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A Review on Processing Technology for Biodiesel Production

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ABSTRACT

Current environmental issues and resource demands are driving the global development of renewable energy. This study reviews various technologies that have been used for biodiesel production till date. 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 ultrasound and microwave assisted reaction. The inconveniences of the conventional method for biodiesel production by alkaline catalysis suggests research towards alternative methods with the non-catalytic transesterification using an alcohol at supercritical conditions proposed as a promising technique for biodiesel production. However, application of this methodology has some limitations, like operating conditions (elevated temperature and pressure and higher amounts of alcohol) which result in high energy costs and degradation of the products generated. Novel approach is also discussed such as the one proposed to convert lipid-rich, dry algae into Fatty Acid Ethyl Esters (FAEE) under microwave-mediated supercritical ethanol (MW-SCE) conditions with a non-catalytic transesterification approach.

Key words: Microwave irradiation, non-catalytic reaction, green chemistry, dimethyl carbonate, sub-critical condition

INTRODUCTION

From the beginning, human being has always been dependant on the use of energy in every field of life such as agriculture, transportation, industry, food and production of electricity (Silitonga *et al.*, 2011; Enweremadu and Mbarawa, 2009). With the increase in population, the requirement of energy has also increased. In tandem with the increasing requirement for the energy, the utilisation of fossil fuels has also increased. Fossil fuel combustion is responsible for the majority of CO_2 emissions caused by mankind. There are several theories as to the causes of climate change but it is widely accepted that the major driving force is the increased levels of greenhouse gases, such as CO_2 and methane, being released into the atmosphere. The level of CO_2 in the atmosphere has increased mainly due to combustion of fossil fuels, cement production, gas flaring, deforestation and changes in land usage. Electricity generation is the largest emitter of CO_2, accounting for approximately 41% of all CO_2 emissions in the US in 2006, followed by the transport sector at 33%. Similarly, in the UK, energy and transport are the sectors responsible for the largest portions of CO_2 emissions (Forster *et al.*, 2007). In an attempt to reduce CO_2 emissions, the

Table 1: Major benefits of biofuels

Environmental impacts
Reduction of greenhouse gasses
Reduction of air pollution
Higher combustion efficiency
Easily biodegradable
Carbon neutral
Energy security
Domestically distributed
Supply reliability
Reducing use of fossil fuels
Reducing the dependency on imported petroleum
Renewable
Fuel diversity
Economic impacts
Sustainability
Increased number of rural manufacturing jobs
Increased farmer income
Agricultural development

European Commission, for example, had set targets within the European Union (EU), requiring EU member states to increase the role of renewable resources in total energy production to 12% by 2010 and ultimately to 20% by 2020 with 33% of electricity production needing to come from renewable resources (Council of the European Union, 2007). The US government has passed the Energy Independence and Security Act (EISA) in 2007 which requires a gradual increase in the production of renewable fuels to reach 36 billion gallons per year by 2022. Furthermore, 28 states have passed their own mandatory renewable energy legislation. For example, Arizona and California will replace 15 and 20% of their electricity sales with renewable energy by 2020, respectively. Texas has a mandate for 5880 MW of renewable electricity capacity by 2015. Similarly other states have mandates to reduce greenhouse gas (GHG) emissions. For instance, Minnesota's strategic goal is to reduce GHG emissions by 80% between 2005 and 2050 (Yang *et al.*, 2011; Hoekman, 2009). As a result, there is a significant drive in research and initiatives for the use of renewable and sustainable fuels to facilitate the development of society while minimizing the impact on the environment. Table 1 shows the main advantages of using biofuels such as biodiesel (Demirbas, 2009).

Renewable energy has grown rapidly in recent years. Overall, renewables produced 16.5% of world primary energy in 2005. Renewable technologies have been growing at rates of 15 to 60% annually since the late 1990s. It is this group of technologies that is projected to grow the fastest in the coming decades, making renewables a highly significant and potentially majority share of world energy (Martinot *et al.*, 2007; Turton and Barreto, 2006). Problems with energy supply and use of fossil fuel are related not only to global warming but also to such environmental concerns as air pollution, acid precipitation, ozone depletion, forest destruction and emission of radioactive substances. These issues must be taken into consideration simultaneously if humanity is to achieve a bright energy future with minimal environmental impacts. Detailed information on these gaseous and particulate pollutants and their impacts on the environment and human bodies have been presented by Dincer (2000, 2001). There is an urgent need to develop green energy strategies for sustainable future without any negative environmental and societal impacts. The concept of sustainable development is something which goes hand in hand with Green Chemistry. In order to achieve sustainable development mankind needs to move away from petrochemical feedstocks to renewable alternatives. One potential pathway to the production of alternative renewable products is the use of agricultural, forestry and municipal waste materials. The move away from our reliance on petrochemical feedstocks to a more sustainable society will result in a significant reduction in our impact on the environment (Fischer and Schrattenholzer, 2001).

The aims of this review are closely tied in with the concepts of renewable materials and sustainability but the key issue is to ensure that the production of these materials is carried out using "green" methods and technology. This study reviews biodiesel production by transesterification of triglycerides from a catalytic standpoint. The need to use heterogeneous catalysts and to replace or complement the current homogeneous catalysts with the heterogeneous ones, to incorporate catalysts that are effective for a broader spectrum of reactants that can tolerate higher levels of impurities are some of the key issues that will be looked into. In this regards, this study examined the reported effects of different catalysts in producing biodiesel fuel. The other part of the review will look into the non-catalytic process of biodiesel production. There have been only a few studies on non-catalytic esterification and transesterification reactions which lead to much simpler purification and environmentally friendly processes (Diasakou *et al*., 1998; Kusdiana and Saka, 2001; Yujaroen *et al*., 2009; Yamazaki *et al*., 2007; Joelianingsih *et al*., 2008). Most of these studies were conducted under pressurized conditions, i.e., supercritical or subcritical conditions of methanol. However the processes revealed in these works are not easily applicable to actual production of biodiesel due to significantly high production and capital costs required. In addition, these processes require severe operating conditions such as high pressure, high temperature and high molar ratio of methanol including uncertain safety aspects. Microwaves have the ability to induce reactions even in solvent-free conditions offering "Green Chemistry" solutions to many environmental problems related to hazardous and toxic contaminants. Due to these advantages, microwaves provide for tremendous opportunities to improve biodiesel conversion processes from different feedstock and oils. The intention of this review is to provide the basics of microwave energy applications specific to biodiesel preparation and processing, preliminary understanding and explanation of microwave effect on the chemical reactions (extraction and transesterification), update on process utilization and improvements and information related to different process configurations and reactor designs available for biodiesel production.

CURRENT BIODIESEL PRODUCTION TECHNOLOGIES USING CATALYSTS

Biodiesel refers to a diesel-equivalent renewable, sustainable, biodegradable fuel derived by chemical modification or specifically by the transesterification (alcoholysis) of fats and vegetable oils (Srivastava and Prasad, 2000; Meher *et al*., 2006). Transesterification is a stepwise process and excess alcohol is used to drive the reaction to the forward direction (pseudo-first order) as detailed in Fig. 1 (Meher *et al*., 2006; Ataya *et al*., 2006). Biodiesel is a clear amber-yellow liquid with a viscosity similar to that of petrodiesel and is generally synthesized via liquid base catalysed transesterification of C_{14}-C_{20} triacylglyceride (TAG) components of lipids with C_1-C_2 alcohols into Fatty Acid Methyl Esters (FAMEs) which constitute biodiesel, alongside glycerol as a potentially valuable by-product. While the use of higher (e.g., C_4) alcohols is also possible and advantageous in respect of producing a less polar and corrosive FAME with reduced cloud and pour points, the current high cost of longer chain alcohols and difficulties associated with separating the heavier FAME product from unreacted alcohol and glycerol, remain problematic (Demirbas, 2009).

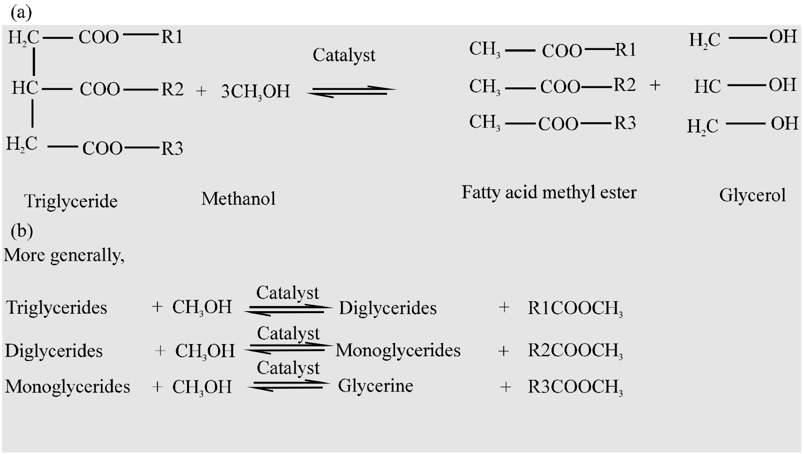

Fig. 1(a-b): Transesterification reactions of glycerides with methanol, (a) Overall reaction and (b) Stepwise consecutive and reversible reactions (Islam *et al*., 2013). The R1, R2 and R3 are alkyl group

Biodiesel, is an alternative fuel for internal combustion engines and can be used directly to run existing diesel engines or as a mixture with crude oil diesel. The main advantages of using biodiesel is that it emits low greenhouse gases and it can reduce net carbon dioxide emissions by 78% on a life-cycle basis when compared to conventional diesel fuel (Mittelbach and Gangl, 2001).

Biodiesel is non-flammable and, in contrast to petrodiesel, is non-explosive with a flash point of 423 K for biodiesel as compared to 337 K for petrodiesel. The biodiesel has oxygen content of about 11-15% in the molecular structure which helps to speed up the combustion process in compression ignition engines and decreases pollutants such as unburned hydrocarbons by 45.2%, particulate matter emissions by 66.7% and carbon monoxide (CO) emissions by 46.7% (Murillo *et al*., 2007; Lapuerta *et al*., 2008).

Biodiesel production requires a feedstock (fat or oil) and an alcohol. Typical raw materials of biodiesel are rapeseed oil, canola oil, soybean oil, sunflower oil and palm oil. Beef and sheep tallow and poultry oil from animal sources and cooking oil are also sources of raw materials. There are various other biodiesel sources: Almond andiroba (*Carapa guianensis*), babassu (*Orbignia* sp.), barley, camelina (*Camelina sativa*), coconut, copra, cumaru (*Dipteryx odorata*), Cynara cardunculus, fish oil, ground nut, Jatropha curcas, karanja (*Pongamia glabra*), laurel, microalgae (*Chlorella vulgaris*), oat, piqui (*Caryocar* sp.), poppy seed, rice, rubber seed, sesame, sorghum, tobacco seed and wheat (Pinto *et al*., 2005). The conventional biodiesel production technique is transesterification by the chemical approach which is a well-developed technology that has been commercialized world wide. The common production methodologies have been well reviewed by other research previously (Srivastava and Prasad, 2000; Knothe *et al*., 2005; Mittelbach and Remschmidt, 2006; Meher *et al*., 2006; Demirbas, 2009; Knothe, 2010; Sharma *et al*., 2011a; Santacesaria *et al*., 2012; Talebian-Kiakalaieh *et al*., 2013; Hama and Kondo, 2013; Atadashi *et al*., 2013; Sani *et al*., 2014). Typically, depending on the quality of the feedstock, either esterification or transesterification reactions are used for biodiesel production. In most cases, a catalyst also is present to increase the rate of reaction and the reaction yield. For the classification of the biodiesel production processes, it is convenient to divide them into two broad categories; catalytic and non-catalytic, where the catalytic is further divided into different sub-groups as shown in Fig. 2.

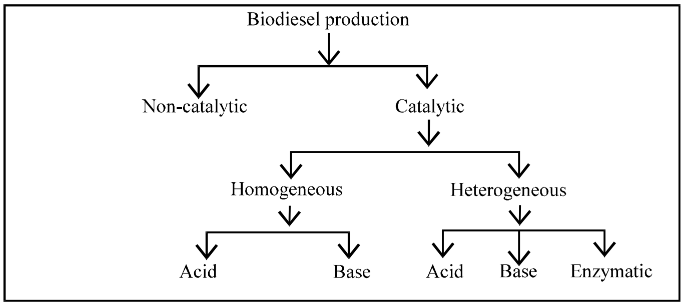

Fig. 2: Classification of biodiesel production processes based on reaction methodology

Homogeneous catalytic reaction: Homogeneous base-catalyzed transesterification is the most common method for biodiesel production whereby sodium hydroxide (NaOH), potassium hydroxide (KOH) and sodium methoxide (CH3ONa) are the most common alkaline (base) catalysts. Sodium methylate (sodium methoxide) is more effective than NaOH and KOH as a catalyst but it is more expensive. Base catalysts are very sensitive to the presence of water and free fatty acids. The amount of sodium methoxide required is 0.3 to 0.5% of the weight of the oil. A higher amount of catalyst (0.5 to 1.5% of the weight of the oil) is required when NaOH or KOH is used. NaOH and KOH also lead to water formation which slows the reaction rate and causes soap formation. Methanol is the most common alcohol used for con-version of fats and oils to biodiesel. Methanol is flamable, so proper handling is required for safety. Since transesterification is a reversible reaction, excess alcohol is used to drive the reversible reaction forward in order to increase the yields of the alkyl esters and to assist phase separation from the glycerol. This method works well if the free fatty acid, moisture and phosphorous contents of oil/fat are less than 0.1 percent and less than 10 ppm, respectively. Oil and fat that have high free fatty acid content will cause soap formation that will pose adverse effects on down stream processing and leads to yield reduction (Canakci and van Gerpen, 2003; Demirbas, 2008a). Methanol and oil do not mix well and vigorous mixing at the beginning of the reaction improves reaction rates. Near the end of the reaction, reduced mixing helps the separation of glycerol and the reaction would precede faster in the top layer which is oil and methanol. The reaction is usually conducted below the boiling point of methanol (60°C) and the reaction may take between 30 to 90 min for completion (Srivastava and Prasad, 2000; Knothe *et al.*, 2005; Van Gerpen, 2005; Mittelbach and Remschmidt, 2006; Meher *et al.*, 2006; Demirbas, 2009; Knothe, 2010). A homogeneous acid catalyst, such as sulfuric acid or hydrochloric acid can also be used (Furuta *et al.*, 2004; Lotero *et al.*, 2005; Jacobson *et al.*, 2008) which does not produce soap and increase the fuel production. However, corrosiveness and the down-streaming separation are the main problems. One advantage of acid catalysts over base catalysts is their low susceptibility to the presence of FFA in the starting feedstock. However, acid-catalyzed transesterification is especially sensitive to water concentration. It was demonstrated previously, that as little as 0.1 wt.% water in the reaction mixture was able to affect biodiesel yields. The reaction is almost completely inhibited at 5 wt% water concentration (Zhang *et al.*, 2003; Canakci and van Gerpen, 2003). Further to that, the use of these strong homogeneous acid catalysts is hazardous, generates much waste water during product washing and the homogeneous catalysts are not recoverable (Zhang *et al.*, 2003). Acid catalysts also require long reaction time for completion and this may not be practical for industrial application. The long reaction time and difficulty in catalyst separation due to the corrosive nature of the catalyst make homogeneous catalysts unfavourable (Zhang *et al.*, 2003; Wang *et al.*, 2006). Though great efforts have been placed in the improvement of this process, it still suffers from high production costs and environmental concerns, e.g., wastewater, chemical disposal and low quality of the glycerol co-product.

The base-catalyzed transesterification cannot handle conversion of Free Fatty Acid (FFA) effectively and often times lead to soap formation. On the other hand, the acid process is limited to only the esterification reaction, i.e., conversion of FFA into biodiesel because the rate of transesterification is too slow to make it feasible for industrial production. Therefore, given an oil source that contains a large amount of FFA, only a combination of the acid and alkaline processes can fully utilize the feedstock oil. As a result, capital investment is doubled, as well as the operating cost, leading biodiesel to cost higher than petroleum diesel. Industrial scale biodiesel production employing homogeneous base or acid-catalyzed process is still favorable worldwide despite the issues discussed earlier. The main reason is due to the fact that it is kinetically much faster than heterogeneously catalyzed transesterification and is economically viable.

Heterogeneous catalytic reaction: Improving the process for biodiesel production has been ongoing for decades. The ideal process would involve a continuous flow reaction that neither deactivate nor consume the catalyst and that minimizes or eliminates the need for multitudinous downstream separation and purification steps. The processes utilizing homogeneous catalysis, involve utilization of a catalyst that is soluble in alcohol. In these systems the catalyst ends up in the by-products and it is not recovered for re-use. The problems with separation and soap formation have prompted researches to explore the use of heterogeneous non-enzymatic catalysts. Heterogeneous catalysis technology has been developed to adapt the natural characteristics of biodiesel feedstock and existing transesterification technology. Utilization of heterogeneous catalyst for biodiesel production has offered some relief to biodiesel producers by improving their ability to process alternative and cheaper feedstock with simplified processes and cheaper manufacturing processes with prolonged catalyst life time. The three factors namely catalytic activity, catalyst life and oil flexibility have tremendous impact on the cost of biodiesel (Yan *et al.*, 2010). Many types of heterogeneous catalysts have been used recently for biodiesel production such as ion exchange resins (Furuta *et al.*, 2006; Park *et al.*, 2008), sulfated oxides (Holser *et al.*, 2006; Alba-Rubio *et al.*, 2010) and heterogeneous base catalysts like transition metal oxide and derivatives (Sreeprasanth *et al.*, 2006; Antunes *et al.*, 2008), boron group base heterogeneous catalyst (Umdu *et al.*, 2009; Xu *et al.*, 2008; Boz *et al.*, 2009; Noiroj *et al.*, 2009; Chen and Fang, 2011; Ilgen, 2011), alkaline earth metal oxides and derivatives (Wang and Yang, 2007; Lopez *et al.*, 2005; Yoo *et al.*, 2010), mixed metal oxides and derivatives (Wang and Yang, 2007; McNeff *et al.*, 2008; Xu *et al.*, 2008; Wang and Yang, 2007), alkali metal oxides and derivatives (Ebiura *et al.*, 2005; Arzamendi *et al.*, 2007), waste material based heterogeneous catalyst (Deka and Basumatary, 2011; Chakraborty *et al.*, 2011), carbon based heterogeneous catalyst (Shu *et al.*, 2010; Dehkhoda *et al.*, 2010) have been used in various biodiesel processes. In general, the heterogeneous catalysts are designed for continuous operation and produce high-purity glycerine (greater than 98%). The product, fatty acid esters, does not require water washing and yields are generally high. However, in most of the solid catalyzed processes, the reaction proceeds at a relatively slower rate compared to the homogeneous catalyzed process. The presence of heterogeneous catalysts turns the reaction mixture into a three-phase system, i.e., oil-methanol-catalyst which protracts the reaction for the purpose of effective mass transfer. For this reason, the reaction conditions of heterogeneous catalysis are intensified to enhance its sluggish reaction rates by increasing reaction temperature (100-250°C), catalyst amount (3-10 wt%) and methanol/oil molar ratio (10:1-25:1). Normally, the heterogeneous catalyst systems operate under high temperature and pressure to achieve conversions greater than 90%, compared to homogeneous catalysts, hence making them more energy intensive (Liu *et al.*, 2008; McNeff *et al.*, 2008). To our knowledge, no heterogeneous catalyst for transesterification is yet commercially available that operates under mild reaction conditions (20-60°C). Other main problems with heterogeneous catalysts are their deactivation with time owing to phenomena, such as poisoning, coking, sintering and leaching (Sivasamy *et al.*, 2009). The problem of poisoning is particularly evident when the process involves used oils (Lam *et al.*, 2010). More general and dramatic is catalyst leaching which not only can increase the operational cost as a result of replacing the catalyst but also leads to product contamination. In general, the best catalysts must have several qualities i.e., catalyze transesterification and esterification, not deactivated by water, stable, do not give rise to leaching, active at low temperature and have high selectivity. More efficient heterogeneous catalysts require improvement in catalytic activity and selectivity. Both these aspects rely on the tailor-design of catalytic materials with desired structure and active site dispersion. It is crucial that the surface of these heterogeneous materials should display some hydrophobic character to promote the preferential adsorption of triglycerides and to avoid deactivation of catalytic sites by strong adsorption of polar by-products such as glycerol and water (Lotero *et al.*, 2005). The catalyst efficiency depends on several factors such as specific surface area, pore size, pore volume and active site concentration. Porous support materials offer such possibilities with controlled large and accessible surface area. The mesoporous characteristic of the support may permit access of bulky molecules (i.e., triglycerides) to the active sites resulting in substantial increase in catalytic activity (Islam *et al.*, 2012).

Solid base catalysts: Of the large variety of heterogeneous catalysts used in transesterification of vegetable oils, most are alkali or alkaline oxides supported over large surface area supports (Antunes *et al.*, 2008). Heterogeneous basic catalysts showed higher reaction rate than solid acids and they have been preferably studied. Heterogeneous base catalysts refer mainly to solids with Brønsted basic and Lewis basic activity centers, that can supply electrons (or accept protons) for (or from) reactants. 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 (Islam *et al.*, 2013). Stronger bases are in general more effective to initiate the transesterification of triglycerides due to its strong ability to adsorb the alcohol to the basic sites of catalyst surface and then to dissociate it into RO- and H+ (Ma *et al.*, 2008). Similar to their homogeneous counterparts, solid basic catalysts are more active than solid acid catalysts. Heterogeneous base catalyzed transesterification for biodiesel synthesis has been studied intensively over the last decade. Table 2 lists types of solid base catalysts (Hattori, 2001, 2004).

These catalysts include mostly alkali, alkaline oxides, large-surface-area material supported alkaline oxides, basic zeolites, hydrotalcites and organic base catalysts. However, although several heterogeneous base catalysts have showed promising activities, so far they have not replaced the homogeneous catalyst in commercial biodiesel production. Brief details are given herein for some of the most common heterogeneous base catalysts.

Table 2: Types of heterogeneous basic catalysts

Single component metal oxides
Alkaline earth oxides
Alkaline metal oxides
Rare earth oxides
ThO_2, ZrO_2, ZnO, TiO_2
Zeolites
Alkaline ion-exchanged zeolites
Alkaline ion-added zeolites
Supported alkaline metal ions
Alkali metal ions on alumina
Alkali metal ions on silica
Alkali metal ions on activated carbon
Alkali metal on alkaline earth oxide
Alkali metals and alkali metal hydroxides on alumina
Clay minerals
Hydrotalcite
Chrysotile
Sepiolite
Non-oxide
KF supported on alumina
Lanthanide imide and nitride on zeolite
Metal nitrides, sulphides, carbides, phosphides
Organic bases (guanidine) grafted on microporous or mesoporous materials

Single and mixed alkali, alkaline oxides: Metal oxides are composed of cations possessing Lewis acid and anions with Brønsted base. Metal oxides are the basic heterogeneous catalysts group most studied of which the most common ones are calcium oxide, magnesium oxide, strontium oxide (Yan *et al*., 2010). Calcium oxide (CaO) is the most widely used as a solid basic catalyst as it presents many advantages such as long catalyst life, high activity and moderate reaction conditions. Metal oxides used in transesterification are classified as single metal oxides (e.g., MgO, CaO and SrO) and mixed metal oxides [A-B-O type metal oxides, where A is an alkaline-earth metal (Ca, Ba, Mg), alkaline metal (Li), or rare earth metal (La) and B is a transition metal (Ti, Mn, Fe, Zr, Ce)] (Kawashima *et al*., 2008; Liu *et al*., 2007, 2008; Montero *et al*., 2009). Basic sites of metal oxide catalysts are believed to be located on oxygen (O) atoms on the catalyst surface because of oxygen atom's ability to interact attractively with a proton. The strength of basic sites for metal oxide catalysts depends upon the tendency of the metal atom to donate electrons. In a metal-O bond, the metal atom is positively charged while the oxygen atom is negatively charged. The stronger the ability of a metal atom to donate electrons, the more negatively the oxygen atom is charged and then the stronger the basic strength (Hattori, 2001). The basicity of single metal oxides (especially, strong basic sites) directly influences the rate of reaction. Bancquart *et al*. (2001) compared activities of several single metal oxides and found that the order of activity followed the intrinsic basicity of the oxides: La2O3>MgO>>ZnO ˜CeO2. Calcium oxide (CaO) is the most frequently applied metal oxide catalyst for biodiesel preparation, due to its cheap price, relatively high basic strength and less environmental impacts (Bancquart *et al*., 2001). The biodiesel yield by the CaO catalyst depends heavily on the reaction temperature and especially the methanol/oil molar ratio. The yield increased from 65 to 99% as the methanol/oil molar ratio was increased from 6:1 to 41:1 at methanol supercritical condition with a catalyst amount of 3.3 wt% (Demirbas, 2007).

The catalytic activity of CaO could be increased by using nano-sized crystalline particles. (Reddy *et al*., 2006) investigated the catalytic activity of nano-crystalline CaO in transesterification of soybean oil and poultry fats under room temperature. Nano-crystalline CaO presented a much stronger activity than laboratory-grade CaO due to its high surface area associated with nano-crystallite sizes. Calcium oxide (CaO) sometimes produces a lower biodiesel yield than expected from its high triglyceride conversion which is usually attributed to the formation of Ca(OCH3)2 on the CaO surface (Watkins *et al*., 2004). As with any other basic catalyst, some careful handling is required in order to use CaO as a solid base catalyst. Its surface sites can be poisoned by contact with room air due to the adsorption of CO_2 and H_2O at the surface of the solid as carbonates and hydroxyls groups. Therefore, the poisonous species must be removed at high temperature (more than 700°C) and exposure to the atmosphere should be strictly prevented before its use (Granados *et al*., 2007). To increase the basic strength of a single metal oxide, mixed metal oxides are synthesized. Kawashima *et al*. (2008), studied A-B-O type metal oxides, where A is an alkaline-earth metal (Ca, Ba, Mg), alkaline metal, or rare earth metal (La) and B is a transition metal (Ti, Mn, Fe, Zr, Ce). The catalysts were prepared through high-temperature calcination of a mixture of transition metal (B) oxide and alkaline metal (A) carbonate. The calcium catalyst series CaZrO3 and CaO-CeO2 catalysts showed highest catalytic activities with methyl ester yields >80% at 60oC with oil/methanol ratio 6:1 and this activity was maintained after 5-7 reaction repetitions.

Supported base catalysts: In spite of activity aspects of single calcium oxide catalysts in biodiesel production, they suffer poor mechanical strength which could cause separation problems and lead to a short life time (Lee *et al*., 2009). Except nano particle CaO, most calcium oxides possess a relatively low surface area which limits the catalytic activity of a solid catalyst. Therefore, there is a demand to develop desirable solid base catalysts with a high activity, a large-surface-area and a sufficient mechanical strength. Solid-base catalysts have been applied in transesterification reaction with variety of supported materials, such as alkaline-earth metals oxides and hydroxides, alkali metals hydroxides or salts supported on alumina, zeolites and hydrotalcites (McNeff *et al*., 2008; Helwani *et al*., 2009). Al_2O_3, SiO_2 and zeolites are among the most used supports due to their large surface areas, proper porosity and stable structures Al_2O_3-supported CaO and MgO catalysts were employed in transesterification of nannochloropsis oculata microalga's lipid into biodiesel (Umdu *et al*., 2009). The supported CaO and MgO catalysts showed higher activities than the corresponding pure oxides and their activities depend upon CaO or Mg loading amounts. Albuquerque *et al*. (2008), studied mesoporous silica (SBA-15 and MCM-41)-supported CaO in transesterification and showed that SBA-15, as compared to MCM-41, was thermally more resistant and interacted more strongly with supported calcium species. The strong interaction between CaO and SBA-15 effectively prevented leaching of active calcium species. The authors noted that the most active catalyst, 14 wt% CaO/SBA-15, resulted in 95% conversion after 5 h for transesterification of sunflower oil at 60°C and a methanol/oil molar ratio of 12. Overall the activity of this series of supported catalysts was not sufficient for industrial application.

Zeolite: As generally recognized, the versatile catalysis ability of zeolites results from their chemical composition, pore size distribution and ion-exchange abilities. A micro-porous inorganic lithium containing zeolite has been shown to be a new generation solid base catalyst for transesterification. Most of these catalysts contain the basic sites (cation) generated by thermal decomposition of the supported salt. The base strength of the alkali ion exchanged zeolite increases with increasing electropositive nature of the exchanged cation. The base strength of the alkali zeolites are controlled by the kinds and quantities of ion-exchanged cations and by the Si/Al ratio of the main zeolite framework. It has been shown that the conversion to methyl ester over NaX faujasite zeolite that was ion exchanged with more electropositive cations was higher than that of the parent zeolite (Puna *et al.*, 2010). To control the basicity of zeolite, two approaches are generally undertaken: ion-exchange with alkali metal ions and the impregnation of basic components on the inner surface of the zeolite pores (Suppes *et al.*, 2004; Nakagaki *et al.*, 2008). Among the zeolite family, zeolite-X, titanosilicates (esp.ETS-4 and 10) and mesoporous zeolites have attracted the most research attention for biodiesel synthesis. Zeolite X is generally accepted as one of the most basic zeolites and the ion exchange of Na-X with larger monovalent cations such as K and Cs increases the basicity markedly (Suppes *et al.*, 2004; Puna *et al.*, 2010).

Clay minerals: The hydrotalcite has been considered of great interest in the transesterification reaction due to its strong basicity, high surface area and pore volume. It consists of natural anionic clay containing carbonate anions intercalated between lamellar double hydroxide, magnesium and aluminum (Wang and Jehng, 2011). The lamellar double hydroxides, although not abundant in nature, can be synthesized in the laboratory at a relatively low cost. The Mg-Al hydrotalcites have been considered of great interest in the transesterification reaction, due to the fact that they are resistant to the presence of water and free fatty acids, show high activities and give no place for leaching (Santacesaria *et al.*, 2012). Hydrotalcites have an ideal formula of $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$. The activation of hydrotalcite by thermal treatments removes the interlayer carbonate, forming the Mg-Al mixed oxides with high specific surface areas and excellent basic properties (Guerreiro *et al.*, 2010).

Non-oxide base: It was reported that sodium carbonate, potassium carbonate and sodium phosphate all catalyzed transesterification; where potassium carbonate showed the highest activity while sodium carbonate and sodium phosphate exhibited almost the same activity which was much lower than potassium carbonate. A 97% biodiesel yield was obtained using sodium phosphate as the catalyst. However, after 5 h of reaction, 55% of the potassium carbonate dissolved but the losses of sodium carbonate and sodium phosphate were 20 and 15%, respectively (Wan *et al.*, 2009; Arzamendi *et al.*, 2008). Guanidine is a good homogeneous catalyst and it can be converted into solid base catalyst by heterogenization by using various supports. For example, guanidine was immobilized on various supports: polystyrene, zeolite Y, mesoporous silica MCM-41, SBA-15 (Meloni *et al.*, 2011). These catalysts showed catalytic activity as high as other conventional non-guanidine based solid catalysts such as calcium carbonate, single metal oxide, mixed zinc-aluminum oxide and hydrotalcites (Bourney *et al.*, 2005; Faria *et al.*, 2008; Balbino *et al.*, 2011; Nguyen *et al.*, 2013).

Solid acid catalysts: Highly reactive homogeneous Brønsted acid catalysts are efficient for transesterification process but they suffer from serious contamination and corrosion problems that require the implementation of good separation and purification steps. More recently, a “green” approach to biodiesel production has stimulated the application of sustainable solid acid catalysts as replacements for such liquid acid catalysts. In this perspective, various solid acids including sulfated metal oxides, H-form zeolites, sulfonic ion-exchange resins, sulfonic modified meso structured silica materials, sulfonated carbon-based catalysts, heteropolyacids and acidic ionic liquids are reviewed as heterogeneous catalysts in esterification and transesterification (Melero *et al.*, 2009a; Shu *et al.*, 2010). Compared to solid acid, solid base provides a faster rate to transesterification under mild condition. Table 3, lists some of the advantages and disadvantages of homogeneous and heterogeneous acid and base catalyst (Lam *et al.*, 2010).

Table 3: Advantages and disadvantages of different types of catalysts used in transesterification for biodiesel production

Type of catalyst	Advantages	Disadvantages
Homogeneous base catalyst	Very fast reaction rate-4000 times faster than acid-catalyzed transesterification	Sensitive to FFA content in the oil
	Reaction can occur at mild reaction condition and less energy intensive	Soap will formed if the FFA content in the oil is more than 2 wt.%
	Catalysts such as NaOH and KOH are relatively cheap and widely available	Too much soap formation will decrease biodiesel yield and cause problem during product purification especially generating huge amount of wastewater
Heterogeneous base catalyst	Relatively faster reaction rate than acid-catalyzed transesterification	Poisoning of the catalyst when exposed to ambient air
	Reaction can occur at mild reaction condition and less energy intensive	Sensitive to FFA content in the oil due to its basicity property
	Easy separation of catalyst from product	Soap will be formed if the FFA content in the oil is more than 2 wt.%
	High possibility to reuse and regenerate the catalyst	Too much soap formation will decrease the biodiesel yield and cause problem during product purification
		Leaching of catalyst active sites may result to product contamination
Homogeneous acid catalyst	Insensitive to FFA and water content in the oil	Very slow reaction rate
	Preferred-method if low-grade oil is used	Corrosive catalyst such as H_2SO_4 used can lead to corrosion on reactor and pipelines
	Esterification and transesterification occur simultaneously	Separation of catalyst from product is problematic
	Reaction can occur at mild reaction condition and less energy intensive	
Heterogeneous acid catalyst	Insensitive to FFA and water content in the oil	Complicated catalyst synthesis procedures lead to higher cost
	Preferred-method if low-grade oil is used	Normally, high reaction temperature, high alcohol to oil molar ratio and long reaction time are required
	Esterification and transesterification occur simultaneously	Energy intensive
	Easy separation of catalyst from product	Leaching of catalyst active sites may result to product contamination
	High possibility to reuse and regenerate the catalyst	

Solid acids catalysts (both Lewis-type such as the mixed and sulfated oxides and Brønsted-type such as sulfonic acid-containing materials) also have the similar advantages as that of heterogeneous base catalysts. One major advantage of solid acid catalyst is the diversity of acidic sites on the surface of the solid acid catalysts with different strengths of Brönsted or Lewis acidity. Several solid acid catalysts have been developed to overcome the disadvantages of homogeneous alkaline catalysts currently used in the industries. The challenging feat is to develop suitable solid acid catalysts for esterifying long-chain acids compared to the shorter acids such as acetic acids (McNeff *et al.*, 2008; Hattori, 2010). However, the ideal catalyst would be bifunctional, containing both Bronsted and Lewis acid sites with a hydrophobic environment protecting the Lewis site from the poisoning effect of water. The Bronsted acid sites promote the esterification and produce some water; Lewis acid sites are more active in promoting transesterification provided that the sites are not poisoned by water (Carrero *et al.*, 2011). The various types of solid acid catalysts differ in acidity, surface area, mechanical resistance, thermal and hydrothermal stability and cost of production. Solid acid-catalysts such as Nafion-NR50, sulfated zirconia and tungstated zirconia have been popularly chosen to catalyze biodiesel-forming transesterification due to the presence of sufficient acid site strength (Lopez *et al.*, 2007). Table 4, lists some of the common solid acid catalyst that has been studies by researches. More in-depth description on heterogeneous acid and

Table 4: Description of some of the common type of solid acid catalyst

Type of solid acid catalyst and description	References
Sulfonic acid Ion-exchange resin	
They are composed of copolymers of divinylbenzene Styrene and sulfonic acid groups grafted on benzene. Catalytic activity depends strongly on swelling properties as swelling capacity controls the reactant's accessibility to the acid sites	Shibasaki-Kitakawa *et al.* (2007), Tesser*et al.* (2010), Liu *et al.* (2009), Feng *et al.* (2011), Caetano *et al.* (2009), Sharma *et al.* (2011), Son *et al.* (2011), Russbueldt and Hoelderich (2009), Melero *et al.* (2009), Hara (2010), Dehkhoda *et al.* (2010)
Mass-transfer restriction affects catalytic activity. Most of the active sites are embedded in the gel matrix, so the resins with macro-pores have high catalytic activity.	
The catalytic activity decreased when the cross-linking degree of polymeric matrix increased	
Mechanical strength and thermo-stability are important for the large-scale applications of resins. Continuous production of biodiesel in a fixed-bed reactor packed with resins was successively operated.	
Esterification of palmitic acid with methanol using poly (vinyl alcohol) cross-linked with sulfosuccinic acid (SSA) resin at 60°C, gave about 90% conversion rate after 2 h. Only about 5% sulfosuccinic acid was leached after 7 recycles. Higher content of sulfonic groups led to better performance by the PVA polymer cross-linked with sulfosuccinic acid. Better catalytic activity of PVA has also been attributed to high swelling capability of PVA in oil and less in methanol. Activity of NKC-9 resin even slightly increased at the first 10 runs, due to breakdown of resin particles under mechanical agitation	
Sulfonated mesostructured materials are promising catalysts for the preparation of biodiesel with over 95 wt.%, for oil conversion reported, under the best reaction conditions: Temperature 180 °C, methanol/oil molar ratio 10 and catalyst loading 6 wt.%	
Sulphonated carbonized natural products such as sugars, starch or cellulose resulting in a rigid carbon material had been used to produce high-grade biodiesel. The activity two times greater than that of liquid sulfuric acid catalyst and much higher than conventional solid acid catalyst	
Catalyst deactivation is caused by salt contaminants and water-swelling. Catalytic active sites on acidic resins can exchange with salt ions contained in oil. Traces of Na, K, Mg and Ca lead to a continuous activity loss	
Amberlyst-15 was poisoned by the presence of water in the reaction medium and its activity was substantially reduced in comparison to the homogeneous sulfuric acid catalyst. The presence of water resulted in poor accessibility of reactants to the acid sites	
Zeolites	
Zeolites have extremely high internal surface area (600 m^2 sec) and high thermal-stability (1000°C), Are crystalline alumino-silicates with a three-dimensional porous structure Can be synthesized with different crystal structures, definitive pore sizes, framework Si/Al ratios and adjustable acid centers. They exhibit high concentration of active acid (Lewis and Bronsted) site	Shu *et al.* (2007), Sasidharan and Kumar (2004), Chung *et al.* (2008)

Table 4: Continue

Type of solid acid catalyst and description	References
The acidic properties of zeolites can be improved by protonation- exchange of the cations contained in the positively charged aluminosilicate cage with protons. Catalytic activity was independent of the pore structure of the zeolites but product yield increased linearly with enhancing the acid strength and with increasing the amount of strong acid sites Lewis-acid sites are mainly present in the micro-porous walls; while Brønsted-acid sites are present on the internal and external surface Internal diffusion resistances are considered to limit reaction rate significantly. Thus, large-pore zeolites are active for the reaction. Large-pore zeolites such as Y, mordenite, and β showed higher activity (biodiesel yield 92%) than the medium-pore ZSM-5 and aluminum containing mesoporous MCM-41. The high pore volume of zeolites favored reaction by rendering the active sites more accessible to the bulky triglyceride molecules. Most of zeolites exhibit not only acidic property but they also provide high activity and selectivity in various acid catalysts as carrier	
Heteropolyacids (HPAs)	
Is a class of acid made up of a particular combination of hydrogen and oxygen with certain metals (i.e., tungsten, molybdenum and vanadium) and non-metals (i.e., silicon, phosphorus). With the advantages of strong Bronsted acidity, stability and high proton mobility, HPAs are favorable as environmentally benign and economical solid catalysts for biodiesel production The Keggin ($H_nXM_{12}O_{40}$) and Dawson ($H_nX_2M_{18}O_{62}$) structures are two of the better known groups. HPAs (e.g., H3PW12O40) are soluble in water and possess acidic strength as strong as sulfuric acid HPAs are significantly higher than conventional acid catalysts in transesterification Their acid strength in the descending order is as follows: $H_3PW_{12}O_{40}$> $Cs_{2.5}H_{0.5}PW_{12}O_{40}$> $H_4SiW_{12}O_{40}$>15%$H_3PW_{12}O_{40}/Nb_2O_5$, 15%$H_3PW_{12}O_{40}/ZrO_2$, 15%$H_3PW_{12}O_{40}/TiO_2$> H_2SO_4> HY, H-Beta> Amberlyst-15 Exchange of protons in HPA can help promote its activity in transesterification of triglycerides Disadvantage of HPAs is their solubility in water and polar solvents. This problem can be overcome by converting it into its salt (e.g., ammonium salt) with decreases of acidity and catalytic activity. Recovery and reutilization of HPAs is difficult. Immobilization of HPAs on carrier is an efficiency method to obtain insoluble catalyst and can be recovered	Kozhevnikov (1998), Alsalme *et al.* (2008), Giri *et al.* (2005), Caetano *et al.* (2008), Narasimharao *et al.* (2007)

heterogeneous base catalyst for transesterification reaction may be found in some excellent reviews by Sharma *et al.* (2011b), Borges and Diaz (2012), Atadashi *et al.* (2013) and Sani *et al.* (2014).

Enzyme-catalyst transesterification: Enzymes are biological catalysts which have enormous potential for reducing energy requirements and environmental problems in the industrial chemicals processes. Enzyme catalyzed transesterification reactions have been extensively used in production of drug intermediates, biosurfactants and designer fats (Shah *et al.*, 2003). Enzymatic approach for production of biodiesel has been extensively reported, although this technology has not received much commercial attention except in China where the first industrial scale for biodiesel production in the world (with lipase as the catalyst at a capacity of 20,000 tons year^{-1}) is in operation (Du *et al.*, 2008). The pros and cons of using lipases as biocatalysts compared to alkaline and acid catalysts for biodiesel production are summarized in Table 5 (Shah *et al.*, 2003; Narasimharao *et al.*, 2007; Fjerbaek *et al.*, 2009; Robles-Medina *et al.*, 2009; Gog *et al.*, 2012).

Table 5: Comparison of enzymatic technology versus chemical (homogeneous alkaline and acid) technology for biodiesel production

		Chemical process	
Parameter	Enzymatic process	Homogeneous alkaline	Homogeneous acid process
FFA content in the raw material	FFA are converted to biodiesel	Soaps formation	FFA are converted to biodiesel
Water content in the raw material	It is not deleterious for lipase	Soaps formation. Oil hydrolysis resulting more soaps	Catalyst deactivation
Biodiesel yield	High, usually around 90%	High, usually >96%	High yields (>90%) only for high alcohol to oil molar ratio, high catalyst concentration and high temperature
Reaction rate	Low	High	Slower than for alkaline process
Glycerol recovery	Easy, high grade glycerol	Complex, low grade glycerol	Complex, low grade glycerol
Catalyst recovery and reuse	Easy, Reusability proved but not sufficiently studied	Difficult; neutralized by an acid Partially lost in post-processing steps	Difficult, the catalyst ends up in the by-products No reusable catalyst
Energy costs	Low temperature: 20-50°C	Medium temperature: 60-80°C	High temperature: >100°C
Catalyst cost	High	Low	Low. However, high cost of equipment due to acid corrosion
Environmental impact	Low; wastewater treatment not needed	High; wastewater treatment needed	High; wastewater treatment needed

Lipases (triacylglycerol acylhydrolases, EC 3.1.1.3) constitute a diverse and ubiquitous family of enzymes which are produced by animals, plants and microorganisms. Lipases from microorganisms (bacterial and fungal) are the most used as biocatalysts in biotechnological applications and organic chemistry. Lipases have been successfully used in novel biotechnological applications for the synthesis of biopolymers and the production of enantiopure pharmaceuticals, flavor compounds, agrochemicals and biodiesel (Jaeger and Eggert, 2002). Lipases are considered hydrolases which naturally hydrolyses triacylglycerol (Salis *et al.*, 2005). Most lipases are capable of converting triglycerides, diglycerides, monoglycerides and free fatty acids to Fatty Acid Alkyl Esters in addition to fat hydrolysis (Akoh *et al.*, 2007). It is the stability of lipases that allows them to catalyze the unnatural reaction of transesterification (Jegannathan *et al.*, 2008). The advantages of using lipases in biodiesel production are: (a) Ability to work in very different media which include biphasic systems, monophasic system (in the presence of hydrophilic or hydrophobic solvents), (b) They are robust and versatile enzymes that can be produce in bulk because of their extracellular nature, (c) Many lipases show considerable activity to catalyze transesterification with long or branched chain alcohols which can hardly be converted to fatty acid esters in the presence of conventional alkaline catalysts, (d) Ability to esterify both FFA and triglycerides in one step without the need of washing step; no soap formation and the ability to handle large variation in raw material quality such as waste cooking oil, (e) Products and byproduct separation in downstream process are extremely easier, (f) The immobilization of lipases on a carrier has facilitated the repeated use of enzymes after removal from the reaction mixture and when the lipase is in a packed bed reactor, no separation is necessary after transesterification, (g) Lipases have higher thermostability and short-chain alcohol-tolerant capabilities; hence making them very convenient for use in biodiesel production (Peilow and Misbah, 2001; Ranganathan *et al.*, 2008; Kato *et al.*, 2007; Robles-Medina *et al.*, 2009; Gog *et al.*, 2012). However, enzymatic transesterification has several drawbacks: (a) Longer reaction time, (b) Higher catalyst concentration is required to completion of reaction, (c) High cost of production (due to high enzyme cost- lipase enzyme makes up 90% of the total cost of enzymatic biodiesel production), (d) The risk that glycerol inhibits the lipase by covering it, due to its accumulation, (e) Initial activity may be lost because of volume of the oil molecule, (f) Although, repeated use of lipase becomes possible after immobilization of lipase on carrier, it loses its activity in 100 days of application (Marchetti *et al.*, 2007; Jeong and Park, 2008; Fjerbaek *et al.*, 2009; Gog *et al.*, 2012). The stability of the lipase is the most important enzymatic characteristics when used in biodiesel synthesis. The environment in a reactor is often more harsh for the enzyme than when in vivo. Therefore, many enzymes do not remain stable when used industrially. The higher temperature, inactivating impurities and aggressive surfaces of the reactors assist in enzyme deactivation and inhibition. In addition to mechanical forces, lower chain alcohols, the by-product glycerol, water content and high alcohol to oil ratios can also cause destabilization and deactivation of the enzyme (Marchetti *et al.*, 2007; Torres *et al.*, 2008; Robles-Medina *et al.*, 2009; Zhang *et al.*, 2009). Therefore, more research is needed in order to be able to use modified lipase on a large scale.

Factor affecting enzymatic transesterification: If such matters as cost, stability, rate and extent of reaction, instability of enzyme in short chain alcohols, among others, can be solved, then enzymatic transesterification for biodiesel production can be applied in commercial biodiesel production. Cost of lipase is the major issue for the industrialization of lipase-mediated bio-diesel production. There are two ways to reduce the lipase cost. One is to reduce the production cost of the lipase which can be realized through new lipase development, fermentation optimization and downstream processing improvement. Another way is to extend the operational life of the lipase and this can be achieved through enzyme immobilization and alcoholysis reaction optimization. Immobilization of lipase is the attachment of the enzyme onto a solid support or the confinement of the enzyme in a region of space. Immobilization can, also, be seen as the transformation of a mobile enzyme to an immobile one which overcomes the longer reaction time and/or the lower enantioselectivity (Jegannathan *et al.*, 2008). Immobilised enzymes or whole-cell biocatalysts also allow enzymes to be held in place throughout the reaction which they are easily separated from the products and be used again repeatedly which is an efficient way to reduce cost of the enzyme. Immobilized enzymes show an increase stability and activity in terms of thermal, chemical and mechanical properties as compare with free enzymes, thereby allowing their applications under harsher environmental conditions (Bhushan *et al.*, 2008; Barberis *et al.*, 2008; Tan *et al.*, 2010).

The most commonly used alcohols are: methanol, ethanol, propanol, iso-propanol, 2-propanol, n-butanol and isobutanol (Coggon *et al.*, 2007). The lower linear alcohols (methanol and ethanol) are the only economically feasible options, however, they found to be liable for deactivation and inhibition of immobilized lipase (Salis *et al.*, 2005; Al-Zuhair *et al.*, 2007). The degree of deactivation is estimated to be inversely proportional to the number of carbon atoms in the alcohol which means that methanol is the most deactivating alcohol (Ranganathan *et al.*, 2008). To overcome the inhibiting effects of lower chained alcohols; stepwise addition of the alcohol has been shown to decrease the deactivation of the enzyme and therefore, increase longevity. Stepwise addition of methanol in the transesterification of olive oil allowed for the repeated use of enzyme and the conversion rate was maintained over 85% after eight cycles (Lee *et al.*, 2002; Matassoli *et al.*, 2009). The other way is by adding of solvents. Solvents are used to protect the enzyme from denaturation by alcohol by increasing alcohol solubility. The use of a common solvent for the reactants and products not only reduces enzyme inhibition but also ensures a homogeneous reaction mixture, reduces the reaction mixture viscosity and stabilizes the immobilized enzyme (Ranganathan *et al*., 2008; Fjerbaek *et al*., 2009). Tert-butanol is the most popular among all these solvents. It is only moderately polar, has stabilizing effects on the enzyme and is not easily influenced by the polarity of other solvents (like water) or by any of the reactants or products (Fjerbaek *et al*., 2009). Tert-butanol and 2-butanol have been suggested as treatments for the regeneration of deactivated lipase (Li *et al*., 2007; Robles-Medina *et al*., 2009). However, several disadvantages of the use of solvents have been identified, these include: (a) Solvent must be separated from the final desired product (biodiesel) which requires addition processing (Vasudevan and Briggs, 2008), (b) The use of organic solvents can compromise safety since they are generally volatile and hazardous and (c) Reactor volumes must also increase to compensate for the additional volume of solvent added to the reaction mixture (Fjerbaek *et al*., 2009).

Pretreatment of immobilized lipase often involves soaking the enzyme in a medium prior to use in the transesterification reaction. This pretreatment is believed to minimize the deactivation of the enzyme which is most commonly due to the use of lower chained alcohols (Ranganathan *et al*., 2008). Pretreatment in a polar organic solvent is thought to transform the enzymes hydrophobic closed active site to a hydrophobic open active site, thus enhancing its activation (Jegannathan *et al*., 2008). Biocatalysts often require a minimum amount of water present to maintain their activity (Jegannathan *et al*., 2008). The optimum water content minimizes hydrolysis and maximizes enzyme activity for the transesterification reaction (Jegannathan *et al*., 2008) even if it is employed with lower chained alcohols (Akoh *et al*., 2007). It has been suggested that the reaction rate of transesterification decreases when over 0.1 g of water is present per gram of dry enzyme. This is believed to happen because the excess water floods the pores of the enzyme support which decreases the enzymes exposure to the reaction medium (Robles-Medina *et al*., 2009). With regards to reaction temperature, most lipases are known to have a fairly large thermal stability with optimal temperature between 30 and 60°C (Marchetti *et al*., 2008). It is important to note that the optimum temperature for a given lipase increases when the enzyme in immobilized (Fjerbaek *et al*., 2009; Tan *et al*., 2010). Considering all the above factors and the advantages, lipase can be used on oils with variable chemical composition which broadens the feedstock base and is of great advantage when waste oils and fats are considered (Du *et al*., 2008; Fukuda *et al*., 2008).

Ultrasonic and microwave assisted catalytic transesterification: Ultrasonic process using sound wave energy vibrates more than 20,000 times per second. These waves are in the range of 20-100 kHz. The industrial application of this energy significantly increased since 1980s and today ultra-sonic waves are used in wide ranges of application such as processing, extraction and atomization (Mason, 2000). Ultrasonic irradiation has three significant influences on reaction: (1) Acoustic streaming mixing, (2) Variation of sonic pressure lead to rapid movement of fluids, (3) Cavitation bubbles formed by liquid breakdown that caused by large negative pressure gradient application in liquid (Mason, 2000). The main effect of ultrasonic waves on chemical reactions comes from formation and collapse of micro-bubbles. The liquid jet effect is cavity collapse that improves them as transfer by disrupting the interfacial boundary layers (Kumar *et al*., 2010). The application of ultrasonication to enhance the transesterification of vegetable oil to biodiesel was reported as early as in 2003 (Stavarache *et al*., 2003). The findings of reduced reaction time, low catalyst application rate and less excess methanol requirement make this unique technology very attractive. Since then, researchers have extensively explored the advantages of ultrasonication and its feasibility for advancing biodiesel production technology. Mixing of oil and alcohol is the main factor that increases the biodiesel yield because both oil and alcohol cannot be miscible completely in conventional processes. Ultrasonic irradiation improves the reaction characteristics by formation of smaller droplets (146-148 nm by 50-70W) compared to conventional stirring system (340 nm by 1000 rpm) by improving the contact area between oil and alcohol (Stavarache *et al*., 2006). Besides, ultrasonic energy can break catalyst to smaller particles to form new sites for subsequent reaction. Therefore, solid catalysts are suitable choice for this process because the catalysts stability is expected to last longer (Mootabadi *et al*., 2010). In addition, ultrasonic irradiation can enhance the enzyme (Novozym435) catalyst activity (Mootabadi *et al*., 2010). There are some reaction parameters that significantly influence the ultrasonic irradiation process: (1) Ultrasonic power, (2) Frequency effect, (3) Catalyst type, (4) Alcohol type. The other main advantages of ultrasonic irradiation process are: (1) shorter reaction time, (2) lower molar ratio of alcohol to oil, (3) lower amount of catalyst (or enzyme) utilization, (5) Increased reaction rate, (6) Enhanced conversion and improved yield. In contrast, this process has some disadvantages such as: (1) The reaction temperature was slightly higher for long reactions, (3) The ultrasonic power must be under control due to the soap formation in fast reaction. Therefore, FAME yield can be reduced by higher frequencies (40 kHz). Definitely this process requires additional technical and scientific enhancement to overcome the drawbacks before commercialization and industrialization can be realized. Salamatinia *et al*. (2010) investigated the ultrasonic process with heterogeneous trans-esterification of palm oil for production of biodiesel. The ultrasonic process dramatically reduced the catalyst weight and reaction time to 2.8% wt and 50 min individually, reaching more than 95% yield. The application rate of catalyst can be reduced by approximately two to three times due to the use of ultrasonication. The ultrasonication process can reduce the transesterification process to tens of minutes and even as low as 1 min (Ji *et al*., 2006; Teixeira *et al*., 2009).

Most researchers believe that the effect of ultrasonication on enhancing transesterification lies mainly in intensifying the mixing of the immiscible methanol and triglyceride phases, especially at the beginning of the reaction. The mixing enhancement is largely due to the collapse of ultrasonic cavitation bubbles and the reduced droplet sizes of low boiling temperature methanol in less-miscible triglycerides (Colucci *et al*., 2005; Wu *et al*., 2007). Another observation was that the ultrasonication does not affect the ester profiles as compared with those from conventional, non-ultrasonication procedures if potassium is used as the catalyst, indicating that ultrasonication does not decompose fatty acids to other chemicals (e.g., radicals) as observed in other organic systems (Stavarache *et al*., 2006). On the other hand, results of improved fatty acid separation were observed under ultrasonication when sodium hydroxide was used as the catalyst (Stavarache *et al*., 2006). The catalysts after ultrasonication maintain their physical and chemical properties and can be reused without significant deactivation. Ultrasonication also showed effectiveness for transesterification catalyzed by enzymes. Under optimized conditions (50% of ultrasonic power or approximately equivalent to 7200 kJ energy input per liter of reacting mixture, 50 rpm vibration, 6% Novozym 435 and 40°C), 96% yield of biodiesel from soy bean oil was achieved in 4 h and the enzyme showed no obvious activity loss (Yu *et al*., 2010; Kumar *et al*., 2011). Mahamuni and Adewuyi (2010) have reported that to maximize the ultrasonication effect, a combination of lower frequencies at higher intensity of irradiation was preferred over higher frequencies and lower intensities of irradiation. The authors commented that higher intensity of ultrasonication is preferred but an optimum intensity must be observed due to the phenomena of that states that when large amount of ultrasonic power enters a system, a much larger quantity of ultrasonic cavitation bubbles is generated in the solution. Excessive bubbles likely merge and form larger and more stable bubbles and, thus, create a barrier to acoustic energy transfer (Mason, 2000; Canals and Hernandez, 2002; Prabhu *et al.*, 2004).

Microwave technology relies on the use of electromagnetic waves to generate heat by the oscillation of molecules upon microwave absorption. The electromagnetic spectrum for microwaves is in between infrared radiation and radio frequencies of 30 GHz to 300 MHz. In microwave-assisted heating, unlike the conventional methods, the heat is generated within the material, thus rapid heating occurs. As a result of this rapid heating, many microwave-assisted organic reactions are accelerated, incomparable with those obtained using the conventional methods. Thus, higher yields and selectivity of target compounds can be obtained at shorter reaction times (Azcan and Danisman, 2007; Saifuddin and Chua, 2004). In addition, many reactions not possible using the conventional heating methods, had been reported to occur under microwave heating. Other than the advantages of rapid heating, microwave non-thermal effects on reaction likely occur, obtaining dramatic increase in the yield even at milder conditions. Evidence on the true existence of non-thermal effects, had been reported and postulates had also been made by several researchers (De La Hoz *et al.*, 2005). The properties of biodiesel obtained by microwave irradiation are similar to the biodiesel obtained by the conventional method. These radiations can influence molecular movements (ion migration or dipole reactions) but not change the molecular structure.

Among some recent studies on the transesterification carried out under microwave irradiation includes the study by Koberg and Gendanken (2012) which reported the transesterification of castor oil with methanol and SrO as a catalyst under a two-stage (extraction and transesterification) and a one-stage method (*in situ* transesterification) using three techniques: conventional heating, sonochemistry and microwave irradiation. For the two-stage method, the authors found the highest yield of biodiesel as 52.7% and a conversion of 99.5% using microwave irradiation as a heating source. On the other hand, 57.2% yield of biodiesel and a conversion of 99.9% were achieved in a one-stage method lasting 5 min using microwave irradiation. In another study to evaluate transesterification of castor oil under microwaves using acid catalysts ($NaHSO_4.H_2O$ and $AlCl_3$) and a base catalyst (Na_2CO_3), best results were obtained at 65°C, 18:1 molar ratio of methanol to castor oil, 7.5 wt% of catalyst with respect to castor oil, 200W microwave radiation power and 120 min of reaction time. The yield obtained were 74, 73 and 90% using $NaHSO_4.H_2O$, $AlCl_3$ and Na_2CO_3, respectively (Yuan *et al.*, 2011). They also found that microwave heating consumes less energy than conventional heating to achieve the same amount of biodiesel (Yuan *et al.*, 2011).

Besides the efficient heating phenomena seen with microwave reactions, there are reports on non-thermal effect as another important contributor for the high rate of reaction. According to the Arrhenius equation the rate of a chemical reaction depends on the pre-exponential factor (A) and the activation energy (Ea) (Lidstrom *et al.*, 2001).

Arrhenius equation:

$$k = Ae\,\frac{-E\alpha}{RT}$$

Some authors have found evidence of the modification of the pre-exponential factor A involving microwave reactions (Binner *et al.*, 1995; Polshettiwar and Varma, 2010). This factor describes the molecular mobility and depends on the frequency of collisions at the reaction interface (Lidstrom *et al.*, 2001). Another aspect to consider is the ability of a polar solvent to efficiently absorb microwave energy and to convert this energy into heat (Lidstrom *et al.*, 2001). Ethanol is more effective as polar solvent in microwave systems compared to methanol and hence induces dipolar polarization as a consequence of dipole-dipole interactions of polar molecules with the electromagnetic field (Perreuz and Loupy, 2006). Microwave irradiation results in a rapid heating leading to an efficient intermolecular mixing and agitation (i.e. increase in effective collisions), therefore, increasing the reaction rate compared to conventional heating. Microwave heating was a useful technique to obtain high biodiesel yields in short reaction times, achieving better performances at lower times compared with conventional heating. In microwave reaction the temperature has low effect on yield which confirms that the influence of microwaves is effective even at low temperatures, contrary to that observed with conventional method. These results are encouraging for the future analysis of transesterification assisted by microwaves using ethanol derived from biomass or using low-quality oils.

NON CATALYTIC BIODIESEL PRODUCTION

Synthesis via supercritical reaction: Researchers have attempted to find novel methods to eliminate or decrease the various types of obstacles in catalytic (alkali and acid catalysed processes) biodiesel production process. Meanwhile, the utilization of lipase (enzymatic catalyzed) has their own disadvantages such as having a high price of catalyst and being time consuming. These limitations of catalytic transesterification processes have led to the exploration and development of new processes. In addition, to make biodiesel more economically viable and competitive, the utilisation of inexpensive lipid feedstock would be highly advantageous, as 70-75% of biodiesel cost arises from the lipid feedstock. However, inexpensive lipid feedstock generally contains a large amount of water and Free Fatty Acid (FFA), making additional purification processing necessary. Thus, economically and technically reliable biodiesel production methodology that can tolerate the high amount of water and FFA must be developed. One such potential method is the non-catalytic transesterification of triglycerides. To minimize the downstream refining steps associated with the conventional biodiesel production process, Diasakou *et al.* (1998) investigated the thermal non-catalytic transesterification of soybean oil with methanol. Reactions were carried out at temperatures below the critical temperature of methanol (240°C), at 220 and 235°C, in a batch stirred tank reactor. Since then, several researchers have continued to study the sub- and supercritical transesterification of various seed oils. The transesterification reaction can occur in the absence of a catalyst when the alcohol is subjected to supercritical conditions. Saka and Kusdiana were first to proposed that Fatty Acid Methyl Ester (FAME) can be produced by supercritical method at 350°C (Saka and Kusdiana, 2001). There is still scarcity of literatures published on the esterification of fatty acids exclusively with sub and supercritical alcohols for the purposes of producing biodiesel. Table 6, provides a comparison of the production of biodiesel by supercritical methanol (SC) and conventional homogeneous alkali-catalyzed transesterification method (Saka and Kusdiana, 2001).

A supercritical fluid (SCF) is a compound, mixture, or element above its critical pressure (Pc) and critical temperature (Tc) but below the pressure required to condense into a solid. Under such conditions, the densities of both liquid and gas phases become identical and the distinction between them disappears. Supercritical fluids (SCFs) possess unique solvent properties that allow them to be used in various applications. At conditions above the critical point (i.e., critical temperature and

Table 6: Comparison between supercritical methanol and conventional homogeneous alkaline method of biodiesel production process (Saka and Kusdiana, 2001)

Parameters	Conventional method	SC method
Reaction time	1-6 h	0.067 h
Reaction temperature	30-65°C	250-350°C
Reaction pressure	0.1 MPa	10-65 MPa
Catalyst	Alkali	None
Free fatty acids	Saponified products	Methyl esters
Yield (%)	96-97	98
Compounds to be removed for purification	Methanol, catalyst and saponified products	Methanol

pressure), the fluid exists in a supercritical phase where it exhibits properties that are in between those of a liquid and a gas. More specifically, SCFs have a liquid-like density and gas-like transport properties (i.e., diffusivity and viscosity). The supercritical properties of methanol are $Tc = 239°C$ and $Pc = 8.09$ MPa. The supercritical state of methanol enhances the miscibility of the oil/methanol mixture due to a decrease in the dielectric constant of methanol in the supercritical state (Marchetti, 2013). Under supercritical conditions, the mixture becomes a single homogeneous phase which will accelerate the reaction because there is no interphase mass transfer to limit the reaction rate. The alcohol under supercritical condition has lower dielectric constant and becomes hydrophobic resulting in higher solubility of triglyceride in alcohol (Kusdiana and Saka, 2004a). The supercritical method requires no catalyst and can achieve near complete conversion in a relatively short time. In addition, the noncatalytic supercritical process potentially has environmental advantages because no waste is generated from catalyst treatment and separation from the final product. Furthermore, this noncatalytic method requires no pretreatment of the feedstock because impurities in the feed do not significantly affect the reaction. When water and FFAs are present in the feed, three types of reactions (transesterification, hydrolysis of triglycerides and alkylesterification of fatty acids) occur simultaneously as shown in Fig. 3 (Kusdiana and Saka, 2004b). Of these, alkyl esterification is faster than transesterification and ensures that all FFAs in the feed, whether present originally or products of triglyceride hydrolysis, are completely transformed into alkyl ester (Warabi *et al.*, 2004a). Warabi *et al.* (2004b), used various supercritical alcohols (methanol, ethanol, 1-propanol, 1-butanol, or 1-octanol) to study transesterification of rapeseed oil and alkyl esterification of fatty acids and showed that transesterification was slower for alcohols with longer alkyl chains.

Table 7 gives a summary of some selected non-catalytic tranesterification studies modified from Pinnarat and Savage (2008). As shown in Table 7, generally to obtain high conversion, a high temperature, pressure and alcohol-to-oil ratios are needed. The supercritical trans-esterification method is more tolerant to the presence of water and FFAs than the conventional alkali-catalyzed technique and hence more tolerant to various types of vegetable oils, even for fried and waste oils. Water in the feedstock can hydrolyze the oil and form FFAs, posing no problem in noncatalytic supercritical processes because esterification of the FFAs will occur at a rate faster than transesterification. Therefore, all FFAs will be converted to their corresponding esters (Warabi *et al.*, 2004a). Finally, water contributes to an easier separation at the end of the supercritical process because the biodiesel product is not miscible in water at room temperature. The non-catalytic transesterification reactions at high temperature and pressure conditions provide improved phase solubility, decrease mass-transfer limitations, provide higher reaction rates and make easier separation and purification steps.

Table 7: Summary of reaction condition for high yield biodiesel production from non-catalytic reaction

Authors	Oil type	T, P	Alcohol: Oil molar ratio	Reaction time (min)	Conversion (%)
Saka and Kusdiana (2001)	Rapeseed oil	350°C, 4.5 MPa	42:01:00	4	95
Demirbas (2002)	Hazelnut kernel oil	350°C	41:01:00	5	95
Madras *et al.* (2004)	Sunflower oil	350°C, 20.0 MPa	40:01:00	40	96
Cao *et al.* (2005)	Soybean oil	330	33:01:00	10	100
Han *et al.* (2005)	Soybean oil	280°C with Propane: MeOH = 0.04	33:01:00	10	100
		280°C with CO_2: MeOH =0.04	24:01:00	10	98
Bunyakiat *et al.* (2006)	Coconut oil, palm kernel oil	350°C, 19.0 MPa	42:01:00	7	95
He *et al.* (2007)	Soybean oil	100-320°C (gradually heat)	40:01:00	25	96
	Soybean oil	310°C, 35.0 MPa	40:01:00	25	77
Silva *et al.* (2007)	Soybean oil (ethanol)	350°C, 20.0 MPa	40:01:00	15	80
Demirbas (2008)	Cottonseed Oil (methanol)	230°C	4:01	8	98
	Cottonseed oil (ethanol)	230°C	4:01	8	75
Vieitez *et al.* (2008)	Soybean oil (ethanol)	350°C, 20.0 MPa	40:01:00	28	78
Varma and Madras (2007)	Castor and linseed oil (both methanol and ethanol)	350°C, 20.0 MPa	40:01:00	40	100
Hawash *et al.* (2009)	Jatropha oil	320°C, 8.4 MPa	43:01:00	4	100
Rathore and Madras (2007)	Groundnut oil, Pongamiapinnata, Jatrophacurcas (both methanol and ethanol)	350°C, 20.0 MPa	50:01:00	5	95
Song *et al.* (2008)	Refined, bleached and Deodorizedpalm oil	350°C, 40.0 MPa	45:01:00	5	95

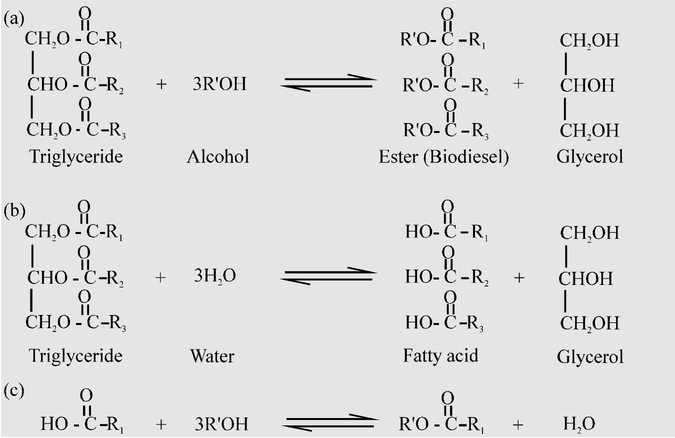

Fig. 3(a-c): Reactions with supercritical alcohol (a) Transesterification of triglycerides, (b) Hydrolysis of triglycerides and (c) Esterification of fatty acids (Reproduce from Kusdiana and Saka, 2004a)

Up to now, non-catalytic biodiesel conversion methods have been limited to the use of supercritical conditions (i.e., temperatures above 250°C and pressures above 10 MPa) (Kusdiana and Saka, 2004a; Ilham and Saka, 2012). Both ethanol and, especially, methanol, have been reported as supercritical fluids for biodiesel synthesis, although other fluids in supercritical conditions (e.g., dimethyl carbonate, methyl acetate) have also been evaluated (Lee and Saka, 2010). In spite of the numerous advantages, the operational and equipment costs for producing biodiesel under supercritical conditions are huge obstacles. Another issue that must be addressed is the thermal stability of biodiesel prepared by non-catalytic SCFs methods. It was found that although all fatty acid methyl esters, including the poly-unsaturated ones, are stable at low temperatures and pressures but they partially decomposed with isomerization from cis-olefin to trans-olefin at high pressure and temperature. It was suggested that, for high-quality biodiesel production, the reaction temperatures in SCFs processes should be maintained below 300°C, for supercritical methanol and lower than 360°C for supercritical methyl acetate with a supercritical pressure higher than 8.09 MPa (Ilham and Saka, 2012).

Enhancement in non-catalytic supercritical reaction: As stated the transesterification rate is low at subcritical (multiphase) conditions but significantly accelerated at supercritical (single phase) conditions. One portion of this acceleration is due to temperature effects and another portion is also due to the presence of a single supercritical phase at supercritical conditions. Therefore, the phase behavior of the mixture in the system is an important consideration in biodiesel production. Supercritical method is not feasible for large scale production because it requires high temperature and pressure for biodiesel production. Thus, most researchers have focused on finding new approaches in this method to decrease the reaction temperature and pressure. To produce high quality biodiesel and reduce the energy consumption, lowering the reaction temperature and pressure are key factors to improve the production with supercritical technology. Co-solvent process is another option in non-catalytic biodiesel production. Use of co-solvent is a way to obtain a single-phase system for noncatalytic transesterification but at potentially lower temperatures and pressures than the values for supercritical alcohol. Co-solvent options are designed to overcome slow reaction time caused by the extremely low solubility of the alcohol in the triglyceride phase. This system is also known as BIOX process which makes use of a co-solvent that helps to overcome the slow reaction time. Cao *et al.* (2005) used propane as a co-solvent for biodiesel production from soybean oil with methanol. In their study, the critical point of the mixture is reduced with increasing amounts of propane which is a good solvent for vegetable oil, allowing a single phase to be formed in the mixture. This use of propane reduces the amount of methanol required and results in a significant reduction in the system pressure. The reaction conditions that gave the best results (98% yield in 10 min) in their study were a temperature of 280°C, propane to methanol molar ratio of 0.05, methanol to oil ratio of 24 and a system pressure of 12.8 MPa (Cao *et al.*, 2005). One another approach is to use either tetrahydrofuran (THF) or Methyl Tetra-Butyl Ether (MTBE) as a co-solvent to generate a one-phase system (Sawangkeaw *et al.*, 2007). The result is a fast reaction, on the order of 5 min and no catalyst residues in either the ester or the glycerol phase. The THF co-solvent is chosen, in part, because it has a boiling point very close to that of methanol. This system requires a rather low operating temperature, 303 K (30°C) (Balat and Balat, 2010). Han *et al.* (2005) used CO_2 as co-solvent and reported that about 0.98 of FAME yield was obtained from a batch reactor in 10 min at 553 K, 14.3 MPa, methanol to oil molar ratio of 24:1 and CO_2 to methanol molar ratio of 1:10.

There is a clean separation of glycerol and the ester. The products obtained finally are water and catalyst free. It is also very easy to recover and recycle the co-solvent. Adding proper co-solvent may lower the critical points of the reacting mixtures which may result in decrease of required temperature and pressure in the reactor.

Another possible way to reduce the required reaction temperature and pressure was proposed by Kusdiana and Saka (2004b). They developed a two-step supercritical methanol process. This process involves the hydrolysis of oil in subcritical water to producing free fatty acids and then followed by the esterification of fatty acids with supercritical methanol to produce methyl esters (biodiesel). In this method, oils/fats are, first, treated in subcritical water for hydrolysis reaction to produce fatty acids. After hydrolysis, the reaction mixture is separated into oil phase and water phase by decantation. The oil phase (upper portion) is mainly fatty acids while the water phase (lower portion) contains glycerol in water. The separated oil phase is then mixed with methanol and treated at supercritical condition to produce methyl esters thorough esterification. Another advantage of the two-step process is that a lower ratio of alcohol to oil is required. Under milder conditions, at 563 K (270°C) and 20 MPa, 90% methyl ester yield was obtained in 15 min via esterification of oleic acid (5:1 methanol to oil molar ratio) with supercritical methanol (Minami and Saka, 2006). Since less excess methanol is necessary in this two-step process, resulting in reducing the energy consumption for recovery of unreacted methanol. The biodiesel produced from this alternate two-step method is cleaner than that from the transesterification of triglyceride alone. No mono- or diglycerides or glycerol appear as by products from the ester formation step since these compounds will have been removed after the first reaction stage (Saka *et al*., 2006). The amount of glycerol in biodiesel phase can be reduced dramatically. The total glycerol content of biodiesel prepared by one-step and two-step supercritical processes were 0.39 and 0.15 wt%, respectively (Saka *et al*., 2006).

Hydrolysis is an important reaction to process oils and fats for the non-catalytic fatty acid esterification. Hydrolysis of triglyceride is a stepwise reaction from triglyceride to diglyceride to monoglyceride which then produces glycerol and fatty acids. At low temperature, two phases occur (oil and water phase). In the first step the unique properties of subcritical water are exploited. The dielectric constant of water decreases from $\varepsilon = 80$ at standard T and P to $\varepsilon = 31$ at 225°C, P = 10.0 MPa, (critical point for water; $T_c = 374.15$°C, $P_c = 22.1$ MPa) (Weingartner and Franck, 2005). The reduction of the dielectric constant with increasing temperature promotes the miscibility between water and the oil, favouring a hydrolysis process. Furthermore, at a constant pressure of 25 MPa, the ionic product of water increases with temperature until it reaches a maximum (10^{-11}) at 250°C. This allows acid and base-catalysed reactions to be performed in high temperature pressurized water with no catalyst (Minami and Saka, 2006). Hydrolysis of vegetable oil in subcritical water (260-280°C) without use of catalyst gave high conversions of 97% with short reaction times of 15-20 min. Conversion doubled when the water to oil molar ratio increased from 3:1 to 10:1. However, further increases in the amount of water gave no effect on conversion (maximum 90%) (Minami and Saka, 2006). These conditions are milder than those reported for the original one step in supercritical methanol (350°C and 20-50 MPa), thus reducing the energy consumption. After hydrolysis, two layers are formed, the upper portion containing fatty acids and the lower portion water with glycerol. In a second step, FAMEs are produced in supercritical methanol after 20 min at 270°C and 7 MPa.

Minami and Saka (2006) studied the kinetics for both the hydrolysis and esterification steps in the two-step process. The esterification reaction sequence is shown below:

- Fatty Acid $\rightleftharpoons$ Fatty Acid$^-$+ H^+ (dissociation of Fatty Acid)
- Fatty Acid +$H^+$$\rightleftharpoons$Fatty Acid+ (protonation of Fatty Acid)
- Fatty Acid$^+$+Methanol$\rightleftharpoons$Fatty Acid Methyl Ester$^+$ +Water (methyl esterification)
- Fatty Acid Methyl Ester$^+$$\rightleftharpoons$Fatty Acid Methyl Ester +H^+ (deprotonation)

In the first step, a fatty acid is dissociated to release a hydrogen ion (a proton). This is followed by the protonation of the carbonyl oxygen of the fatty acid. Alcohol then attacks the protonated carbonyl group and a protonated ester is formed upon the release of a water molecule. A final proton transfer yields the fatty acid methyl ester.

The introduction of non-catalytic means to produce biodiesel using supercritical methanol via the one step method and two step method (Kusdiana and Saka, 2004b, 2001) has triggered many further research works utilizing wide range of raw materials or with certain improvements and modifications in the recent years. Up to now, non-catalytic biodiesel conversion methods have been limited to the use of supercritical conditions (i.e., temperatures above 250°C and pressures above 10 MPa). However, the supercritical conditions used to drive the reaction gave rise to high operational and equipment costs. In this regard, noncatalytic biodiesel conversion with the conditions under ambient pressure must be developed. Isayama and Saka (2007) developed an alternative new process with other potential reactants such as methyl formate and methyl acetate of carboxylate esters to produce fatty acid methyl esters (biodiesel) with triacin from oils and fats without producing glycerol. Similarly non-catalytic supercritical dimethyl carbonate (DMC) method has been developed by Ilham and Saka (2009), based on the direct transesterification of triglycerides with dimethyl carbonate at the condition of 350°C and 20 MPa. In the study, dimethyl carbonate rather than methanol was selected as a reactant for non-catalytic supercritical treatment. The authors have reported a yield of 97.4% was achieved using conditions of 300°C and 20 MPa for 20 min with a molar ratio of DMC to lipid feedstock of 42:1 via a batch system. As shown in Fig. 4, the byproduct of the transesterification reaction with DMC is glycerol dicarbonate. In general, DMC is a versatile chemical due to its eco-friendliness, chemical reactivity and superior physical properties compared to methanol. DMC are being produced from methanol and carbon dioxide thereby making it a true green reagent. The growing interest is mainly due to its low persistence, low bioaccumulation and high biodegradability. It has also low toxicity, absent of any

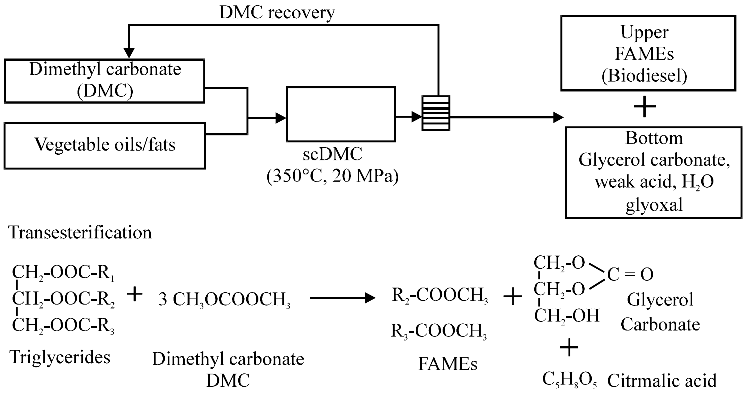

Fig. 4: Non-catalytic one-step transesterification reaction with triglyceride and DMC (Kwon *et al.*, 2014)

irritant or mutagenic effects. The economic value of by-products such as glycerol carbonate and glycerol dicarbonate, from the non-catalytic transesterification using DMC as a methyl donor, is higher than that of glycerol (Ilham and Saka, 2009).

To enhance the reaction, others have also studied the use of porous material (due to its intrinsic physical properties such as tortuosity and absorption/adsorption) such as activated alumina or charcoal has been carried out (Kwon *et al.*, 2012). These properties of the porous material significantly enhanced the reaction rate. This strategy provided the continuous process for biodiesel and the main driving force for such reaction was temperature rather than pressure. Among the porous materials screened, mesoscale and macroscale porous materials were suitable to increase the reaction rates. This strategy can simultaneously increase the esterification of FFA and the transesterification of triglycerides into a single step with a reaction time of 1-2 min. The noncatalytic biodiesel can be achieved under ambient pressure and it was shown that the main driving force behind the non-catalytic transesterification of the lipid feedstock with DMC in the presence of the porous material was temperature rather than pressure. The numerous pores in the material served as micro reaction chambers and ensured that there was enough contact time between the liquid triglycerides and the gaseous DMC which enabled the completion of the transesterification (Kwon *et al.*, 2014). The authors have shown that the highest Fatty Acid Methyl Esters (FAMEs) yield achieved was 98±0.5% within 1-2 min at a temperature of 360-450°C under ambient pressure. Compared to the optimal conditions reported by other authors (i.e., 300°C) (Ilham and Saka, 2012), the experimental temperature used by Kwon *et al.* (2014) was relatively high. The relatively high temperature used did not cause thermal decomposition of the FAMEs. This can be explained by the fast reaction rate and the relatively short retention time of FAMEs and byproducts. The fast reaction rates made it possible to convert the lipid feedstock into biodiesel via a continuous flow system without the application of increased pressure (Kwon *et al.*, 2014). This suggested that the commonly used supercritical conditions could be avoided; resulting in huge cost benefits for biodiesel production.

INNOVATIVE TECHNOLOGY

As mentioned before high transesterification yields require high temperature, high pressure and high alcohol to oil molar ratio. Indeed, high temperature and pressure require high initial investments (equipment costs) for the implementation of such processes and safety management policy. As a result of the high alcohol to oil molar ratio, greater energy consumption in the reactant pre heating and recycling steps is unavoidable. To increase the technical and economic feasibility of supercritical method, further studies are required to reduce the energy consumption and operating parameters of this process.

Microwaves, as an energy source, produce heat by their interaction with the materials at molecular level without altering the molecular structure. Microwaves are non-ionizing radiations i.e., electromagnetic waves with low energy content that therefore cannot ionize the atoms crossed. These radiations can influence molecular movements, such as ions migration or dipole rotations but do not change the molecular structure (Varma, 2001; Refaat *et al.*, 2008). Polar solvents with low molecular weight and high dielectric constant, irradiated by microwave, undergo a rapid increase in temperature, thus reaching faster their boiling point. Biodiesel production from microalgae requires extraction of oils and lipids from the cellular mass prior to their transesterification. Supercritical conditions can be applied in direct extractive-transesterification of vegetable oils and algal oils. Water at supercritical conditions can act as organic solvent and thus eliminating the need for solvent use. It has been demonstrated that simultaneous extraction and transesterification (in situ transesterification) of the wet algal biomass in supercritical methanol conditions (Patil *et al*., 2011). In a microwave-assisted extraction and transesterification process, it is anticipated that the reaction can be conducted at atmospheric pressures and temperatures merely close to the boiling point of methanol with much shorter reaction time (Refaat *et al*., 2008; Patil *et al*., 2010; Barnard *et al*., 2007).

CONCLUSION

The biodiesel market represents a relatively young business started about 15 years ago, driven by two main factors: new environmental regulations and the dramatic increase of the price of oil. The competitiveness of biodiesel is hindered by the price of vegetable oils. Among all current transesterification methods, the reaction with homogeneous base catalysis is still a common and commercial method. Besides the traditional methods, non-catalytic synthesis of biodiesel or supercritical method have been highlighted in this review as there is enormous potential of applying supercritical fluid technologies in production of biodiesel. However, as for any emerging technology, it also presents some weaknesses. Future efforts should move forward to simpler, cost effective and “greener” SCFs processes, leading to high yields of a quality biodiesel fuel. New non-edible potential sources of vegetable oil such as microalgae and jatropha oil will ensure that biodiesel production does not compete with resources for food industry, as they will help to reduce costs and increase social acceptance. A proof-of-concept study has been made to convert rapeseed oil into fatty acid butyl esters by means of microwave irradiation without using a catalyst. High conversions can be reached when the transesterification of triglycerides with 1-butanol was performed under near-critical or supercritical conditions. Microwave heating is an attractive method to perform high-temperature chemistry since the reaction mixture can be heated up considerably faster under carefully controlled conditions. Additional studies into the economic viability of any of the approaches mentioned should be made before we can safety talk of a green chemical industry for biodiesel production.

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