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Advances in solid-catalytic and non-catalytic technologies for biodiesel production

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ABSTRACT

The insecure supply of fossil fuel coerces the scientific society to keep a vision to boost investments in the renewable energy sector. Among the many renewable fuels currently available around the world, biodiesel offers an immediate impact in our energy. In fact, a huge interest in related research indicates a promising future for the biodiesel technology. Heterogeneous catalyzed production of biodiesel has emerged as a preferred route as it is environmentally benign needs no water washing and product separation is much easier. The number of well-defined catalyst complexes that are able to catalyze transesterification reactions efficiently has been significantly expanded in recent years. The activity of catalysts, specifically in application to solid acid/base catalyst in transesterification reaction depends on their structure, strength of basicity/acidity, surface area as well as the stability of catalyst. There are various process intensification technologies based on the use of alternate energy sources such as ultrasound and microwave. The latest advances in research and development related to biodiesel production is represented by non-catalytic supercritical method and focussed exclusively on these processes as forthcoming transesterification processes. The latest developments in this field featuring highly active catalyst complexes are outlined in this review. The knowledge of more extensive research on advances in biofuels will allow a deeper insight into the mechanism of these technologies toward meeting the critical energy challenges in future.

1. Introduction

Today's struggle for existence is the struggle for sustainable energy. Considering the economic development and therefore high consumption, the present demand of earth's energy (14 terawatt (TW)/y) will increase to 28–30 TW/y by 2050 [1]. The known petroleum reserves are limited and will eventually run out. In consequence, the inadequacy of fossil fuel and the increase in demand of energy are the driving force concerning the future energy security around the world. Fossil fuel consumption causes the emission of carbon dioxide into the atmosphere, resulting in collapse of balance between the carbon dioxide released to environment and the gas absorbed by plants. According to world climate report [2], the ongoing trend of using traditional energy sources aid to increase the carbon dioxide levels from 8600 to 13,000 million metric tons of carbon by 2050. Hence, researches have been directed toward the development of renewable, non-toxic and carbon–neutral alternative fuels. The efficient production of clean energy is the vital breakthrough of modern science to keep up-to-date on *cutting-edge* research. It was reported that [3]:

> *"Scientists have the moral duty to inform the general public of the urgency and complexity of the energy problem."*

An update on the advances production technique can reinforce the biodiesel as an *alternative clean fuel.* Biodiesel refers to the lower alkyl esters of long chain fatty acids, which are synthesized either by transesterification with lower alcohols or by esterification of fatty acids [4] shown in Fig. 1. The transesterification can be carried out either using catalytic (homogeneous or heterogeneous) or non-catalytic process. Presently, most of the commercial production of biodiesel worldwide uses homogeneous base or acid

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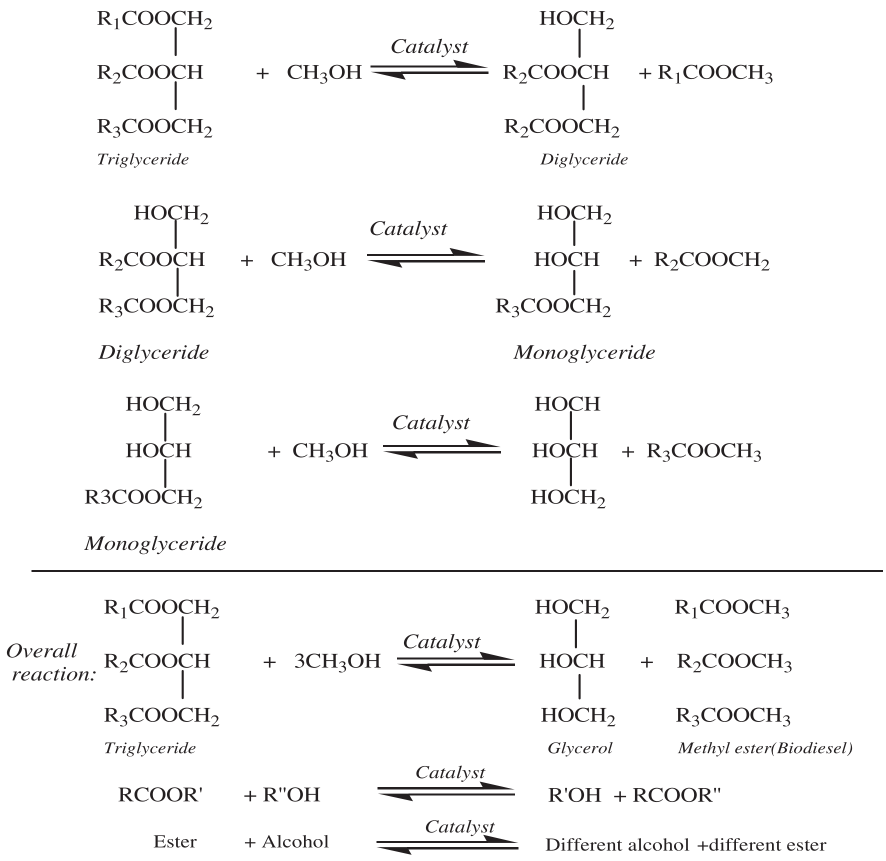
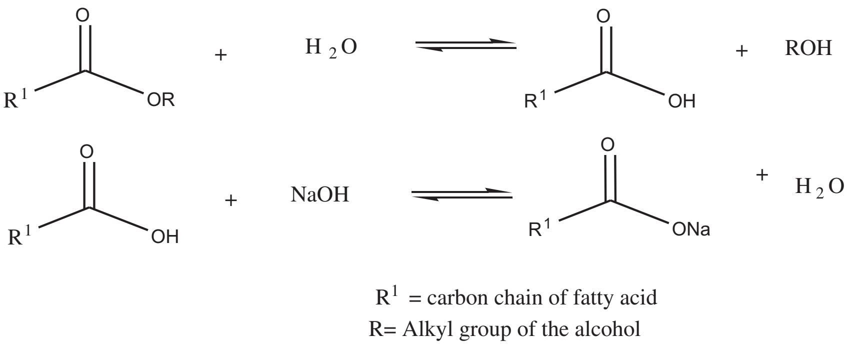


Fig. 1. Overall transesterification reaction.

catalysts. Homogeneous catalyst dispersed in a solution of reactants, has many potential advantages over solid phase and could be designed rationally to be selective and highly active. However, the main problem of this process is the undesirable production of soap which requires energy intensive separation operations [5].



It was reported by King [6] that separation processes represent more than half of the total investment in equipment for the fuel industries. Therefore, it is reasonable to state that the separation costs are a decisive factor in the final analysis of a new process. In addition, the production process is fairly corrosive and cannot be reused [7]. Hence, a great effort has been *placed toward* the development of solid catalysts aiming to make a cost efficient process.

From a process perspective, the heterogeneous catalysts in contrast to the homogeneous catalysts have the benefit of the elimination of several steps of washing of biodiesel, ensuring thereby, higher efficiency and profitability of the process. For the classification of various types of heterogeneous catalysts, it is convenient to divide them into two broad categories, soild-acid and solid-basic catalyst (Fig. 2). In particular, layered double hydroxides (LDHs) have attracted much interest as solid base catalysts for vegetable oil transesterification [8,9]. LDHs have showed efficient catalysts for esterification reaction due to its high basic properties; however, the catalyst works rarely for the transesterification reaction [10]. Thus, most of the secondary feedstocks such as waste oil and most other non-food feedstocks containing high FFA are more desirable in acid catalyzed reaction than basic-catalyzed reaction [11]. Several recent studies have reported on technical and economical feasibility for biodiesel production through heterogeneous acid-catalyzed transesterification [12,13]. Consequently, the acid catalytic reaction is of particularly interest for biodiesel production; however, the acid catalysts show lower catalytic activity in

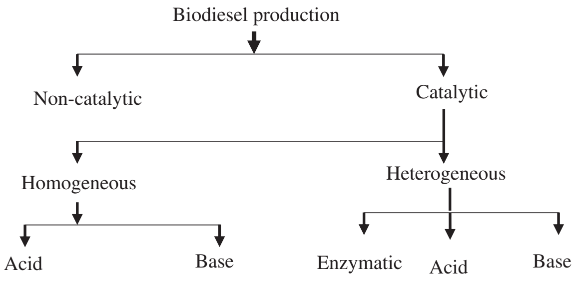


Fig. 2. Classification of catalyst used for biodiesel production.

transesterification reactions compared with basic catalysts. Thus, this low activity of catalyst is usually compensated by higher operating temperatures.

The development of non-catalytic supercritical process offer many opportunities over solid-acid or solid-base catalyzed system. With regard to the FAME production efficiency, biodiesel production by supercritical process requires a minimum number of processing steps because the feedstock pretreatment to remove moisture and free fatty acids, as well as some of the product post-treatment steps, such as neutralization, washing and drying, are not necessary [14,15]. Besides, molecules in the substances have high kinetic energy like gas and high density like a liquid in supercritical stage [16]. Therefore, the chemical reactivity in supercritical fluid can be enhanced, as reported by He et al. [17]. As a consequence, several studies focussed exclusively on non-catalytic process as forthcoming transesterification processes [18,19]. There are various process intensification technologies based on the use of alternate energy sources such as ultrasound and microwave to accelerate the reaction rate.

A state-of-the-art review of the comparison of different biofuel synthesis process is necessary to highlight recent advances, remaining difficulties and future progress. Process comparison refers to a holistic approach that should be taken into account in order to search suitable method and thereby minimization of overall processing cost. Few review papers have been published on this subject. Application of heterogeneous catalysts for biodiesel production have been reviewed by some researchers [20–23] and the influence of some operating and reaction conditions on the process, the kinetics models describing the ethanolysis process rate and the FAME yield were mainly focused. Reviews on the different process intensification techniques such as cavitational reactors, microwave irradiation, microchannel reactor, oscillatory flow reactor along with the optimized reaction parameters, catalyst properties, leaching aspects have been published [24–27]. Some attentions have been paid on the heterogeneous basic and acid catalysts [28–33] especially, calcium oxide, oxide from waste shell and hydrotalcite/layered double hydroxide and their catalytic activity, selectivity, catalyst loading, catalyst reusability were reported. Works on the design of the heterogeneous catalyst considering the catalyst pore architecture, surface polarity and acid–base properties have been discussed aiming to find effective catalyst for biodiesel production [11,34]. An alternative approach to produce biodiesel based on supercritical technology as an alternative to the conventional homogeneous alkaline catalyzed method have been highlighted [35,36]. Several recent reviews have concentrated on possible environmental and social impacts associated with biodiesel production, government's incentives, opportunities and challenges in biodiesel production [37–41]. The technologies for extracting the vegetable oil from the seed, and its subsequent refining and conversion into biodiesel and the exhaust emissions of a diesel engine have been outlined in recent years [42–52]. The present review is specifically concerned with the comparison of advanced biodiesel process with the existing methods to the purpose of evaluate efficient methods for promoting biodiesel technologies. The latest developments in this field featuring highly active catalysts are outlined and highlighted the drawbacks of certain practices in this review that can be considered in future areas of research.

2. Development of heterogeneously-catalyzed process

2.1. Catalyst support/carrier used in biofuel production

Supports/carrier can provide higher surface area through the existence of pores where active component can be anchored. Most of the solid catalyst used for biodiesel production have two different components namely, active components and support. The choice of a particular support depends on the nature of application and reaction conditions. The elementary preparation steps and the quality of the raw materials strongly affect the support properties. The active components are responsible for the principal chemicals reaction. When the active component is a metal, it should be in a sufficiently dispersed form to give a large specific surface area and consequently in a maximum activity [53]. Promoters or additives on the other hand, are added to ensure the structural integrity of the catalyst or to increase the catalyst activity and selectivity.

Attempts to improve the support properties have been ongoing for decades. More efficient catalytic processes require improvement in catalyst activity and selectivity. Both aspects rely on the tailor-design of catalytic materials with desired structure and active site dispersion. Porous support materials offer such possibilities with controlled large and accessible surface area [54]. Though porous supports offer the opportunity to disperse a relatively large amount of active component, large molecules (triglycerides) is inaccessible to the active sites of catalyst. The mesoporous characteristic of the support may permit access of bulky molecules (i.e. triglycerides) to the active sites resulting substantial in increase catalytic activity. If, as some workers [55] have suggested, the triglyceride molecule can be diffused into catalyst having pore diameter of more than 5 nm then, diffusion of the triglyceride molecule could be restricted when the diameter of the catalyst was less than 5 nm and this would in turn, be decreased the catalytic activity. Thus, the development of porous supported catalyst for biodiesel production is an active area of research in many academic and industrial laboratories. Various support materials have been reported to be used in biodiesel production especifically, high performance porous zirconia, titania and alumina catalyst, have shown great promise in terms of their catalytic, thermal, and mechanical stability for long-term continuous esterification and transesterification reactions [56–58]. Brahmkhatri et al. [59] used mosoporous (SBA-15) supported on Tungstophosphoric acid in simultaneous free fatty acids esterification and triglyceride transesterification raction and found that the catalyst gave 90% yield of biodiesel. Liang et al. [60] achieved a high yield of biodiesel (>95%) from canola oil using mesoporous Al-SBA-15 catalyst with tunable pore size (Fig. 3a). However, the information on the mass transfer properties remained unexplored. It is to underline that the relatively small pores could plug during impregnation, especially if high loading of active component is sought [61]. With this mind, MCF (mesocellular foam) silica support could be a practical alternative support material to address the challenges associated with small pores [62]. This sponge-like foam has a three-dimensional structure with large, uniform spherical cells (15–50 nm) that are accessible via large windows (5–20 nm), and thus provides an open structure that favors mass transfer [63]. It could be especially, suitable support material where big reactant molecules are involved.

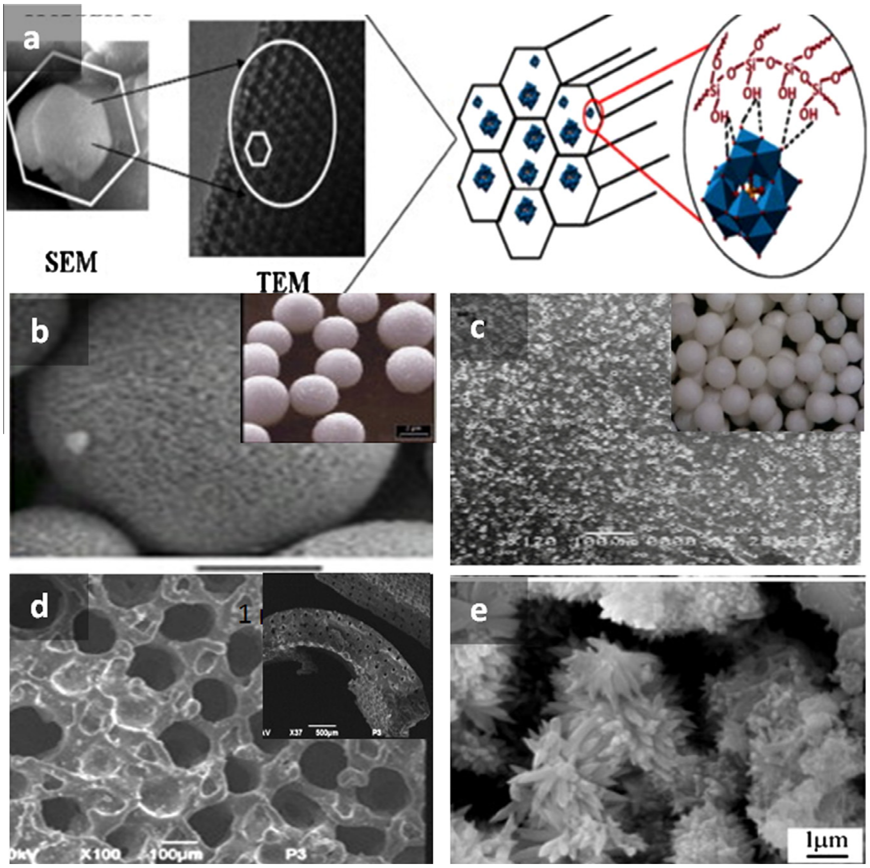


Fig. 3. Application of porous support in biodiesel production.

Modification of support microstructure has attracted much attention in recent years, because of their unique properties, leading to promising applications in catalysis. A solid microspheres catalyst with honeycomb array of channels was fabricated by Borges et al. [64] and reported the improved efficiency of catalyst in biodiesel production for continuous packed-bed industrial reactor (Fig. 3b). The vital role of macroscopic porous support in determining performance in transesterification of vegetable oil with methanol has been studied by McNeff et al. [65] and Islam et al. [66]. The authors reported that the macroscopic porous support amenable to continuous fixed bed biodiesel production (Fig. 3c and d). Recently, the fabrication of novel structured CaO catalyst has been developed by Liu et al. [67]. The results revealed that the preferred nucleation and growth of CaO nuclei along the growth directions led to flower-like architectures which is potential catalyst for biodiesel production (Fig. 3e). However, the powder structured catalyst could be difficult to separate from the reaction medium. In addition, the small particle size gives rise to several problems such as high pressure drops, poor mass/heat transfer, poor contact efficiency and difficulties in handling and separation [66]. There are also possible health risks caused by inhalation of small particles. Therefore, the fabrication of structured catalyst with macroscopic form could be useful for industrial applications, as proposed by sevaral researchers [66,67]. Based on survey of the literature, few important properties of support materials are listed below:

- Inertness. Ideally, support materials should have no catalytic activity leading to undesirable side reactions [68].
- Stability at high temperature reactions and regeneration conditions [69].
- Shape, preferably, spherical in order to minimize the resistance to transport of reactants and products [70,71].
- Porosity, including average pore size and pore size distribution. To achieve a higher degree of dispersion of the active component, it is necessary to prepare catalysts in a highly porous form. The active metal component is usually deposited on the surface of a porous or non support [72,73], as shown in Fig. 4. A common route to control the porosity of solid materials to be prepared at high temperatures involves the use of pore formers, which generally are organic compounds that render a porous structure with undefined geometry after the corresponding thermal treatment [66,71].
- Size, the activity of the catalyst has been reported to be dependent on the particle size. Smaller particles can be expected to exhibit higher rate of reaction, or consequently conversions for a given volume of reaction mass due to increased external surface available [74].
- The support materials should have a high surface area and desirable mechanical strength to permit dispersion of the metal, and hence the catalyst life [74].
- Low cost.

Materials with low surface area are generally useful in supporting very active catalytic components in reactions where further side reactions may affect the activity and selectivity, while materials with high surface areas are widely used in precious metal catalysts preparation [68]. In addition, the catalytic behavior of the supported particles depends strongly on their interactions with the support [69]. The active species in catalysts can be either in the metallic (nickel, platinum, Paladium) or metal oxide form or other forms (e.g. sulfides). Among the support materials, alumina, zirconia have received *considerable attention* for *catalytic* reactions as a support owing to its high surface area, stability at high temperature reactions (>800 °C) and easily available [75].

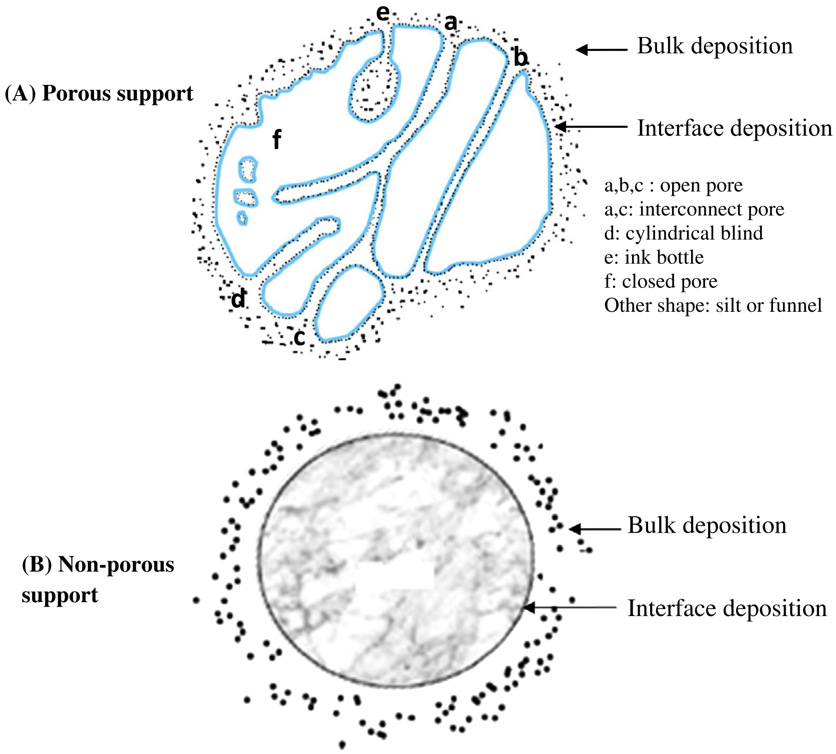


Fig. 4. Schematic representation of the supported catalytic particles.

2.2. Supported-catalysts employed for biodiesel production

There are many supported catalysts employed for biodiesel production. For the classification of various types of supported catalysts, it is convenient to divide them into two broad categories, soild-acid and solid-basic catalyst.

2.2.1. Biodiesel production with solid acid-catalyst

Since heterogeneous catalysis is a surface phenomenon, the extend to acidity of a catalyst affects its catalytic activity, simply because of the variation in the number of acid sites. As a result of the development of solid acid catalyst for biodiesel production, the relationship between catalytic activity and strength of acidity has been the subject of an increasing number of investigations in recent years. Super acidic sulfated zirconia (SO_4/ZrO_2) [76], tungstated zirconia (WO_3/ZrO_2) [77], sulfated tin oxide (SO_4^{2-}/SnO_2) [78] and Tungstated zirconia–alumina (WZA) [79] have been evaluated for the transesterification of vegetable oil at temperature in the range of 150–250 °C. Among them, WO_3/ZrO_2 catalyst was found to be most favorable to the transesterification reaction and resulted in more than 90% yield at 200 °C with 15:1 methanol to oil ratio. The catalyst was found to be suitable for transesterification reaction due to the coexistence of tetragonal zirconia with the amorphous tungsten oxide. Recently the activity of several acid catalysts using different ratio of TiO_2/SO_4 synthesized via sol–gel technique in the transesterification of soybean oil with methanol at 120 °C has been ranked in reference to their ratio of TiO_2/SO_4 such as $TiO_2/SO_4(5:1) > TiO_2/SO_4(10:1) > TiO_2/SO_4\ (20:1)$ [80].

It was reported that the low activity of TiO_2/SO_4 (20:1) is related to its low amount of Brønsted acid on its framework, due the insufficient amount of sulfuric acid used in its preparation. The results are in good agreement with the experimental reactivity observed in case of SO_4^{2-}/TiO_2 and SO_4^{2-}/ZrO_2 catalysts [81]. However, the inconvenience of these catalysts lies toward the deactivation owing to leaching of SO_4^{2-} species to the biodiesel. Leaching of the sulfate group and low activity toward transesterification were undesirable factors that might be avoided by using sulfated titania–silica catalysts, as proposed by Shao et al. [82]. However, synthesis of sulfated titania–silica catalysts from low cost sources is appealing and commendable. Moreover, the way of the reducing deactivation of the catalysts has been suggested by Yadav et al. [76]. It was proposed that the catalyst prepared from chloro sulfonic acid precursor dissolved in an organic solvent, instead of the conventional impregnation of H_2SO_4 could reduce the leaching of sulfate under reaction condition.

Shu et al. [83] reported on sulfonated carbon-based solid acid used as catalyst for transesterification of cottonseed oil with the methanol at 260 °C. It was reported that the catalyst was more active due to their high acid site density. Unfortunately, it is not clear up to what extent the acid site of catalyst is responsible for high conversion, though it has potential for industrial scale biodiesel production. Moreover, the acid sites may have been involved in important side reactions, such as the double dehydration of glycerol to produce acrolein at reaction temperatures of above 250 °C, involving the condensation of glycerol molecules to produce glycerolethers [84,85]. Therefore, further investigation is necessary on sulfonated carbon-based solid acid to find out this aspect.

Recently, much effort has been placed toward the development of solid acid catalyst for simultaneous esterification and transesterification reactions in low grade feedstocks [86–90] For instance, Kulkarni et al. [91] studied simultaneous esterification and transesterification low quality canola oil with methanol using hydrous zirconia supported 12-tunstophosphoric acid. They found that the catalyst was most active in methanolysis at the operating condition of 3 wt% of catalyst, molar ratio of oil to methanol of 1:9, at 200 °C for 10 h, reaching 90% of FAME yield. Likewise, several attempts have also been made to use the variety of 12-tungstophosphoric acid catalyst in simultanious esterification and transesterification reactions. For example, Srilatha et al. [92] reported the production of biodiesel from used cooking oil containing high free fatty acid by a two-step heterogeneously catalyzed process over

12-tungstophosphoric acid (TPA) supported on Nb_2O_5 catalyst. The catalyst showed high FAME yield reaching maximum value of 90%, as it possessed maximum number of strong acid sites. Same research group [93] assessed the effect of various reaction parameters on the ester yield using 12-Tungstophosphoric Acid (TPA)/Nb_2O_5 catalyst. It was found to exhibit maximum *yield* of 92%, which could be accounted for by the high acidity of the catalyst. The stability of the catalyst was ascertained by ensuring no leaching of active phase from the support. Some studies concerning the esterification and transesterification reactions simultaneously using sulfated tin oxide enhanced with SiO_2 ($SO_4^{2-}/SnO_2–SiO_2$) as super acid solid catalyst have been reported [31]. The catalyst was found to be a very active catalyst under the reaction conditions, typically from low-grade oil with high free fatty acid content, reaching >90% of FAME yield.

The activity of acid catalyst was improved further by incorporating functional groups to the catalyst. The bifunctional solid catalysts were reported as an alternative to the biodiesel production in order to develop simultaneously the esterification and transesterification reaction. Since esterification and transesterification reactions share a common molecular mechanism, the reactions using bifunctional catalyst takes place simultaneously [94]. According to the method, the esterification takes place between free fatty acids (RCOOH) and methanol (CH_3OH) whereas transesterification takes place between monoglyceride (RCOOR) and methanol adsorbed on acidic site of catalyst surface (Fig. 5). One of the examples of the use of bifunctional catalyst in biodiesel production was carried out by Kondamudi et al. [95] who reported the use of *Quntinite-3T catalyst* showing bifunctional properties in the conversion of FFA and TG into biodiesel. The high catalytic activity was achieved under the optimized reaction conditions; 10 wt% of the catalyst at 75 °C and 2:1 methanol to oil—a yield over 96% of methyl esters was achieved. With regards to the stability of the catalyst, up to five consecutive reutilization runs were carried out without significantly affecting the conversion and selectivity of the catalyst. Thus, the satisfactory recycling tests reveal a higher structural integrity of the catalyst. Yin et al. [96] have also reported the use of organophosphonic acid-functionalized silica as a bifunctional catalyst for biodiesel production. The catalyst showed excellent catalytic performance reaching maximum biodiesel conversion of 89.94% under the optimized conditions which was ascribed to its strong Brønsted acidity and amphiphilicity of catalyst.

The acid–base type of catalysts has been reported by Macario et al. [97] for biodiesel production from MCM-41. It may be mentioned that the MCM-41 have the charecteristics of acidic sites and it can be accommodated a wide variety of cations such as Na^+,K^+, Ca^{2+}, Mg^{2+} that attributed to its basic nature [27].Thus, the acid MCM-41 catalyst was prepared by hydrothermal synthesis procedure. Later, the cation such as potassium (K) was loaded on different materials by ionic exchange methods for preparation of acid–base type catalyst [97]. It was reported [97] that the K loading of MCM-41 increased the conversion of triglyceride to a great extent (97%). However, the reclycling of recovered catalyst showed decrease in biodiesel yield which could be attributed to the leaching of metal from the catalyst.

Some amphoteric metal oxides, such as PbO, PbO_2, Pb_3O_4 and Ti_2O_3 have attracted attention from researchers because of their basic–acid properties. Singh et al. [98] compared the activities of a series of metal oxides–PbO, PbO_2, Pb_3O_4 and Ti_2O_3, with methanol/oil ratio 7:1 at 225 °C to find the most suitable candidate for the transesterification of of soybean Oil. Among the catalyst tested, the most active was Pb_3O_4 and found to be most favorable toward the transesterification and resulted in more than 89% of the biodiesel yield. However, further testing showed Pb content in the glycerol and biodiesel products was as high as 2000 ppm which implied some dissolution of the catalyst.

In order to increase the stability and strength of acidity of catalyst, Sreeprasanth et al. [99] exploited the Fe–Zn double-metal cyanide complexes (DMC) for biodiesel production. The DMC catalyst has higher activity in sunflower oil transesterification most likely because of higher concentration of acid sites on the surface and surface hydrophobicity. It was found that the DMC catalyst's activity still retained a high proportion (96.5%) of catalytic activity in the methyl ester formation reaction, even after many cycles of successive reuse. The application of other hybrid catalyst in biodiesel synthesis, including zirconia, titania and alumina, have also been demonstrated by McNeff et al. [65]. The recycling experiment

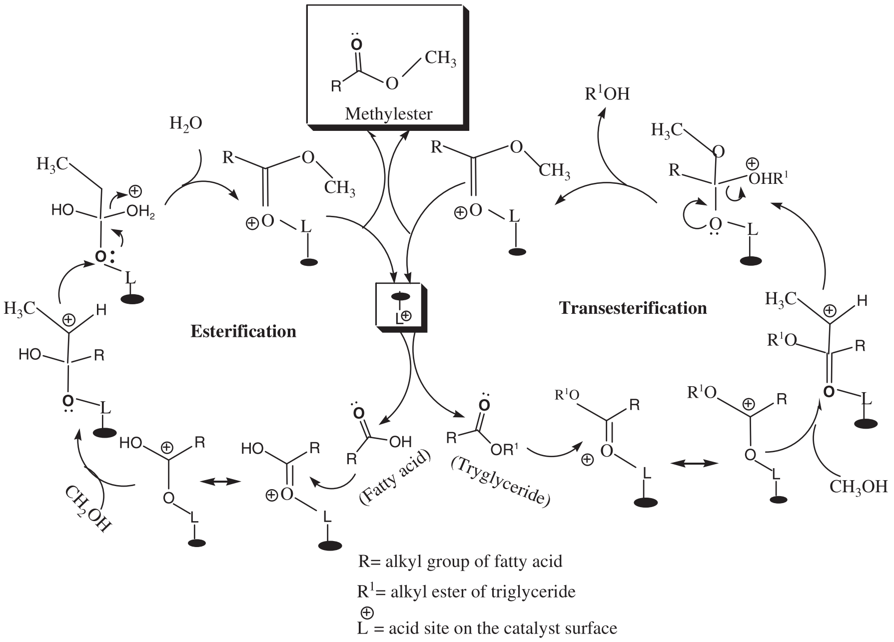


Fig. 5. Mechanism of simultanuous esterification and transesterification reaction.

showed that the catalysts was maintained a high yield of biodiesel (90%) over the course of 10 h of continuous operation. From the view point of stability of catalyst, this catalyst is very important, however, the active sites of the catalyst responsible for high activity is unknown and further investigation is necessary needed in this direction.

A strategy for preparing novel sulfonic acid carbon-based solids has been developed by several researchers [100–103]. The sulfonation of incompletely carbonized carbohydrates such as starch, cellulose, D glucose and sucrose leads to a rigid carbon material consisting of small polycyclic aromatic carbon sheets. Dehkhoda et al. [103] prepared a carbon-based solid acid catalyst by sulfonation of biochar material. This catalyst was employed to simultaneously catalyze esterification and transesterification reaction to synthesize biodiesel when canola oil with large amounts of free fatty acids was used as feedstock. The solid acid consisted of a flexible carbon-based framework with highly dispersed polycyclic aromatic hydrocarbons containing sulfonic acid groups. It was concluded by the authors [103] that the high catalytic activity and stability of this catalyst was related to its high acid site density, hydrophobicity that prevented the hydration of -OH species, hydrophilic functional groups ($-SO_3H$) that gave improved accessibility of methanol to the triglyceride and FFAs, and large pores that provided more acid sites for the reactants.

Many papers have published describing the use of weak solid acid catalyst for biodiesel production. For instance, Brito et al. [104] reported the activity of several commercialized Y-type zeolites in a continuous tubular reactor at atmospheric pressure. According to the authors, under a good thermally stable reaction condition, catalysts were obtained with good reactivity and selectivity to methylester. The other researchers investigated transesterification of fried oil with methanol over zeolite Y at different concentrations [105]. The catalytic effect has been tested within a temperature range 60–476 °C and conversion was reported to be at 98% for the zeolite Y catalyst. In particular, these catalysts presented an appreciable activity for reactions when n hexane and THF were used as co-solvents. It was reported that the regenerated zeolite Y was less deactivated over time than fresh catalyst. However, the use of the catalysts still needed high temperatures (476 °C) in order to be effective. Some other works, weak solid acid catalyst of vanadium compound has been reported the active catalyst for biodiesel production, such as Fe^{3+} vanadyl phosphate, vanadyl phosphate [106,107]. The vanadyl phosphate catalyst showed the highest activity under optimized reaction condition. It has been reported to catalyze the methanolysis of vegetable oil at 180 °C with over 79% of oil conversion in 1 h [107]. This type of catalysts exhibit varied activities depending on the formation of active species (V^{3+}, V^{4+}, V^{5+}) and reaction temperature where, V^{3+}, V^{4+} and V^{5+} were active, intermediate and inactive species respectively. It was reported that the activity of these catalysts slightly increased with increasing the reaction time. However, longer reaction time increases the production cost of biodiesel.

The evolution of solid acid catalyst concerning the biodiesel synthesis technologies shows three major advances, as per literature reviewed (Fig. 6). Due to high FFA content in low grade feedstocks, the alkali catalyzed transesterification reaction to produce biodiesel gives low biodiesel yield because FFA reacts with alkali to form soap, resulting in serious emulsification and separation problems. Thus, the production of biodiesel by a solid acid catalytic process has been developed to minimize the aforementioned problems. Several recent studies have proved the technical feasibility of biodiesel production via heterogeneous acid-catalyzed transesterification. The acid catalysts are known to show a much lower catalytic activity in transesterification reactions, compared with alkaline catalysts, and this lack of activity is usually compensated by operating at higher temperatures. However, some non-edible feedstocks are considered as a high free fatty acid (FFA) feedstock, in which commercial acid catalyzed transesterification, is not a suitable choice to produce biodiesel [108]. Thus, super acidic catalyst has been proposed as an alternative one over the traditional acid catalyzed system. Further, two-step catalytic process has been proposed to increase the selectivity of catalyst toward the transesterification reaction. In a first step, a feedstock pretreatment is performed in which the free fatty acid content is reduced by the use of an acid catalyst such as sulfuric acid or ferric sulfate and in a second step a basic catalyst is used to produce biodiesel [109,110] Though, the two-step method also faces the problem of catalyst removal in both steps. The catalyst removal problem in the first step can be avoided by neutralizing the acid catalyst, using extra alkaline catalyst in the second step. The use of extra catalyst will increase the cost of biodiesel production. Hence, bifunctional solid acid catalyst was proposed as an alternative one in order to precede simultaneously esterification and transesterification reaction. Most of the reported bifunctional solid catalysts can be classified in two main groups: inorganic and organically-functionalized. The organically functionalized catalyst contains both of the Brønsted and Lewis acid sites which is superior in transesterification reaction compare to those of the inorganically functionalized catalyst [111]. As reported by the researchers [12] that the solid acid catalyzed transesterification reactions are initiated or promoted via the abstraction of proton from the reactant (alcohol), followed by rate of transesterification reaction (Fig. 7). Since the ability of acids to abstract a proton from an alcohol is directly connected to the acid strength, stronger acids are in general more

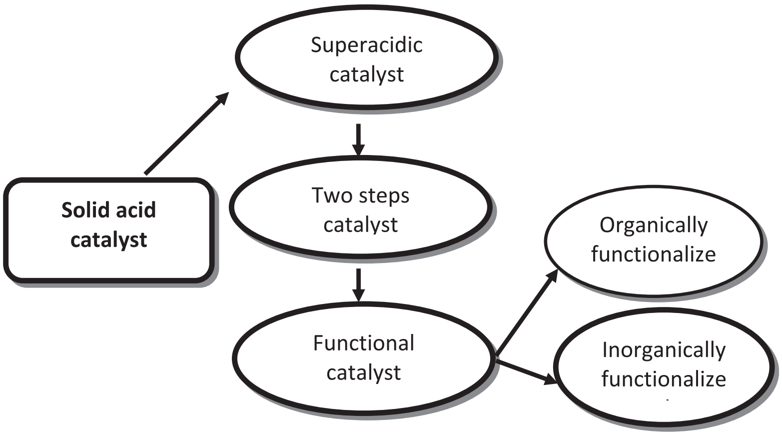


Fig. 6. Advances in solid acid catalyst in biofuel production.

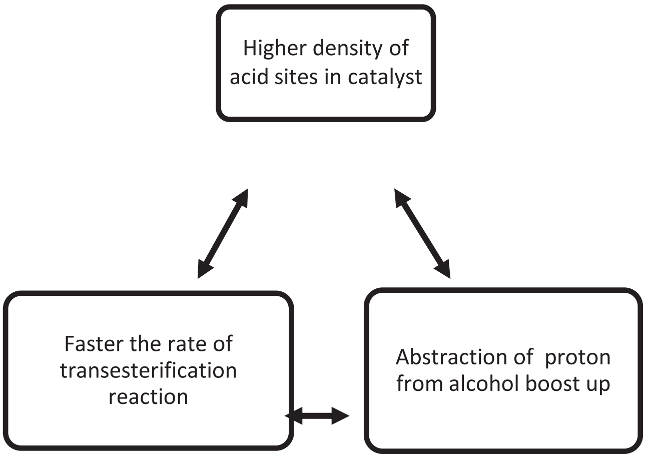


Fig. 7. Factor affecting the acid catalyzed biodiesel production.

effective to initiate the transesterification of triglycerides. In this connection, questions regarding the nature of Brønsted and Lewis acid sites, their number, strength, and location as well as cooperative effects should be clarified. In recent years, several scientific advances have provided new highly active and stable soild-acid catalyst for biodiesel production. Though, the biodiesel produced by using solid-acid catalyst in the temperature range of 120–450 °C is highly energy intensive; hence a study has to be considered at lower temperature range.

2.2.2. Biodiesel production with solid base-catalyst

Solid-base catalysts have been applied in transesterification reaction of variety of supported materials, such as alkaline-earth metals oxides and hydroxides, alkali metals hydroxides or salts supported on -alumina, zeolites, and hydrotalcites. The KNO_3, K_2CO_3, KOH, KI supported on Al_2O_3 catalysts showed high yield of biodiesel (>90%) due to more basic sites forming either K_2O supported on Al_2O_3 species produced by thermal decomposition or Al–O–K groups formed by salt–support interactions [66,112,113]. Ma et al .[114] and Kim et al. [115] investigated the activity of $K/KOH/\gamma\text{-}Al_2O_3$ and $Na/NaOH/\gamma\text{-}Al_2O_3$ catalyst in the transesterification reactions. It was pointed out that the catalyst's activity is closely related to the basic nature of the catalyst. The strong basic sites (super basic) promote the transesterification reaction at low temperature (60–70 °C), while the basic sites with medium strength require a higher temperature to process the reaction [11].

Since the ability of bases to abstract a proton from an alcohol is directly connected to the base strength, stronger bases are in general more effective to initiate the transesterification of triglycerides. It was reported by Chorkendorff and Niemantsverdriet [116] that the metal oxide provides sufficient adsorptive sites for alcohol in transesterification reaction and concluded that the high transesterification activity of catalyst might be due to the manifestation of the dissociation of alcohol to RO^- and H^+ on basic sites of metal oxide catalyst surface. Thus, the generation of active oxide phases such as, K_2O phases on $K/KOH/\gamma\text{-}Al_2O_3$ and $NaAlO_2$ phase on $NaNO_3/\gamma\text{-}Al_2O_3$ increased the basicity as well as the transesterification activity, as reported by Ma et al. [114] and Islam et al. [66]. The catalyst was found most promising for higher FAME yield of 95%; however, a small portion of metal content such as K^+ or Na^+ leaching was observed in methanol.

Ilgen et al. [117] recently reported the use of KOH loaded MgO instead of typical alkali loaded alumina type solid base. The KOH/MgO is an active and promising heterogeneous solid base catalyst for the production of biodiesel from canola oil. The catalyst with 20 wt% KOH loaded on MgO and after being calcined at 500 °C for 5 h gave the highest basicity which is responsible for higher FAME yields (>95%). Similar FAME yield (92%) has been obtained using CaO/Al_2O by Pasupulety et al. [118]. However, X-ray diffraction result validated that the catalyst was contaminated by H_2O, O_2, CO_2, and other gaseous substances contained in air during storage for reaction. Therefore, thermal treatment before reaction was recommended to improve the catalytic activity and to avoid the gaseous contamination.

Using commercial hydrotalcite MgO/Al_2O_3 (Mg: Al = 3), Xie et al. [113] achieved oil conversions of up to 66% at methanol reflux temperature for the transesterification of soybean oil after a 9 h residence time. Albuquerque et al. [119] have evaluated the MgCa and MgAl oxides catalysts in the transesterification of sunflower oil and have emphasized the influence of molar ratio of metal oxide on the yield of biodiesel. Highest activity was found for a Mg:Ca molar ratio of 3.8, with a FAME yield of 92%, for a methanol:oil molar ratio of 12, at a reaction temperature of 60 °C and 2.5 wt.% of catalyst whereas for Mg:Al at molar ratio of 5.8 the yield reaches a value of 60%. The best performance was observed for the series of MgCa oxides, which could be attributed to the presence of strong basic sites on the surface, mainly associated with $Ca^{2+}\text{–}O^{2-}$ pairs. Moreover, the catalyst could be suitable by reason of easy separation of the catalyst through simple filtration of the catalyst.

High ester yields have also been obtained with Mg/MCM-41, Mg–Al Hydrotalcite, recrystalized hydrotalcite. Particularly, Mg-Al hydrotalcite showed the highest activity (conversion 97%) due to the high basic strength [120]. It may be mentioned that the metal content from oxide catalyst might be leached as a direct consequence of a saponification reaction. Thus, it would also be of great interest from a practical point of view to investigate the effect of ultrasonication on the stability of catalyst.

Several alkali-doped metal oxide catalysts were evaluated by MacLeod et al. [121] the activity in the transesterification of rapeseed oil to biodiesel. Of those evaluated, $LiNO_3/CaO$, $NaNO_3/CaO$, KNO_3/CaO exhibited greater than 99% conversion in a 3 h test. The formation of active centres O^- by substitution of M^+ ion after calcination (600 °C) might have been responsible for the higher activity. There is also some degree of mass transfer limitation, possibly caused by the formation of a glycerol film limiting access to the active sites of the catalyst.

The application of solid *superbase catalysts* such as, Eu_2O_3/Al_2O_3 and KF/Eu_2O_3 in the transesterification of soybean oil has been reported by several researchers [122,123]. The intrinsic basic character of this catalyst system has been probed by TPD-CO_2, wherein it has been observed that the super-basic sites at a temperature of greater than 350 °C could be responsible for higher catalytic activity (>90%). The result demonstrated that the strength of the basicity of the solid catalysts has a direct relationship on the yield of biodiesel production. Thus, the success was based on the ability to prepare catalysts with strong basicity that can make the catalysts efficient for biodiesel production.

The number of well-defined calcium oxide (CaO) complexes that are able to catalyze transesterification reactions efficiently has been significantly expanded in recent years (Fig. 8). The catalytic activity of waste eggshell and oyster shell has been investigated for the transesterification of vegetable oil with methanol [124,125]. CaO decomposed from waste eggshell ($CaCO_3$) and oyster shell ($CaCO_3$) at high temperature has been shown to exhibit the high activity for the transesterification of soybean oil at 70 °C due to its superior basic strength. However, the catalyst underwent significant deactivation during the first reaction cycle probably due to deactivation of the strongest most accessible base sites. The causes of CaO catalyst deactivation have been reported by several authors [126,127]:

(a) The ambient CO_2 and H_2O adsorbed on the basic sites of catalyst;

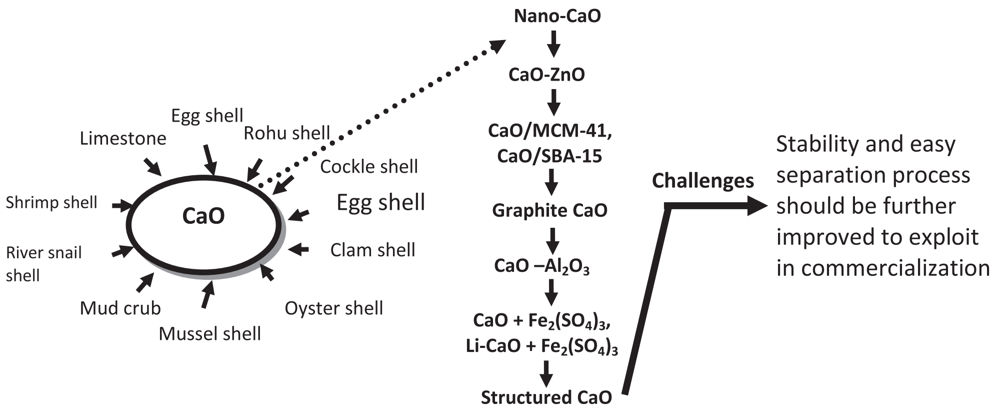


Fig. 8. Recent advances of calcium oxide catalyst for biofuel production.

(b) the basic sites come into contact with H_2O contaminates the reactants; and

(c) the leaching of Ca content which displays the homogeneous contribution toward the base-catalyzed transesterification and thereby, contaminate biodiesel with the leached Ca species.

According to European standard, calcium content of biodiesel is limited to 5 ppm [126]. Recently, the evidence of soap formation during the transesterification reaction has been observed (Fig. 9) by Endalew et al. [127] which could reduce selectivity of the CaO catalyst. All the information provided above affects the lifetime expectancy of CaO catalyst. Thus, the future study should be taken into account considering the aforementioned inconveniences lay on CaO catalyst.

Nano-catalyst stands recently in the center of research due to its large specific surface areas to accelerate selectivity toward the transesterificaton reaction [128]. For example, Reddy et al. [129] reported nano-calcium oxides for biodiesel production at room temperature. However, the separation of CaO from biodiesel after the reaction is very difficult due to gel formation in the lower glycerol layer. The mixture of CaO–ZnO obtained by thermal treatment of calcium zincate at 400 °C is an active and tolerable with FFA for the ethanolysis of sunflower oil [85]. The catalyst showed high activity reaching FAME yield of 90 wt.% using an ethanol:oil molar ratio of 20:1, at 78 °C in the presence of 3 wt.% of catalyst. Calcium manganese oxide [130], Calcium magnesium oxide [131], calcium tin oxide [132] and CaO–MoO3–SBA-15 [133] catalysts were recently identified as an active heterogeneous catalyst for biodiesel production from animal fat; however, the catalyst activation or deactivation mechanisms, its behavior in the production using different feetocks as well as the impacts of its use on the quality of the product remained unclear. Moreover, the catalysts have demonstrated to be less resistant to the reutilization in the ethanolysis, which is due to lixiviation of the active phase.

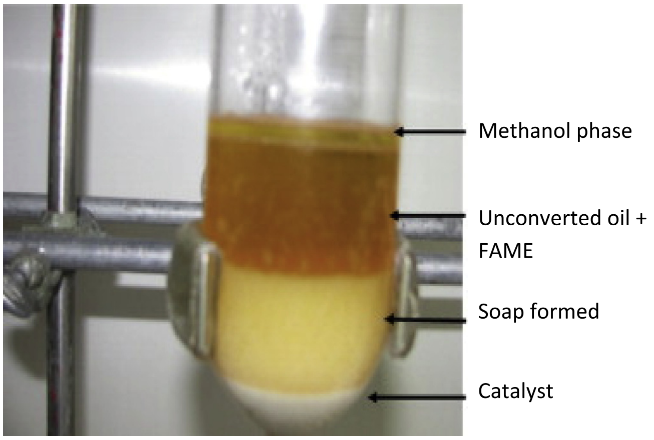


Fig. 9. Soap formation in CaO catalyzed transesterification reaction.

To prevent the lixiviation of catalyst, Sun et al. [134] synthesized CaO/SBA-15 solid base catalyst for biodiesel production. It was reported that the interaction between CaO and silica is strong enough to prevent the lixiviation of the active phase in methanol. A biodiesel yield of as high as 99.1% was achieved on the 0.5Ca/SBA-15 catalyst at a reaction temperature of 200 °C for 8 h. Likewise, graphite oxide (GO) supported CaO was reported as stable in transesterification reaction and maintained high activity (>90%) after four consecutive reaction cycles [135]. It was speculated that the presence of abundant oxygen-containing functional groups on the surface of carbon supports was the key factor for the fabrication of active and stable carbon-supported CaO catalysts. A solid Ca/Al composite oxide-based catalyst was applied transesterification of rapeseed oil with methanol [136]. The results revealed that the catalyst calcined by 1000 °C reused for at least seven cycles with FAME yields maintained above 87%. The catalyst was easily separated from the reaction mixture, as it is insoluble in methanol and methyl esters. Endalew et al. [127] explored new solid $CaO + Fe_2(SO_4)_3$ and $Li–CaO + Fe_2(SO_4)_3$ catalysts which catalyzed a simultaneous esterification and transesterification of jatropha curcas oil with FFA content in a single step. The reaction was performed under reaction conditions of 60 °C reaction temperature, 3 h of reaction time, 6:1 M based alcohol to oil ratio, 5 wt.% catalyst to achieve the conversion of about 98%. However, the catalysts were deactivated by the presence of atmospheric CO_2. Avoidance of atmospheric contact may increase the life of these active base catalysts. Recently, an interesting idea of structure-controlled CaO catalysts has been employed for biodiesel production. A conclusion has been reached by Liu et al. [67] who reported that the flower-like CaO architectures predominantly exposed active O^{2-} on (222) and (400) favorable planes of CaO, resulting in obvious enhancement of catalytic activity and high yield of biodiesel (95%). However, no result regarding the stability of catalyst has been provided.

In similar to CaO, SrO derived from thermal decomposition of $SrCO_3$ and nanocrystalline MgO have been shown to have high applicability for transesterification reaction [137,138]. The conversion over nanocrystalline MgO was 98% compared with 95% over SrO. In the case of MgO, microwave energy could increase the reaction rate because of the microwave radiation that increases the catalyst's interaction with the reactant. Dias et al. [139] took a step forward in the development of these catalysts, reporting the synthesis of similar catalysts, though instead of SrO, a mixture of SrO and MgO was employed as catalyst for the transesterification of soybean oil. Though the catalysts exhibited high FAME yield (95%), fast catalyst deactivation was observed. Thus, important research efforts should be directed in their stabilization and regeneration in transesterification reaction.

The catalytic activity of various Ca-containing catalysts-$CaMnO_3$, $Ca_2Fe_2O_5$, $CaZrO_3$, and $CaO–CeO_2$ in the transesterification of vegetable oil has been compared [140] In particular, $CaZrO_3$ and $CaO–CeO_2$ catalysts retained a high durability even after 7 cycles of successive use. The active species calcium methoxide-like compounds appear to be favored to increase the catalytic activity after calcination at 900 °C. Similarly, the use of supported base catalysts – $Ca(NO_3)_2/Al_2O_3$,$LiNO_3/Al_2O_3$, $Mg(NO_3)_2/Al_2O_3$ and $NaNO_3/Al_2O_3$ was disclosed in a recent paper [8]. Good results in transesterification of palm kernel oil were obtained using $Ca(NO_3)_2/Al_2O_3$ and $LiNO_3/Al_2O_3$ followed by calcination at 450 °C for 3 h whereas calcined $Mg(NO_3)_2/Al_2O_3$ and $NaNO_3/Al_2O_3$ catalyst possessed an inactive magnesium and sodium-aluminate phase, resulting in very low methyl ester formation. A new generation of stable and active aluminum, tin and zinc oxides $((Al_2O_3)_X(SnO)_Y(ZnO)_Z)$ hybrid catalyst has been prepared by Macedo et al. [141]. The catalyst was found a high proportion (80%) of its catalytic activity in the transesterification reaction and recycled it without apparent loss of its activity.

The step forward has come more recently with the discovery of the sodium molybdate (Na_2MoO_4), which offer more stability under the reaction condition [142]. The reusability test demonstrated that the catalyst was found to be completely restorable after being washed in the transesterification reaction. A cellulose catalyst was reported as a more stable catalyst in transesterification reaction [143]. The results revealed that the catalyst retained a high proportion (93%) of its catalytic activity even after more than 50 cycles of successive reuse. The reason attributed to the better stability of catalyst was attributed to the presence of polycyclic aromatic carbon sheets which is hydrophobic and do not allow a water layer to form on its surface.

The development of mesoporous solid is currently an area of extensive research in biodiesel production, which offers many opportunities over microporous materials by being more accessible to reactants. The use of mesoporous catalysts such as KI/silica [144] and $MgO{\cdot}MgAl_2O_4$ [67] have been reported for the transesterification of vegetable oil. Some of these research findings were proven the potential application of catalyst for transesterification reactions; however, from the practical point of view, handling of small particles in large quantities is difficult and limits the possibilities to recover for reuse. In addition, the mesopores of the catalyst can be collapsed at moderate to high temperatures with consequent deactivation of the catalyst, as reported by Sivasamy et al. [7]. Hence, an advanced method of for the synthesis of stable porous catalyst should be taken into account for future area of research.

2.2.3. Ultrasound-assisted biodiesel production

Many research groups have recently focused on the ultrasound-assisted biodiesel production approach to accelerate the reaction rate. A comprehensive review on the current status of ultrasonic assist transesterification was reported by Ramachandran et al. [145] who concluded that the ultrasonic irradiation showed great enhancements on the reaction parameters particularly, yield and reaction time. The yield of biodiesel synthesized using ultrasound was found to be 30–40% more when compared to the corresponding results obtained using conventional stirring reactor system. Choudhury et al. [146,147] reported from the study of biodiesel synthesis from crude *jatropha curcas* that the ultrasound could be enhanced the mass transfer characteristics of the system with 20% reduction in activation energy, as compared to mechanically agitated systems. Ultrasonic-assisted biodiesel synthesis using alkaline earth metal oxides (BaO, SrO) catalyst which have higher basicity, lower solubility in alcohol has been reported by Mootabadi et al. [148]. After 1 h, by using alcohol/oil molar ratio of 9:1, the conversion of oil reached 95%. However, the reusability test of the catalyst indicated the severe drop of activity in the catalyst.

The researchers have been given a great concern about increasing the stability of catalyst (Fig. 10). Kumar et al. [149] studied the stability of Na/SiO_2 catalyst by performing the reusability test. It was reported that the catalyst was maintained yield 97% after three times of successive reuse. A conclusion has been reached by Deng et al. [150] who reported that the mixed Mg/Al oxides catalyst might be deactivated by the surface absorption of by-product glycerol as well as the collapse of the layered structure. Thus, after removing the glycerol on the surface, the catalyst was maintained 90% of FAME yield after 8 times of successive reuse. Same research group [151] have reported another study on the nano Ca–Mg–Al solid base catalyst under ultrasonic radiation in microaqueous media. The yield of 95% biodiesel from Jatropha oils was established with 30 min of reaction time. The catalyst could be reused twelve times after washing of the adsorbed glycerol from the surface of catalyst with ethanol. Recently, Guo et al. [152] have reported the use of Brønsted acidic ionic liquid-based catalyst for Biodiesel production from soybean oil with methanol using under ultrasound irradiation. The optimal conditions were: methanol/oil molar ratio of 9:1, 1.0 wt.% catalyst in oil, ultrasound power of 200 W, and reaction temperature of 60 °C. Under these conditions, the conversion of triglycerides to fatty acid methyl esters was about 93.2% within the reaction time of 60 min.

The effect of alcohol oil molar ratio was investigated by Kalva et al. [153] for the transesterification with ultrasound assistant process and the maximum yield of 98% was obtained at the alcohol to oil molar ratio of 12:1. It was reported that the low intensity of microturbulence could generate enormous interfacial area by cavitation bubbles in oil at the methanol to oil ratio of 12:1, which accelerate the transesterification reaction. In another paper, Choudhury et al. [154] reported that the optimum temperature for the highest yield using ultrasound assistant process was close to boiling point (65 °C) of methanol. The authors envisaged that the influence of cavitation bubbles at this temperature could be negligible and ultrasonic micro-streaming could provide necessary convection in the system to enhance transesterification reaction. Ultrasonic can also grind the catalyst into smaller particles to create new active sites for the subsequent reaction. Thus, the solid catalyst is expected to more active in the ultrasonic-assisted process [155–158]. More recently, a single-step ultrasonic synthesis of biodiesel from high FFA containing vegetable oil like Jatropha curcas using chlorosulfonic acid as a catalyst has been reported by Choudhury et al. [159]. A high conversion rate (93%) was obtained within 4 h, though commercial viability of the catalyst has not been performed.

Ultrasound is known to manifest its chemical and physical effect on a liquid–liquid heterogeneous reaction system through cavitation bubbles. The chemical effects are in terms of the generation of radicals through the dissociation of gas and vapor molecules during the transient collapse of the cavitation bubbles, whereas the physical effects are in terms of the generation of strong convection through microstreaming or microturbulence [160–162]. The chemical effect attribute to the manifestation of the dissociation of lcohol to RO^- and H^+ on basic sites of catalyst surface while the physical effect depends on the intensity of mixing in the reaction system [116,163]. It was reported [147,154,159] that the physical mechanism only responsible for the beneficial action of ultrasound was the formation of fine emulsion between oil and methanol. Due to this, the interfacial area between the reactants increases enormously, assisting to enhance the transesterification reaction

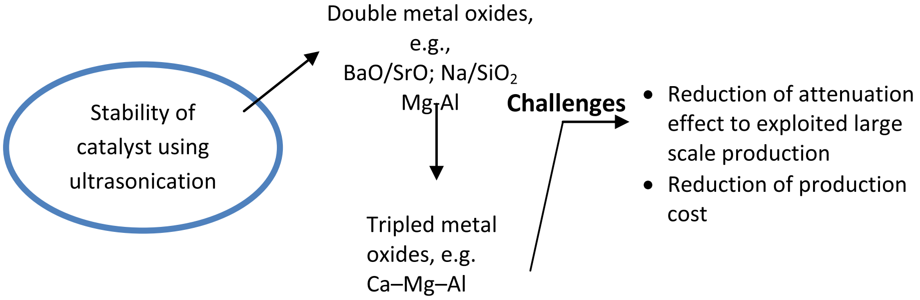
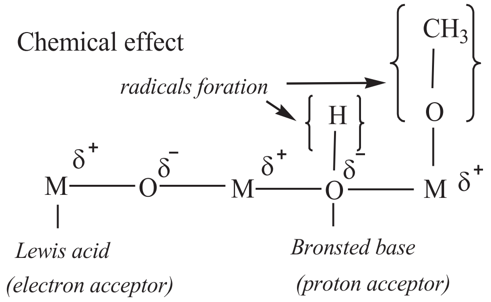


Fig. 10. Stability of catalyst using ultrasound-assisted biofuel production.



Several attempts have been directed by authors to identify the physical mechanism of the enhancement caused by ultrasound. Sivassankar et al. [164] reported that the degassing of the reaction medium intensifies the transient collapse of the cavitation bubble which boosts up the transesterification process. A conclusion has been reached by Bhasakar et al. [165] that the microstreaming produced by ultrasound has a beneficial effect in that it generates a fine emulsion between immiscible phases and increases the interfacial area, which enhances reaction kinetics in the heterogeneously catalyzed reaction. Kalva et al. [153] presumed that the ultrasound provides the mechanical energy for mixing in which the microturbulence generated due to radial motion of bubbles leading to intimate mixing of the immiscible reactants and thus, initiating the transesterification reaction. As reported by Choedkiatsakul et al. [156] that loss of efficiency in the ultrasonic waves transfers through the liquids may be due to the coalescence of small cavitation bubbles into larger ones which act as a barrier to that wave's transfer and the decoupling effect. Thus, it is very important to optimize ultrasound wave amplitude to get higher yield of biodiesel. Despite the faster resultant rate of reaction, the addition of homogeneous catalysts to the ultrasound-assisted biodiesel production is not an attractive idea because of the problems of subsequent product purification and waste management that are seen in the conventional process.

2.2.4. Microwave-assisted biodiesel production

The microwave-assisted route is another method for the synthesis of biodiesel gaining more significance in recent years. Several researchers have been directed toward the development of microwave irradiation process to accelerate the transesterification reaction. Zhang et al. [166] reported that the optimal conditions of reaction temperature 60 °C, methanol/acidified oil mass ratio 2.0:1, catalyst loading 3 g, microwave power 360 W and reaction time 90 min, achieving a biodiesel yield of 98%. Khemthong et al. [167] found that the maximum yield of fatty acid methyl esters reached 96.7% under the optimal condition of reaction time of 4 min with 900 W microwave power, methanol-to-oil ratio of 18:1, and catalyst loading of 15%. Jaliliannosrati et al. [46] obtained high yield of FAME (97.29%) under the optimum conditions: 12.21 min irradiation time, 8.15 ml KOH catalyst loading and 331.52 rpm agitation speed in the 110 W microwave power system. A conclusion has been reached by Li et al. [57] that the reaction time of microwave assisted transesterification was shorter compare to conventional method. Similarly, Yuan et al. [168] reported that the reaction time of biodiesel synthesis using microwave irridation was decreased by 180 min in comparison with conventional heating under the same reaction conditions. The enhanced chemical reaction rate could be due to the following reasons, as speculated by several researchers [169–171].

- Energy transfer from microwaves to the material is believed to occur either through resonance or relaxation, which results in rapid heating and thus, it delivers energy directly to the reactant.
- Microwave assists more molecular friction and collisions in reaction medium, giving rise to intense localized heating and thereby accelerating the chemical reaction.

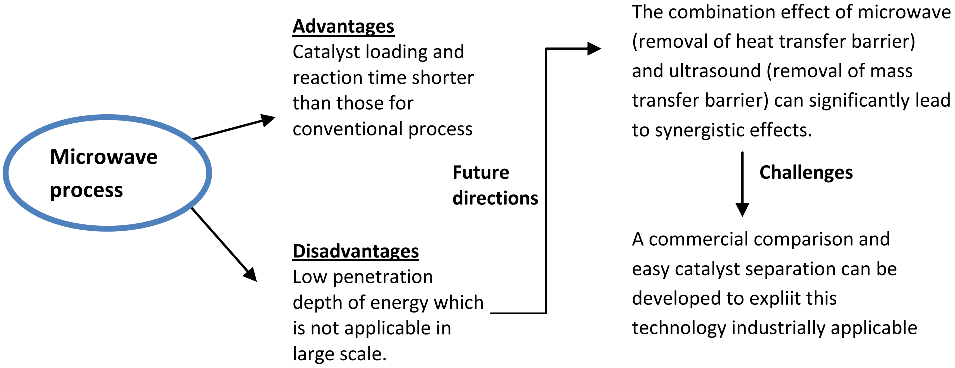


Fig. 11. Advances of microwave-assisted technology in biofuel production.

Motasemi et al. [12] estimated the energy consumption during the biodiesel production using microwave irradiation. It was reported that the average of 2.1277 kW h electrical energy can be produced from one kg biodiesel, while production of one kg biodiesel needs only 0.4681 kW h electricity. Important to underline that the most important limitation of this process is scaling the production up to the industrial scale (large-scale) due to the low penetration depth (a few centimetres) of microwave radiation into the absorbing material. Thus, the combination effect of microwave (removal of heat transfer barrier) and ultrasound (removal of mass transfer barrier) could overcome the limitation of these techniques (Fig. 11). Recently, Gole et al. [172] have reported that the synthesis of biodiesel from non-edible oil using sequential combination of microwave and ultrasound assisted method. It was concluded that the reaction time for the esterification and transesterification using ultrasound alone was 60 min and 20 min respectively and it reduced to only 15 min and 6 min for the combination approach. However, the limitation of this technique leads to high energy consumption for maintaining higher temperature condition. Thus, this emerging technology needs to be further investigated to exploite this approach up to the industrial application. Moreover, easy catalyst separation process is one of the major challenges to highlight real progress of this technology. Hence, an advanced method of non-catalytic supercritical studies is on the anvil.

3. Non-catalyzed biodiesel production

In a more recent development, non-catalytic supercritical transesterification provides a new way of producing biodiesel fuel from bio-based oils (triglycerides) [173,174]. It was reported that biodiesel can be produced at a relatively fast rate without the presence of catalyst by heating up to supercritical stage of methanol, ethanol, propanol and butanol [175]. Thus, the reaction temperature especially supercritical had a favorable influence on FAME yield [176] as shown in Fig. 12. Many methods have been proposed for biodiesel production in supercritical (SC) technology including-SC methanol [177,178], SC ethanol [179], SC methanol with CO_2 as a co-solvent [180] and SC carbon dioxide with enzyme [181]. He et al. [178] subjected soybean oil to transesterification process in the absence of catalyst with the supercritical methanol and found that the maximum biodiesel yield can be obtained at 310 °C. However, the side reactions of unsaturated fatty acid methyl esters (FAME) at reaction temperature above 300 °C lead to much loss of material. Gradual heating procedure could effectively reduce the loss of materials caused by the side reactions of unsaturated FAME, as proposed by He et al. [178] but the high temperature is still very much energy intensive for biodiesel production.

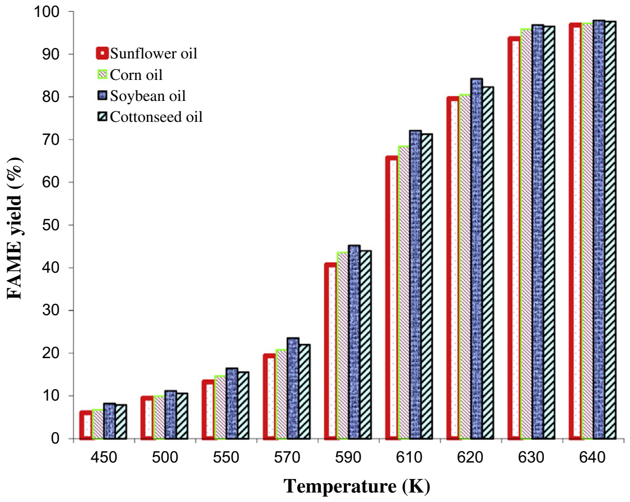


Fig. 12. Changes in yield percentage of methyl esters as treated with supercritical methanol at different temperatures as a function of reaction temperature.

Various co-solvents, such as hexane, heptane, tetrahydrofuran (THF), toluene, nitrogen (N_2) and carbon dioxide (CO_2) had been employed in transesterification process with varying success [182–185], since they are able to reduce supercritical temperature during the reaction. Sawangkeaw et al. [186] studied the effect of tetrahydrofuran (THF) and hexane as co-solvents on production of biodiesel via transesterification in supercritical methanol. The addition of co-solvent allowed the reaction to be completed under milder conditions due to the lower critical properties of the reaction mixture. Moreover, as their boiling points of are close to that of methanol (65 °C, 66 °C and 69 °C for methanol, THF and *n*-hexane, respectively) both co-solvent and methanol could be recovered simultaneously at the end of reaction and recycled. It was reported by Abbaszaadeh et al. [187] that the CO_2 as a cosolvent provide in a single phase that takes only seconds at ambient temperature and pressure (Fig. 13). A some what related conclusion has been reached by Pinnarat et al. [188] who reported that the CO_2 is a good solvent to allow reaction mixture in a single phase at relatively lower temperature. This could be achieved through the presence of co-solvent molecules which enhanced the local density of the mixture homogeneity by attracting solvent around them [189]. Thus, the supercritical method with cosolvent could provide improved phase solubility, decrease mass transfer limitations and provide higher reaction rates. Though, the usage of co-solvents in biodiesel production process can also be highly selective depending on feedstocks and process condition [190]. Thus, future studies on the effect of co-solvents at low methanol to oil molar ratios are necessary to clarify the role of co-solvents in biodiesel production with SCM.

Demirbas [191] and Yoo et al. [192] applied CaO and metal oxide (SrO, CaO, ZnO) catalysts for biodiesel production with SCM, where maximum conversion is achieved at relatively low temperatures and pressures compared with catalyst-free conditions. The addition of heterogeneous catalysts to the SCM reaction is not a striking initiative to lower the operating parameters, since the subsequent catalyst separation is not easier and cannot be recycled unlike the homogeneous catalysts. Thus, further studies on heterogeneous catalysts in the SCM reaction, such as the effect of water and FFAs, and the reusability of catalysts would be a demand of advanced research.

The influence of process parameters has been optimized for non-catalytic transesterification by several researchers to get high yield of biodiesel. Hawash et al. [179] found that the conversion of

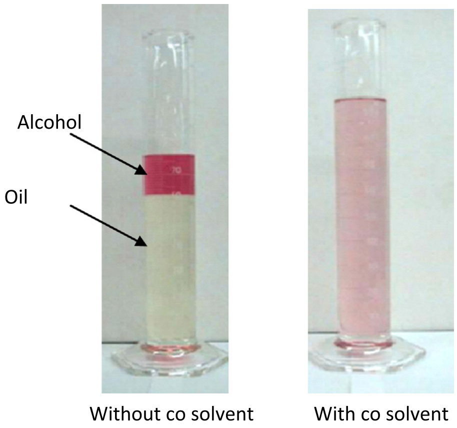


Fig. 13. Mixture of oil and alcohol with the use and without the use of co-solvent.

Jatropa oil almost tripled when the temperature increased from 239 to 340 °C. Similar results have been reported by Ilham et al. [16]. After 12 min of reaction at 350 °C and pressure 200 bar, rapeseed oil treated with supercritical dimethyl carbonate reached 94% yield of fatty acid methyl ester. Likewise, the conversion was 96% in case of coconut oil and palm kernel oil over the same temperature range with molar ratio of methanol to oil 4 and the reaction time of 10 min [193]. Other results consistent with these findings are from Silva et al. [194]. However, the conversion below the solvent critical temperature is very low. It should be noted that the critical temperatures of methanol and ethanol are 240 and 243 °C (Table 1), respectively, and, therefore, the conditions at 200 °C represent a subcritical state of the medium, as classified by Madras et al. [181]. However, the yield drastically increased when the temperature was changed from subcritical to supercritical state for transesterification with methanol or ethanol. This could be due to the absence of mass transfer interphase under these conditions to limit the reaction rate. However, the temperature beyond the super the supercritical, the FAME yield could be dropped [14]. According to Gui et al. [14] the temperature above supercritical, unsaturated fatty acids such as oleic acid and linoleic acid tends to decompose via isomerization of the double bond functional group from cis-type carbon bonding ($C{=}C$) into trans-type carbon bonding ($C{=}C$), which is naturally unstable fatty acids. Therefore, it was highly possible to drop FAME yield with increasing temperature especially at conditions beyond the supercritical point. Although the transesterification of triglycerides at higher temperature and pressure has been analyzed in detail, the kinetic expression which could correlate the experimental data over wider range of pressure and temperature should be taken into account for further studeis. The influence of different alcohols on supercritical transesterification has also been investigated. For instance, in methanol, the conversion increased from 78% to 96% with the increase in temperature [195]. A similar trend was observed for conversions in ethanol but the conversions were higher. Higher conversions in ethanol may be attributed to the solubility of the oil in the system [196]. Because the solubility parameter of ethanol is lower than that of methanol and is closer to the solubility parameter of the oil, the conversions are higher in ethanol compared to the conversions obtained in methanol. A number of researchers have demonstrated the importance of different variables influencing the rate of reaction, and among them the temperature and molar ratio of alcohol to oil seem to be the most important.

Table 1
Critical temperatures and critical pressures of various alcohols.

Alcohol	Critical temperature (°C)	Critical pressure (bar)
Methanol	240	81
Ethanol	243.2	64
1-Propanol	264.2	51
1-Butanol	287.2	49

Few studies have focused on the costs of investment under the supercritical conditions. With regard to environmentally friendly aspects, biodiesel in SCM does not require any catalysts and does not generate significant wastes. Moreover, this method is highly tolerant against the presence of water in oils/fats, thus, being applicable for various low-grade waste oils/fats [197]. However, the usage of energy intensive synthesis process is the main disadvantageous to push this technology from laboratory to industrial scale (Fig. 14). Thus, future study should focus on the reduction of extreme operating parameters while maintaining the high conversion rate.

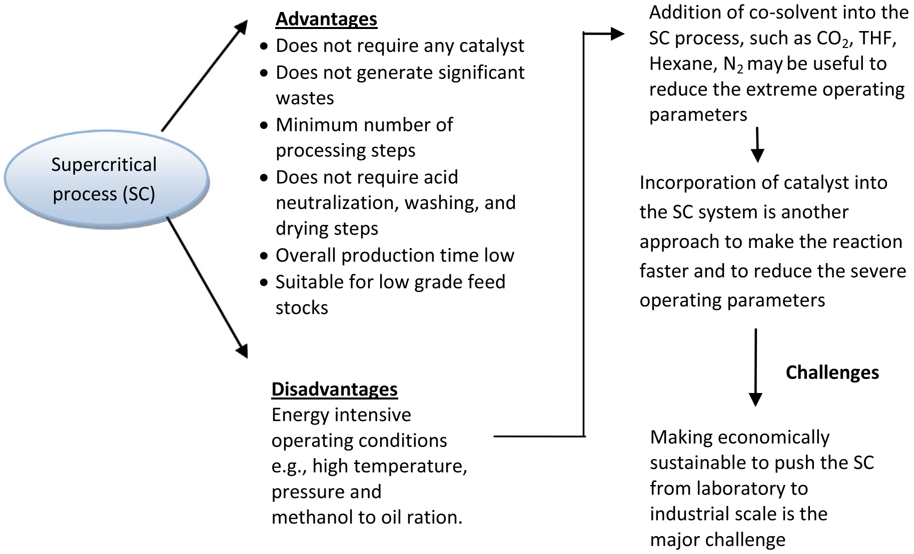


Fig. 14. Recent progresses in supercritical process.

4. Challenges and future outlook

A number of studies have been reported on using solid basic or acidic *catalyst for biodiesel production having a* size of nanometer to macroscopic scale [67,198] shown in Fig. 15. Since nanocatalysts have a large surface area compared to macroscopic catalyst, they are attractive candidates as catalysts for biodiesel production. Despite the high percentage of fatty acid methyl ester (FAME) (>90%) achieved by nano catalysts [199–202], many of the catalytic systems have not been commercialized because of the difficulties encountered when trying to separate such catalysts from the reaction media. One of the main reasons to consider heterogeneous catalysis for industrial processes is the ease of catalyst separation after the reaction. It may be pointout that the separation processes represent more than half of the total investment in equipment for the fuel and chemical industries [6]. Thus, the separation and easy handling process need to be developed further to exploit the nanocatalyst for industrialization. In addition, the small particle size gives rise to several problems such as high pressure drops and poor

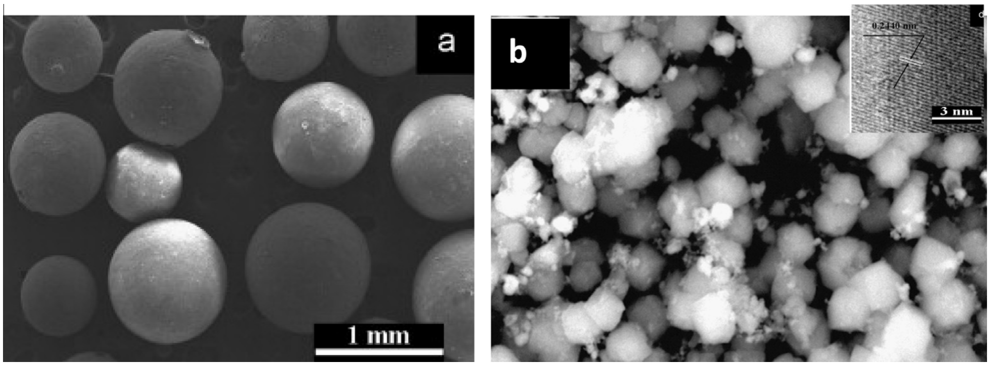


Fig. 15. Catalyst employed for biodiesel production; (a) macro catalyst; (b) nano catalyst.

contact efficiency [203,204]. Therefore, the extensive work should be invested with emphasis placed on optimum reactor design to overcome the addressed issues.

Identifying the active site of catalyst is the initial step to design and optimization of a new catalyst. In simulating the active site, one should consider the effects of the local environment on the active site as well the influence of process variables. Moreover, the structure/selectivity relationships needs for nanocatalyst to make it potential for biodiesel production. The incorporation of catalytic functional group into nanocatalyst may create new kinds of assemblies to enhance selectivity toward the transesterification reaction.

The utilization of macrocatalyst catalyst in transesterification reactions could be a practical in view of following advantages; (i) easy of separation of the catalyst by simple filtration, (ii) the catalyst is easy to handle and reusable for several times. However, leaching is one of the main hurdle in both of nano and macro catalyst. Hence, further research should be addressed on the the elementary mechanisms that lead to deactivation or degradation of catalyst structure. In this case, the incorporation of stabilizer into the catalyst may be one of the approaches to anchor the active site of catalyst and thus, control the leaching or deactivation of catalyst. Additionally, fabrication methods of macro or nano catalyst should be developed to the point where size and functionality of materials can be controlled. In the design of a catalyst, the shape should also be taken into account, as the shape preferably; spherical could minimize the abrasion of catalyst in the reaction medium [205].

Recently, mesoporous catalysts have received a great attention for biodiesel production. May be mentioned that porous materials offer the large accessible surface area for catalyst to react. Does mesoporous catalyst benefit from long-ranged ordering of porosity? It was reported by Sivasamy et al. [7] that the mesopores of the catalyst can be collapsed at moderate to high temperatures with consequent deactivation of the catalyst. Thus, the stability of mesopores properties of catalyst is crucial for the future direction of research. It may be reasonable to state that the triglyceride molecule can be diffused into catalyst having pore diameter of more than 5 nm [206] shown in Fig. 16. The diffusion of the triglyceride molecule could be restricted when the diameter of the catalyst was less than 5 nm and this would in turn, be decreased the catalytic activity [207]. Besides, the catalyst with high mechanical strength is essential, which could be decisive for long term stability of catalyst.

There are various process technologies based on the use of alternate energy sources such as, ultrasound and microwave. These

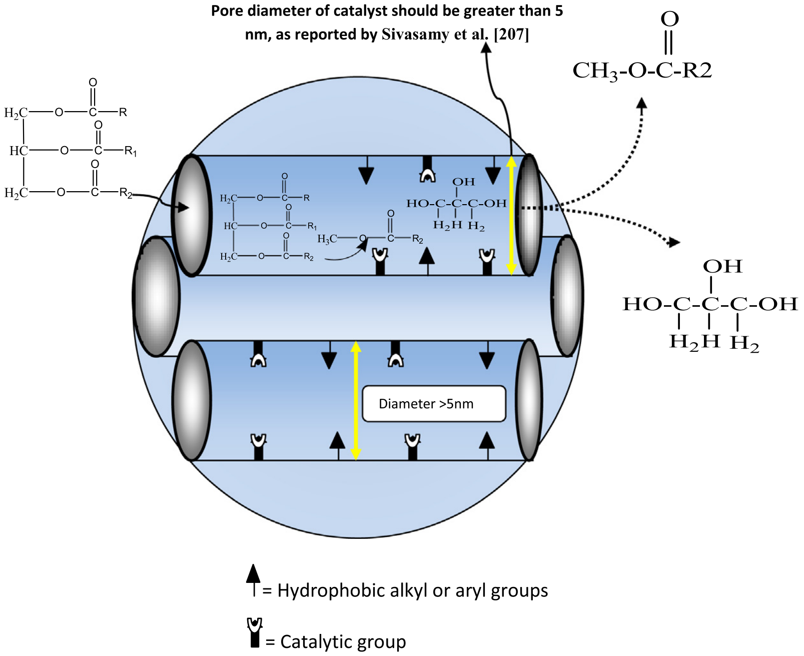


Fig. 16. Schematic of mesoporous hydrophobic group for FA esterification with alcohol.

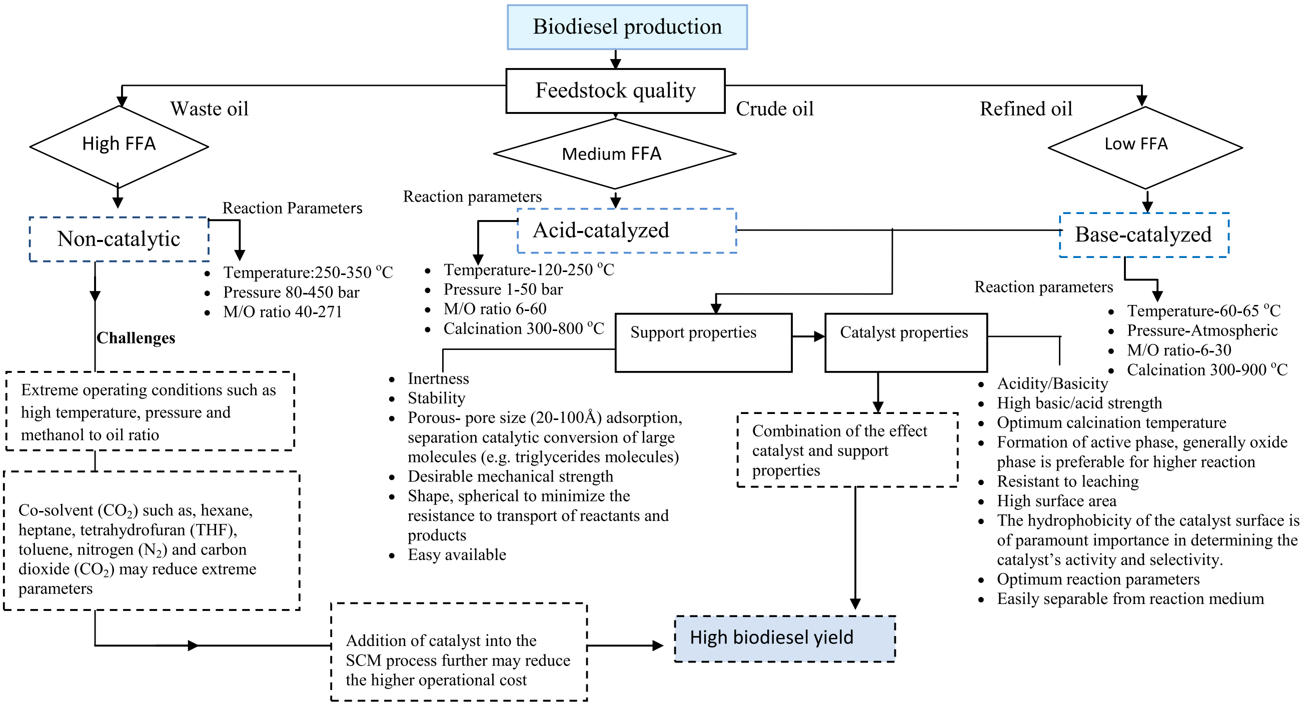


Fig. 17. Design of catalyst consideration of biodiesel production.

techniques have certain limitations such as attenuation effect in the case of ultrasound while uncontrolled heating for microwave and low penetration depth of energy inside the reactant. The limitation of these techniques could be overcome by the combinational approach and the combination effect of microwave (removal of heat transfer barrier) and ultrasound (removal of mass transfer barrier) can significantly lead to synergistic effects. Thus, this could improve the yield of biodiesel and reduce the process time as compared to conventional methods. Process integration refers to a holistic approach that should be taken into account in order to achieve the minimization of the overall investment cost, higher product yields and an efficient process design. Therefore, an approach to choose proper catalyst for biodiesel production is proposed in Fig. 17.

The magnitude of biofuel impacts depend on the prize and availability of feedstock. A more sustainable biofuels strategy would be a utilization of widely available agricultural biomass feedstocks to the largest extent possible, ultimately drawing upon lignocellulosic biomass instead of only the edible oils and triglyceride fractions. The first generation biofuel have drawbacks in that they depend on feedstocks that are not sufficiently available to satisfy the demands currently met by fossil fuel. Thus, the development of second and third generation biofuels that utilize lignocellulosic biomass and algae could be a better option to allow large scale production of sustainable biofuels. It is worth mentioning that the waste carbon dioxide exists in plenty and causing a negative impact on the environment by including contributing to the greenhouse effect. With this in mind, it would be striking to utilize waste carbon dioxide as a potential unlimited feedstock for biodiesel production that can be employed as drop-in replacements for fossil fuels.

5. Conclusions

Several research efforts have been made to continually search for a more economical transesterification route at different temperatures using either in the presence or absence of catalysts. From a process perspective, the heterogeneous catalysts have the benefit of the elimination of several steps of washing of biodiesel, ensuring thereby, and higher proficiency. A great variety of solid acid/base catalysts have been reported in the literature with a high yield (>90%) of biodiesel. However, it is not possible with any of the catalysts presented in this review to possess simultaneously a strong acid/base, high surface area and inexpensive catalyst production. Certainly, a compromise needs to be reached in each case. Several recent studies have reported the technical feasibility of biodiesel production via heterogeneous acid-catalyzed transesterification. However, the acid catalysts are known to show a much lower catalytic activity in transesterification reactions, compared with alkaline catalysts, and this lack of activity is usually compensated by operating at higher temperatures. Thus, the design of the solid acid catalyst with economic, versatile and efficient and economically viable is the major challenge. The development of a new class of recyclable bifunctional solid catalyst with higher tolerance to water and FFA might be one of the approaches to reduce operation cost of biodiesel. There are various process intensification technologies in biodiesel production based on the use of alternate energy sources such as ultrasound and microwave. However, it is important to underline that the most important limitation of this process is scaling the production up to the industrial scale due to the low penetration depth (a few centimetres) of microwave radiation into the absorbing material. Thus, the combination effect of microwave (removal of heat transfer barrier) and ultrasound (removal of mass transfer barrier) could overcome the limitation of these techniques. Though, viability of these processes should be proved by economical analysis to push the technology from laboratory to industial scale. Supercritical fluid has recently received attention as a new reaction field for biodiesel production, as it is highly tolerant against the presence of free fatty acids and water in oil or fats. Compared to the catalyzed method, the non-catalytic supercritical method can be applied for various types of oil/fats and their wastes as a raw material to produce biodiesel. Biodiesel production with SCM has remarkably strong advantages, such as fast reaction time, feedstock flexibility and environmental friendliness, but its extreme operating parameters, such as higher temperatures of 350–400 °C, pressures of 200–450 bar, and methanol to methanol to oil ratio of 40–271 are the major challenges from the research point of view. Biodiesel feedstocks including pure vegetable oils, waste cooking oils, and animal fat will become heavier and sourer with time. This will require future catalysts, which are higher in activity, more poison tolerant and stable for longer periods. Furthermore, the diversification of feedstocks and conversion technologies would be a potential mainstay for the long-term security of the supply of sustainable biofuels. Ultimately, we hope to see a holistic utilization of waste feedstock and carbon dioxide through the most efficient processes, resulting in a cleaner, more sustainable basis for the production of biofuels.

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