissimilar phase during the transesterification reaction. Though, the homogeneous catalyst was widely used in industries they possess certain impediment during esterification and transesterification process (Baskar et al., 2018). The use of homogeneous catalyst generates a high amount of wastewater during separation, recovery and purification. The separation of wastewater from the desired product has augmented the overall cost of production. In regards, the introduction of heterogeneous catalysts for the transesterification process has gained wide attention. Heterogeneous catalysts can be separated easily from the reaction mixture and can be reused for a certain number of cycles. A heterogeneous catalyst highly reduces saponification and they are designed in such a way to catalyze both esterification and transesterification without any pre-treatment (Dossin et al., 2006).

Nanocatalyst is grouped under heterogeneous catalyst, have created a wide response in the catalytic improvement due to the nano-sized solid nature (Leung et al., 2010; Rattanaphra et al., 2011). The space for nanocatalyst in the catalytic technology has reached tremendous deliberation because of the electric delocalization with a strong chemical bond as noted in metal nanoparticles. Nanomaterials are better than microscopic particles owing to its size-dependent property achieved by steric effects. The atomic coordination at the surface of the catalyst is strongly influenced by the reactivity of the species (Liu et al., 2010). The factors influencing the catalytic activity of the nanomaterials are the shape and homogeneity of the nanomaterials. The high surface area of base materials helps in grafting the composite nanoparticles with supports such as oxides, zeolites and carbon substance. The other factors influencing the catalytic performances are the acidic and basic properties of the nanomaterials (Polshettiwar et al., 2011). It was reported that porosity and dosage of the catalyst also influence the catalytic performances. The various heterogeneous nanocatalyst used for the transesterification reaction includes alkaline earth oxides, hydrotalcite, zeolites band sulfated oxides (Shylesh et al., 2010).

5. Solid acid heterogeneous catalyst

5.1. Zeolites

Zeolite holds distinctive acidic sites, shape and selectivity. The pore structure and electric field at the surface of zeolites attribute excellent catalytic performance. Transesterification of soybean oil using modified zeolite (La/zeolite ß) were investigated. The three-dimensional structure enhances the acid-catalyzed reaction more effectively. The catalyst was prepared by the ion-exchange method in the suspension of lanthanum nitrate under the continuous stirring condition for 3 h. The suspension was dried and calcinated at 250°C for 4h. The low conversion of 48.9% was obtained due to the agglomeration and modification of La^+. The low conversion of biodiesel was also due to the weak bronsted acid site (Zhang et al., 2014). Also, the transesterification of *Pongamia pinnata* was studied using 1:10M ratio of oil to methanol and 0.575 g of Hß-zeolite K-10. The conversion of 59% was achieved after 24 h of reaction time (Bankovic–Ilic et al., 2017).

The potential of NaX zeolites loaded with KOH for the production of biodiesel was investigated. The yield of 85.6% was obtained by loading 10% of base oxide to NaX for 2 h at 125°C. It was reported that the conversion decreased to 48.7% due to leaching of KOH and the low conversion was due to the presence of trace amount of glycerides at the final stage of the product (Shu et al., 2007). Zeolites were reported for the esterification process in which removal of FFA was achieved with methanol and ZSM-5 (MFI) as a catalyst. It was observed that the catalytic efficiency in FFA removal was based on the acidic strength of the zeolites. The catalyst ZSM-5 (MFI) was efficient in FFA removal due to cracking of FFA pore structure (Karmee and Chadha, 2005). NaY zeolites along with Ultra Stable Y zeolites were reported for the catalytic conversion of FFA to oils. This type of catalyst calcinated 300°C for 3 h showed a shorter conversion time of 10 min and 60 respectively (Marchetti et al., 2007).

5.2. Heteropolyacids

Heteropolyacids and their corresponding salts are called as oxygenated compounds which are predominantly used for the transesterification reaction. Heteropolyacids (HPA) such as $H_4PNbW_{11}O_{40}$, $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$ and $H_4SiMo_{12}O_{40}$ were reported for better catalytic performance. In order to increase the catalytic performance, HPAs were incorporated into highly porous materials with high surface area (Xie et al., 2007). The heteropoly acid WO_3/ZrO_2 was reported with a yield of 95% with the catalyst concentration of 15% (w/w). The yield was high due to the moderate acidity and porosities for the interference of catalyst and methanol under controlled conditions (Chung et al., 2008). Similarly, the activity of $H_4PNbW_{11}O_{40}/WO_3\text{-}Nb_2O_5$ was also investigated after calcination at 500°C for 180 min for the transesterification of triolein. It was observed that the generation of bronsted acid sites at the surface has created insoluble material without any significant dissolution of the acid in the reaction medium (Sharma et al., 2011). The loading of HPAs on to SBA supported molybdophosphoric acid ($H_3PMo_{12}O_{40}$) were tested for the transesterification of karanja oil. The loading capacity of 2.5% was found to optimum and it was noted that an increase in the concentration resulted in the blockage of silica mesopores. The yield of 81.8% was observed at 140°C for 300 min and stirring rate of 250 rpm (Jothiramalingam and Wang, 2009). The catalytic activity of $Cs_{2.5}H_{0.5}PW_{12}O_{14}$ with bis-clyclodextrin catalyst for biodiesel production from waste cooking oil was studied. The maximum yield of 94.2% was observed at 65°C for 180 min and catalyst concentration of 3 % (w/w) (Katada et al., 2009). The catalyst known as Amberlyst-15, were used as heteropoly acids for biodiesel production from waste cooking oil. Amberlyst-15 has offered good resistance during the conversion of fatty acid. The conversion of 88.6% was noted at 65°C and 10% (w/w) as catalyst (Khayoon and Hameed, 2013).

5.3. Other acid catalyst

The use of aluminium hydrogen phosphate ($Al(H_2SO_4)_3$) as catalyst was reported for the alcoholysis of waste vegetable oil. The high conversion of oil (81%) was achieved at 220°C for 50 min using 16:1 ratio of methanol to oil ratio and 0.5% (w/w) of catalyst concentration. The highest conversion was achieved due to the covalent interaction of aluminium with pores of $AlCl_3$ ($-SO_3H$) promoting hydrophilicity of the catalyst to interact with methanol (Zou et al., 2013). The impregnation of ammonium metatungstate on SnO_2 the formation of WO_x clusters promoted the protons for the generation of bronsted acid sites. The maximum conversion of oil (72.5%) was achieved at 180°C after 300 min of reaction time using oil to methanol ratio of 1:30 and 5% (w/w) of catalyst (Talebian-Kiakalaieh et al., 2013).

The final product containing methyl esters and FFA was obtained using Bronsted and Lewis sites known as macroporous vanadium phosphate (P-OH and V=O). This catalyst was efficient in obtaining FAME but one disadvantage associated with this type of catalyst was the generation of wastewater (Ramachandran et al., 2011). The copper vanadium phosphate with the three-dimensional network was reported for transesterification of soybean oil using methanol. The maximum conversion of 65.5 % was obtained using methanol to oil ratio of 6.75:1 at 65°C and 1.5% (w/w) of catalyst concentration (Xie and Yang, 2012). Various cation exchange resins such as Amberlyst-31 WET, CH-A and NKC-9 were reported for the transesterification reactions (Chen et al., 2011; Domingues et al., 2013). The sulfated zirconia alumina catalyst was investigated for transesterification process and was found to have the yield of 78.2 % when the catalyst was calcinated at 490°C for 4 h (Kouzu et al., 2011). The cation and anion exchange resins, Diaion PA306S and Diaion PK208LH were studied for esterification and transesterification reaction. It was observed that anion exchange resins adsorbed the wastewater and glycerol which also increased the yield of the final product in bench-scale reactors (Jiang et al., 2013). $Zr(SO_4)_2$ with PVA were reported for the conversion of FFA were result showed that the catalyst was efficient in conversion only when loaded to the catalytic polyvinyl hybrid membranes (Yee et al., 2011).

6. Heterogeneous base catalyst

6.1. Alkaline metal oxides

Alkaline metal oxides have been used predominately for the production of biodiesel as they require mild operating conditions and energy. They are classified under high basic strength of the metal and the activity of catalysts, based upon the synthesis and thermal method for the activation process (Sharma et al., 2011). The most used metal oxides for transesterification reaction is CaO. They have high activity towards the production of biodiesel because of the basic strength of the material. The main challenge of using this catalyst is maintaining the stability for a longer run. Increased stability of catalyst was reported by incorporating CaO with other oxides such as MgO, ZnO, SiO_2 and Al_2O_3 . (Shibasaki-Kitakawa et al., 2013).

The use of CaO as a catalyst for transesterification was reported with a yield of 93.9%. The catalyst showed better catalytic performance because of the crystalline nature throughout the surface area with the same pore volume (Shi et al., 2010). The nanorods containing positive metal ions (cations) and negative ions (anions) were used for the production of biodiesel from olive oil using ZnO nanorods as a catalyst. The use of this catalyst was reported with a yield of 94.8% at 150°C for 8 h. The synthesized nanomaterials were also used in flow type batch reactor for the production of biodiesel using supercritical water (Jamil et al., 2020). The use of Magnesium Oxide (MgO) was used for transesterification of sunflower and rapeseed oil into biodiesel. The high yield was achieved due to the selectivity of the catalyst under low optimal conditions. The selectivity and the active site of nanostructured MgO have made the production of biodiesel more efficient (Molina, 2013). The calcinated MgO at 600°C for 8 h were reported for the conversion of triacetin to biodiesel. The yield of 92 % was found to be effective using 12:1 ratio of methanol to oil and 5% (w/w) of catalyst loading. The same catalyst MgO was efficient under supercritical conditions with the yield of 91% using 39.6:1 ratio of methanol to oil in a batch reactor (Levy et al., 2014; Verziu et al., 2008). BaO and SrO were reported for the transesterification of palm oil for the production of biodiesel. The reaction was conducted under ultrasound conditions for the effective production of biodiesel. The yield of 95% was obtained on using both the catalyst using 9:1 ratio of methanol to oil and 2.8% (w/w) of catalyst concentration. Strontium oxide (SrO) was examined for the production of biodiesel from rapeseed oil under supercritical conditions. This catalyst was found to have minimum weight loss by dissolution with high catalytic activity. The same catalyst was investigated for the production of biodiesel from soybean oil. The yield of 90% was obtained at 65°C using 3% (w/w) of catalyst loading (Tatsuo-Tateno, 2004; Zabeti et al., 2009).

6.2. *Earth mixed metal oxides*

The metallic oxides (CaO-Nd_2O_3) prepared by the co-precipitation method was investigated. The yield of 86.3% was obtained at 65°C with 5% (w/w) of catalyst and 15:1 ratio of methanol to oil. The higher yield of biodiesel from *Jatropha curcas* was obtained due to the high-density base sites which are responsible for better catalytic performance (Yoo et al., 2010). The use of TiO_2-ZnO nanocatalyst was used for the transesterification of palm oil. The yield of 92.2% and 83.2% were obtained on using TiO_2-ZnO (200 mg) and free ZnO (250 mg) respectively under the optimized conditions at 60°C for 5 h and oil to methanol ratio of 1:6 (Tatsuo-Tateno, 2004). The heterogeneously mixed metal oxides were commonly used for the production of oil from algae. The yield of 32.6% obtained from *Scenedesmus obliquus* was reported for KOH-SrO as a catalyst. The low yield of biodiesel was obtained due to the lack of residual purification during the extraction of oil. Also, the yield of 29% was obtained when free SrO was used as a catalyst (Madhuvilakku and Piraman, 2013).

The effect of CaO-Al_2O_3nanocatalyst for the production of biodiesel was investigated. The studied showed better catalytic performance and the catalyst effectively reduced the soap formation. It was also reported that it is mandatory to monitor the amount of catalyst loading as they play a significant role in the final yield of the product (Veillette et al., 2017). The magnetic nanocatalyst (KF/CaO-Fe_3O_4) was for the transesterification of biodiesel from beef tallow. The catalyst was found to show a positive outcome in the yield of biodiesel due to basicity of the catalyst and the use of magnetic particles were effectively reused by applying an external magnetic field for the recovery of the catalyst (Teo et al., 2016). The transesterification of *Pistacia chinensis* oil was used for the production of biodiesel using CaO-CeO_2 as a catalyst. The catalyst was found to be efficient with a yield of 91%. The catalyst was reported to be reused with any loss in activity for five cycles (Kumar, 2016).

6.3. Oxides as support

The use of oxides as support is reported to reduce the mass transfer limitations in the liquid phase as they provide high surface through the resistance of pores. The solid base potassium supported by alumina was studied for transesterification of soybean oil to biodiesel. The catalytic efficiency was better due to high basicity of the catalyst noted as 6.75 mmol/g. The high yield of 87% was obtained after 8h using a molar ratio of 15:1 and 6.5% (w/w) of catalyst (Yu et al., 2010). The same potassium was incorporated to zinc oxide prepared by impregnation method at 600°C for 5 h. The basicity of the catalyst was found to be 1.47 mmol/g with the yield of 87% from soybean oil, using 3% (w/w) as catalyst and 10:1 of alcohol to oil ratio in 9 h of time (Xie et al., 2006). The use of alumina loaded with sodium and NaOH as a catalyst for transesterification of soybean oil using hexane and methanol was studied. The surface area of alumina was found to decrease from 143.1 to83.2 m^2/g when they were incorporated to sodium hydroxide. The yield of 83% was achieved when the catalyst was used without any modifications (Xie and Huang, 2006).

7. Functionalized acid/base as catalyst

The acid-base catalyst also known as a bi-functional catalyst has many advantages because of its high stability than other types of catalyst. Bi-functional catalyst has the facilities of catalyzing both esterification and transesterification simultaneously. This catalyst reduces the cost involved during the pre-treatment process with help of uniformly disturbed active sites of acid and basic nature. Ferric manganese doped with sulfated zirconia solid acid was used as a bi-functional catalyst for transesterification of waste frying oil to biodiesel. It was observed that the fatty acid content was reduced to 0.3% with a maximum yield of 96.05% of biodiesel. The optimum conditions achieved during the production of biodiesel were noted at 180°C, 600 rpm of stirring speed, and 1:20 ratio of oil to methanol and 3% (w/w) of catalyst loading. This bi-functional catalyst was reused and the activity was found to be stable till the sixth cycle, enabling good catalytic activity of catalyst (Kim et al., 2004). Quintinte-3T was used as a bi-functional catalyst for transesterification and esterification of vegetable oils. This catalyst was prepared by sol-gel method, reported for high yield of 96% at 75°C in 2 h with 10% (w/w) of catalyst concentration and 1:12 ratio of oil to methanol (Alhassan et al., 2015).

The bi-functional catalyst, Mo-Mn/α-Al_2O_3-MgO was used for the transesterification of waste cooking oil to biodiesel. The yield of 91.4% was obtained at 100°C for 4 h of reaction time, 27:1 ratio of methanol to oil, 500 rpm of agitation speed and 15% (w/w) of catalyst concentration. The catalyst was observed to be stable till 8 cycles without major loss in yield of biodiesel (Sirisomboonchai et al., 2015). The bi-functional catalyst $MnCeO_x$ (acid-base) was effectively studied for biodiesel production. The maximum production of biodiesel was achieved in 5 h of reaction time, 1% (w/w) of catalyst loading and at 200°C of reaction temperature. The activity of the catalyst was enhanced by the synergistic effect of acid and basic sites along with surface and textural properties of the catalyst (Kondamudi et al., 2011). Thus the bi-functional catalysts can be used for the production of biodiesel from various feedstocks. The different type of heterogeneous catalyst including acid, base and functionalized catalysts are listed in table 1.

8. Modernistic pathway towards heterogeneous catalyst

8.1. Ionic liquid as catalyst

The use of Ionic Liquids (ILs) as a catalyst for the production of biodiesel has increased recently due to the limitation associated with other catalysts. ILs are considered as salt material in a liquid state with a melting point below 100°C. These liquids are also used as solvents for other types of reactions as they possess cations and anions. ILs has unique properties such as thermal stability, dissolubility with various inorganic/organic compounds under low vapour pressure (Chiappe and Rajamani, 2011). The functionalized ILs with lewis and bronosted acid were reported with a yield of 98.5% with a minimum generation of waste and no saponification. The basic mechanism includes the interaction of H+ ions to produce methoxide. This further reacts with triglycerides molecule to form methyl ester and diglycerides. The following final step includes the reaction of diglycerides to form monoglycerides to produce methyl ester and glycerol (Ab Rani et al., 2011). The selection of ILs is mainly based upon hydrogen acidity, basicity and polarization effects. The strong bronsted acidity of pyridinium is reported with a yield of 81% in 3 h. Also, the use of Di-cationic Bronsted Acidic Ionic Liquid (DAILs) was reported with the yield of 95-96% using (TMEDAPS, HSO_4). The novel IL catalyst was used for the transesterification of rapeseed oil using 1, 4 butane sulfonate and hexamethylenetramine produced 98.3% in 7h at 70°C (Zuo et al., 2012).

The effect of functionalized lewis acids with ILs was evaluated for the transesterification reaction. The functionalized catalyst $[Et_3NH]Cl\text{-}AlCl_3$ was reported with a yield of 98.5% under the optimum conditions of 5 mmol of methanol, 5 g of soybean oil at 70°C for 9 h (Fan et al., 2013). The researchers evaluated the effect of $[Et_3NH]Cl\text{-}MgCl_2$ and $ZnCl_2$ under optimum conditions. The low yield of biodiesel was observed due to the low acidity of metal ions. The steric hindrance and presence of long-chain carbon with complex mass transfer were also reported for the low yield of biodiesel. The Jatropha oil with an acid value of 13.8 mg KOH/G was studied for biodiesel production using MCl addition (Li et al., 2010; Liang et al., 2009). It was found that the yield was maximum (94%) was obtained by the addition of $[BMIM](CH_3SO_3)\text{-}FeMCl_3$. The main reason for the increase in the production was due to a stronger acidity of trivalent metallic ions (Guo et al., 2013). The esterification and transesterification of waste palm oil were studied using BMIM $[H_2SO_4]$ and (Et_3NHSO_4). The yield of 96.6% was reported to be high under the optimal conditions using (Et_3NHSO_4) as a catalyst. The high yield was obtained because of the interaction of the longer side chain of the catalyst with methanol and methoxide ions. The use of hydroxides such as [BMIM][OH] was evaluated for the synthesis of biodiesel. The yield of 87% was reported at 120°C for 8h with methanol to oil ratio of 9:1 (Ullah et al., 2017).

ILs with solid support was extensively studied for biodiesel production as they provide high surface area and porosity for the reaction to proceed faster. The solid support, [BMIM][Ntf_2]and free ILs [BMIM][PFO] catalyst were compared for high biodiesel yield. It was identified that solid support catalyst was reported with the yield of 99% whereas free ILs catalyst was found to have only 83% in 0.5 h of time. It was noted that solid-supported ILs produced biodiesel at a shorter time than acid ILs which requires 13h of time (Zhou et al., 2012). The lipase-catalyzed transesterification in ILs suspension was studied. The immobilized *candida antarcitica* lipase B (Novoenzyme 435) was examined for transesterification of waste cooking oil. The use of (CaLB) with ILs (OMIM) [PF6] showed good synthetic activity for the production of biodiesel owing to its hydrophobicity of cation and reduced nucleophilicity of anions. The biphasic system has added advantage for easy separation of desired products (Abreu et al., 2005). Similarly, [C_{16}MIM] and [C_{18}MIM] [NtF_2] immobilized with lipase was evaluated, were NtF_2 showed higher activity with a yield of 90.29%. The high yield was achieved due to the operational stability of anions at monophasic system. Immobilization of ILs onto ion exchange resin support such as [Sn (3-hydroxy 2-methyl 4-pyrone)$_2$ (H_2O_2)] was used as a catalyst for biodiesel production. The maximum yield of 93% was achieved in 3 h and the yield was found to show a decrease (58%) when they were used for next cycles (De Diego et al., 2011; Lapis et al., 2008). The list of various ILs used for the production of biodiesel is listed in Table 2.

8.2. Carbon as a catalyst

The active sites of the catalysts directly influence the activity because of the presence of water molecules. The hydrophobic surface of the ordered carbon material acts as the ideal support for anchoring of various materials. The use of carbon material has an additional advantage as they could withstand even at high operating conditions without any change in the overall structural framework of the material. The carbon materials synthesized from biomass is a recent trend involving three major processes such as hydrothermal carbonization, template-directed method and direct carbonization. These methods are usually synthesized by the impregnation method followed by calcinations (Reza et al., 2014). The catalytic activity of carbaneous sulphanated catalyst was reported for the transesterification reaction. The stability of the catalyst is highly maintained by porosity and strong bonding to the substrate. The activity of the catalyst was reported to decrease due to the adsorption of reactants at the surface. Also, the stability of the catalyst was reduced due to the weak bonding attributed by leaching of active sites (Kang et al., 2014; Konwar et al., 2016).

The nanographene (-SOH), one of the amorphous carbon has drawn wide attention for biodiesel because of its high catalytic activity. The multi-walled carbon nanotubes (MWCT) were tested for the alcoholysis of palm fatty acid distillate. It was observed that yield of 93.4% was obtained at 170°C in 180 min using 2% of catalyst and 20:1 ratio of methanol to oil (Shuit and Tan, 2014).

The activated carbon material was used as support for the esterification of palmitic acid. The heterogeneous acid known as HPAW and HPAM$_0$ were easily incorporated on the carbon surface due to high porosity of carbon. Though the incorporation was effective, the yield of biodiesel was not convincing due to the limitation of ions movements to the catalytic centre (Alcaniz-Monge et al., 2013). The effect of copper incorporated on activated carbon prepared by sol-gel method was used as a catalyst for the esterification of biodiesel. The conversion of FFA was found to be effective (95%) in 360 min at 65°C using 10:1 ratio of methanol to oil and 7% of copper material (Ong et al., 2014).

The yield of 90% of biodiesel was obtained at 65°C using SO_3-H-SWCNH as a catalyst. The yield was achieved in 300 min using 3% as catalyst and 33:1 ratio of methanol to oil. They showed good catalytic effect as the surface area of SWCNH was increased due to oxidation which simultaneously enabled the opening of mesoporous (Poonjarernsilp et al., 2014). The use of acid incorporated with carbon, 4-sulfophenyl activated carbon was reported for biodiesel production. The yield of 95% was achieved at the optimum condition of 20:1 ratio of methanol to oil, 10% of catalyst concentration in 7 h at 65°C (Malins et al., 2015). Graphene Oxide (GO) was reported for the transesterification of lipids. The catalytic efficiency was facilitated by the diffusion at the surface of the carbon. The transesterification reaction proceeded by microwave irradiation with the conversion of 95.1% in 40 min at 60°C (Cheng et al., 2016). The base materials incorporated with activated carbon was used for transesterification of palm oil to biodiesel. The yield of 94% was achieved using KOH/AC as a catalyst for biodiesel production using 1:1 ratio of methanol to oil, 5% as catalyst concentration at 70°C (Dehkhoda et al., 2010).

8.3. Mesoporous and macroporous as a catalyst

The poor accessibility of active site in case of conventional catalytic system is associated with the diffusion limitations (Gaudino et al., 2005). Tailoring of porous solids with high surface area helps in the development of the activity of the catalyst. Silicates, one of the mesoporous materials actively helps in the transesterification reaction. Mesoporous materials including M4IS, Sodium silicate, TEOS were reported for the transesterification process (Galarneau et al., 2006). The mesoporous silicates including SBA-15, SO_4/ZrO_2 were actively grafted with sulphonic acid. The size of silica (below 6nm) helps in the diffusion and FFA conversion using SBA-15. The functionalized silica with MPTS was effectively reported for both palmitic esterification and triolein transesterification reactions (Pirez et al., 2012).

The two-dimensional structure is known as BA-15p 6 mm were reported to be not effective in the molecular transport in bulk media. In order to enhance the connectivity 3 dimensional la3d KIT-6 mesoporous silica enhances the connectivity during FFA esterification. The use of surface template mesoporous support was widely used for the transesterification/esterification reaction as they help in maintaining diffusion limitations with the help of pore structure. The other diverse pathway is the incorporation of macroporous to hydrotalcite for the transesterification process. Synthesis of bimodal pore macropore structured material for the incorporation to hydrotalcite increases the surface density in the reaction media using ordered hierarchical materials (Woodford et al., 2012). The investigation of Ni and Pt supported SBA-15 and SBA-16 for the production of biodiesel was studied. The results showed that SBA-15-Ni was efficient in alcoholysis to achieve the yield of 89% at the optimal conditions of 2.5% (w/w) as a catalyst in 4 h at 60°C(Barron-Cruz et al., 2011). Titanium incorporated SBA-15 was used for biodiesel production from Jatropha oil. The methyl ester yield of 98.4% was obtained at 200°C in 3 h using108:1 ratio of methanol to oil (Chen et al., 2013). The biodiesel yield of 99.6% was achieved by oil to alcohol molar ratio of 1:9 and catalyst concentration of 3% (w/w) in 1 h at 60°C and 250 rpm from rapeseed oil. The biodiesel yield was decreased to 92% after five cycles. The activity of Li2SiO3 was found to be stable with 96.1% of biodiesel yield after six cycles. The biodiesel yield was decreased to 94.6±0.5% when the catalyst reused from 7 to 10 times (Long et al., 2011; Wang et al., 2011).

8.4. Metal sulfur as a catalyst

The use of certain heterogeneous catalyst was reported for biodiesel reduction that contains high oxygen and acidity level which relinquished its application in the transportation sector. Hence, striving efforts were spotted out for the development of biodiesel through decarboxylation and hydrodeoxygenation process over specific catalysts (Furimsky, 1983).

Several types of catalyst have been reported for the production of biodiesel including nickel, noble metal, bimetallic, sulphide free HDO catalyst open up contemporary approach towards the development and selection of highly effective catalyst for the biofuel production. The production of biodiesel by hydrodeoxygenation was reported to show similar properties to that of fossil diesel (Donnis et al., 2009; Kubicka and Kaluza, 2010; Peng et al., 2012).

Direct hydrodeoxygenation and deoxygenation isomerization are the two process involved in the production of biodiesel. Studies show that direct hydrodeoxygenation converts the deep fats under high temperature and pressure using CoMO/NiMO as catalyst (Donnis et al., 2009; Snare et al., 2006). The fuels obtained using these methods were reported with high cetane number, but the main drawback associated with this process was the poor cold flow properties which reduce the quality of fuels. In case of the isomerization process, linear paraffin is obtained with alkanes of high cetane number (Krar et al., 2011, 2010). Isomerization is consistently noted by NEXBTL and Ecofining process using Pt as a catalyst. Since HDO process is exothermic activity and phase separation of the catalyst should be monitored constantly to avoid deactivation. It was reported that low temperature with increased stirring rate and low concentration of the catalyst was excellent for HDO biodiesel production process (Tiwari et al., 2011). The proposed carbon-chain filling and carbon shortening strategy for the production of green diesel in the presence and absence of hydrogen was investigated. The carbon number (C-14-18) was reported for C-C filling strategy whereas, C-6-9 were reported for gasoline (Zhang et al., 2015). The schematic representation of sulfur catalyst in the production of green diesel is given in Fig. 2.

8.5. Biomass as a catalyst

The use of heterogeneous catalyst has been addressed with certain issues like the formation of the three-phase system. This system inhibits the transesterification reaction due to the immiscible nature of the reactants and catalyst. The three-phase system also decreases the rate of diffusion at high temperature as the mass transfer rate is limited within the bulk material (Sani et al., 2014). The other issues associated with heterogeneous catalyst are leaching, micro-porosity and active sites of the material. The main drawback of using these catalysts are the cost involved during the preparation and utilization for a particular reaction. In order to overcome these issues, utilization of industrial waste material and renewable biomass has gained wide attention owing to its inexpensive nature (Macario and Giordano, 2013; Smith et al., 2013). This bio-based green catalyst also known as green catalyst utilizes biological sources such as carbon and calcium as a catalyst for transesterification.

These bio-based green catalysts are non-toxic, non-corrosive as it is prepared from natural biomass. The green catalyst eliminates the production of wastewater which is highly noted on using a homogeneous catalyst. The green catalyst is also termed as a bio-degradable catalyst as it does not require any sophisticated disposal methods (Sanjay, 2013; Lam et al., 2010; Luque et al., 2012). The conventional base heterogeneous catalyst has been replaced by various natural organic wastes containing calcium carbonate as the main component. The presence of calcium and other trace elements including magnesium and strontium carbonate are predominantly found in animal bones, shells, coral fragment and waste fish scale (Oliveira et al., 2013). The calcium carbonate ($CaCO_3$) is converted to calcium oxide at a high temperature which is highly utilized as an active catalyst for the production of biodiesel. The biomass-derived catalyst has drawn wide attention among researchers due to the simple and inexpensive route of synthesis (Correia et al., 2014).

The use of the waste fish scale of *labeorohita* for the transesterification using soybean oil was investigated. The catalyst was calcinated around 600-1000°C for 2 h. The maximum biodiesel yield of 97.7% was reported at 70°C for 5 h using catalyst concentration of 1.01% (w/w) and methanol to oil ratio of 6.27:1 (Chakraborty and RoyChowdhury, 2013). The maximum biodiesel of 98% was reported on using waste coral fragment as catalyst (calcinated at 700°C). The optimized reaction temperature was noted at 65°C for 2 h of time with methanol to oil ratio of 15:1 (Roschat et al., 2012). The optimized transesterification condition at 60°C for 4 h was reported for palm oil using duck eggshell as a catalyst. The catalyst was reported to be calcinated at 900°C for 4 h with a maximum yield of 92.9%. The empty fruit bunch based boiler ash was used for the transesterification of palm olein. The yield of 90% of methyl esters was found to be at 60°C of reaction temperature, 30 min of reaction time, 15:1 ratio of methanol to oil and 3% (w/w) of catalyst loading (Boey et al., 2011). The yield of 98% was achieved using EFB (Empty Fruit Bunch) as a catalyst. The authors reported that impregnation of oxides (KOH) on EFB were effectively for biodiesel production with the optimum conditions of 15% (w/w) of ash as a catalyst in 45 min at the temperature of 65°C (Yaakob et al., 2012). The waste animal bones calcinated at 800°C was found to be effective with the yield of 96.78% at 65°C using 1:18 ratio of oil to methanol, 20% (w/w) as a catalyst and 200 rpm of stirring speed (Obadiah et al., 2012). The sulfonation with concentrated H_2SO_4 incorporated with palm trunk waste was studied for catalytic activity at 150°C by varying sulfonation time. The biodiesel was found to show an increase due to the total acid density of the catalyst in 2-6 h (Ezebor et al., 2014). The different types of modern catalysts are listed in table 3.

9. Factors influencing efficiency the heterogeneous catalyst

The major factors influencing the heterogeneous catalyst are thermal treatment, calcination temperature, hydrophobicity/ hydrophilicity, surface area, porosity and leaching process. It is necessary to monitor these parameters has a direct impact on the yield of biodiesel. Influence of thermal treatment and calcination temperature plays a similar role in determining the final yield of biodiesel. It was reported that calculations of materials at a high temperature greater than 900°C liberated carbon and hydroxide species. The calcination was reported to increase the surface area and porosity of the catalyst ensuring active interaction of catalyst with methanol. Calcination at very high temperature decreased the basicity of the reactant material which decreases the activity of the catalyst (Cakırca et al., 2019; Granados et al., 2007; Xie et al., 2007).

The yield and purity of the biodiesel depend upon the temperature as the purity of biodiesel was decreased when the temperature was maintained between 100-500°C. The effect of calcinated CaO/SnO_2 for the production of biodiesel was investigated. The maximum yield of 94.33% was obtained when the catalyst was calcinated at 1050°C. The results also showed that the yield was low when the catalyst was calcinated at 500°C (Sharma et al., 2010). The influence of hydrophobicity and hydrophilicity was also studied as they influence on catalytic performances. The hydrophobic species at the surface of the catalyst helps in the adsorption of the oil and also helps in controlling the deactivation of the catalyst (Xie and Zhao, 2013). The use of modified sulfonic mesoporous group was reported to control the deactivation of the catalyst at the surface. This modification was reported to show the good effect on the increase in surface area and pore volume due to the exposure to high temperature (Lotero et al., 2005; Sreeprasanth et al., 2006). The other problem with heterogeneous catalyst was the leaching of catalyst on the liquid system. The presence of SO_3 species in the catalyst was reported to be sensitive to water vapour and in the liquid system the sulfur species easily leach out and decreases the activity of the catalyst (Corma et al., 1994; Kiss et al., 2006)

10. Significance of heterogeneous catalyst design

Various factors play an articulate aspect all along in the design of the catalyst. It was reported that reactivity of the catalyst was evaluated by a selection of proper supports as they are a key factor for the activity and selectivity of the catalyst. The high surface area of the mesoporous support material help in achieving high dispersion and strong interactions at the surface of the metal. Nickel supported on slightly reducible supports such as Zirconia and titania exhibited high selectivity due to defect on oxygen sites whereas catalytic supported on non-reducible materials such as alumina and silica, the conversion was less due to lower activity of the catalyst (Ambursa et al., 2016). The deactivation of the catalyst plays a significant role in the yield of biodiesel. The stability and activity of the catalyst were indicated by sulfur-free steam. The adsorption of sulfur blocks the active site and also initiates the deactivation process. The addition of Rh and NI to the reaction mixture helps in maintaining the stability and activity of the catalyst (Gutierrez et al., 2009; Lakhapatri and Abraham, 2009; Zong et al., 2007).

The effect of weak and medium acidity of SAPO-11 with Ni-metal was investigated. It was observed that they showed high catalytic activity due to the synergistic effect of Ni and acidic support. The stability of mesoporous silicate supported catalyst was stable for 5 h of a reaction than commercial silicates. The basic supports were utilized less as the catalytic support consume a huge amount of energy which was evident on using CoMo/MgO. It was found that the catalyst was effective only at a high temperature of 350°C. The activity of the catalyst also depends upon redox properties of the supports (Lakhapatri and Abraham, 2011). The removal of water during HDO process is a major challenge as they show a negative impact on the overall yield. The generation of water is minimized by the addition of H_2S and CO atoms. The exposure of the catalyst to high temperature and pressure reduces the acidity which shows a great impact on the yield of biodiesel. The influence of H_2 pressure also showed a direct influence on the yield of biodiesel. It was reported that the yield showed a decrease from 66 to 59% due to the influence of H2 in the reaction medium (Kim et al., 2015).

11. Economic impact of heterogeneous catalyst selection

Use of vegetable oil and alkali catalysts for the production of biodiesel is considered a cost-effective process as they utilize less number of unit operations. Thus, the relatively require minimal investment compared to other potential alternatives. Selection of heterogeneous catalyst plays a significant role in biodiesel production due to the reusability of catalysts for several cycles (Chen and Xu, 2016; Chouhan and Sarma, 2011). The source of catalyst preparation also plays a vital role in the economic aspect. Calcium oxide, one of the heterogeneous alkali catalysts has drawn wide attention because they are prepared from waste materials at a minimal cost. Heterogeneous acid catalysts tends to show better economic performances when feedstock containing higher FFA are used. The use of heterogeneous acid catalyst has an advantage with respect to economic view as they can be easily separated and reused. This type of catalyst is less corrosive and does not require washing to be performed in order to purify the product. The other technologies such as enzyme-catalyzed and supercritical transesterification were preferred as they tolerate high free fatty acid and water content for the conversion of biodiesel. But these methods could not compete with an acid catalyst in economic terms. Various studies revealed that the alkaline catalyst was cheaper than other catalysts. The authors compared the effectiveness of alkaline, immobilized catalyst and soluble enzyme catalyst. Hence, the techno-economic investigation was done with these three technologies for the production of biodiesel from spent oil containing 5% FFA. The studies showed good efficiency towards alkaline catalyst with the pre-esterification process. In terms of economic value, the heterogeneous alkaline catalyst has gained significant value as they produce a low generation of wastewater during the transesterification process.

The total investment cost is reported higher using a heterogeneous alkaline catalyst. But the operating cost was low with respect to the unitary production cost of biodiesel (Kouzu and Hidaka, 2012). Comparing to a heterogeneous catalyst, homogeneous catalyst requires high investment as they require additional equipment for product separation and purification. In order, to reduce the capital cost of construction material and equipment, carbon steel was introduced for alkali catalyzed. Recovery of the byproducts valuable for the market is one of the possible ways to make economically feasible biodiesel production with less total investment. Recycling of the catalyst and excess alcohol plays a vital role in obtaining high-quality glycerol as they are the most crucial entry in biodiesel production. This recycling concept has added great concern to researchers. Catalyst is recycled such that the co-product glycerol is used for algal consumption for the production of low-cost feedstock for biodiesel production (Jegannathan et al., 2011). Conventional reactor with catalytic distillation (CD) was also reported for biodiesel production. The use of catalytic distillation process was reported to reduce the number of equipment needed for biodiesel production and purification. Thus, the use of catalytic distillation led to a significant reduction in capital and production costs making this technology economically efficient (Karmee et al., 2015). Biochar was used as a catalyst for biodiesel production from waste cooking oil. The economic analysis of biochar-based biodiesel production optimized the biodiesel cost (1.91$) and payback period (2.06 years) (Lee et al., 2020).

12. Reactors for biodiesel production using heterogeneous catalysts

Heterogeneous catalysts were used in reactors for the production of biodiesel. Free fatty acids present in the acidified oil were continuously esterified using methanol in the presence of heterogeneous nanocatalyst NKC-9 cation-exchange resin in a fixed bed reactor. FFA conversion was reported to increase with an increase in methanol to oil ratio and decreases with increase in moisture content in initial feedstock (Gaurav et al., 2016). Stirred tank and fluidized bed reactors operation under different mode was designed and performance was studied for biodiesel production (Feng et al., 2011). A continuous reactor was designed for the production of high-quality methyl esters (biodiesel) from palm oil. A microporous membrane made with TiO_2/Al_2O_3 was packed with potassium hydroxide catalyst supported on palm shell activated carbon. The maximum conversion of palm oil to biodiesel in the reactor was obtained at 70°C with 157.04 g catalyst per 1 litre of the reaction mixture (Baroutian et al., 2011; Narayanan C M, 2019). Thus, the heterogeneous nanocatalyst is more suitable for the design of reactors for biodiesel production.

13. Practical implications and scientific future perspectives

A large number of studies demonstrate that heterogeneous catalysts have more effects in biodiesel production. The heterogeneous catalysts have low environmental effects because it's had low solubility and reusability in nature. But, reusability and the use of the catalyst in successive cycles are still doubtful. The main reason for doubtful reusability is the organic materials are deposition on the active site of catalyst. The heterogeneous catalyst simplifies the biodiesel production process and reduces the production cost, in which easy separation, no soap formation. Several studies demonstrate the heterogeneous catalysts, but many studies not explained process mechanisms, kinetics and catalytic activity in biodiesel production. Currently, more industries using the homogeneous catalyst for biodiesel production due to a lack of in-depth research in the heterogeneous catalyst. A large of heterogeneous catalyst are studied and it shows different advantages and disadvantages (Mardhiah et al., 2017). Some studies the heterogeneous catalyst is synthesized from waste source, which is highly economically feasible (Ling et al., 2019). In overall, the heterogeneous catalyst is a prominent catalyst for low cost and sustainable biodiesel production, but more elaborated research needed. Very few works only available in techno-economic analysis of biodiesel production using heterogeneous, more studies are needed for economic analysis.

Conclusions

The increased demand for fuel in both the industrial and transportation sector has led to the development of a more sustained supply of fuels. The demand for biofuel will increase to 50% by 2025. The large scale production of biofuel is less efficient and this can be overcome by the usage of heterogeneous solid catalyst. Heterogeneous solid catalyst serves best for commercial biodiesel production by increasing the efficiency of the biodiesel production process. They are more environmentally friendly and economical. The most advanced heterogeneous catalyst for biodiesel production is base nanocatalysts, acid nanocatalysts, and bi-functional nanocatalysts. By through reviewing the functions of heterogeneous catalyst bi-functional nanocatalysts are found to be best for biodiesel production, catalyzing transesterification and esterification reaction of oils and fats at the same time.

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Table 1. Effect of reactions conditions on biodiesel production using heterogeneous catalyst

	Reaction conditions					
Catalyst	Catalyst concentration (%, w/w)	Temperature (°C)	Time	O/M ratio (v/v)/ %	Biodiesel yield (%)	Reference
CaO	--	100	-	-	91	Yoosuk et al., 2010
Lithium-Doped ZnO	5	65	-	12:1	96.3	Xie et al., 2007
Tetramethyl guanidine on silica gel	-	-	3 h	-	86.73	Faria et al., 2008
CaO	5	70	5 h	6.9:1	97.73	Du et al., 2004
Na_2PEG 300	6	70	5 h	30:1	99	Fabbri et al., 2007
KF/Zn(Al)O	3	65	3 h	6:1	95	Xu et al., 2008
WO_3-ZrO_2-Al_2O_3	10	200	10 h	-	65	Park et al., 2008
SZ	1	65	2 h	-	95	Muthu et al., 2010
Ruthenium	0.5-3	40	2 h	-	46	Furuta et al., 2006
Mn doped ZnO	8	50	50 min	1:7	97	Baskar et al., 2017
ICdO5	-	200	1 h	-	84	Alves et al., 2014
$S_2O_8^{2-}$—ZrO_2	-	110	4 h	20:1	100	Wang et al., 2016
SBA-15 with sulphonic acid	-	100	8 h	1:15	86.2	Shah et al., 2004
$CoAl_2O_4$	7	140	-	1:6	80	Perez et al., 2016
ZSM5 with KOH	35	-	24 h	1:12	95	Saba et al., 2016
$Sr_3Al_2O_6$	1.3	-	61 min	25	95.7	Rashtizadeh et al., 2014
CZO	12	55	50 min	1:8	97.71	Baskar and Aiswarya, 2015b
Mg/$MgAl_2O_4$	3	110	-	12:1	95.7	Rahmani Vahid and Haghighi, 2017
HY-340	-	200	1	30:1	94.2	Reyes et al., 2012
CaO-MoO_3-SBA-15	6	-	50 min	50:1	83.2	Xie and Zhao, 2014
Fe doped ZnO	12	55	50 min	1:10	93%	Baskar G, 2016
Ti/SiO_2	5	65	4 h	30:1	98	Kaur et al., 2018
Zinc doped calcium oxide	6	55	80 min	9:1	89	Naveenkumar and Baskar, 2019
Clay with zinc oxide	8	55	50 min	9:1	97.43	Kalavathy and Baskar, 2019)
Alumina doped calcium oxide	8	65	90 min	9:1	92.5	Cherian et al., 2019

Table 2. Different type of ionic liquids used for biodiesel production

Source	ILs Liquid/support	Reaction conditions	Yield (%)	Reference
-	*Pseudomonas cepacia* lipase with [BMIM][NTf$_2$]	-	73.9	Gamba et al., 2008
-	[C$_{18}$MIM][NtF$_2$]	-	98.6	Ha et al., 2007
-	[C$_{18}$MIM][PF$_6$]+Lipase	180 bars, 4 h	82	
-	[C16][C$_{18}$MIM][NtF$_2$]	60°C, 6 h	98	Ruzich and Bassi, 2010
Soybean oil	[EMIM](CFSO$_3$)+Lipase	12 h, 50°C	80	Ha et al., 2007
Jatropha oil	[BMIM](CH$_3$SO$_3$)-FeCl$_3$	120°C	99.7	De Diego et al., 2011
Jatropha oil	Pyridinum based IL [BSPy](CF$_3$so$_3$]	100°C 6 h	95.1	Li et al., 2010
Waste cooking oil	[BMIMHSO$_4$]	160°C, 1 h	95.65	Ullah et al., 2015
Soybean oil	[Et$_3$NH]Cl/AlCl$_3$	70°C, 9 h, Recycle-6 times	98.5	Liang et al., 2009
Soybean oil	Modified N-methylimidazolium (PS-DVB)	12:1 (Methanol to oil ratio) Catalyst concentration-2.5%, speed-570 rpm, 10 h	97.25	Liang et al., 2009
Waste cooking oil	[MorMe A][Br]	70°C, 6 min in Microwave	98	Lin et al., 2013
Cotton seed oil	[IMC$_2$OH]	4 h, 55°C, 0.4% of catalyst, 12 parts of methanol	98.5	Liang and Yang, 201
Waste cooking oil	IL[TBP][OH]	-	82	Ullah et al., 2014
Waste cooking oil	[BMIM][HSO$_4$]	11:1 (Methanol to oil), IL Dosage-9.17%, microwave power-168W for 6.43 h and reused for 6 cycle	98.83	Ishak et al., 2017
Soybean oil	1,2 bis (3-methylimidazolium-yl) ethylene imidazolide	60°C, 2.5 h, 1:15, 4%	99.6	Fan et al., 2013

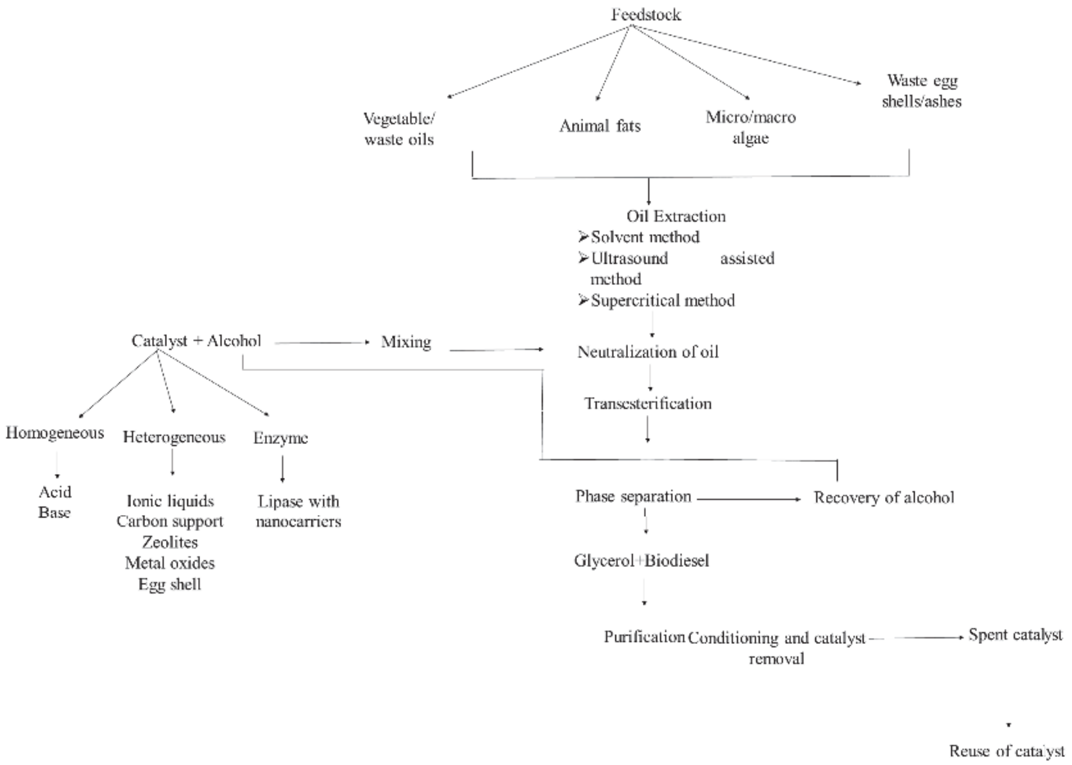
Table 3. Modern heterogeneous catalyst used for biodiesel production

Catalyst	Reaction conditions				Yield (%)	Reference
	Catalyst concentration (%, w/w)	Temperature (°C)	Time (h)	O/M ratio (%, v/v)		
Na_2SiO_3	0.5	230	0.5	-	95.6%	Yin et al., 2010
MCM-41	8	200	4	12:1	95	García-Sancho et al., 2011
KOH on activated carbon	31.3	60	2	1:20	87	Buasri et al., 2012
Capiz shell	3	60	6	1:8	93.2	Suryaputra et al., 2013
Egg shell	5	65	1	1:12	94.52	Niju et al., 2014
$Na_2SiO_3@Fe_3O_4/C$	7	55	80 min	1:7	97.9	Zhang et al., 2015
MoO_2Cl_2 on activated carbon					97	Mouat et al., 2016
CaO/dolomite catalyst	3	65	3	1:6	90	Cakirca et al., 2019

Figure Captions:

Fig. 1. Schematic representation for the production of biodiesel by transesterification process

Fig. 2. Schematic representation of sulfur catalyst in the production of biodiesel



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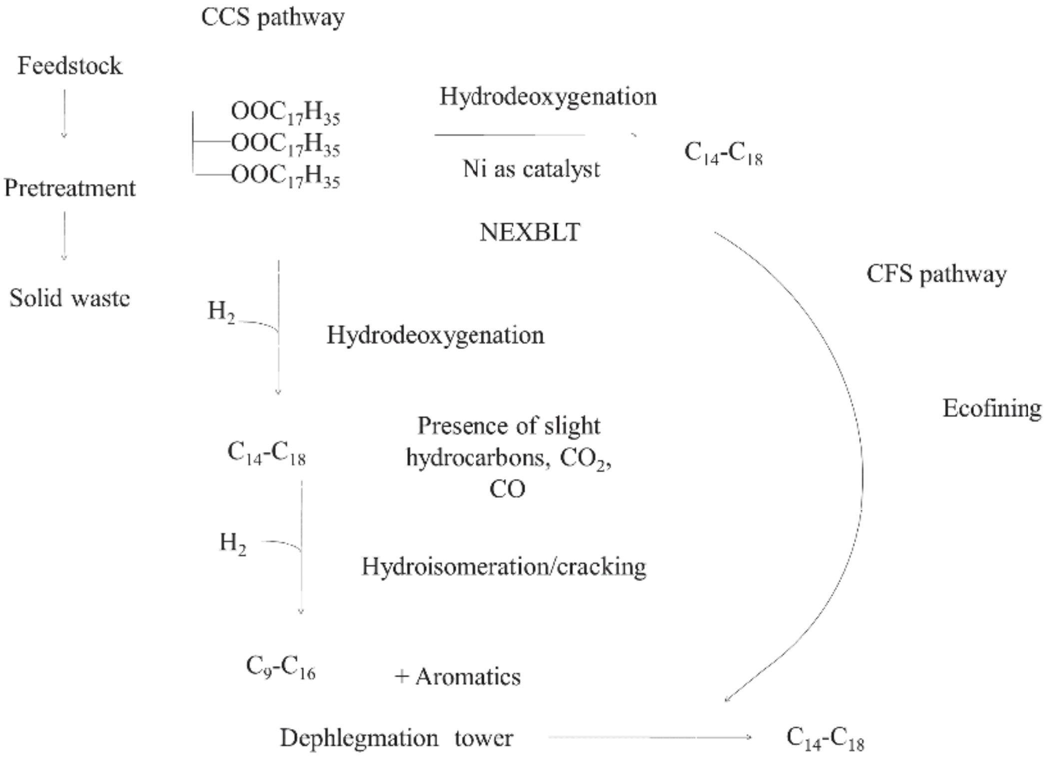

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