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Advances in nano-catalysts based biodiesel production from non-food feedstocks

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Abstract

This paper aims to examine the influence of various catalysts on biodiesel production, especially from non-food feedstocks with an ambition to optimize the catalytic biodiesel production. Homogenous acid catalysts are mainly used in biodiesel production, but they cannot be recovered and demand costly fuel purification as being corrosive. Similarly, enzyme catalysts are expensive in industrial-scale production of biodiesel. However, heterogeneous catalysts simplify the easy separation of product and by-products from the catalyst along with catalyst reusability and reduction of waste. Solid acid and base catalysts offer more advantages due to their non-toxicity, high surface area, reusability, higher stability and the simplicity of purification. Heterogeneous base catalysts yield better activity than heterogeneous acid catalysts, however, they cannot esterify large amounts of free fatty acids (FFAs) in non-food feedstocks. The solid acid catalysts have the added advantages of being more tolerant to high amounts of FFAs and being able to simultaneously esterify FFAs and transesterify triglycerides in cheap feedstocks like waste cooking oil. Recently, an array of inorganic, organic and polymeric solid acid and nanomaterial-based catalysts have been developed using cheap feedstock. However, the issues of low reactivity, small pore sizes, low stabilities, long reaction times, and high reaction temperatures still need to be solved. These developments of producing efficient, cheap, durable, and stable solid acid and nanomaterial-based catalysts have been critically reviewed in this study. Furthermore, the challenges and future perspectives of production of biodiesel and its industry growth have also been discussed.

Keywords: Biodiesel; Homogeneous catalysts; Heterogeneous catalysts; Solid acid catalysts; Nano-catalysts; Non-food feedstock

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1. Introduction

Renewable fuel production has been a topic of research for more than a century and is expected to continue due to depletion of fossil fuel and increasing environmental concerns over their consumption, including rising CO_2 emissions (Armaroli and Balzani 2007). According to the international energy report by the U.S. Energy Information Administration (EIA) in 2016, total world energy use is expected to increase by more than half over the next three decades, driven by global industrial and transportation growth (EIA 2016). For example, world liquid fuel use in 2012 was 90,000,000 barrels per day (b/d) with the figure expected to rise to 100,000,000 b/d in 2020 and to 121,000,000 b/d in 2040. As a result, CO_2 emissions, especially from fossil fuel consumption, will increase, as is projected in Figure 1(b). The consequence of this could be global temperature increases (global warming). If temperatures increase by more than 2 °C, it is estimated the cost will be hundreds of millions of human lives and other species lost (Atabani et al., 2012). Therefore, the world's fastest-growing energy source over the next three decades is going to be renewables, as seen in Figure 1 (a). This relates to renewable energy use increasing by an average 2.6% per year between 2012 and 2040.

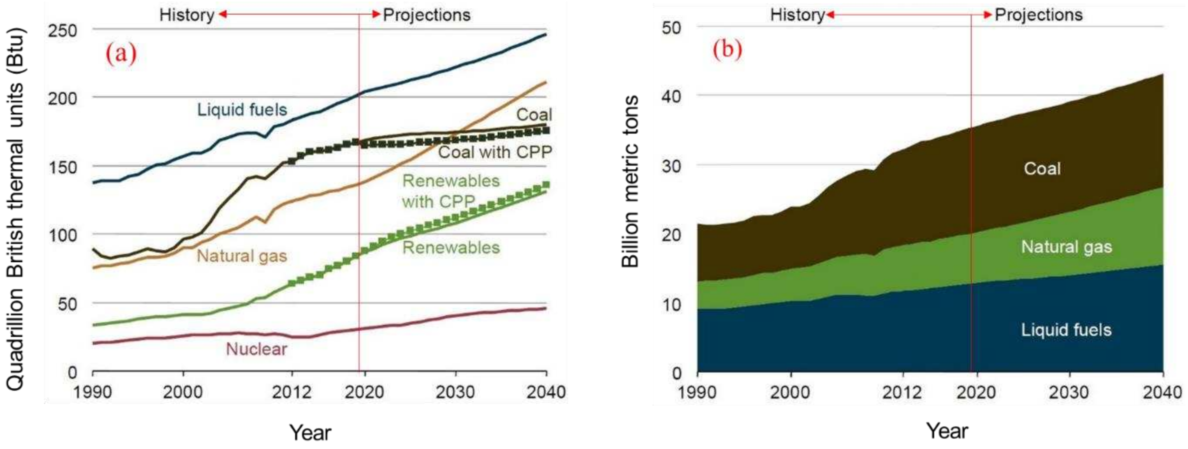
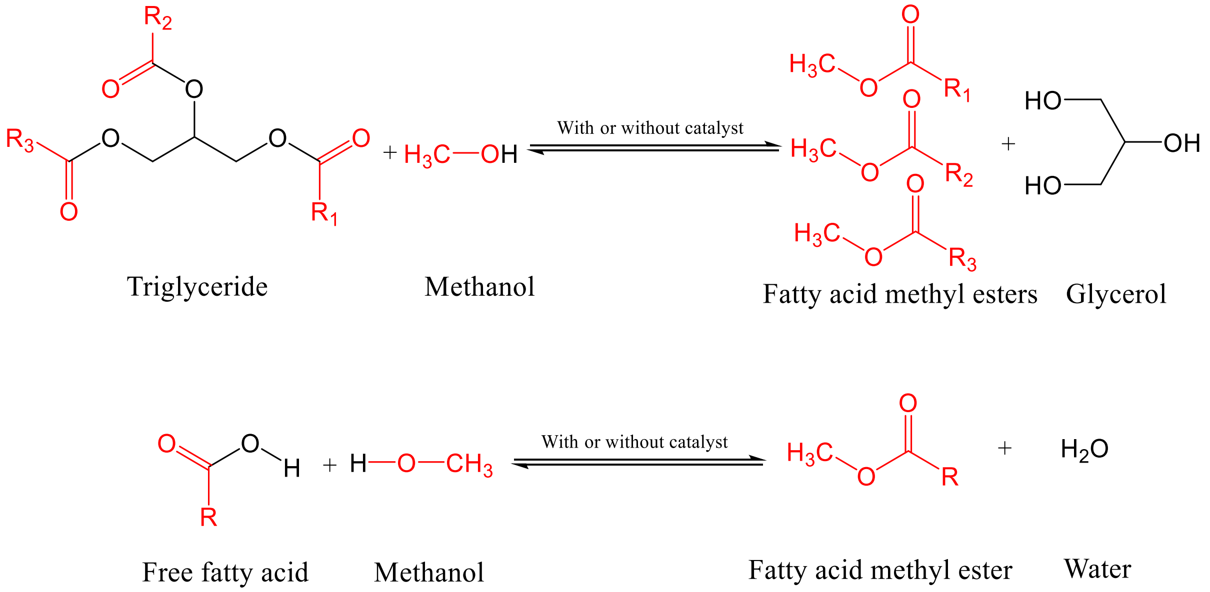


Figure 1. Total world energy consumption by energy source from 1990 to 2040 (a), and world energy-related carbon dioxide emissions by fuel type from 1990 to 2040 (b) (EIA 2016).

Many researchers have investigated the possibility of partially/totally replacing crude oil and its derivatives with an alternative fuel. In 1893, Rudolf Diesel invented the use of peanut oil in a model diesel engine. This marked the beginning of the use of vegetable oils in diesel engines as opposed to petro-diesel. However, it has been highlighted that vegetable oils could not be used effectively in engines due to high viscosity, low volatility, and cold flow behaviours (Bezergianni and Dimitriadis, 2013). This led to exploration to try to overcome these problems, leading to the concept of biodiesel in 1980s. Research continues extensively with a view to producing a source of renewable and sustainable energy to meet global demand and supply (Koh and Ghazi, 2011; Salvi and Panwar, 2012; Kumar et al., 2013; Younis et al., 2014). Biodiesel is an environment-friendly fuel, non-toxic and biodegradable source of energy and it can be made by esterification and transesterification reactions of vegetable oils or animal fats with low molecular weight of alcohol in the presence or absence of catalysts as shown in Scheme 1 (Gardy et al., 2014, 2016, 2017; Likozar et al., 2014a, 2016). An estimated 90% of the worldwide biodiesel is produced through transesterification using vegetable oils with homogeneous base catalysts (Gardy et al., 2016).



Scheme 1. Biodiesel production from TG/FFA with methanol

However, usage of virgin/edible vegetable oils poses dilemmas of food versus fuel (Rathore et al., 2016; da Conceição et al., 2016; Cordero-Ravelo and Schallenberg-Rodriguez, 2016). In addition, the biodiesel industry faces the problems of limited feedstocks and their constant supplies around the year and high fuel cost (Nizami et al., 2016). Therefore, various non-food feedstocks including waste cooking oil (WCO), micro-algae, non-edible seed oils, and animal fats along with low-cost technologies have been emerged in attempts to reduce the cost of fuel and to commercialize its products in both developing and developed countries (Akhtar et al., 2019; Capodaglio et al., 2018; Gardy et al., 2018; Shahzad et al., 2017; Rehan et al., 2018; Nizami et al., 2017a,b; Likozar et al., 2014b). However, as shown in Figure 2 the production of biodiesel around the world using different feedstocks is mainly depended on climate, local soil conditions and availability of feedstocks (Gardy 2017).

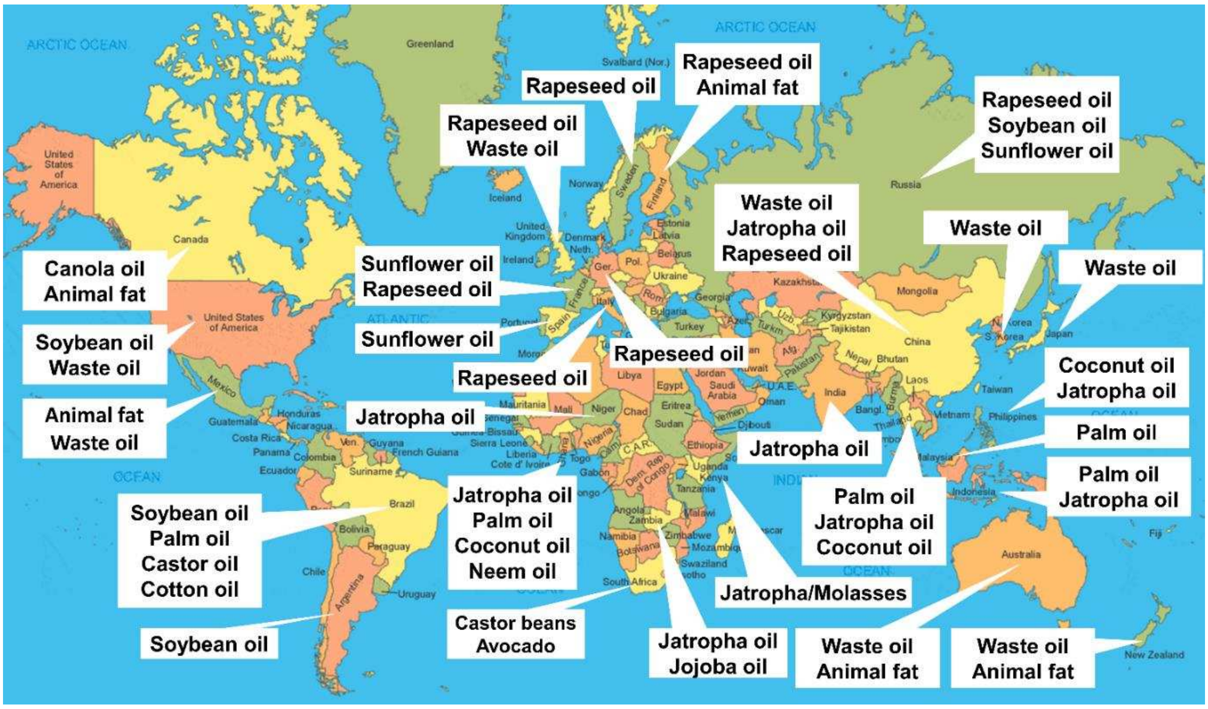


Figure 2. Production of biodiesel around the world from different raw materials

The non-food feedstocks although offer promising future feedstocks for the biodiesel industry, but they contain high amounts of free fatty acids (FFA) (> 1 wt.%), moisture (> 0.5 wt.%) and other impurities that form soap (fatty acid salt), aqueous quenching and difficulties in products separation when transesterified using homogenous base catalysts (Gardy, 2017; Lee et al., 2014; Munir et al., 2019). Therefore, homogenous acid catalysts are used to catalyze these materials into biodiesel. However, these catalysts are very corrosive and cannot be recovered, and result in costly fuel purification processes (Balat and Balat, 2010; Osatiashtiani et al., 2016). Similarly, enzyme catalysts are costly in industrial-scale applications and not favorable for biodiesel production (Sharma et al., 2011). Heterogeneous catalysts, therefore, have gained significant interest as alternative catalysts for optimized biodiesel production from non-food feedstocks (Semwal et al., 2011). In addition, easy separation of product and by-products from the catalysts are possible by these catalysts (Gardy et al., 2014).

Heterogeneous base catalysts exhibit higher catalytic activity than heterogeneous acid catalysts. However, they are unable to esterify large amounts of FFAs from non-food feedstocks (Sharma et al., 2011). Therefore, solid acid catalysts are more beneficial and efficient for non-food feedstocks containing high FFAs via simultaneous esterification and transesterification processes. Consequently, these catalysts have been extensively studied as offering the biodiesel industry an alternative to homogeneous catalysts. Moreover, they offer the advantages of eliminating the aqueous quenching step, readily separation from the reaction medium, regeneration while recycling the catalyst and are less sensitive to raw materials that contain a high amount of FFAs as compared to other types of catalysts (Leung et al., 2010).

Many inorganic, organic and polymeric solid acid catalysts have been recently explored with an aim to optimize biodiesel production using cheap feedstocks (Borges and Diaz, 2012). However, there remain some challenges to be overcome including low reactivity, reduced surface area, and porosity, low stabilities, long reaction times as well as high reaction temperatures with the use of solid acid catalysts (Ramachandran et al., 2013). Moreover, some solid acid catalysts suffer from a low concentration of acid sites, significant amount of catalyst requirement, deactivation, leaching of acid sites, mass transfer (diffusion) limitation, and side reaction (poisoning) problems. For instance, the calcination at a high temperature of sulfonated solid acid catalysts destroys catalyst templates, reducing their catalytic activities along with making the process more energy intensive.

Surface functionalization of solid acids catalysts is an efficient route for introducing some important functional groups on the internal or external surfaces, but in some cases it reduces the catalyst surface area and porosity. Therefore, further, development is critical to prevent deactivation of catalyst sites and produce more efficient, cheap, durable, and stable solid acid catalysts in order to overcome current problems associated with catalytic biodiesel production (Gardy 2017), which is the focus of this paper. This review aims to examine the influence of various homogeneous and heterogeneous catalysts on biodiesel production, especially from non-food feedstocks. A focus has been given to the role of nano-catalysts among the solid acid catalysts to optimize the overall biodiesel production process. Moreover, the current limitations with the use of various catalysts and their possible solutions are discussed in detail.

2. Role of catalysts in biodiesel process

A catalyst changes the rate of esterification and transesterification reactions without being consumed. Lower activation energy is normally obtained for catalytic esterification and transesterification reactions compared to non-catalytic processes. The catalytic esterification and transesterification processes could be classified into two categories which are homogenous and heterogeneous catalysts. The catalyst and reactant can function in the same phases for homogenous catalysis whilst they are in different phases for heterogeneous catalysis. There has been significant research in recent years on the various catalysts and their classification and modifications to produce biodiesel (Figure 3) and improve the quality of the produced fuel. The effects of particle size (PSD = nm to mm), shape (e.g. spherical, needle, hexagonal, etc.), porosity (e.g. microporous, macroporous, mesoporous, mixed, etc.), type (e.g. solid acid and base) and process conditions (e.g. calcination and pH) on catalyst preparations as well as reaction kinetics, mass transfer, scale-up and optimization of esterification/transesterification processes have been extensively studied (Gardy 2017; Likozar et al., 2016; Osatiashtiani et al., 2016; Silveira et al., 2019; Borah et al., 2019; Manayil et al., 2017)

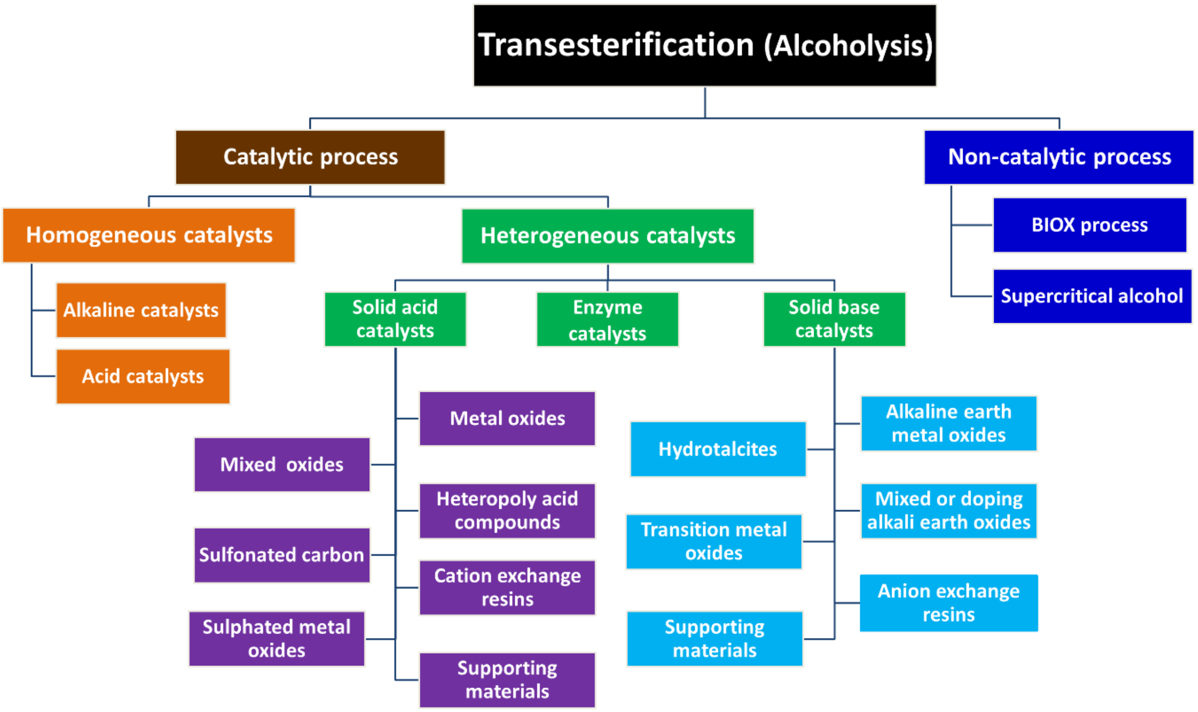


Figure 3. Classification of transesterification processes for biodiesel production

2.1 Homogenous catalysts in biodiesel production

Several homogenous catalysts have been studied to observe different reactions, including esterification, ester hydrolysis, and transesterification. In homogeneous catalysis reactions, the catalyst is normally in the same phase as the reactant. The homogeneous catalysts can be divided into two categories that are homogenous acid and base catalysts. The most commonly homogenous catalysts used for transesterification reaction are alkalis such as sodium hydroxide (NaOH), KOH, $NaOCH_3$ and $KOCH_3$ (Tyson et al., 2004). Gerpen (2005) has reported that when FFAs are present in the oil or fat feedstock, the alkali catalyst reacts to form soap and water in the initial step. Therefore, he has utilized an acid catalyst such as sulfuric acid (H_2SO_4) to remove the saponification process by esterification of the FFAs into methyl esters. This is then transesterified with alkali catalyst into biodiesel. The kinetics of both acid- and alkali-catalyzed reactions have been extensively studied to find the rate of the reaction. As a result, the alkaline-catalyzed transesterification reaction is much faster than the acid-catalyzed reaction (Lin 2013; Kattimani and Venkatesha, 2013). The biodiesel production processes using homogeneous catalysts are presented in the following sub-sections.

2.1.1 Acid-catalyzed transesterification

The acid catalyzed reaction is an esterification process using various acids such as H_2SO_4, H_3PO_4, hydrochloric acid, boron trifluoride (BF_3) and organic sulfonic acids ($R\text{-}SO_3H$) (Samios et al., 2009). Acid catalysis is a two-stage process. The first stage involves reactions of oils and alcohol in the presence of acid catalysts and the second stage utilizes the oil produced, with a lower acid value, to re-transesterify with methanol using alkali catalysts such as sodium or potassium hydroxide. Several studies have reported that using homogeneous acid catalysts is more suitable for feedstocks having high FFAs and water contents as compared to base catalysts (Fukuda et al., 2001; Hara et al., 2009).

However, it has been reported that the acid-catalyzed transesterification reactions are much slower than the alkaline-catalyzed reactions (Koh and Ghazi, 2011) and the use of acidic catalyst requires costly equipment to resist acid corrosion, which adds costs to the expenses of the biodiesel production process (Lee et al., 2014). This catalytic process is also not recommended for using a higher concentration of acidic catalyst such as H_2SO_4 and temperature, this is mainly due to the transesterification process could lead to the formation of ether from the dehydration of alcohol and burn some of the oil and ultimately reduce the FAME yield (Canakci and Van, 2001; Keyes 1932).

2.1.2 Alkali-catalyzed transesterification

A standard approach for biodiesel production from pure vegetable oils is the alkali-catalyzed transesterification process. The stoichiometry of the reaction indicates that 3 moles of fatty esters (biodiesel) with 1 mole of glycerol are formed from 1 mole of triglyceride and 3 moles of alcohol. The optimum molar ratio of the alkali-catalyzed reaction was found to be 6:1 for obtaining higher than 98% of methyl ester yields (Zhang et al., 2003). The most effective alkali catalysts for the transesterification process are KOH, NaOH, $KOCH_3$, and $NaOCH_3$ (Ma and Hanna, 1999). Several researchers have found that the alkali metal methoxide (methoxide salts) have higher catalytic activities for transesterification reaction as compared to their corresponding hydroxides (Felizardo et al., 2006; Marris 2006). However, the presence of more than 0.5 wt.% of FFA content in the feedstocks enhances soap formation, produces a low yield of biodiesel and complicates the separation of by-products (Koh and Ghazi, 2011). In addition, this type of catalyst results in the low yield of FAME when the feedstock contains more than 0.06 wt.% of water (Luque and Melero, 2012). This is due to the high sensitivity of alkaline catalysts towards FFAs and moisture in the feedstock. The presence of water also reduces the biodiesel yield and consumes more catalyst during the process (Koh and Ghazi, 2011). Therefore, pre-treatment of the FFA and moisture containing feedstock is critical for an efficient alkali-catalyzed transesterification reaction. This catalytic process is recommended only for raw materials with a low FFA (< 0.5 wt.%) and moisture content (< 0.06 wt.%). In addition, the removal and recycling of this kind of catalyst from the product and by-product are relatively difficult due to its solubility (Gardy et al., 2016, 2017).

2.2 Heterogeneous catalyzed transesterification

The current processes for biodiesel production using homogeneous catalysts have many limitations, including corrosion, separation from products/by-products, high sensitivity to water and FFAs in feedstocks, soap formation, requiring aqueous quench and neutralization process steps (Woodford et al., 2012). Therefore, the design and development of suitable heterogeneous catalysts to produce biodiesel from different cheap non-food feedstocks are critical for simultaneous esterify of FFAs and transesterify of TG (Gardy et al., 2018; Lee et al., 2014; Lee and Wilson, 2015; Hattori and Ono, 2015). The heterogeneous catalysts are divided into the solid base and solid acid catalysts.

2.2.1 Solid base-catalyzed transesterification

The solid base catalysts show higher catalytic activities for high purity feedstock containing very low FFAs (Lee et al., 2014; Wilson and Lee, 2012). A range of solid base catalysts has been widely examined for their catalytic activities to produce biodiesel from different feedstocks. Some of these catalysts have demonstrated good performance, including alkaline earth oxides (Zhao et al., 2013; Verziu et al., 2011; Çakırca et al., 2019; Pandit and Fulekar, 2017) alkali metal doped alkali earth oxides (Malhotra and Ali, 2019; Montero et al., 2010), hydrotalcites (Reyna-Villanueva et al., 2019), and supported alkali metals or alkaline earth oxides (Kaur and Ali, 2011; Liu et al., 2012).

Many other solid base catalysts have been tested in the transesterification of biodiesel from different raw materials showing good catalytic activity, some even at low temperature. This provides a commercially viable way to decrease production costs for the biodiesel industry. However, the main problems encountered for commercial exploitation of such catalysts are: slow reaction rate (high basicity of alkaline earth oxides having low solubility in methanol) (Tangy et al., 2016), catalyst leaching (Lee et al., 2014; Wilson and Lee, 2012; Verziu et al., 2008; Wen et al., 2010a), dissolution of catalyst in the reaction medium (solid-liquid-liquid phases) (Mbaraka and Shanks, 2006), unsuitability for feedstocks containing high FFAs (Borges and Díaz, 2012) and some catalysts having a low activity, low porosity with low surface area (Taufiq-Yap et al., 2011). Furthermore, it is difficult to create a catalyst possessing simultaneous qualities as a strong basic, high surface area, large pore size, cheaper and chemically stable. Therefore, more research need to be carried out to find cheap and more efficient catalysts for transesterification of raw materials containing FFAs by designing or developing suitable solid base catalysts.

2.2.2 Solid acid-catalyzed transesterification

In the late 1930s, the Houdry process used solid acid catalysts in catalytic cracking (Hattori and Ono, 2015). Since then, a wide range of solid acid catalysts has been designed, developed and examined for their catalytic activities in different applications to replace homogenous catalysts. Their use eliminates drawbacks associated with liquid acid catalysts, including corrosion, quenching steps, toxicity, environmental issues, and non-reusability. Their potential in conventional biodiesel production from different feedstocks has, therefore, been the subject of recent studies (da Conceição 2016; Fu et al., 2013; Soltani et al., 2017a; Yap 2016; Mahto et al., 2016). Solid acid catalysts are less active, require higher reaction temperature and longer time than solid base catalysts for transesterification reaction. However, solid acid catalysts are more stable and could be effectively used simultaneously for both transesterification and esterification of feedstocks containing high FFAs and water (Hara 2009; Lotero et al., 2005). This advantage has resulted in the recent development of a wide range of solid acid catalysts to obtain biodiesel from various feedstocks. They include zeolites (Jeon et al., 2019; Osatiashtiani et al., 2017), clays (Bálsamo et al., 2019), metal oxides and mixed metal oxides (Pandit and Fulekar, 2019; Prabu et al., 2019), supported acids (Vieira et al., 2017; Aziz et al., 2017), sulphated metal oxides in particular sulphated zirconium oxide ($H_o \geq -14.52$) (Shi et al., 2017; Elimbinzi et al., 2018; Rabee et al., 2017) and sulphated titanium oxide ($H_o \leq -14.52$) (Gardy et al., 2016, 2017, 2018), heteropoly compounds (Kurhade et al., 2019), sulfonated carbon based materials including carbon nanofibers; carbon nanotubes; biochar; amorphous carbon; graphene oxide; sugar; and waste (Guan et al., 2017; Tran et al., 2016; Baig et al., 2016; Tan et al., 2019; Bora et al., 2018; Rahimzadeh et al., 2018; Wu et al., 2019) and cation exchange resin (Zhang 2016; Fu et al., 2016).

In simultaneous esterification and transesterification reactions, the performance of this type of catalyst depends on the accessibility of reactant to the active sites (Brønsted and Lewis acids) to initiate the reaction. Solid acid catalyst would also simplify and provide an economical way for pre-treating raw materials containing high FFAs. There have been many studies exploring how to increase the amount of active acid sites, surface hydrophobicities, pore sizes, the accessibility of reactant molecules (e.g. triglycerides size = 5.8 nm)) to the active sites inside micro-pores, fast separation of catalyst from reaction medium by introducing the magnetic properties to the catalyst; minimize leaching of active acid sites and, reduce the diffusional limitations for producing cheap biodiesel (Gardy 2017). Despite numerous good results solid acid catalysts for esterification and transesterification reactions are still far from being perfect in order to be used for industrial biodiesel applications. Major barriers are low activity at lower temperatures, water sensitivity/resistance, leaching of active sites, low surface area, poor porosity, deactivation, mass transfer limitation, thermal instability by destruction and degradation of catalyst structure, a large amounts of methanol to oil ratio, high temperature and long reaction time, particularly for cheap feedstocks such as WCO. There are also limited reports on developed solid acid catalysts for cheap and readily available feedstocks, such as WCO, without the need for pre-treatment. Therefore, more research is needed to design a better and suitable catalyst for the esterification and transesterification processes.

2.3 Enzyme-catalyzed transesterification

The transesterification reaction of vegetable oils or animal fats can also be carried out through the enzyme-catalyzed process. The biocatalytic transesterification process is more advantageous than the homogenous acid- and alkali-catalyzed transesterification, as there is no saponification problem during purification and neutralization issues. In addition, the reaction utilizes mild conditions and can be used for feedstocks with high FFA content (Shahid and Jamal, 2011). The most common enzyme catalysts used for biodiesel production is lipase (e.g. Novozym 435 and Lipozyme IM-77) (Fukuda et al., 2001; Shahid and Jamal, 2011). The enzymatic catalysts can be used completely for converting raw materials containing high FFAs into FAME (Fukuda et al., 2001). However, enzyme catalysis has demerits in its higher production costs due high cost of enzyme catalysts, longer reaction time and the limited reuse and regeneration of the catalyst. The biodiesel yields obtained from this process have also been reported as being unfavorable compared to the homogenous alkali-catalyzed reaction, making it less economical (Shahid and Jamal, 2011; Koh and Ghazi, 2011).

3. Optimization of biodiesel production through nanomaterial-based catalysts

Nanotechnology has attracted great interest in the last few years for biodiesel production (Nizami et al., 2018). Nano-catalysts are prepared by chemical (including sol-gel, microemulsion, hydrothermal, polyol, and chemical vapor); physical (including high energy ball milling, inert gas condensation, laser pyrolysis, pulse vapor deposition, flash spray pyrolysis, electrospraying and melt mixing); and biological (including microorganism assisted biogenesis, biotemplates assisted biogenesis and plant extracts assisted biogenesis) methods. Research on nano-catalysts has been carried out by using alkaline earth metal oxides (Zhao et al., 2013), supported metal oxides (Montero et al., 2010), magnetic catalysts (Gardy et al., 2018; Ambat et al., 2019; Ghalandari et al., 2019). Zhao et al. (2013) have reported the effect of different particle size and surface areas of calcium oxide catalysts in transesterification reaction of canola oil and methanol. Recently a number of studies have been published on nanomaterial-based catalysts to produce surface modified (impregnation) nanoparticles (NPs) with increased surface acidity/ basicity (Toh-Ae et al., 2014; Radoman et al., 2015). This is very important to develop new catalysts with enhanced catalytic activity in biodiesel production processes that use cheap raw materials with FFAs. The acid-based catalysts have the advantage of facilitating both transesterifications of triglycerides and esterification of FFAs simultaneously with no soap formation (Lee and Wilson, 2015). In the following sections, various nanomaterials-based catalysts including CaO, SrO, MgO, Al_2O_3, TiO_2, ZrO_2, SiO_2, ZnO, along with magnetic nanoparticles-based and carbon-based nano-catalysts are discussed in detail.

3.1 Development of nanomaterial-based metal oxides catalysts

3.1.1 Development of nanomaterial-based CaO catalyst

Calcium oxide is the most studied and promising catalyst among all alkaline earth single metal oxides for biodiesel production due to its availability, high basic strength, its lesser environmental impact, its lower cost and long catalyst lifetime (Colombo et al., 2017). The catalytic activity of alkali earth oxides catalysts in the transesterification process depends on their basicity strength and its origin that is believed to appear as ion pairs [M^{+2}-O^{-2}] in coordination environments (Hattori 1995). This basicity can arise in different ways, including cationic defect site in the lattice and surface terminations as shown in Figure 4.

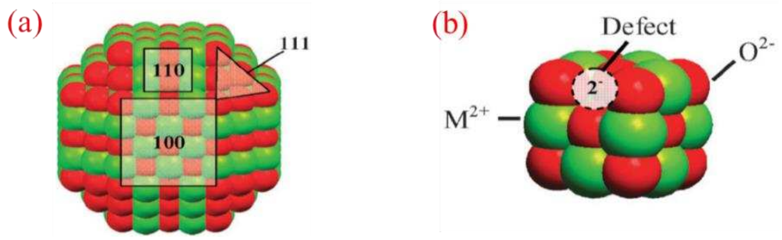


Figure 4. Origin of basicity in an alkaline earth oxides (a) crystal facet termination on the surface crystal and (b) defects in lattice. Reprinted figure with permission from (Wilson and Lee, 2012). Copyright (2012) RSC

Venkat Reddy et al. (2006) examined the effect of CaO nano-crystalline on the soybean oil transesterification at room temperature for 24 h with 1.3 wt.% catalyst and 1:27 mole ratio of oil to methanol to obtain > 99 % conversion. They also noted that the deactivation of the catalyst after 8 cycles might be due to the impurities of CaO. Liu et al. (2008) studied the effect of water on the catalytic activity of CaO and found that the use of an appreciate water level (up to 2.8 %) in the transesterification reaction medium enhanced the catalyst activity of CaO, and improves the FAME yield. This is because of the O^{-2} attracts proton from the water to form hydroxide anion on the surface of the catalyst. However, the addition of water more than 2.8 % into methanol could result in saponification due to hydrolysis of FAME under basic condition (OH^-) to form FFAs. Kouzu and Hidaka (2012) also reported the catalytic activity of CaO at low concentration ratio corresponding to calcium methoxide (Ca-OMe) or the surface of CaO as an initial active sites catalyses the transesterification reaction as illustrated in Figure 5. Veljković et al. (2009) studied the kinetic of calcined CaO at 500 °C for transesterification process of biodiesel production from sunflower. The reaction was performed using 6:1 mole ratio of methanol to oil, 2 h reaction time, 1 wt.% catalyst and 60 °C to achieve 98 % of FAME yield. Moreover, they noted that the rate of reaction at the beginning of transesterification process depends on a rate mass transfer of the reactants and this became faster with an active surface of CaO catalyst.

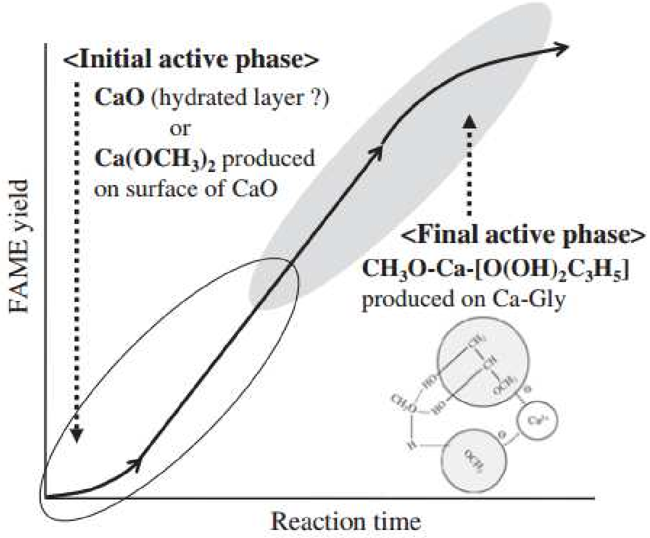


Figure 5. Transesterification reaction showing the variation in active phase of CaO at low concentration ratio with methanol. Reprinted figure with permission from (Kouzu and Hidaka, 2012). Copyright (2012) Elsevier

The catalytic activity of CaO with different particle size was also evaluated by Zhao et al. (2013) in the transesterification of canola oil and methanol using a batch reactor at optimum conditions of 65 °C, methanol to oil molar ratio of 9:1 and 600 rpm stirring speed. The biodiesel yield over nano-CaO was nearly 81 %. The CaO having a smaller average particle size of 27.3 nm and a high surface area (HSA-nano-CaO) of 89.3 m^2/g showed higher activity compared to nano-CaO with an average particle size of 37.3 nm with a lower surface area of 22.3 m^2/g. Moreover, 100 % biodiesel yield was attained under fixed reaction temperature and molar ratio using only 0.3 wt.% of HSA-nano-CaO compared to 4.0 wt.% of nano-CaO, reducing the time of reaction to half. They have also reported the effect of reusability of catalysts on the FAME yield, which slightly dropped after 12 cycles.

Alonso et al. (2009) examined the influence of different lithium loading on CaO and the activation temperature of Li-doped CaO catalyst in the transesterification of food-grade sunflower oil to form biodiesel. They found that 4.5 wt.% of Li loading was needed to promote the catalytic activity of CaO for biodiesel production whilst the activation temperature of Li-doped CaO catalyst required a temperature above the melting point of lithium nitrate (Li precursor). Likewise, Watkins et al. (2004) studied the impact of lithium contents in the range of 0.26–4.0 wt.% onto the CaO catalyst for glyceryl tributyrate transesterification. They reported that the basic strength of Li-doped CaO samples have a $17.2 > pK_{BH^+} > 15$ whilst for the bulk CaO has $10 > pK_{BH^+} > 8$. CaO catalyst showed poor catalytic activity for transesterification reaction with only 2.5% conversion for 20 min whilst loading 1.23 wt.% of Li on CaO increased the conversion to 100% within the same period of time. Kawashima et al. (2008) examined the combination of different types of metal oxides on the transesterification of rapeseed oil with a 6:1 mole ratio of methanol to oil at 60 °C to form 90 % of FAME yield using $CaTiO_3$, $CaZrO_3$, $CaMnO_3$, $Ca_2Fe_2O_5$ and $CaO\text{-}CeO_2$ catalysts. They found that the calcium-containing catalysts showed high catalytic activities for transesterification reaction. Major drawbacks of this kind catalyst are poor catalytic activities, unsuitability for feedstocks containing high FFAs, deactivation, dissolution of CaO particles in the methanol or the unstable CaO phase being dragged out by FFAs in the raw material to form organosol (calcium soap) which competed with the FAME yield and created difficulties for FAME separation from the by-product (Phillipp and Fujimoto, 1992).

3.1.2 Development of nanomaterial-based MgO and SrO catalysts

MgO and SrO have also shown good catalytic activity in the transesterification process to produce biodiesel from different feedstocks. Verziu et al. (2008) obtained around 80 % of FAME yield with MgO as the catalyst using optimum reaction conditions; 1:4 rapeseed oil to methanol ratio, 70 °C, 2 h and 300 mg of catalyst. They also found that the catalyst can be re-used without any reactivation/regeneration after recycling from the reaction. Wang and Yang (2007) earlier reported the use of MgO catalyst to produce biodiesel using soybean oil and supercritical/subcritical methanol at optimum conditions of 1000 RPM, 3 wt.% nano-MgO, 260 °C, 30 MPa, 10 min of reaction time with 36:1 methanol to oil mole ratio to convert 100 % of soybean oil. Liu et al. (2007) studied the production of biodiesel through transesterification reaction of soybean oil over SrO catalyst having strong basicity of $H_0 = 26.5$ and 1.05 m^2/g BET surface area. $SrCO_3$ being used as a promising solid base precursor for synthesizing of SrO at 1200 °C for 5 h. The reaction was conducted using 12:1 methanol to oil mole ratio, 3 wt.% catalyst, reaction temperature (65 °C) and time (30 min). They also reported that the catalyst could be re-used for 10 cycles with a slight decrease in the yield of biodiesel. The reaction mechanism over SrO also revealed that the catalytically active phase was the surface of SrO catalyst to form CH_3O^-.

Berger et al. (2007) reported that doping of lithium ion (Li^+) with MgO using chemical vapor deposition increases the surface basicity. The influence of caesium (Cs) impregnated to MgO on the structure and basicity in the tributyrin transesterification reaction was reported by Montero et al. (2010). It was found that the Cs doping MgO (CsNanoMgO-C) catalyst enhanced the rate of tributyrin transesterification (100 % conversion within 3 h), but the surface of the

CsNanoMgO-C catalyst deactivated after one cycle. There were a number of reasons reported for this, including leaching of Cs, the large agglomeration post-transesterification, surface reconstruction, and sintering of spent catalyst. Taufiq-Yap et al. (2011) described newly mixed metal oxides for catalyzing the transesterification reaction of non-edible Jatropha curcas oil to produce biodiesel. The catalyst demonstrated good activity with optimum reaction conditions; 25:1 molar ratio of methanol to oil, 3 h, 120 °C, and catalyst loading of 3 wt.% for various Ca/Mg atomic ratios to produce FAME with 70 to 90 % yield range. They found that the catalytic activity after five consecutive runs without any treatment was slightly reduced. This reduction was due to the dissolution of bulk CaO in the methanol or the unstable CaO phase being dragged out by FFAs in the raw material to form organosol (calcium soap) which competed with the FAME yield and created difficulties for FAME separation from the by-product. It has been reported, however, that the surface of the mixed oxides (MgO:CaO) resist the deactivation by CO_2 (Phillipp and Fujimoto, 1992).

3.1.3 Development of nanomaterial-based ZnO and ZrO_2 catalysts

Zinc oxide (ZnO) and zirconium oxide (ZrO_2) have been also studied for esterification and transesterification reactions to produce biodiesel (Jitputti et al., 2006; Karmee and Chadha, 2005). It was reported that ZnO can catalyze crude palm kernel and coconut oils to produce 86.1 and 77.5 % FAME yield, respectively, while 64.5 and 49.3 % of FAME yield could be achieved using 3 wt.% of ZrO_2 catalyst with crude palm kernel and coconut oils, respectively, being raw materials. Macedo et al. (2006) studied the transesterification of soybean oil over ZnO-Al_2O_3 and SnO-Al_2O_3 catalysts at optimum conditions of 4 h of reaction time, 5 wt.% catalyst and 60 °C reaction temperature to obtain 80 % of FAME yield. Madhuvilakku and Piraman (2013) have also developed TiO_2-ZnO nano-catalyst for biodiesel production from palm oil. They reported that the synthesised mixed oxide catalyst did not form any specific structure with exhibiting good catalytic activity compared to ZnO catalyst. The developed nano-catalyst displayed catalytic activity at optimum reaction conditions of 60 °C reaction temperature, 5 h reaction time, 6:1 mole ratio of methanol to oil, and 200 mg catalyst loading to reach 92 % of FAME yield and 98 % of conversion.

Soltani et al. (2017b) have recently examined the surface modification of mesoporous ZnO material by sulfuric acid to form a solid acid catalyst for biodiesel production from the esterification of palm fatty acid distillate containing 90 % of FFAs. The mesoporous ZnO catalyst was synthesised via hydrothermal treatment followed by the post-sulfonation treatment to introduce the sulfonic acid groups as shown in Figure 6. The catalyst showed high surface area (305.62 m^2/g) with average pore size of 3.16 nm and high acid density (1.72 mmol/g). The reaction was performed using 9:1 methanol to oil mole ratio, 2 wt.% of catalyst amount, 120 °C, 1.5 h reaction time to reach 95.6 % of yield. This catalyst exhibited good activity in acid-catalysed esterification of palm fatty acid distillate with methanol and a high stability for spent catalyst up to 5 cycles followed by loss of active sites in run 8. The activity of the catalyst was mainly related to the acid strength of acid sites.

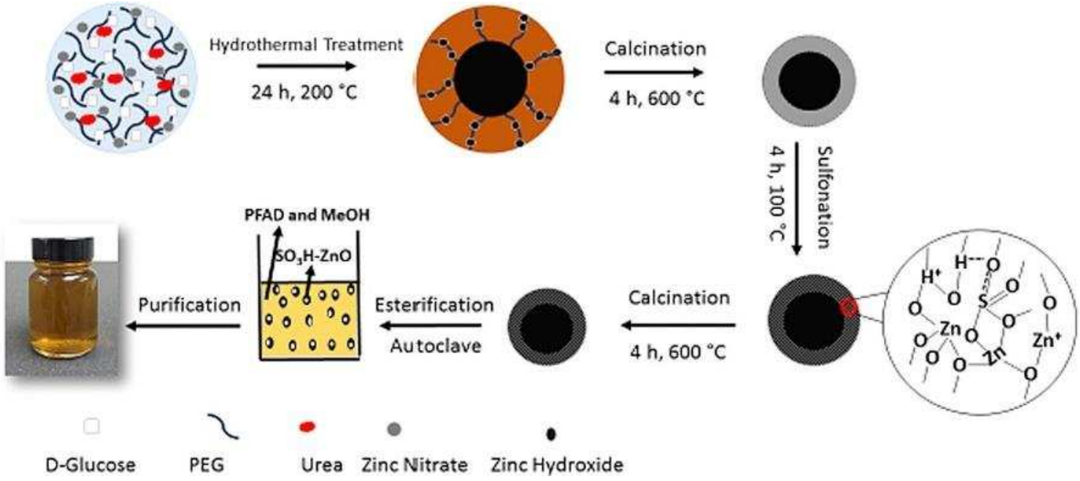


Figure 6. Proposed schematic for the synthesis of sulfonated mesoporous ZnO. Reprinted figure with permission from Soltani et al., 2017b. Copyright (2016) Elsevier

Lopez et al. (2008) compared the catalytic activities of commercial sulphated zirconia with calcined amorphous mixed oxides at between 400 and 900 °C for the esterification of caprylic/palmitic acid and transesterification of tricaprylin. They found that sulphated zirconia was the most effective catalyst of those evaluated. The spent catalyst was regenerated by re-impregnation with sulfuric acid followed by calcination at 500 °C. It was reported that leaching of sulphate ions from the catalyst in the polar media was dependent on the percentage of sulphur loading, calcination temperature, reaction media and reaction temperature. Although leaching of sulphate ions in water as a by-product from esterification reaction form HSO_4^- or H_2SO_4 which increases rate of reaction, it leads to interference of homogenous and heterogeneous catalytic activity, poisoning of active sites and pore blockage of the sulphated zirconia catalyst were occurred, which later affects the activity of the solid catalyst. The same finding has been drawn by other researchers (Garcia et al., 2008; Muthu et al., 2010). More recently, Raia et al. (2016) have studied the activity ofSO_4/ZrO_2 catalyst in the simultaneous esterification and transesterification for Jatropha curcas L. oil containing 14.29 % of FFAs with ethanol. The catalyst was prepared by impregnation method followed by calcination at 550 °C for 3 h. Despite the high acidity of catalysts, it showed low activity for esterification of FFAs and transesterification of TG in jatropha curcas L. oil after 8 h at 150 °C, 10 wt.% of catalyst and 10:1 mole ratio of ethanol to oil with 800 RPM mixing rate. The authors concluded that SO_4/ZrO_2 catalyst was more effective in the esterification reaction rather than transesterification of TG. However, Garcia et al. (2008) reported the preparation of zirconium oxide and the sulfonating process have a significant influence on the activity of prepared SO_4/ZrO_2 catalysts.

3.1.4 Development of nanomaterial-based TiO_2 catalyst

According to the literature, titanium dioxide nanoparticles are among the most widely studied for their use in photocatalysis, catalyst support, gas sensors, medicine, pigments, cosmetics and solar cells (Bagheri et al., 2014; Dai et al., 2017). This is due mainly to their favourable properties, including acidity, good mechanical and chemical stability, high reactivity, low toxicity, and high reusability wide band gap, high surface area, low cost, and easy availability (Bourikas et al., 2005; Ahmed et al., 2014). A wide range of recent studies on synthetic routes have been undertaken to fabricate surface modified/impregnation TiO_2 nanocatalyst to increase surface acidity for biodiesel production involving the use of cheap raw materials containing free fatty acids (Toh-Ae et al., 2014; Radoman et al., 2015). The solid acid catalysts can facilitate simultaneous esterification of FFAs and transesterification of triglycerides without soap formation (Lee and Wilson, 2015; Shu et al., 2010).

Sulphated doped TiO_2 is a good example of a solid super-acidic ($H_0 \leq -14.52$) catalyst that has also been used in petroleum refining processes in petrochemical industry (Nishikiori et al., 2013; Noda et al., 2005) and showed better performance compared to other sulfated metal oxides. The higher catalytic activity is because of the acidic strength of the TiO_2 particles that is further enhanced by SO_4^{-2} groups loading onto TiO_2 surface. The super acidity of sulphated TiO_2 catalysts reported being possibly based on Lewis acid and Brønsted acid sites, whereas Brønsted acid sites formation were linked to high sulphate groups in the catalyst (Noda et al., 2005). Thus, the Brønsted acid sites are very important for the catalytic activity of acid catalysts (Sun et al., 2005; Noda et al., 2003). Similarly, many studies showed that sulphate ions incorporated into the metal oxides catalysts enhanced their acidic properties, catalytic activities, higher selectivity with reduced catalyst deactivation (Refaat, 2011). Several other sulfated metal oxides have been tested in the esterification and transesterification reactions for their activities and stabilities.

Ropero-Vega and co-workers (2010) compared the catalytic activity of SO_4/TiO_2 catalyst synthesised using different sulfonating agents [(H_2SO_4 and $(NH_4)_2SO_4$] for esterification of oleic/linoleic acids with ethanol. All prepared catalysts were shown to have Brønsted and Lewis acid sites by the formation of pyridinium ions. The authors found the lowest effective catalyst was the one prepared with sulfuric acid precursors which had a low loading of sulphur. This acid strength was not enough to carry out the esterification of oleic/linoleic acids. Conversely, the SO_4/TiO_2 catalyst synthesised with ammonium sulphate had higher Brønsted acidity, which led to the highest activity with 82.2 % conversion after 3 h at 80 °C with 10:1 ethanol to FFA mole ratio and 2 wt.% of catalyst loading. It was concluded that preparation and sulfonating methods are important for preparing sulphated titania for the esterification reaction. In a different study, Zhao et al. (2014) synthesised a high surface area sulphated nano-titania for esterification of acetic acid with n-butanol. The TiO_2 with exposed (Colombo et al., 2017), as shown in Figure 7, support was prepared by a one-step hydrothermal method without any template followed by sulfonation using impregnation method and then calcination at 450 °C to form a super acidic catalyst. The authors postulated that this novel method allowed the synthesis of a mesoporous SO_4/TiO_2 with sulphate content of 793.8 μmol/g. The DRIFT-pyridine detected the presence of both Brønsted and Lewis acid sites. The pyridine adsorbed onto Brønsted acid sites exhibited two bands at 1640 and 1539 cm^{-1} whilst the band at 1440 cm^{-1} was attributed to that coordinatively bound to Lewis acid sites. Optimal reaction conditions of 120 °C reaction temperature, 1.2 mole ratio of n-butanol to acetic acid, 0.18 g of catalyst loading, and 2.5 h reaction time, enabled a 92.2% of butyl acetate yield. The reusability of the catalyst was tested through four consecutive runs. After four catalytic runs a significant fall in the yield to 52.1% was evident. This was due to the adsorption of water on the surface of the catalyst and the deposit of butyl acetate molecules which inhibited the contact between reactant molecules and the active sites. However, soaking of the spent catalyst in sulfuric acid followed by the calcination could help to regenerate activity.

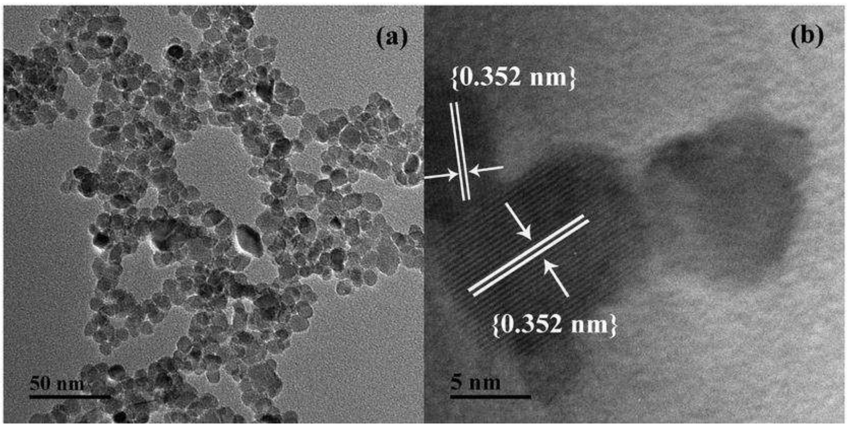
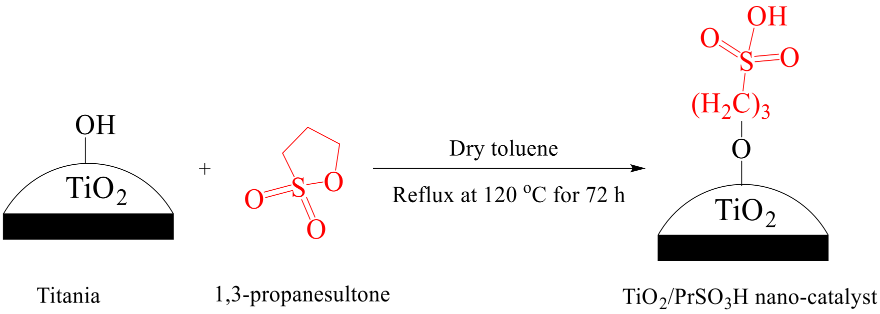


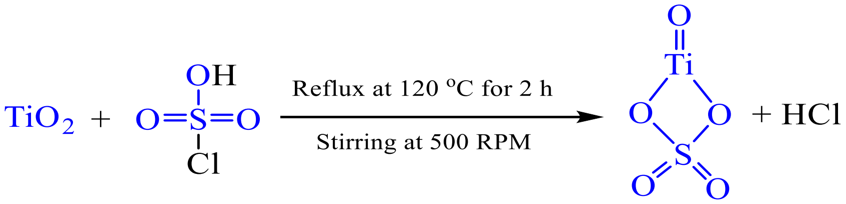
Figure 7. TEM (a) and HRTM (b) images of sulphated TiO_2. Reprinted figure with permission from (Zhao et al., 2014). Copyright (2014) Royal Society of Chemistry

Gardy et al. (2017) have recently developed $TiO_2/PrSO_3H$ catalyst by the reaction of TiO_2 NPs support with an extremely reactive sulfoalkylating agent to increase the surface acidity of TiO_2 nano-catalyst as shown in Scheme 2. It was found that 98.3 % of FAME can be obtained after 9 h of reaction time with 1:15 molar ratio of waste cooking oil to methanol, 60 °C reaction temperature and 4.5 wt.% of a catalyst loading. The enhanced catalytic performance mainly relates to the loading of propyl sulfonic acid groups on the surface of TiO_2 NPs which increased the proportion of Brønsted acid sites, according to the DRIFTS analysis. It was also found that the one-step post-surface functionalisation strategy with hydrophilic functional groups ($-SO_3H$) enhanced the acid strengths of the catalyst providing more acid sites for the reactants, and improved the accessibility of methanol to the triglycerides/free fatty acids by increasing the pore volume/size of the catalyst. The solid acid catalyst was re-used in four consecutive runs without significant loss of catalytic efficiency.



Scheme 2. Proposed protocol for the synthesis of $TiO_2/PrSO_3H$ catalyst. Reprinted figure with permission from (Gardy et al., 2017). Copyright (2017) Elsevier.

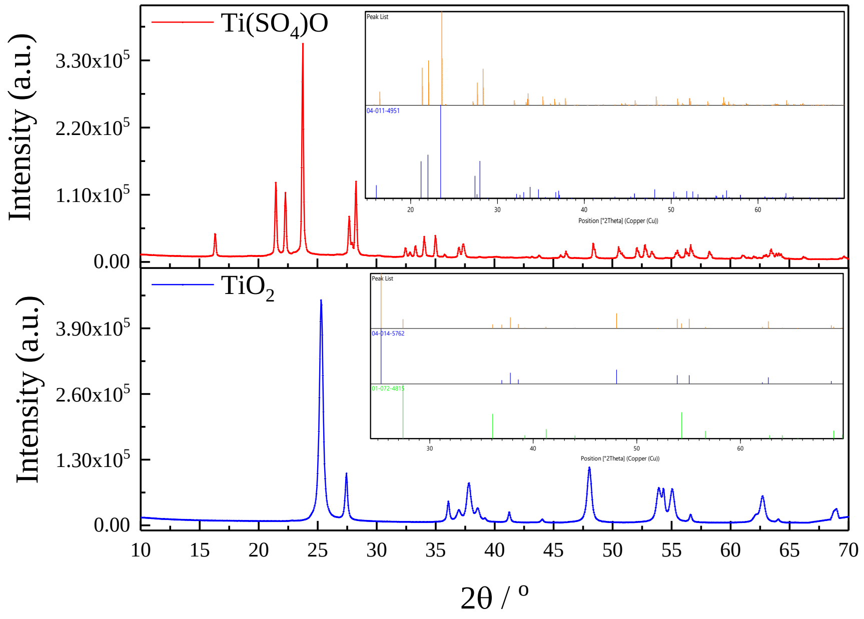
In another recent study (Gardy et al., 2016), a stable titanium sulphate oxide (titanium oxysulfate) was synthesised by reacting of titania particles with chlorosulfonic acid at room temperature as shown in Scheme 3. At high temperature, chlorosulfonic acid slowly generates sulphur trioxide and hydrochloric acid gas. The sulphur trioxide is a very aggressive electrophilic reagent that rapidly reacts with titania particles to form titania/sulfonic acid. In the presence of a reflux for 2 h, the formed product is slowly converted into the sulphated titanium oxide or oxysulfate titania [$Ti(SO_4)O$].



Scheme 3. Proposed protocol for the preparation of $Ti(SO_4)O$ solid acid catalyst. Reprinted figure with permission from (Gardy et al., 2016). Copyright (2016) Elsevier

The results showed that the $Ti(SO_4)O$ catalyst were non-uniformly distributed particles and with all XRD diffraction peaks matched with titanium sulphate oxide as shown in Figure 8. It was found that the obvious change in the chemical structure makes the $Ti(SO_4)O$ nano-catalyst more stable compared to all reported sulphated metal oxide catalysts and the acidity of the developed $Ti(SO_4)O$ catalyst (3.45 mmol/g) is also much higher than the TiO_2 particles (0.28 mmol/g). The catalyst can be used for converting cheap raw materials to biodiesel under a reaction time of 3 h, catalyst to UCO ratio of 1.5 wt.% and methanol to UCO ratio of 9:1 at 75 °C reaction temperature up to eight times without deactivation of the active sites.

(a)



(b)

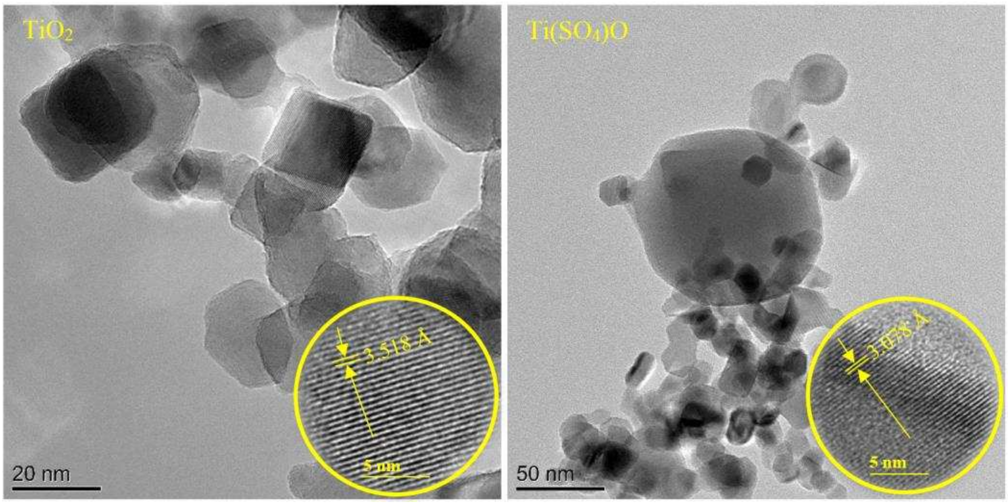


Figure 8. (a) XRD patterns and (b) TEM images of TiO_2 and $Ti(SO_4)O$ catalyst samples at room temperature. Reprinted figure with permission from (Gardy et al., 2016). Copyright (2016) Elsevier.

Sulphated titania-silica nanomaterial was used as a solid acid catalyst in esterification reaction of acetic acid and glycerine (Yang et al., 2003). The sol-gel method was used to prepare this catalyst followed by calcination at 500 °C for 1 h. The sulfate ions were introduced to the TiO_2-SiO_2 support by impregnation method and then re-calcined at 400 °C for 3 h. This catalyst (SO_4/SiO_2-TiO_2) showed a high surface area 550 m^2/g and super acidity ($H_0 \leq 12.7$). The super acidity corresponded to the nature of S=O from sulfate ions coordinated to the TiO_2-SiO_2. The catalyst exhibited good catalytic activity with 91.4 % of conversion under mild conditions. The combination of TiO_2 and SiO_2 generated stronger acid sites compared to separate metal oxides. The conclusions were drawn that the catalytic activities depend on the percentage of TiO_2, sulfate loading, calcination temperature for the final gel, and interaction between sulfate ions and TiO_2 in the support. Embong et al. (2014) have also synthesized the SO_4/SiO_2-TiO_2 super acidic catalyst from a cheap and available silica source. The catalyst was tested for the transesterification of decanter cake and found to have good catalytic performance (91 % of FAME yield after 5 h at 120 °C using 15:1 mole ratio of methanol to oil and 13 wt.% of catalyst to oil). In a different study similar activity was reported on transesterification reaction of waste soybean oil using SO_4/SiO_2-TiO_2 catalyst (Shao et al., 2013). The authors reported that the catalyst showed good catalytic activity (93.8 %) on the first run and then the catalytic activity drastically decreased to 21 % of conversion. This was possibly due to the poisoning of the active site and leaching of sulfate ions. The thermogravimetric analysis (TGA) results revealed a weight loss of 20 % from 140 to 380 °C for the fresh catalyst.

Sulphated trinary metal oxides have been also used to improve the stability and activity of the solid acid catalyst in cheap feedstocks. Li et al. (2010) investigated the performance of SO_4/ZrO_2-TiO_2/La in the esterification and transesterification of acid oil (~60 % of FFAs). The catalyst support was prepared by precipitation method followed by sulfonation process. It was found that a conversion 97.8 % achieved under the conditions of the catalyst amount of 10 wt.%, 80 °C, 2 ml of methanol/g of oil, and 5 h. The catalyst was also reused for five consecutive cycles without any treatment of the recycled catalyst and enabled a conversion of 93.6 %. The impregnation of lanthanum (La^+) to the ZrO_2-TiO_2 improved the catalytic stability of sulphated ZrO_2-TiO_2. However, loading of lanthanum above 0.1 wt.% leads to a reduction of the number of sulphate groups linked to the surface of ZrO_2-TiO_2 catalyst support. Low reactivity, high amount of catalyst, deactivation, low concentration of acid sites, small pore sizes, leaching of acid sites, long reaction times, separation and high reaction temperatures are the main drawbacks of using sulphated titania catalysts in industrial applications.

3.2 Development of carbon-based nano-catalysts

Carbon-based materials, including carbon nanofibers (Stellwagen et al., 2013); carbon nanotubes (Guan et al., 2017; Shuit and Tan, 2014; Zhang et al., 2014); biochar (Dehkhoda et al., 2010); amorphous carbon (Hara 2010); graphene oxide (Mahto et al., 2016); sugar (Wang et al., 2015a; Fu et al., 2015); and waste (Fu et al., 2013; Shu et al., 2010), have grown in significance as solid acid catalysts for biodiesel production utilizing different feedstocks. However, the main drawbacks of this type of catalyst are deactivation, thermal instability, a large amount of methanol to oil ratio, side reactions of active sites, high temperature and long reaction time (Mahto et al., 2016). Sulfonic acid functional groups modify these types of catalyst on the carbon support as active sites. Stellwagen et al. (2013) have developed a solid acid catalyst from the functionalization of carbon nanofibers (CNF) by aryl sulfonic acid groups using selective diazonium coupling reaction for the transesterification of triolein. They found that the maximum total acid sites (sulfonic acid groups) load on the CNF could be 0.62 mmol/g with high reactant molecule accessibility to the Ar-SO_3H sites. The catalytic performance of the CNF-Ar-SO_3H catalyst reached 72 % of methyl oleate yield after 4 h at 120 °C, 1:10 of triolein to methanol mole ratio, and 0.75 g of catalyst. The catalyst, after simple treatment, could be re-used for 4 cycles with slight deactivation based on the titration of acid sites result.

Sulfonic acid functionalized carbon nanotubes (CNT) have also been tested in biodiesel production from different feedstocks including cottonseed oil, bio-oil, palm fatty acid distillate, and trilaurin. Shuit and Tan (2014) have recently examined the effect of sulfonation routes, including in-situ polymerization of poly(sodium-4-styrene sulphonate); in situ polymerisation of acetic anhydride and sulfuric acid; thermal decomposition of ammonium sulphate; and thermal treatment using concentrated sulphuric acid, on the multi-walled CNT for the esterification reaction of palm fatty acid distillate to form biodiesel. It was reported that the acid density sites of synthesized catalysts were between 0.016 and 0.061 mmol/g. The sulfonated multi-walled CNT through in situ polymerization of 4-styrene sulfonate gave 93.4 % of FAME yield after 3 h at 170 °C with 20:1 methanol to oil mole ratio and catalyst loading of 2 wt.%, due to the high acid density sites loading on the multi-walled CNT. Another example of sulfonation of multi-walled CNT by thermal treatment at 210 °C with concentrated sulphuric acid is reported by Shu et al. (2009).

The synthesized catalyst had a high acid site $–SO_3H$ density (2.04 mmol/g) loading, surface area (41.27 m^2/g) and average pore size (43.90 nm). The large pore of the catalyst allows better accessibility of the FFAs and TG for contact with active sites. The highest yield of 89.9 % of biodiesel was obtained from cottonseed oil under optimized reaction conditions of 240 °C, 240 RPM mixing rate, 1.5 wt.% catalyst loading, 2 h and 20:1 methanol to oil mole ratio. The catalytic activity of the spent catalyst decreased after a few runs because of sulfonic acid leaching and the swelling effect of the catalyst. Guan et al. (2017) have recently reported FAME yield of 97.8 % from the transesterification of trilaurin in ethanol at reaction conditions of 150 °C, 1 h, 3.7 wt.% catalyst loading, 1:20 trilaurin to ethanol mass ratio. However, the spent catalyst lost around 13 % of its activity after 1 h of reaction in the first re-used cycle. This was despite the loss of catalyst surface area and agglomeration of CNTs.

Amorphous carbon bearing $-SO_3H$, -COOH and -OH groups as a solid acid catalyst was tested for its efficiency and stability for esterification of oleic acid (Hara 2010). The catalyst had a high acidity of H_0 = -8 to -11 with low surface area (2 m^2/g). The low surface area was related to the large amount of hydrophilic groups into the bulk of the catalyst. The results exhibited high catalytic esterification activity of oleic acid with 99.5 % conversion. Dehkhoda et al. (2010) tested three types of sulfonated biochar as solid acid catalysts for transesterification of canola oil. The catalyst has been prepared via concentrated sulfuric acid and fuming sulfuric acid. The total acid site loading was found to be 36.3-83.4 μmol/g and all catalysts performed at 65 °C for 24 h, 5 wt.% of catalyst loading with 15:1 methanol to oil mole ratio. The acidity of prepared catalysts attributed entirely to the Brønsted acid sites showed good catalytic activity for feedstocks containing low amount of FFAs.

Mahto et al. (2016) have also demonstrated the suitability of single step sulfonation of graphene oxide as a solid acid catalyst for the esterification of oleic acid. The high surface area, ample amount of sulfonic acid groups, π-π stacking interaction and cavities between thin layers, facilitate adsorption of reactants of the solid acid catalyst to convert 97.6 % of oleic acid after 4 h at 100 °C with 0.1972 mole of methanol in 2 ml of oil and 5 wt.% of catalyst loading. The re-usability of the catalyst was found to decline in the first cycle because of the blockage of –SO_3H groups.

Another important group of carbon based catalysts used in biodiesel production is that formed from sugar. Fu et al. (2015) have recently synthesised solid acid catalyst from β-cyclodexrins via incomplete hydrothermal carbonization followed by sulfonation process. The catalyst tested for simultaneous esterification and transesterification of triolein containing 50.2 wt.% of oleic acid. The catalytic activity was found to reach 80 % of FAME yield after 12 h reaction time at 85 °C with 30:1 methanol to oil mole ratio and 5 wt.% of catalyst. Recycling of spent catalyst showed a gradual decline in the conversion to 79 % after six cycles. They found the main reason for the deactivation of the catalyst was restricted access of the active sites (hydrophobic groups of the polyaromatic carbon sheets by the formation of a water layer during the washing process or water as by-product from the reaction).

Sulfonated carbonaceous materials from waste of vegetable oil and microalgae residue have also been used as solid acid catalysts in biodiesel production. Fu et al. (2013) have synthesised an inexpensive and stable solid catalyst with a high density of active sites (4.25 mmol/g) from microalgae residue via in situ hydrothermal carbonisation with sulfuric acid. The activity of the synthesised catalyst was tested for the esterification of oleic acid and transesterification of triolein. The catalyst displayed good stability after 6 cycles with high catalytic activity even though it has a low surface area of below 1 m^2/g. It was concluded that the highly catalytic activity attributed to the high density of acidic –SO_3H groups, the hydrophilic –COOH and –OH groups and strong affinity between the hydrophilic parts of the reactant molecules and the –OH groups bonded to carbon catalyst matrix. The same conclusion was extracted from the study of Shu et al. (2010) who reported a way to prepare an inexpensive solid acid catalyst based on carbon from sulfonation of vegetable oil asphalt. The resulting catalyst was tested in the simultaneous esterification and transesterification of cottonseed oil containing 50% of oleic acid. They achieved 80.5 and 94.8 wt.% of FFAs and TG conversions, respectively, when the catalyst performed in an autoclave under optimum conditions of 220 °C reaction temperature, 4.5 h reaction time, 0.2 % of catalyst to oil mass ratio and 16.8 molar ratio of methanol to oil. A study on the deactivation of materials bearing -SO_3H, -OH, and -COOH catalysing the esterification reaction has been reported by Fraile et al. (2015). The authors found that the high surface acid density of -SO_3H, -OH, and -COOH on the catalyst also esterified as a side reaction according to the NMR results for recovered catalyst. The proposed mechanism for the esterification reaction and side reaction for partial deactivation of catalyst is shown in Figure 9.

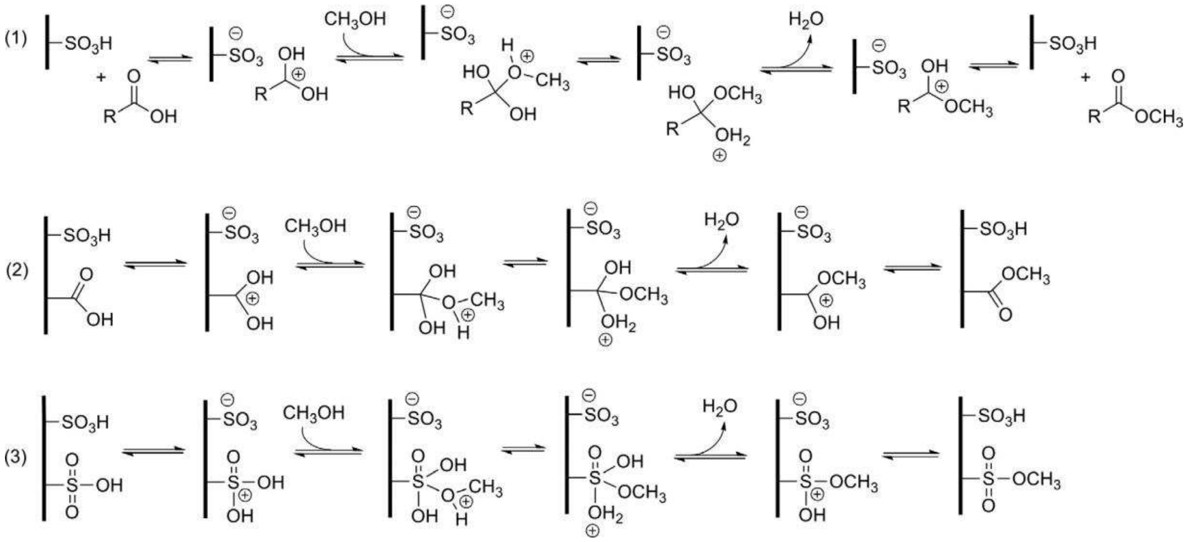


Figure 9. Proposed mechanism by Fraile et al. (2015) for the esterification reaction (1), the partial deactivation of the catalyst by side reactions (2) and (3). Reprinted figure with permission from (Fraile et al., 2015). Copyright (2015) Elsevier.

The main drawbacks of this type of nano-catalyst are deactivation, thermal instability, a large amounts of methanol to oil ratio, side reactions of active sites, high temperature and long reaction time in most cases are required.

3.3 Development of mesoporous nano-catalysts

Mesoporous nano-catalysts have attracted significant attention in biodiesel production research because of their high surface area, large pore sizes, and better accessibility, which facilitate reactants diffusion into the interior of the catalyst's acidic sites to the active sites. Since the discovery of porous materials in the early 1990s, different methods have been developed in the designing and development of such materials with excellent texture properties such as pore size, stability, and active sites to improve their performance in various reactions. The pore size can range from 15 to 300 Å based on the synthesis method and interaction between precursor and template particles (Melero et al., 2006). A wide range of mesoporous nano-materials have been synthesized recently and according to IUPAC can be classified as ordered and non-ordered (Wan et al., 2007). Among them, ordered mesoporous carbon and ordered mesoporous silicate have been mostly studied due to their high surface area, uniform pore-size distribution, large pore volume, controllable wall composition, optimum mass transfer properties, and high thermal and mechanical stabilities. Their large pore sizes generally facilitate the reactant molecules, i.e. TG (5.8 nm), to penetrate into the pore channels and contact the active sites (Mbaraka et al., 2006; Wu et al., 2014a). Sol-gel, polymeric precursor, microwave and hydrothermal are some of the critical synthetic processes for fabricating mesoporous materials (Song et al., 2018; Soltani et al., 2017; Xie et al., 2016). Mesostructured nano-catalysts can be prepared via post-synthesis procedure such as grafting methods and direct synthesis like co-condensation reactions. Direct synthesis is the co-condensation process of siloxane (i.e., tetraethyl orthosilicate or tetramethyl orthosilicate), and organosiloxane (mercaptopropyl-trimethoxysilane) precursors in the presence of the structure-agent template. While post-synthesis is the surface modification process of silica with organic precursors (i.e., 3-mercaptopropyltrimethoxysilane) as presented in Figure 10. An example is propyl sulfonic acid modified mesostructured material as a solid acid catalyst prepared by post oxidation route (Melero, 2006).

Mbaraka et al. (2006) synthesized uniform mesoporous SBA-15-$PrSO_3H$ nano-catalyst in the presence of Pluronic P123 template followed by post-oxidation of mercaptopropyl groups with hydrogen peroxide (H_2O_2). This catalyst had a high surface area (920 m^2/g) with a pore size of 48 Å and was effectively used for the esterification of FFAs in pre-treated beef tallow under optimum conditions of 120 °C, 20:1 methanol to FFAs mole ratio, and 30 min reaction time to reach 92 % of conversion.

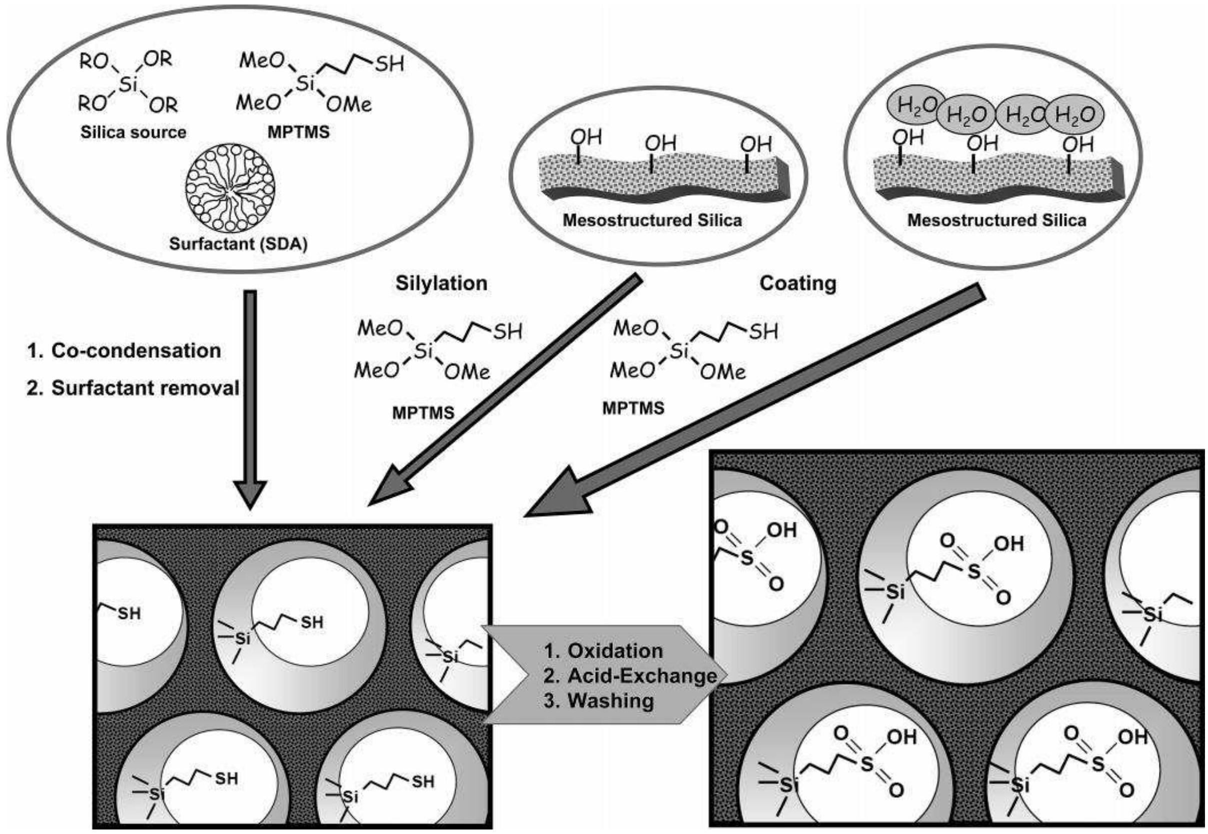


Figure 10. Mesostructured silica functionalised with propyl sulfonic acid ($PrSO_3H$) groups synthesised by post-oxidation of thiol groups. Reprinted figure with permission from (Melero 2006). Copyright (2006) American Chemical Society

Melero et al. (2010) studied the influence of different solid acid catalysts based on sulfonic acid incorporated with meso-structured SBA-15-type for transesterification of palm oil containing high FFAs. The sulfonic acid functionalized mesostructured SBA-15 were synthesized via co-condensation method with different silanes in the case of propylsulfonic acids modified SBA-15-$PrSO_3H$ and in arene sulfonic acids modified SBA-15-$ArSO_3H$, but post-synthesis grafting was used for perfluorosulfonic acid modified F-SBA-15-SO_3H. The synthesized catalysts (Figure 11a) showed high surface areas (404-712 m^2/g) with narrow pore diameters (8.2 - 9.6 nm) and acidity (0.28 - 1.17 meq/g). The SBA-15-$PrSO_3H$ and SBA-15-$ArSO_3H$ exhibited good thermal stabilities up to 350 °C, while perfluorosulfonic acid modified SBA-15 progressively decomposed after 250 °C. The transesterification reaction was carried out in a batch reactor (autoclave) made of stainless-steel at 150 °C, 20:1 methanol to oil mole ratio and 6 wt.% of catalyst loading for 2 h, resulting in 70, 80 and 90 % FAME yields over SBA-15-$PrSO_3H$, SBA-15-$ArSO_3H$, and F-SBA-15-SO_3H, respectively. This was mainly dependent on the molecular environment nature of the sulfonic acid sites, giving higher acid strength than SBA-15-$ArSO_3H$ and SBA-15-$PrSO_3H$. Likewise, the aromatic ring in SBA-15-$ArSO_3H$ had higher acid strength than SBA-15-$PrSO_3H$ due to the resonance effect of the ring (i.e., electron withdrawing environment leads to higher Brønsted acid sites). Therefore, higher acid strength in the catalyst improved the catalytic performance of the catalyst. However, the spent F-SBA-15-SO_3H was deactivated after first the run compared to other mesoporous nano-catalysts. This can be explained by the non-stability of Si-O-C bonds in polar media. The same explanation is reported by Zuo et al. (2013) that when they studied the microwave-assisted transesterification process of soybean oil and 1-butanol over these catalysts.

The hydrophobisation process was carried out to solve the issues in the relation with the interaction between reactant molecules, FAME and surface interaction of the silica catalyst (surface polarity issue) and provide a hydrophilicity-hydrophobicity balance for SBA-15-Ar-SO_3H catalyst in the transesterification process as shown in Figure 11b (Melero et al., 2010). It was found that the catalytic activity increased by 10 % even though the surface and pore size decreased after hydrophobisation (incorporating alkyl/aromatic groups directly into the silica framework). The spent catalyst, however, was reused for three consecutive cycles without any deactivation owing to the hydrophilicity-hydrophobicity balance.

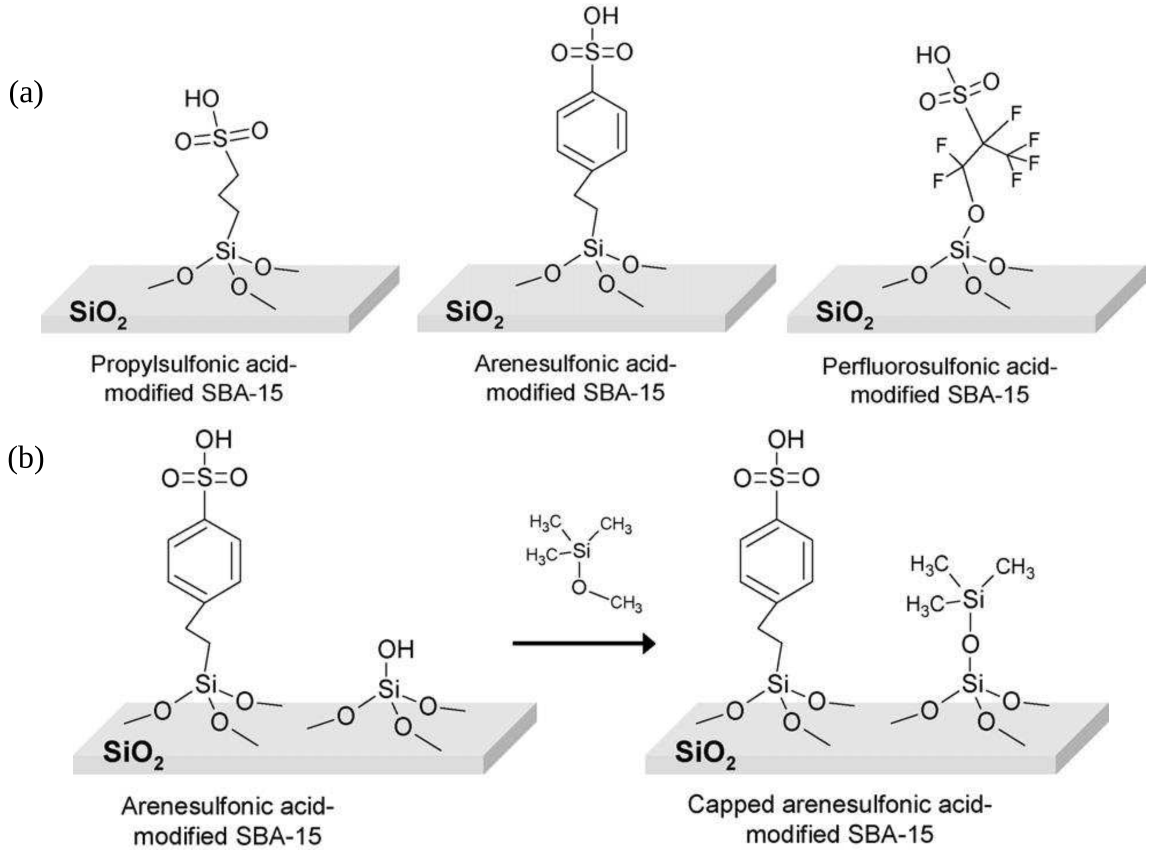


Figure 11. (a) Sulfonic acid functionalised mesostructured SBA-15 catalysts, and (b) hydrophobisation of SBA-15-ArSO_3H catalyst. Reprinted figure with permission from (Melero et al., 2010). Copyright (2010) Elsevier

Yi et al. (2015) have recently tested the catalytic performance of SO_4/Zr-SBA-15 in biodiesel production via transesterification and observed 95.2 % of FAME yield under reaction conditions; 6:1 WCO to methanol mole ratio, catalyst loading of 3 wt.% at 160 °C within 3 h and the catalyst was also recycled for 6 runs. Soltani et al. (2017a) have recently examined the surface modification of mesoporous ZnO material by sulfuric acid to form a solid acid catalyst to be used in biodiesel production via esterification reaction of palm fatty acid distillate containing 90 % of FFAs. The mesoporous ZnO catalyst was synthesized via hydrothermal treatment followed by the post-sulfonation treatment to introduce the sulfonic acid groups. This catalyst showed high surface area (305.62 m^2/g) with an averaged pore size (3.16 nm) and high acid density (1.72 mmol/g). The reaction was performed using 9:1 methanol to oil mole ratio, 2 wt.% catalyst loading, 120 °C, 1.5 h to reach 95.6 % of yield. The catalyst exhibited good activity in acid-catalyzed esterification reaction of palm fatty acid distillate and methanol as well as high stability for spent catalyst up to 5 cycles followed by loss of active sites in run 8. The catalytic activities were mainly due to the acid strength of acid sites.

Sulfonated mesoporous materials are of particular interest for transesterification reactions because bulk reactants are too large (TG size = 5.8 nm) to be incorporated into the small pore. Hence, Valle-Vigón et al. (2012) reported a novel route for preparing highly functionalised mesoporous silica-carbon composites (uniform carbon layer ~30 %) with large pore size (10 - 29 nm). The high surface area (590 m^2/g) catalyst was tested in the esterification of maleic anhydride, succinic acid, and oleic acid with ethanol. Steps for the synthesising procedure for the catalyst preparation are depicted in Figure 12.

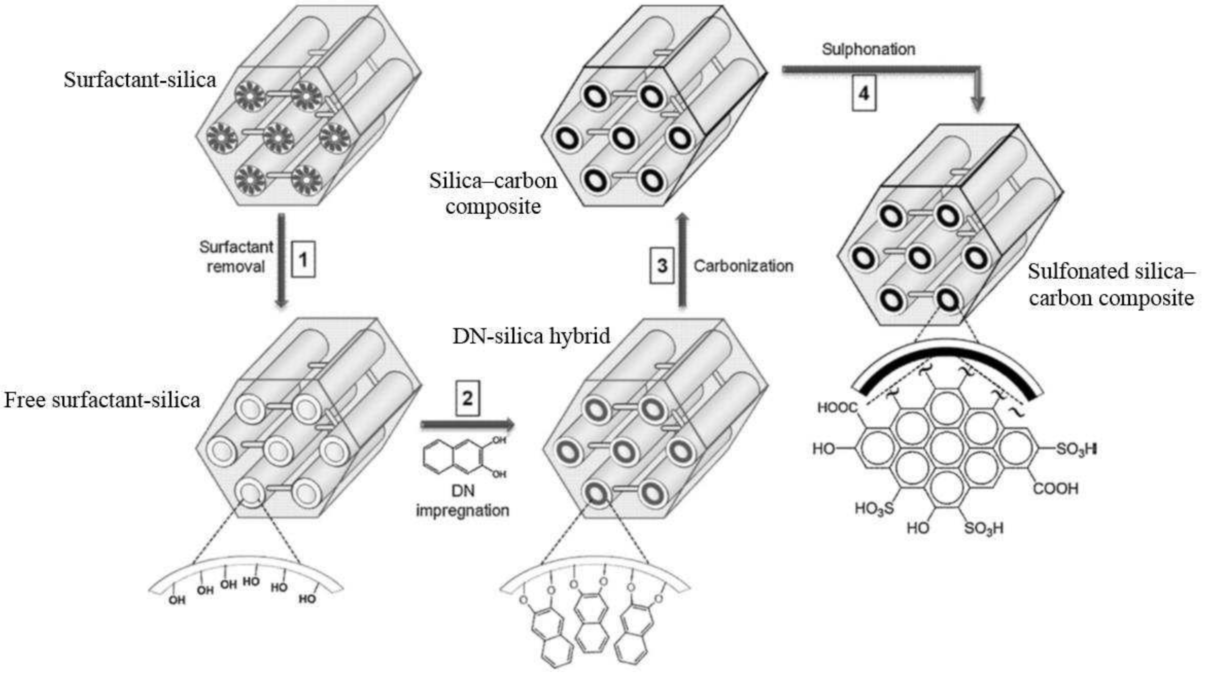


Figure 12. Schematic shows all four steps for the preparation of sulfonated silica-carbon composite. Reprinted figure with permission from Valle-Vigón et al. (2012). Copyright (2012) Elsevier

According to this study, it is important to have a large number of surface silanol groups to maximize the amount of carbonaceous deposited within the silica pores. The results revealed a high product yield formations over the use of this catalyst. However, the authors found that the sulfonation step caused the collapse of the total pore structure and the catalyst was suitable only at a reaction temperature below 150 °C. According to their TGA results this was because of –SO_3H decomposition in the catalyst between 150 and 650 °C. The same observation, in terms of harsh conditions creating a destruction and degradation of structure uniformity, was reported by Wang et al. (2007).

Dacquin et al. (2012) published a novel work focused on pore-expansion up to 14 nm with hexagonal symmetry of SBA-15-Pr-SO_3H catalyst for esterification reaction of palmitic acid and transesterification reaction of triolein and tricaprylin. The pore expansion led to a decrease of the surface area, but it accelerated the initial rate of reactant molecules to active sites in both reactions. This indicated that the reactant molecules have good accessibility to contact with sulfonic acid sites and because of that, the catalytic activity increased by > 3 times in both reactions. The conclusion was drawn that the catalytic activity was greatly dependent on pore dimensions or texture properties. Another remarkable hierarchical meso-macro-porous solid acid catalysts via dual-templating routes employing liquid crystalline surfactants (soft template) and a good dispersion of polystyrene beads (hard template) have been designed by Dhainaut et al. (2010) for esterification reaction of long chain palmitic acid and transesterification of Tricaprylin. The post-synthesis obtained –SO_3H grafting groups in the catalyst from 3-mercaptopropyl trimethoxysilane followed by post-oxidation with H_2O_2. These catalysts showed a very high surface area (938 - 976 m^2/g) and large pore sizes (34.6 - 98.2 nm) as shown in Figure 13.

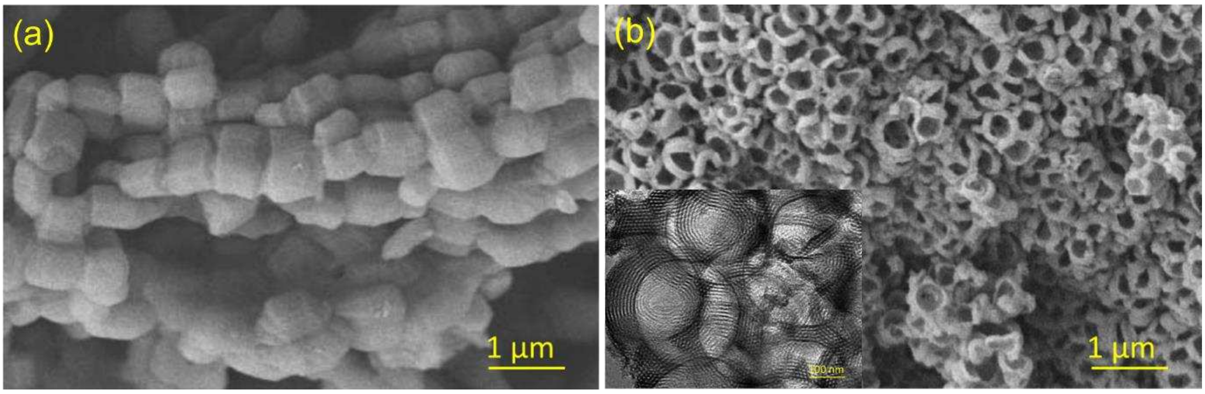


Figure 13. Morphological images of SBA-15 and SBA15 hierarchical macroporous–mesoporous silicas. Reprinted figure with permission from (Dhainaut et al., 2010). Copyright (2010) Royal Society of Chemistry

The preliminary results for macro-mesoporous SBA-15-Pr-SO_3H catalyst have been proven to be successful in increasing the catalytic activity of the esterification/transesterification reactions by 2 fold as compared to SBA-15-Pr-SO_3H catalyst. The authors explained that the rapid increase in initial rates of esterification/transesterification reactions was a result of the presence of large channels (macro-pore) enhancing the mass transfer for the bulky reactant molecules into the active sites which are located within the mesoporous in the pore network solid acid catalyst. The proposed steps, as shown in Figure 14, for the meso-macro-porous silicas catalyst preparation is reported by Lee (2014) in a comprehensive review paper. Despite numerous good results, major barriers are instability, deactivation, side reactions of active sites, water resistance, mass transfer limitation, long reaction time and high temperature, particularly for cheap feedstocks such as WCO.

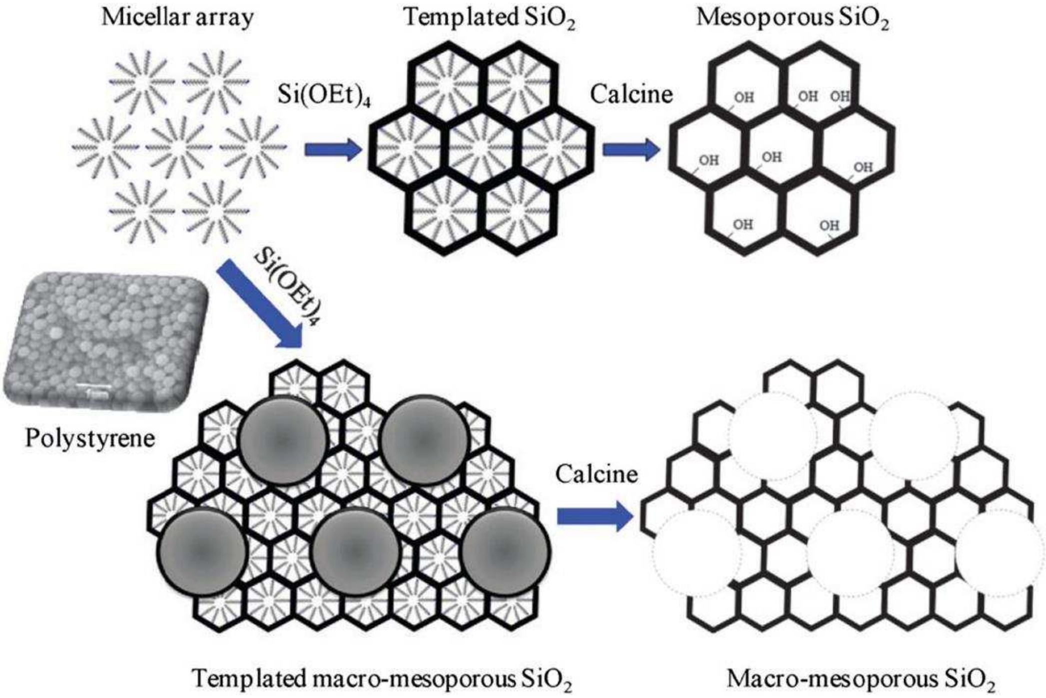


Figure 14. Proposed protocol for synthesis of hierarchical meso-macroporous silicas (Lee 2014)

3.4 Development of magnetic nanoparticles-based catalysts

Magnetic nanoparticles-based catalysts design has received considerable attention and become the main feature of biodiesel production from cheap feedstocks. This is because magnetic properties in nanoparticles-based catalysts are an excellent approach for separating the catalyst from the reaction media, which could overcome the centrifugal techniques and ultrafiltration options of such catalysts for usage in industrial separating the catalysts. A wide range of magnetic nano-materials have been recently synthesized and used for biodiesel production from cheap feedstocks. Among them, heteropolyacids (HPAs) and iron oxide (Fe_3O_4) materials have attracted a good deal of attention owing to their acidity, easier separation and reusability. The HPAs have been classified into three categories: the primary and the secondary and the tertiary (hierarchic) structure of HPAs as depicted in Figure 15 (Mizuno and Mison, 1998).

Duan et al. (2013) recently designed easily separable heteropolyacids (HPAs) supported on magnetic nanoparticles with acid content 0.429 - 0.579 mmol/g for the esterification of palmitic acid. The catalyst exhibited good activity to give 90.2 % of conversion with an optimum reaction performance at 65 °C, 6:1 mole ratio of methanol to oil, 8.2 wt.% of catalyst loading for 2 h reaction time. The catalyst was easily separated from the reaction using an external magnet without activity loss and could be used for 5 cycles of esterification. It was, conversely, found that the catalyst limited water tolerant and the structure of HPAs was destroyed after the addition of water (1 wt.%) in feedstock because of weak bonding between HPAs and the support magnetic nanoparticles. Moreover, it has been reported that the parent HPAs are not suitable catalysts in biodiesel production because of their low surface area, low number of accessible acid sites and high solubility in the polar media (Lee, 2014; Sani et al., 2014). Therefore, this class of catalyst is not suitable for the synthesis of biodiesel without modifications like a homogenous acid catalyst. Different strategies, including Cs^+, K^+, $NH_4^{+,}$ and Ag^+ ion-exchanged Keggin HPAs, have been used to overcome these limitations during esterification and transesterification reactions (Zhao et al., 2013; Gong et al., 2014).

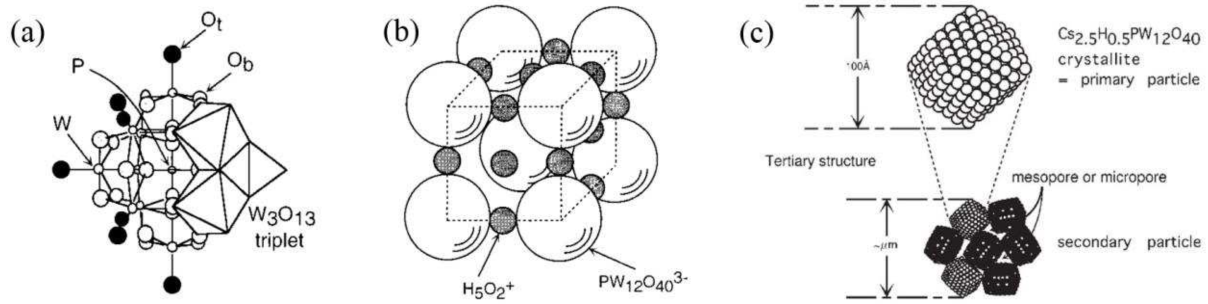
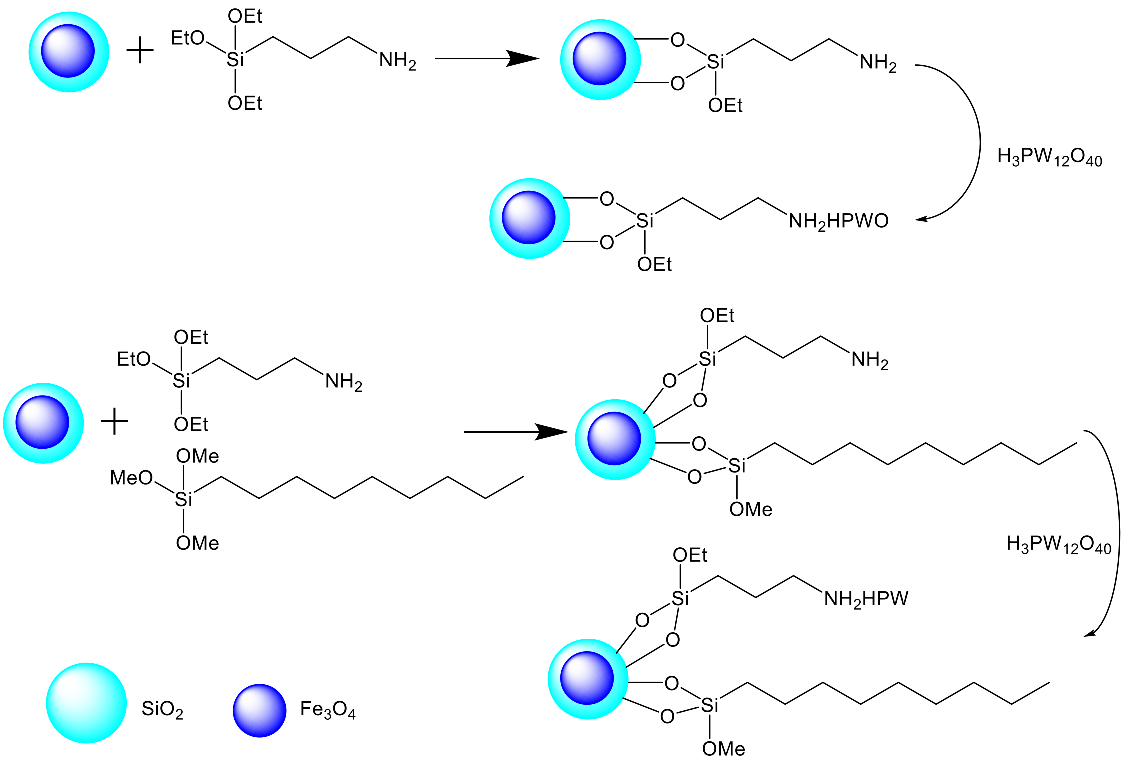


Figure 15. (a) Primary (Keggin structure, $PW_{12}O_{40}$), (b) secondary ($H_3PW_{12}O_{40}.6H_2O$) and (c) an example for tertiary ($Pt–Cs_{2.5}H_{0.5}PW_{12}O_{40}$) HPAs structures. Reprinted figure with permission (Mizuno, N. and M. Misono, 1998; Okuhara and Nakato, 1998). Copyright (1998) American Chemical Society and copyright (1998) Springer Nature

Narasimharao et al. (2007) studied the impact of Caesium external layer on the structure of $Cs_xH_{3-x}PW_{12}O_{40}$ (where x = 0.9 - 3) for the esterification of palmitic acid and transesterification of glyceryl tributyrate. It was found that the monovalent Cs had a good effect on the solubility, surface area and average pore size of the parent HPAs catalyst. It was also reported that the catalytic activity increased with Cs content up to x = 2.0 - 2.3 due to the variation of surface area and the total acid sites. A further increase of Cs content leads to a drop in catalytic activity. Low loading of Cs salts on HPAs showed slight dissolution of active sites (loss of Brønsted acid sites) whilst high loading of Cs salts (x = 3) revealed the stability in hot methanol after 6 h. The $Cs_xH_{3-x}PW_{12}O_{40}$ (x = 2.3) showed the greatest number of accessible surface acid sites with 100 % conversion of the palmitic acid at optimum conditions of 6 h reaction time, 1.9 wt.% of catalyst loading, 30:1 mole ratio of methanol to oil and 60 °C reaction temperature. The catalyst can be re-used for three consecutive cycles with negligible loss of activity and selectivity.

Li et al. (2009) found that the double acid sites ($Zn_{1.2}H_{0.6}PW_{12}O_{40}$ nanotubes) catalyst perform effectively in the esterification reaction of palmitic acid, and transesterification reaction of WCO containing 26.86 wt.% of FFAs and 1 wt.% of moisture. The study eliminated the need to treat WCO and afforded maximum conversion (> 97.2 %) at optimum reaction conditions of 28:1 methanol to oil mole ratio, 65 °C, 12 h, and 2.5 wt.% of catalyst loading. This was because of the synergistic effect of Brønsted and Lewis acidic sites with the high surface area of synthesized $Zn_{1.2}H_{0.6}PW_{12}O_{40}$ nanotubes catalyst. The catalyst was re-used for 5 cycles with negligible loss of activity. Zhang et al. (2009) also fabricated water tolerant, zirconium dodeca tungstophosphate $Zr_{0.7}H_{0.2}PW_{12}O_{40}$ nanotubes (ZrHPW) with double acid sites, the catalyst for transesterification of WCO containing 26.89 wt.% of FFA and 1 wt.% of moisture. The synthesised ZrHPW catalyst has a high surface area (256 m^2/g) and displayed a remarkable enhancement in the activity (98.9 % of conversion) in comparison with parent HPAs as catalysts under the optimum reaction conditions of 20:1 methanol to oil mole ratio, 65 °C, 2.1 wt.% of catalyst loading and 8 h of reaction time. This high catalytic activity owes to the high acidity (double acidic sites inside and outside the channel tube) and distribution of active sites on the catalyst outer surface. The catalyst was reused for 6 cycles with a slight reduction of the conversion (Zhang et al., 2009).

Gong et al. (2014) have recently used picolinic acid modified 12-tungstophosphoric acid (PA-HPAs) catalyst for the esterification of oleic acid as shown in Scheme 4. The prepared catalyst has shown a very strong acid sites according to the potentiometric titration with n-butylamine. It was reported that a 100 % conversion of oleic acid was obtained at optimum condition of 10:1 mole ratio of methanol to oil, 5 h reaction time, 7 wt.% of catalyst loading, and 80 °C. This is because of Brønsted acid sites and high amount of Lewis acid sites can activate the carbonyl group in oleic acid. The catalyst was reused for 4 consecutive cycles after washing with methanol and heat treatment at 110 °C.



Scheme 4. Schematic steps of SiO_2-MNP-1-HPW and SiO_2-MNP-2-HPW preparation. Reprinted figure with permission from (Gong et al., 2014). Copyright (2014) Elsevier

Several studies showed that the catalytic activity of magnetic sulfated ternary metal oxides could be improved by fast separation of solid super acidic catalysts from the product and by-products (Gardy et al., 2018; Alhassan et al., 2015; Guan et al., 2010; Wu et al., 2014b). Guan et al. (2010) proposed super paramagnetic sulfated ternary metal oxides as an alternative way for fast catalyst separation from the reaction and low energy consumption. The uniform and highly dispersed iron oxide nanoparticles were prepared by co-precipitation method followed by growing zirconia on iron oxide nanoparticles surface. While the introduction of boron oxide into the solution was to inhibit the nucleation and grain growth of zirconia by delaying the phase transformation of zirconia nanoparticles from tetragonal to monoclinic. This catalyst has the potential to overcome the limitation for separating solid acid catalysts from products and by-products of the reaction. The acidity of synthesized catalyst displayed stronger ($H_0 < -13.8$) than 100 % sulfuric acid ($H_0 = -12$). The activity of this catalyst was tested at different calcination temperatures (400-900 °C) for the esterification reaction of acetic acid with n-butanol. The improved yield of 97 to 98 % was reported under optimal reaction conditions of 100 °C, 4 h reaction time, 850 RPM mixing rate, and 1 atm. nitrogen pressure.

Wu et al. (2014b) proposed a super paramagnetic polysulphated trinary metal oxides catalyst for the transesterification of cottonseeds with methyl acetate. The core was made from iron oxide and prepared by co-precipitation method. Titania and zirconia was introduced to the iron oxide core by another co-precipitation with different mole ratios of Zr/Ti/Fe, followed by impregnation of sulphate ions from $(NH_4)_2S_2O_8$. The final gel was calcined at 550, 650 and 750 °C for 3 h. The synthesised catalysts showed super acidity (155.3 ± 0.9 to 598.6 ± 1.3 μmol/g) with polysulphate ions coordinated to ZrO_2-TiO_2-Fe_3O_4 catalyst support. It was found that SO_4/ZrO_2-TiO_2-Fe_3O_4 catalyst calcined at 550 °C enabling a FAME yield of 98.5% after 10.8 h at 50 °C with 21.3 wt.% of catalyst and 13.8 ml of methyl acetate per g of seed. The effects were observed of different mole ratios of Zr/Ti and calcination temperatures on the sulphated trinary metal oxides in the transesterification reaction. The acidity of the catalyst increased with the addition of an appreciable amount of titania (3:1 mole ratio of Zr:Ti) into the catalyst texture due to the formation of Zr-O-Ti units during the calcination . This resulted into more sulphur species being adsorbed on the surface and inhibit the zirconia grain growth. As a result, the number of Lewis acid sites increased which enhanced the catalytic activity of the catalyst. The catalyst was re-used for 8 cycles with a slight decrease in activity.

A bifunctional magnetic sulphated ternary metal oxide catalyst has recently been designed by Alhassan et al., (2015). The catalyst [Fe_2O_3-MnO-SO_4/ZrO_2] was prepared via impregnation method followed by calcination at 600 °C for 3 h. This catalyst performed good catalytic activity (96.5 ± 0.02 % of FAME yield) for transesterification of WCO under optimum conditions of 180 °C reaction temperature, 20:1 mole ratio of methanol to oil, 3 wt.% of catalyst loading, and 600 RPM stirring rate. Loss of catalytic activity occurred after 6 re-runs of the spent catalyst because of pore blockage and sulphur leaching. Therefore, the spent catalyst has to be re-impregnated with sulfuric acid followed by re-calcination of the gel.

Gardy and co-workers (2018) have recently designed a super paramagnetic sulfated ternary metal oxides via stepwise deposition of alumina and iron oxides onto commercial TiO_2 nanoparticles, as shown in Figure 16, for converting waste cooking oil to biodiesel fuel. It was found that the designed nano-catalyst exhibited a high acid loading and Brønsted acid character arising from surface sulfate and persulfate functionalised ternary metal oxides by chlorosulfonic acid, and strong magnetic character generating from hematite nanoparticles. The transesterification results showed that SO_4/Fe-Al-TiO_2 exhibited promising catalytic activity under optimum process conditions of 90 °C, a 10:1 molar ratio of methanol:WCO molar, 3 wt.%

catalyst, and 2.5 h reaction. It was also reported that the developed magnetic nano-catalyst showed excellent stability and recyclability employing magnetic separation and thermal regeneration for over 10 consecutive reactions cycles with WCO.

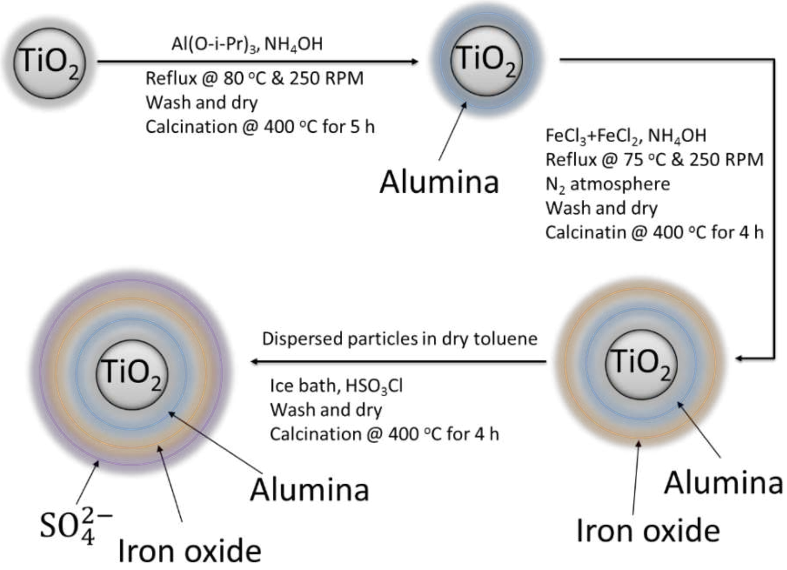


Figure 16. Proposed schematic diagram for synthesised SO_4/Fe-Al-TiO_2 catalyst. Reprinted figure with permission from (Gardy et al., 2018). Copyright (2018) Elsevier

All in all, the catalytic activity of sulphated magnetic catalysts depends mainly on the precursors, type of sulfonating agent, calcination temperature, amount of sulphate content, and crystallinity of the nano-catalyst. However, low activity at lower temperatures, water sensitivity, leaching of active sites, low surface area, and poor porosity are still the main drawbacks of these materials based nano-catalysts. Therefore, more research is needed to design a better catalyst for biodiesel production from cheap raw materials. Despite numerous good results, aforementioned and also summarised in Table 1, developed nanomaterials based catalysts for esterification and transesterification reactions are still far from being perfect in order to be used for industrial biodiesel applications. However, the main problems encountered for commercial exploitation of such catalysts are instability, deactivation, side reactions of active sites, water resistance, mass transfer limitation, long reaction time, high temperature, slow reaction rate, catalyst leaching, dissolution of catalyst in the reaction medium (solid-liquid-liquid phases), unsuitability for feedstocks containing high FFAs and some catalysts having a low activity, low porosity with low surface area. Furthermore, it is difficult to create a catalyst possessing simultaneous qualities as a strong acid and base, high surface area, large pore size, cheaper, easily separable and chemically stable. Therefore, more research need to be carried out to find cheap and more efficient catalysts for transesterification of raw materials containing FFAs by designing or developing suitable solid base catalysts.

Table 1. Summary of some developed nanomaterials based catalysts for esterification/transesterification processes

Feedstock	Alcohol to oil ratio	Catalyst		Time	Particle size, nm	T/°C	**Yield %/Conversion %**	Catalyst recycled	References
		Type	Amount, wt.%						
Croton megalocarpus oil	9:1	2%-WO_3/silica mesoporous-macroporous	4.5	45 min	3.18	70	96 Y	[*]NR	Aziz et al., 2017
Non-edible oil	30:1	PD-En-SO_3H	4	4 h	[*]NR	100	>85 Y	4	Pan et al., 2017
Trilaurin	20:1	Sulfonated MWCNT	3.7	20 min	[*]NR	170	~90 C	[**]NR	Guan et al., 2017
Palm oil	20:1	Sulfonated-graphene oxide	10	14 h	[*]NR	100	>98 Y	4	Nongbe et al., 2017
Palm kernel oil	6:1	SO_4/ZrO_2	1	1 h	[*]NR	200	90.3 Y	[*]NR	Jitputti et al., 2006
Palm datty acid distillate	20:1	Amberlyst 15	30	6 h	[*]NR	60	>95 Y	15	Talukder et al., 2008
Palm oil	30:1	Mg-Al-CO_3 (hydrotalcite)	7	6 h	Few µm	100	87 Y	[**]NRC	Trakarnpruk et al., 2008
Lauric acid	3:1	$H_3PW_{12}O_{40}/Ta_2O_5$	3	3 h	*NR	78	70 Y	*NR	Xu et al., 2008
Jatropha curcas L. oil	9.88:1	SO_4-ZrO_2/Al_2O_3	0.5	4 h	[*]NR	150	90 Y	[*]NR	Yee et al., 2011
Soybean oil	9:1[b]	Na/NaOH/γ-Al_2O_3	20	2 h	[*]N.R.	60	94 C	[**]NRC	Kim et al., 2004
Soybean oil	25:1	CaO/MgO	5	3 h	24-68	120	90 Y	5	Taufiq-Yap et al., 2011
Soybean oil	15:1	Calcined LDH (Li–Al)	1	3 h	~25 nm	65	78-83 Y	1	Shumaker et al., 2008
Soybean oil	6:1	20-nano-MgO/TiO_2	0.1	1 h	[*]N.R.	225	95 C	[**]NRC	Mguni et al., 2012
Soybean oil	20:1	KI/Mg-Al	5	8 h	[*]N.R.	70	>90 Y	[**]NRC	Tantirungrotechai et al., 2010
Ethyl butyrate[a]	4:1	MgO/CaO	62 mg	1 h	[*]N.R.	60	60 C	[**]NRC	Albuquerque et al., 2009
Waste cooking oil	12:1	3.5-K-CaO	7.5	[*]N.R.	~40	65	98 ± 2 Y	3	Kumar et al., 2012
Waste cooking oil	50:1	MgO/TO_2	10	6 h	21.4 nm	170	92 Y	[**]NRC	Wen et al., 2010a
Waste cooking oil	15:1	SO_4/SnO_2SiO_2	3	3 h	[*]NR	150	92 Y	[*]NR	Lam et al., 2009
Used cooking oil	9:1	SO_4-ZrO_2/MCM-41[***]	5	30 min	1-30	60	97 C	5	Dehghani and Haghighi, 2017
Used cooking oil	9:1	SO_4/SiO_2-TiO_2	3	4 h	10.8	200	90 Y	4	Peng et al., 2008
Used vegetable oil	40:1[***]	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	3	1 h	10	260	92 Y	[**]NR	Shin et al., 2012
Sunflower oil	12:1	SO_4-ZrO_2/MCM-41	14.6	2 h	[*]NR	200	92 Y	[*]NR	Jiménez-Morales et al., 2011
Sunflower oil	4:1	CaO	1.4	2 h	22-34 nm	75	92 C	3	Verziu et al., 2011
Sunflower oil	6:1	CaO	1	2 h	3-15 µm	60	98 Y	[**]NRC	Veljković et al., 2009
Sunflower oil	1:4	MgO	300 mg	40 min	1-4.5	70	98 Y	7	Verziu et al., 2008
Sunflower oil	6:1	16-nano-CaO/NaX	10	6 h	5-25	60	94 Y	[**]NRC	Luz Martínez et al., 2010
Sunflower oil	12:1	MgO/$MgAl_2O_4$	3	3 h	11 nm	110	95 C	2-6	Vahid and Haghighi, 2017
Canola oil	15:1	15-Kf/nano-γ-Al_2O_3	3	8 h	[*]N.R.	65	98 ± 2 Y	3	Boz et al., 2009
Jatropha oil	12:1	1.75-Li/CaO	5	2 h	500	65	>99 C	[**]NRC	Kaur et al., 2011
Triacetin	6:1	Fe/Mg-Al	1	40 min	[*]N.R.	60	100 C	[**]NC	Macala et al., 2008

[a] Catalyst activated at 800 °C and a stirring rate of 1250 RPM was used. [b] n-Hexane used as co-solvent. * N.R: Not reported. [**]NRC: Not recyclable catalyst. [***]Super critical methanol

4. Challenges and future perspectives in catalytic biodiesel production

In recent years, apart from feedstock choice, choice of catalyst, a method of production, other factors that affect the production and its cost such as research on blending and use of additives for biodiesel quality improvement have been the main area of research. The basis for the study on these properties was that they promise to reduce the production cost together with improvement in biodiesel efficiency, with the prospects of commercialization of the biodiesel production and applications on a large scale.

4.1 Characteristics of catalysts for biodiesel production

The utilization of inexpensive feedstock, such as WCO, for biodiesel fuel production (Alhassan et al., 2015), helping to reduce environmental pollution while cutting production cost (Wang et al., 2015b; Sani et al., 2014; Atabani et al., 2012). The biodiesel quality and yield could be significantly affected by many features of catalysts that are used in the esterification and transesterification processes such as the surface area, particle size distribution and surface acidity/ basicity of the catalysts (Refaat 2011). This has led to the development of many novel recyclable nano-catalysts as an alternative to the conventional corrosive homogeneous acid catalysts (Sani et al., 2014; Gong et al., 2014). These conventional homogenous acid catalysts resulted in reactors corrosion and required further washing with neutralization steps to remove them from the biodiesel and its by-products (Lee, 2014). There have been numerous recent studies into the development of different classes of solid base and acid nano-catalysts but, about biodiesel production from cheap feedstocks containing high amount of FFAs, water and other impurities, they still suffer from deactivation, leaching of acid sites, mass transfer (diffusion) limitation, and side reaction (poisoning) problems. All in all, these catalysts are not highly water tolerant, cheap and, in some cases, low thermal stability, uneasy separable from the reaction media and leaching of nano-catalysts have been reported. Therefore, more research needs to be carried out to design or develop of new efficient, water-resistant, cheap and green magnetic nano-catalysts for esterification and transesterification reactions from cheap feedstocks.

Many researchers are continuously investigating to develop new nano-catalysts and their modifications with further improved catalytic properties. There are methods researched using different modified solvents without catalysts such as supercritical methyl acetate to further improve biodiesel quality and yield (Saka and Isayama, 2009). The reusability of a new immobilized lipase catalyst was studied after 5 uses, demonstrated a reduction in manufacturing cost (per tonne) to approximately 2000 $/ton. This was still higher than the alkaline process by 206 % but less than the conventional enzymatic process by 324 % (Jegannathan et al., 2011). Thus, an enzymatic catalyst can compete with the homogenous alkaline catalyst by increasing its reusability, and with the fact that the lipase cost is reducing with time, could be used to reduce biodiesel production costs.

4.2 Applicability and limitations of biodiesel

The biodiesel has many advantages, such as its environmental friendliness, renewability, availability, higher combustion efficiencies and biodegradability, and higher cetane number, as an alternate fuel to petro-diesel. The blending of biodiesel with petro-diesel also results in better engine performance as compared to using pure biodiesel (Leung et al., 2010). Moreover, biodiesel has a higher flash point which makes its handling and transportation safer. The high lubricity of biodiesel, because of its higher viscosity, helps to reduce engine wear and thus to extend the engine life (Phan and Phan, 2008).

The disadvantages of biodiesel include limitations in agricultural feedstock availability; lower oxidation stability and storage capability over prolonged periods; operational challenges at low temperatures, lower energy content and higher NO_x emissions (Misra and Murthy 2011; Joshi and Pegg 2007; Moser 2009). However, the engine emissions working on biodiesel results in lower emissions of unburned hydrocarbons, sulfates, polycyclic aromatic hydrocarbons (PAHs), carbon monoxide, nitrated polycyclic aromatic hydrocarbons and particulate matter (Sheehan et al., 1998; Wen et al., 2010b; Chouhan and Sarma, 2011; Sharma et al., 2011; Borges and Díaz, 2012). The impact of blended biodiesel on exhaust emissions from a bus was studied by Sheehan et al. (1998). It was found that net CO_2 emissions from the bus were reduced by 78.45 % by using pure biodiesel as compared to petro-diesel. The net CO_2 emissions reduced to 15.66 % when blended to B20 (Sheehan et al., 1998). The most critical pollutant found in higher quantities from engines running on biodiesel than from petro-diesel was NO_x. Bhale et al. (2009) studied the effect of different blending of mahua methyl ester (MME) with ethanol. Their result showed that blending 80 % biodiesel with 20 % ethanol reduces the amount of NO_x emitted compared to the pure product. This is due to the higher value of latent heat causing decrease in temperature thus reducing NO_x emissions. Another disadvantage of the biodiesel is its poor cold flow properties. Various additives can be added in biodiesel fuel to reduce the solidifying temperature and increase the oxidative stability of biodiesel (Misra and Murthy, 2011; Pullen and Saeed, 2012; Lv et al., 2013; Chastek 2011; Keskin et al., 2007).

4.3 Future perspectives

Energy consumption is inevitable in human existence. The biodiesel industry is emerging as an alternate source of energy, biodiesel being eco-friendly, readily available and biodegradable, for managing the increasing energy demands in all sectors including residential, industrial and transportation. The biodiesel industry faces few problems but research over the past 20 years, and still ongoing, offers the possibility of such problems being overcome, providing an opportunity to reduce the cost of fuel in commercial applications in developing countries, as adopted in some western, developed countries. The problem faced by the industry of higher biodiesel production cost from catalytic process and vegetable oils feedstocks has led to the advent of implementing heterogeneous catalysts and various new cheaper feedstocks, including non-edible oil plant and animal resources.

The effect of various additives on the biodiesel quality have been studied (Misra and Murthy, 2011; Keskin et al., 2007). The additive choice depends on factors such as its impact on fuel efficiency, diesel engine exhaust emissions, fuel oxidation stability, and fuel quality to EN and ASTM standards, for global production and applications. Moreover, the choices of solvents, polymers, antioxidants, and metal additives and blends of biodiesel to improving the biodiesel quality should be studied. The biodiesel production cost should be taken into consideration while research on these parameters has been carried out. Despite so many efforts and development in biodiesel quality and yield, there remains many challenges and areas for further work such as the need for improvement in cold flow properties, viscosity and oxidation stability. The pre-blending of various feedstocks, as well as post-blending of biodiesels from different sources, can help to produce high-quality biodiesel economically feasible. Thus, an investigation into the type and amount of catalyst and use of an additive able to provide biodiesel performance comparable to fossil diesel is essential and should be on-going with the hope of one day being able to replace reliance on fossil fuel.

5. Conclusions

In the biodiesel industry, solid acid catalysts have been extensively examined as an alternative to homogeneous catalysts in simultaneous esterification and transesterifion using non-food feedstocks and cheap biomass under mild conditions. Their advantages over other catalysts include, (1) they are less sensitive to raw materials containing higher amounts of FFAs (2), they provide simultaneous transesterification of TG and esterification of FFAs (3), they eliminate the aqueous quenching step (4), they are easily separable from the reaction media, and (5) they can be regenerated while recycling the catalyst. A wide range of inorganic, organic and polymeric solid acid catalysts have been recently explored to biodiesel production using cheap feedstock oils, but some issues remain and still need to be resolved. Low reactivity, small pore sizes, low stabilities, long reaction times as well as high reaction temperatures are the main challenges of using solid acid catalysts in industrial applications. Furthermore, some solid acid catalysts suffer from a low concentration of acid sites, high amount of catalyst, deactivation, leaching of acid sites, mass transfer (diffusion) limitation, and side reaction (poisoning) problems. Surface functionalization of solid acids is an efficient route to introducing some important functional groups on the internal or external surface, but it reduces the surface area and porosity of the solid acid catalyst. Therefore, further, development is needed to prevent deactivation of catalyst sites and produce efficient, cheap, durable, and stable solid acid catalysts to overcome current problems associated with biodiesel production.

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Graphical Abstract