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Biodiesel Production with Solid Catalysts

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1. Introduction

Biodiesel is usually produced by transesterification of vegetable oils or animal fats with chemical catalysts, especially in the presence of strong acidic or basic solutions, such as hydrochloric acid, sulphuric acid, sodium hydroxide, sodium methoxide and potassium hydroxide. Homogeneous alkali catalysts can convert triglycerides to their corresponding fatty acid methyl esters (FAMES) with high yield, less time and low cost. However, separating the catalyst from the product mixture for recycling is technically difficult. After reaction, the catalyst should be neutralized or removed with a large amount of hot water, which will produce a large amount of industrial wastewater.

Typical plant oils, such as soybean oil, rapeseed oil and palm oil, are the main edible oils. They are not suitable as raw materials, particularly in developing countries due to limited supply and high cost. Therefore, low-cost lipids, such as non-edible oils (e.g., *Jatropha* oil), animal fats and waste oils, are used as ideal feedstocks. Such oils usually contain some water and free fatty acids (FFAs) that will form soap when homogeneous base catalysts are used. On the other hand, homogeneous acid catalysts are corrosive to equipment. Solid heterogeneous catalysts are used to overcome these problems, because they are non-corrosive, non-toxic, and easily-separated for recycling. Reusability of heterogeneous catalysts makes continuous fixed-bed operation possible. Such continuous process can minimize product separation and purification costs, make it economically viable to compete with commercial petroleum-based diesel fuel. This chapter describes solid heterogeneous catalysts for biodiesel production and their typical catalytic mechanism.

2. Heterogeneous solid catalysts

In laboratory-scale experiment, heterogeneous processes could be run in a continuous mode with a packed-bed continuous flow reactor. Heterogeneous catalysts were easily separated from the products, water-washing process and neutralization steps were avoided. Contaminated water from this process was greatly reduced, and the sewage treatment fees were also minimized. New types of heterogeneous catalysts have mushroomed and developed in recent years.

2.1 Heterogeneous acid catalysts

Acid catalysts can simultaneously catalyze both esterification and transesterification, showing a much higher tolerance to FFAs and water than basic homogeneous catalysts (e.g.,

NaOH and KOH). Homogeneous acid-catalyzed reaction is about 4000 times slower than the homogeneous base-catalyzed reaction (Lotero et al., 2005). Heterogeneous acid catalysts performed less activity, but they are favorable for low-qualified oil feedstocks with high FFAs. Now, synthetic solid acids have already amounted to hundreds of species, most of them can be used in esterification and transesterification reactions. Solid acids keep stable activity in conversion of low-qualified oils or fats to biodiesel. Currently developed solid acid catalysts are introduced in the following sections: cation exchange resin (i.e. Amberlyst-15 and NR50), mineral salts (i.e. ferric sulfate, zirconium sulfate, alum phosphate and zirconium tungsten), supported solid acid and heteropolyacid catalysts.

2.1.1 Ion-exchange resins

Ion-exchange resins are widely used in important industrial processes for both separation and reaction applications. They are less expensive than lipase and supercritical methanol. Ion exchange resins also help to separate biodiesel and glycerol. Shibasaki-Kitakawa et al. (2007) found catalytic activity of anion-exchange resins correlated positively with cross-linking degree and particle size. The activity of acid ion-exchange resins for the esterification reaction is influenced by the accessibility of reactants to the matrix anchored sulfuric acid groups located at the surface or inside the resins. Mass-transfer restriction is another factor affecting catalytic activity. Internal diffusion was found to cause mass-transfer restriction and is rate-limiting for regular resins. Most of the active sites are embedded in the gel matrix, so the resins with macro-pores have high catalytic activity. Furthermore, the catalytic activity decreased when the cross-linking degree of polymeric matrix increased. Reusability is an important evaluation index for industrial applications of resins. Mechanical strength and thermo-stability are important for the large-scale applications of resins in biodiesel production. Ion exchange resins usually don't change catalytic property for long time operation at low temperature (< 100 °C).

Caetano et al. (2009) studied esterification of palmitic acid with methanol using poly(vinyl alcohol) cross-linked with sulfosuccinic acid (SSA) resin at 60°C, about 90% conversion rate was achieved after 2 h. Only about 5% sulfosuccinic acid was leached after 7 recycles. Activity of NKC-9 resin even slightly increased at the first 10 runs, due to breakdown of resin particles under mechanical agitation (Feng et al., 2010). Continuous production of biodiesel in a fixed-bed reactor packed with resins was successively operated (Shibasaki-Kitakawa et al., 2007; Liu et al., 2009; Feng et al., 2011). After 500 h, conversion yield of FFAs still kept over 98%. Amberlyst-15 performed high activity at 100 °C in the fixed-bed, and a 97.5% FAMES yield was achieved (Son et al. 2011). Combination of fixed-bed reactor with supercritical CO₂ may develop a continuous process that is preferred for massive biodiesel production. 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 (Russbueldt and Hoelderich, 2009). Deactivated catalyst can be recovered to its original activity by acid washing. It was found that temperature has negligible effect on water-swelling, but the water absorbed on the resin surface can be extracted by excessive methanol (Tesser et al., 2010)..

2.1.2 Zeolites

Zeolites are crystalline alumino-silicates with a three-dimensional porous structure. They can be synthesized with different crystal structures, definitive pore sizes, framework Si/Al ratios and adjustable acid centers to have some important catalytic properties. Aluminum

atoms and ions in skeletons and porosity supply the acidic sites. Zeolites have extremely high internal surface area (600 m²/s) and high thermal-stability (1000 °C), as the most popular solid catalysts. Acidic-shape selectivity is a significant feature of zeolite, derived from the influence of pore size and shape on a reaction. Zeolites were used in biodiesel production as a heterogeneous catalyst. Pérez-Pariente et al. (2003) studied the selective synthesis of fatty monoglycerides with Zeolites. Compared with reaction parameters, catalyst properties have more effects on monoglyceride yield.

Zeolite β is a high silica zeolite with both Lewis-acid sites and Brønsted-acid sites, containing an intersecting three-dimensional structure of 12-membered ring channels (Shu et al., 2007). Lewis-acid sites are mainly present in the micro-porous walls. On the contrast, Brønsted-acid sites are present on the internal and external surface. Zeolite β does not exhibit high activity in transesterification, but it can be used for selective removal of FFAs in waste oil (Chung et al., 2008).

HY zeolite has a large number of weak acid sites. When one Si⁴⁺ is substituted by an Al³⁺, the zeolite framework generates one Brønsted acid site. On the other hand, one Na⁺ cation neutralizes one acid site. Furthermore, hydroxyl groups formed by ion exchange of HY zeolite with ions, such as Ca²⁺, Mg²⁺ and La³⁺, can strengthen the acidic sites. Acidity of zeolite can also be adjusted by introducing protons with dilute hydrochloric acid. Sasidharan and Kumar (2004) found that 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 (biodiesel yield < 30%). The high pore volume of large-pore zeolites favored reaction by rendering the active sites more accessible to the bulky triglyceride molecules. However, H β -Zeolite catalyzed transesterification of crude *Pongamia pinnata* oil gave low yield of 59% at a long reaction time (24 h) (Karmee and Chadha, 2005). Internal diffusion resistances are considered to limit reaction rate significantly. Thus, large-pore zeolites are active for the reaction with satisfactory reaction rate.

Most of zeolites exhibit not only acidic property, but they also provide high activity and selectivity in various acid catalysts as carrier. Bifunctional catalyst can usually be prepared by combining active catalytic sites on an acid zeolite. Shu et al. (2007) introduced La ion into zeolite β with La(NO₃)₃ as the ion exchange precursor. La/zeolite β resulted in higher conversion with higher stability than zeolite β because it has more external Brønsted acid sites available for the reactants. Triglyceride conversion yield of 48.9 wt% was obtained at 60 °C for reaction time of 4 h.

2.1.3 Heteropoly acids (HPAs)

A heteropoly acid 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). Heteropoly acid is frequently used as a re-usable acid catalyst in chemical reactions, but their long term stability and performances are not yet fully characterized. With inherent advantages of strong Brønsted acidity, stability and high proton mobility, HPAs are favorable as environmentally benign and economical solid catalysts. Owing to their unique physicochemical properties, HPAs are profitably used in homogeneous, biphasic and heterogeneous systems. There are many types of heteropolyacids, and the Keggin (H_nXM₁₂O₄₀) and Dawson (H_nX₂M₁₈O₆₂) structures are two of the better known groups (Kozhevnikov, 1998). HPAs (e.g., H₃PW₁₂O₄₀) are soluble in water and possess acidic strength as strong as sulfuric acid. HPAs solubility can be changed via alkali-exchange, and modified HPAs exhibiting significantly higher activity.

HPAs are excellent and environmentally benign acid catalyst for the production of biodiesel, which are tolerant to contaminations contained in oil resources such as FFAs and water. The Keggin HPA (i.e., $H_3PW_{12}O_{40}$) is soluble in methanol, and the use of Keggin heteropolyacids for triglyceride (trans)esterification has been reported. Alsalmeh et al. (2008) studied the intrinsic catalytic activity of Keggin HPAs, indicating activity of HPAs is significantly higher than that of the conventional acid catalysts in (trans)esterification. Their acid strength in the descending order is as follows: $H_3PW_{12}O_{40} > Cs_{2.5}H_{0.5}PW_{12}O_{40} > H_4SiW_{12}O_{40} > 15\%H_3PW_{12}O_{40}/Nb_2O_5, 15\%H_3PW_{12}O_{40}/ZrO_2, 15\%H_3PW_{12}O_{40}/TiO_2 > H_2SO_4 > HY, H\text{-Beta} > Amberlyst-15$. HPA is able to efficiently promote the esterification with a similar performance to sulfuric acid. However, the recovery and reutilization of HPAs is difficult. The main 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. It is reported that partial exchange of ammonium salt in 12-tungstophosphoric acid with offers more acidic strength to the catalyst than the fully exchanged ammonium salt (Giri et al., 2005). Exchange of protons in HPA can help promote its activity in transesterification of triglycerides. The protons replacement has similar effects on activity as cations concentration increase. $Cs_xH_{3-x}PW_{12}O_{40}$ ($x = 0.9-3$), one kind of insoluble Keggin HPAs, offers excellent performance in (trans)esterification (Narasimharao et al., 2007). The catalytic activity of Cs-salts decreases as the content of Cs in HPW grows, due to the decrease of pH and the increase of conductivity of colloidal solutions in direct relation with the acidity of surface layers of primary particles. Furthermore, low-Cs loading on HPAs shows some dissolution of an active acid component after reflux in hot methanol, while high-Cs loading on HPAs is stable in hot methanol. Immobilization of HPAs on carrier is also an efficiency method to obtain insoluble catalyst. Such supported solid acids performed high thermal-stability even under reaction conditions of 200 °C. Caetano et al. (2008) used tungstophosphoric acid, molybdophosphoric acid and tungstosilicic acid immobilized by sol-gel technique on silica to catalyze esterification of palmitic acid with methanol. The higher heteropolyacids load on silica, the lower the catalytic activity is observed. Tungstophosphoric acid-silica (with 4.2 wt.%) showed the highest catalytic activity, 100% palmitic acid conversion was achieved after 30 h reaction time with methanol. Zięba et al. (2010) tested catalytic performance of Amberlyst-15, Nafion-SAC-13, polyaniline-sulfate, silver and cesium salts of HPAs in transesterification of triglycerides with methanol. $Cs_2HPW_{12}O_{40}$ was the most active catalyst due to its highest strength of acid sites, but the great affinity toward glycerol led to its deactivation during recycling process.

2.1.4 Supported acid catalysts

Supports can provide higher surface area through the existence of pores where acidic sites can be anchored. Supports should be modified during preparation of catalysts to anchor catalytic species and obtain reusability. Furthermore, some amorphous carriers also showed good activity for (trans)esterification. Metal oxides are widely used as catalyst supports because of their thermal and mechanical stability, high specific surface area, and large pore size and pore volume. Because solid acids function the same as H^+ in sulfuric acid for (trans)esterification, sulphonated metal oxides, such as $SO_4^{2-}/Al_2O_3, SO_4^{2-}/TiO_2, SO_4^{2-}/ZrO_2, SO_4^{2-}/SnO_2$ and SO_4^{2-}/V_2O_5 (Garcia et al., 2008) can supply more acid species. Such solid acids are usually prepared by impregnating the hydroxides from ammonia precipitation of corresponding metal salt solutions with aqueous sulfuric acids followed by calcination. In

addition to acid amount and acid strength adjustment, the catalysts are satisfactorily active in a heterogeneous liquid–solid system and are recoverable and reusable.

A cheap and high efficiency solid acid catalyst (SAC) derived from sulfonation of carbonized D-glucose or sucrose was reported, and used in transesterification of vegetable oil with alcohol (Shu et al., 2009; Toda et al., 2005; Zong et al., 2007). The catalyst was prepared from carbohydrates by carbonizing at 400 °C under N₂ atmosphere and then sulphonating at 150 °C. The solid acid catalyst can also be prepared by direct sulphonation of lignin consisting of polyethers and C-C linked phenylpropanes as shown in Fig. 1. The carbon carriers are amorphous, polycyclic aromatic carbon sheets containing SO₃H groups as active sites (Shu et al., 2009; Toda et al., 2005). The polycyclic carbon sheets can absorb long-chain hydrocarbon for reactants in solution to access SO₃H groups. Hydrolysis of cellulose to saccharides using such amorphous carbon bearing SO₃H, COOH, and OH function was studied (Suganuma et al., 2008). Phenolic OH groups bonded to the grapheme sheets can absorb β-1,4 glycosidic bonds and provide good access of reactants in solution to the SO₃H groups in the carbon material.

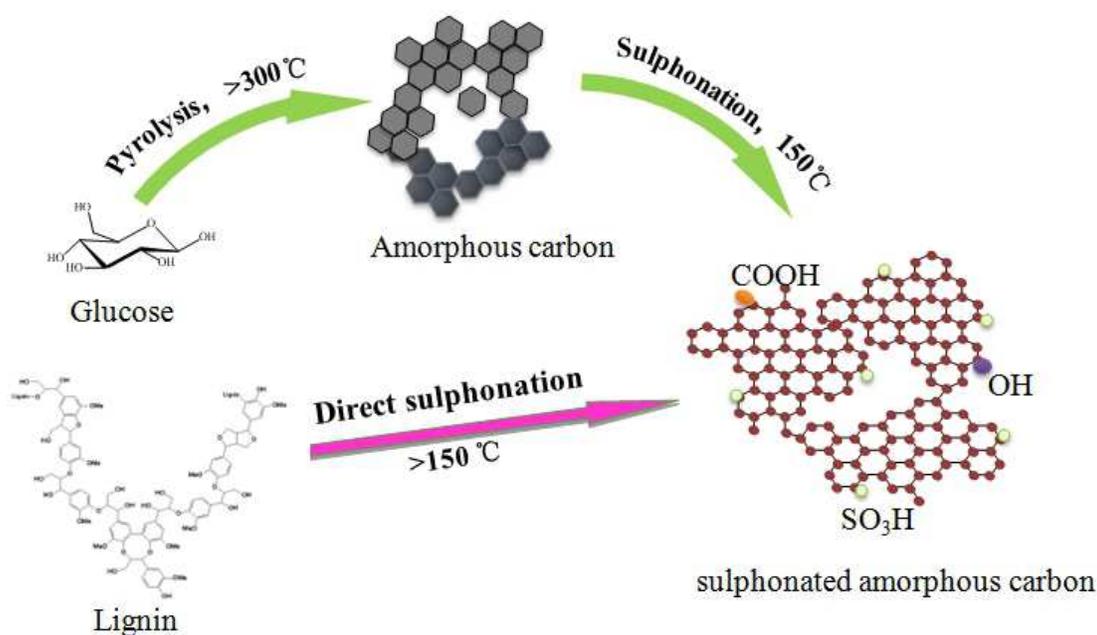


Fig. 1. Preparation process of sulphonated amorphous carbon from glucose and lignin.

Zong et al. (2007) utilized SAC as a solid acid catalyst for transesterification of waste oil (27.8% FFAs) with methanol. The reaction was carried out at 80 °C for 15 h, a high yield of above 90% obtained as compared with below 80% yield when sulfated ZrO₂, Amberlyst-15 and niobic acid were used. SAC was also used for other types of organics reactions, such as oxidations of organic compounds (e.g., sulfides, tertiary amines, aldehydes) with hydrogen peroxide (Shokrolahi et al., 2008). Specific surface area, pore size, pore volume and active site concentration on the surface of catalyst are effective factors on catalytic activity. Stability of the active sites is important for their industrial applications.

2.2 Heterogeneous base catalysts

The transesterification of vegetable oils or animal fats to biodiesel by chemical catalysts, especially in the presence of a strong basic solution, such as sodium hydroxide and

potassium hydroxide, has been widely used in industrial production of biodiesel. Such basic solutions can transform triglycerides to their corresponding FAMES with higher yield at lower temperature and shorter time than those by acid catalysts. However, separating the catalysts from products is technically difficult. Moreover, natural vegetable oils and animal fats usually contain small amounts of FFAs and water, which can have significant negative effects on the transesterification of glycerides with alcohols, and also hinder the separation of FAMES and glycerol due to saponification of FFAs. Compared with basic solutions, solid base catalyst is preferred due to easy separation.

Heterogeneous base catalysis has a shorter history than that of heterogeneous acid catalysis. Solid bases refer mainly to solids with Brønsted basic and Lewis basic activity centers, that can supply electrons (or accept protons) for (or from) reactants. Heterogeneous base-catalyzed transesterification for biodiesel synthesis has been studied intensively over the last decade. Low-qualified oil or fat with FFAs and water can be used. However, the catalytic efficiency of conventional heterogeneous base catalysts is relative low and needs to be improved. Various types of catalytic materials have been studied to improve the transesterification of glycerides. Heterogeneous base catalysts, such as hydrotalcites, metal oxides, metallic salt, supported base catalyst and zeolites are introduced herein details.

2.2.1 Hydrotalcites

Hydrotalcites (HTs) are a class of anionic and basic clays known as layered double hydroxides (LDHs) with the formula $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$. HTs consist of positively charged brucite-like layers and interstitial layers formed by CO_3^{2-} anions, and water molecules compensate the positive charge resulting from the substitution. LDHs have strong alkali sites and high stability with good adjustability of composition and structure. However, low surface area affected its catalytic activity. Mg/Al mole ratio and calcination temperature are the determining factors for the base-catalyzed activities. HTs with a 3:1 molar ratio of Mg to Al have the highest basicity and activity (Xie et al., 2006). Decomposition of HTs after calcination yields a high surface area Mg-Al mixed oxide, which presumably exposes strong Lewis basic sites. During calcination process, the interlayer water is lost first, followed by dehydroxylation and decomposition of interlayer carbonate to CO_2 , which generate a porous structure and specific surface area ranging from 150 to 300 m^2/g (Lee et al., 2009). Furthermore, Mg^{2+} can be replaced by Zn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , and Al^{3+} by Cr^{3+} , Ga^{3+} , Fe^{3+} . HTs substituted with copper have a relatively uniform porous structure with decreased specific surface area. For iron substituted HTs, microporosity features developed, pore size decreased and specific surface area increased. The initial study by Cantrell et al. (2005) on biodiesel synthesis with HTs indicated magnesium content has obvious effects on catalytic activity. Increase of both magnesium content and electron-density enhances alkaline of HTs and finally increases biodiesel yield.

As classical solid base materials, calcined HTs were widely used as catalyst in the production of biodiesel (Brito et al., 2009; Deng et al., 2010). The basicity and surface area of HTs can be tuned by modifying chemical composition and preparation procedure. A co-precipitation method usually used to synthesize HTs with Mg/Al molar ratio of 3/1 using urea as precipitating agent. In previous work (Xie et al., 2006), transesterification process was carried out with reflux of methanol, methanol/soybean-oil molar ratio of 15/1, reaction time of 9 h and catalyst amount of 7.5%, and oil conversion rate was only 67%. In the work of Brito et al. (2009), waste oil as feedstock, biodiesel production was performed at temperatures ranging from 80 to 160 °C, methanol/oil molar ratio from 12/1

to 48/1 and catalyst concentration from 3 to 12%, respectively, and 90% biodiesel yield was achieved.

It is known that HTs present lamellar structure thus not pose accessibility restrictions of vegetable oil molecules to catalyst sites. Improvement of specific surface area becomes necessary to obtain high catalytic activity. Deng et al. (2011) synthesized a series of nanosized HTs by a modified co-precipitation method. SEM images of HTs and calcined HTs were given in Fig. 2. Variables of temperature, solution pH and ageing time have a strong influence on the final basicity of the mixed oxides. Mg-Al ratio in the precursor HT depends on the basic properties of these sites. In the transesterification experiment using Mg-Al HT catalysts, 95% biodiesel yield was achieved from *Jatropha* oil in 1.5 h. Pre-mixture of HTs with methanol is essential to optimize catalyst activity to avoid lagging in reaction activity due to mass diffusion. Xi et al. (2008) tested influence of water on the activity and stability of activated Mg-Al HTs. In the presence of certain amount of interlayer water, Brønsted base sites were active. However, high degree of hydration caused rapid deactivation of the catalyst. Mg-Al HT shows relatively robust activity in the presence of water or FFAs tolerate, which is an attractive feature for biodiesel production.

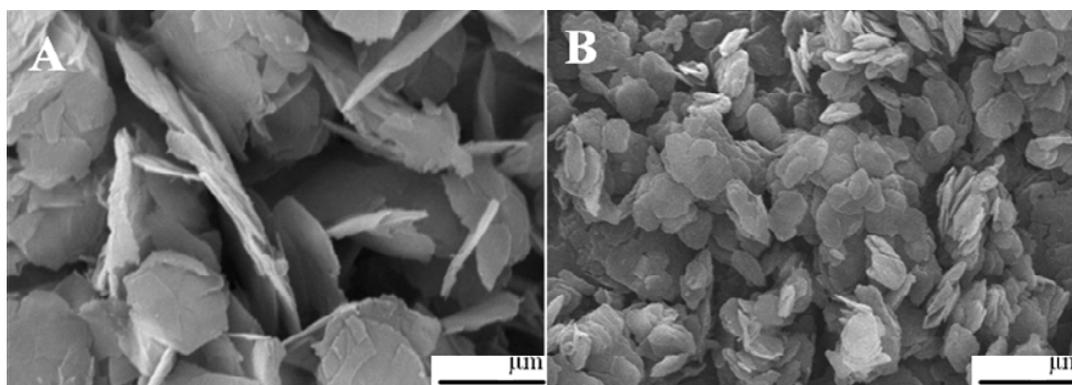


Fig. 2. SEM images of (A) hydrotalcite and (B) calcined hydrotalcite at 500 °C for 6 h.

2.2.2 Metal oxides

Metal oxides are composed of cations possessing Lewis acid and anions with Brønsted base. 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; Liu et al., 2008; Montero et al., 2009). Early studies on heterogeneously catalyzed transesterification were focused on the catalysis by single metal oxides. The basicity of oxides (especially, basic sites) directly depends on reaction rate. A comparison of several metal oxides (MgO, CeO₂, La₂O₃ and ZnO) indicated that the most basic one is La₂O₃, followed by MgO, CeO₂ and ZnO (Bancquart et al., 2001).

The order of activity among alkaline earth oxide catalysts is BaO > SrO > CaO > MgO. 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. Reddy et al. (2006) used CaO as solid base catalyst in the transesterification of soybean oil, only 2% biodiesel yield achieved. However, the intrinsic basicity of nano-CaO is much higher, 99% biodiesel yield was obtained with nano-CaO. In addition to specific surface area, other

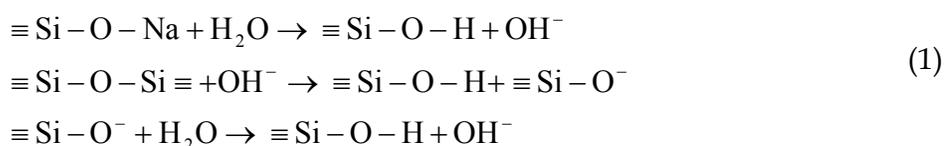
variables such as temperature and molar ratio of methanol to oil also influenced the catalytic activity. A measured amount of water in oil is wonderful for promotion of catalytic activity. Study showed 95% biodiesel yield was obtained using CaO as catalyst in present of about 2 wt% water (Xi et al., 2008). SrO has basic sites stronger than $H_0 = 26$. It can catalyze many chemical reactions, such as oxidative coupling of methane, selective oxidation of propane, nitro-Aldol reactions and mixed Tishchenko reactions. Liu et al (2007) reported SrO performed high catalytic activity to convert soybean oil to biodiesel with a yield over 95% at temperature below 70 °C for 30 min. MgO has weak basic strength and low solubility in methanol. It is usually produced by direct heating of magnesium carbonate or magnesium hydroxide. There is a striking linear correspondence between the catalytic activity and surface basicity of MgO. High reaction temperature (e.g., 523 °C) and high pressure (e.g., 24 MPa) are usually needed for achieving a high biodiesel yield (Wang and Yang, 2007).

To increase the basic strength of a single metal oxide, mixed metal oxides are synthesized. Peterson et al. (1984) prepared CaO-MgO and found that it provided higher catalytic activity than CaO powders for transforming rapeseed oil to biodiesel. Catalytic activity tests were performed for CaO-TiO₂, CaO-MnO₂, (CaO)₂-Fe₂O₃, CaO-ZrO₂ and CaO-CeO₂ samples, approximately 90% biodiesel yield were obtained (Kawashima et al., 2008). The Ca catalysts were found to have higher basicity and activity. Such catalysts performed noticeably decreased activity in transesterification when ethanol or branched alcohols was used, attributed to the steric effects on the catalytic activity of these catalysts. Furthermore, active sites of metal oxides are easily blocked by adsorbing intermediates (diglyceride, monoglyceride) or products. Deactivated catalysts can be recovered nearly to the initial value through calcination.

2.2.3 Metallic salts

Inorganic solid bases, such as sodium silicate (Guo et al., 2010), vanadyl phosphate (Serio et al., 2007), calcium zincate (Rubio-Caballero et al., 2009) and calcium methoxide (Liu et al., 2008), are low-cost and easy-to-use heterogeneous catalysts. Reports on metallic salts catalyzed conversion in biodiesel preparation are rare. Here, only sodium silicate, vanadyl phosphate (VOP) and calcium zincate are reviewed.

Sodium silicate was used as starting materials to synthesize γ -zeolite, NaY zeolite, and NaX zeolite. Guo et al. (2010) used sodium silicate to catalyze the transesterification reaction for the first time. It catalyzed soybean oil to biodiesel with a yield of almost 100% under the conditions: sodium silicate of 3.0 wt %, a molar ratio of methanol/oil of 7.5:1, reaction time of 60 min, reaction temperature of 60 °C, and stirring rate of 250 rpm. In addition to high catalyst activity, sodium silicate also has other similar characteristics to supported-solid base catalysts. Most of basic sites were in the interior of the solid catalyst due to low surface area and high density of the basic sites. The calcined sodium silicate could tolerate 4.0 wt% water or 2.5 wt% FFAs contained in soybean oil. The water tolerance is related to its special crystal and porous structure. In the presence of high amount of water, a sequential hydration will occur in three steps:



As a result, Si-O-Si bridges would be hydrolyzed and H_4SiO_4 monomers are sequentially released. Such series of reactions not only produce OH⁻, but also avoid the formation of soap. Furthermore, sodium silicate could also be used to catalyze dehydration of glycerol. Long et al. (2011) used sodium silicate as catalyst for transesterification of rapeseed oil for several recycles, and subsequently the used sodium silicate without any modification was catalyzed for the hydrothermal production of lactic acid from glycerol at 300 °C. A yield of 80.5% lactic acid and only minor amounts of formic, acetic acid and acrylic acid were produced.

Previous applications of VOP were mainly in hydrocarbon oxidation, dehydration and isomerization (Serio et al., 2006). Serio et al. (2007) confirmed that VOP-based catalysts were very active in the transesterification of vegetable oil with methanol despite their low specific surface area. VOP was deactivated due to a progressive reduction of vanadium (V) species from V^{5+} to V^{4+} and V^{3+} by methanol. Because the deactivation is reversible and catalyst activity can easily be restored by calcination. Rubio-Caballero et al. (2009) investigated the use of calcium zincate in the methanolysis of sunflower oil for biodiesel production. The activated calcium zincate at 400 °C is stable against lixiviation, attributed to its strong interaction with a much less soluble zinc oxide. But, calcium zincate is more sensitive to water (> 0.2 wt.%) rather than FFAs. Calcium methoxide has a moderate surface area, relative broad particle size distribution, narrow pore size distribution, strong basicity, long catalyst lifetime and better stability in organic solvent (Liu et al., 2008). It has tremendous potential to replace some homogeneous catalysts.

2.2.4 Supported base catalysts

Alkali metals (Li, Na, K) and alkaline earth metals (Mg, Ca, Ba) are the most common sources of super basicity, and selected as the active species of supported catalysts for biodiesel synthesis. They are frequently used in the metallic form or as various ionic forms of hydroxide, halide, carbonate and nitrate, such as K^+ , Li^+ , La^{3+} , KOH, NaOH, KF, K_2CO_3 , KNO_3 (Shu et al., 2007; Sun et al., 2008; Vyas et al., 2009). Alumina, silica, zinc oxide, zirconium oxide and zeolite were used as supports for these catalysts. Surface basicity is the primary determinant of catalyst activity, then the specific surface area and pore volume (Sun et al., 2008). During the preparation of such catalysts, the mechanical intensity and surface area of carriers can be adjusted to obtain different basic intensities and activity sites.

Almost all supported base catalysts were synthesized via loading of active species on carriers by covalent bond, ionic bond or physical adsorption. Despite of formation of M-O-carrier (e.g., Al-O-K, Si-O-Na and Ca-O-K), other possible interactions of the alkali species with supports include formation of solid solutions and acid-base reactions. Hydroxyl groups introduced to the surface of solids play an important role in transesterification reaction (Xie et al. 2006). The hydroxyls with alkali species enhance the catalytic activity.

As a most popular carrier, Al_2O_3 has almost all noteworthy properties such as high temperature resistant, high surface area, high porosity, low density and transition crystalline phase existed in a wide temperature range. Furthermore, it serves as carrier with both solid acid and base. Most super basicity sources can be well dispersed on the Al_2O_3 support in the form of a monolayer at a low loading. Furthermore, alumina is more resistant than other supports (e.g., SiO_2 , CaO and zeolite) for alkali species. Taking $\text{KNO}_3/\text{Al}_2\text{O}_3$ as an example, it is usually prepared by impregnation and subsequent calcination at 500 °C (Xie et al. 2006). K^+ ions replaced protons of isolated hydroxyl groups to form Al-O-K groups. The Al-O-K groups and K_2O derived from KNO_3 are active basic species. The base strength could be

tentatively denoted as $15 < H_0 < 18.4$ by using Hammett indicator. Basic strength of $\text{KNO}_3/\text{Al}_2\text{O}_3$ was influenced by KNO_3 loading and temperature. The 35% $\text{KNO}_3/\text{Al}_2\text{O}_3$ sample calcined at 500°C had the highest basicity. However, the sample prepared at 700°C was most stable. Because part of potassium species are loss by a solid-solid reaction leading to formation of spinels or penetration into the subsurface.

Aends and Sheldon (2001) indicated that such kind of catalyst is unstable during reaction, mainly due to M-O-Al decomposed in present of methanol. Arzamendi et al (2007) confirmed that NaOH reacted with the support to form aluminates during preparation of $\text{NaOH}/\text{Al}_2\text{O}_3$. Leaching of sodium species from Al_2O_3 was also found. Furthermore, problems of high cost, difficult preparation and easy poisoning by absorption of H_2O and CO_2 should be solved. The supported solid base catalysts are excellent for transesterification of triglyceride, but a higher temperature is needed.

3. Catalytic mechanism

3.1 Heterogeneous solid acid-catalyzed esterification mechanism

Low-cost feedstocks need pretreatment (esterification) to remove FFAs before base-catalyzed transesterification reaction. The esterification path is relatively simple reversible reaction as follows:



In the reaction (2), FFA is converted to FAME. When homogenous acid (e.g., sulfonate acid, phosphorus acid and hydrochloric acid) was used, esterification reaction is a process that FFA supply hydroxide and methanol supply proton without intermediate process.

Different to homogeneous catalysis, heterogeneous catalytic process is known to follow a carbonium ion mechanism. The mechanism of solid acid-catalyzed esterification consists of following steps as shown in Fig. 3. Firstly, solid catalysts provided protons, and carbonyl carbon was protonated. Next, nucleophilic attack of CH_3OH on the carbonium ion formed a tetrahedral intermediate. Finally, FAME was produced after proton migrated and the intermediate broke down, and proton was reformed.

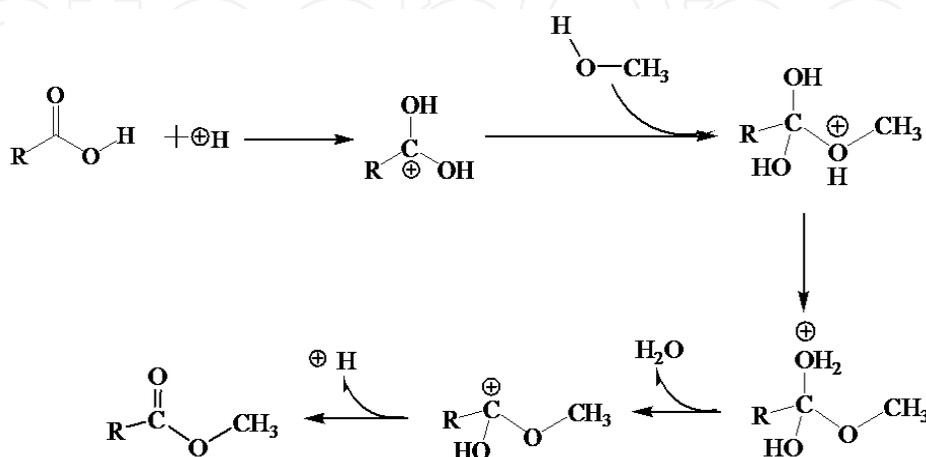


Fig. 3. Solid acid-catalyzed reaction mechanism of esterification.

The esterification reaction path is slightly different in various acidic species types. The whole reaction process is through proton-exchange. Tesser et al. (2005) proposed a kinetic model based on the following hypotheses: (1) major part of the active sites are occupied by methanol in a protonated form, and the rest part are also occupied; (2) fatty acid, water and methyl ester reach proton-exchange equilibrium with the protonated methanol; (3) inside the resin particles, an Eley-Rideal mechanism occurs between protonated fatty acid and the methanol. Deviate from the mechanism shown in Fig. 3, steps of protonation of carbonyl carbon, nucleophilic attack, proton migration and breakdown of intermediate are undergoing in a proton-exchange way.

3.2 Transesterification mechanism

The transesterification reaction involves catalytic reaction between triglyceride and alcohol (e.g., methanol, ethanol, propanol and butanol) to form biodiesel (FAMES) and glycerol (Fig. 4). In the reaction, three consecutive reactions are required to complete the transesterification of a triglyceride molecule. In the presence of acid or base, a triglyceride molecule reacts with an alcohol molecule to produce a diglyceride and FAME. Then, a diglyceride reacts with alcohol to form a monoglyceride and FAME. Finally, an monoglyceride reacts with alcohol to form FAME and glycerol. Diglyceride and monoglyceride are the intermediates in this process.

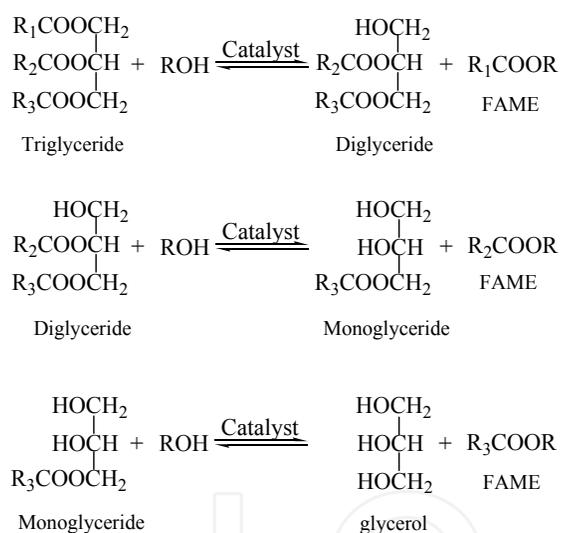


Fig. 4. Transesterification reactions of glycosides with alcohol.

3.2.1 Mechanism for heterogeneous acid-catalyzed transesterification

Acidic or basic functional groups in the active sites of solid catalysts catalyze the reaction by donating or accepting protons. Acid-catalyzed reaction mechanism for the transesterification of triglycerides is shown in Fig. 5. Firstly, triglycerides are protonated at the carbonyl group on the surface of solid acid. Then, a nucleophilic attack of the alcohol to carbocation forms a tetrahedral intermediate (hemiacetal species). Unstable tetrahedral intermediate leads to proton migration, followed by breakdown of the tetrahedral intermediate with assistance of solvent. After repeating twice, three new FAME as products were produced and the catalyst was regenerate. During the catalytic process, protonation of carbonyl group boosts the catalytic effect of solid acid catalyst by increasing the electrophilicity of the adjacent carbonyl carbon atom.

Different with Brønsted acids, Lewis acids [e.g., $\text{Fe}_2(\text{SO}_4)_3$, titanate complexes, carboxylic salts, divalent metal pyrone] act as electron-acceptors via the formation of a four-membered ring transition state (Abreu et al., 2004; Di Serio et al., 2005). The reactant triglyceride and metal form a Lewis complex, which assists solid Lewis acids during process of the carbonyl groups activating for a nucleophilic attack by the reactant alcohol. The triglyceride carbonyl coordinates at a vacant site in the catalytic active specie. Formation of a more electrophilic species is responsible for the catalytic activity. Stearate metals (Ca, Ba, Mg, Cd, Mn, Pb, Zn, Co and Ni) were tested as catalysts for methanolysis of soybean oil (2.0 g) with methanol (0.88 g) at 200 °C (Di Serio et al., 2005). A high FAMES yield (96%) and a low final FFAs concentration (<1%) were obtained in a relatively short reaction time (200 min).

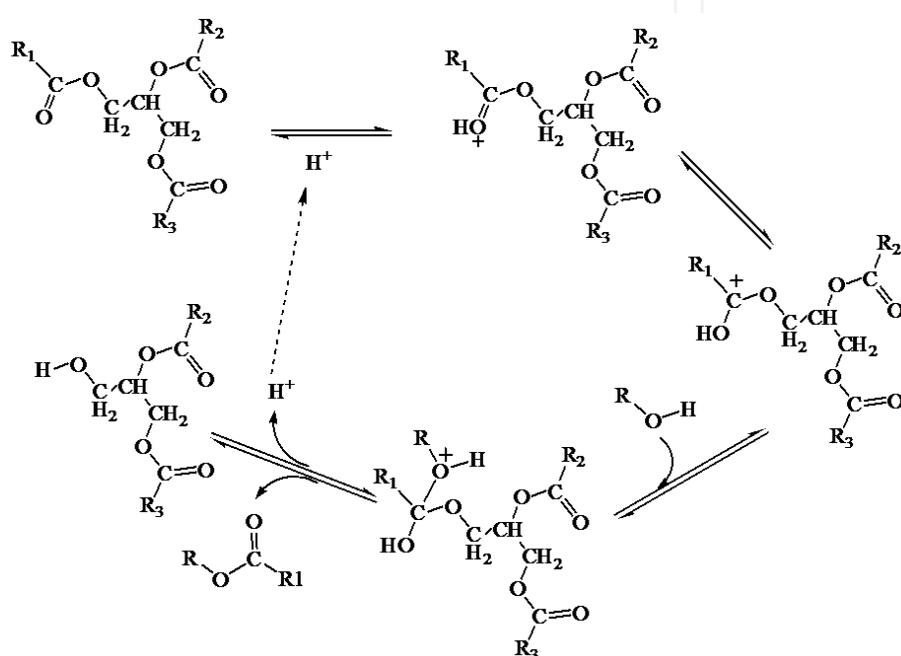


Fig. 5. Acid-catalyzed reaction mechanism of transesterification.

3.2.2 Mechanism for heterogeneous base-catalyzed transesterification

Base-catalyzed crude oil to biodiesel gets more studies than acid-catalyzed method. In base-catalyzed process, OH^- or CH_3O^- ions performed as active species. Catalytic reactions started on the surface of heterogeneous base (Fig. 6). The mechanistic pathway for solid base-catalyzed transesterification seems to follow a similar mechanism to that of a homogeneous base catalyst. First, ion-exchange proceeded after methanol absorbed on the surface of solid base, producing catalytic active specie (CH_3O^-) which is strongly basic and highly catalytic active. Secondly, nucleophilic attack of CH_3O^- on the carbonyl carbon of triglyceride formed a tetrahedral intermediate. Thirdly, rearrangement of the intermediate resulted in the formation of FAME. Finally, protons were converted to diglyceride ion to generate diglyceride. This sequence was then repeated twice to yield glycerol and biodiesel.

Formation of CH_3O^- is different according to solid base types. Taking CaO as an example, surface O^{2-} is the basic site, which can extract H^+ from H_2O to form OH^- , and OH^- extracts H^+ from methanol to generate CH_3O^- (Liu et al., 2008). It is interesting that CaO generates more methoxide anions in the presence of a little water (less than 2.8% by weight of crude oil), avoiding formation of soap. Surface oxides or hydroxide groups depend on the basicity

and catalytic activities. The basic strengths of Na/CaO and K/CaO are slightly lower than that of Li/CaO (Ma and Hanna, 1999). The presence of the electron-deficient M^+ on the support enhances the basicity and activity of the catalysts towards the transesterification reaction.

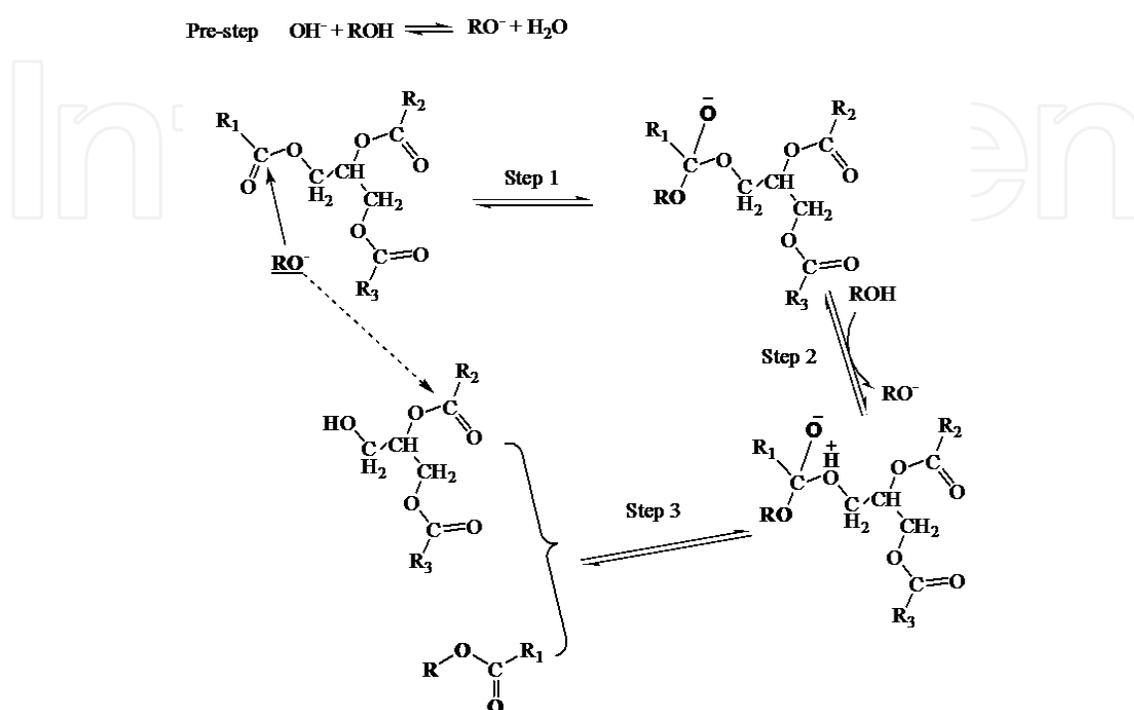


Fig. 6. Base-catalyzed reaction mechanism of transesterification.

4. Other methods or technologies

4.1 Microwave technology

Microwave heating has been widely used in many areas to affect chemical reaction pathways and accelerate chemical reaction rates. Microwave irradiation can accelerate the chemical reaction, and high product yield can be achieved in a short time. Microwave irradiation assisted biodiesel synthesis is a physicochemical process since both thermal and non-thermal effects are often involved, which activates the smallest degree of variance of polar molecules and ions such as alcohol with the continuously changing magnetic field. Upon microwave heating, rapid rising of temperature would result in interactions of changing electrical field with the molecular dipoles and charged ion, leading to a rapid generation of rotation and heat due to molecular friction. Dielectric properties are important in both the design calculations for high frequency and microwave heating equipment. Furthermore, dielectric constant depends on frequency, and is strongly influenced by temperature, mixed ratio and solvent type.

In Azcan and Danisman's work (2007), microwave heating effectively reduced reaction time from 30 min (for a conventional heating system) to 7 min. Ozturk et al. (2010) studied microwave assisted transesterification of maize oil, using a molar ratio alcohol/maize-oil of 10:1, and 1.5% w/w NaOH as catalyst. A 98.3% conversion rate is obtained using methanol for 5 min. Based on special heating manner, microwave irradiation performed well in transesterification of vegetable oil with heterogeneous base. Hsiao et al. (2011) introduced

nano-powder calcium oxide as solid base in converting soybean oil to biodiesel. A 96.6% of conversion rate was obtained under conditions of methanol/oil molar ratio of 7:1, amount of catalyst of 3.0 wt.%, reaction temperature of 65 °C and reaction time of 60 min. While a biodiesel conversion rate exceeded 95% was achieved under conditions of 12:1 molar ratio of methanol to oil, 8 wt.% catalyst, 65 °C reaction temperature and 2.0% water content for 3 h (Xie et al., 2008). Microwave irradiation is also used for extraction of bioactive compounds for value-added products, including oil extraction systems. Microwave heating can be used for biodiesel production by in-situ simultaneous extraction and transesterification from oil seeds.

4.2 Ultrasonic technology

There are three primary effects on an object under ultrasound: (1) Mechanical effects; (2) Cavity effects; (3) Thermal effects. The above effects of ultrasound not only change the structure of the object, but also lead to chemical reactions. Ultrasonic radiation is a relative new technique that results in the formation and collapse of micro-scale bubbles in liquid to generate local high temperature and high pressure. So, it is used as alternative energy source to promote reactions. The cavitation in ultrasonic wavelength is the phenomenon of expansion and contraction of the transfer media bubbles. Ultrasonic energy is propagated into solution by the destruction of pressurized micro-bubbles into small droplets. Furthermore, ultrasonication device placed near the liquid-liquid interface in a two-phase reaction system benefited for producing large interfacial areas (Wu et al., 2007). Cavitation induced by ultrasound has significant effects on liquid phase reactions. When ultrasound irradiation increased from 30 to 70 W, the mean droplet size decreased from 156 nm to 146 nm. Nevertheless, effect of droplet size on biodiesel yield was not studied.

Ultrasound has a short wavelength, slow transfer rate, and high energy transmittance as the vibrating type energy. Irradiation of ultrasonic energy has been used for the (trans)esterification of vegetable oils to shorten reaction time and to increase product yield (Deng et al., 2010). A comparison study between conventional and ultrasonic preparation of beef tallow biodiesel was carried out (Teixeira et al., 2009). The results showed that conversion rate and biodiesel quality were similar. The use of ultrasonic irradiation decreased reaction time from 1 h to 70 s. In addition to the mentioned advantages, ultrasonic can promote the deposition of glycerol at the bottom of reactor. Stavarache et al. (2007) investigated a bench-scale continuous process for biodiesel synthesis from neat vegetable oils under high power, low frequency ultrasonic irradiation. Reaction time and alcohol-oil molar ratio were mainly variables affecting the transesterification. Their research confirmed that ultrasonic irradiation is suitable for large-scale processing of vegetable oils since relatively simple devices can be used to perform the reaction. In the process, however, real irradiation time decreased during increasing pulse interval for tuning temperature, leading to biodiesel yield decrease. To reduce the effect of irradiation time loss, reaction temperature should be kept constant.

Mass transfer resistance is one of the main reasons for poor catalytic performance of solid catalysts in (trans)esterification. Very fine ultrasonic emulsions greatly improve the interfacial area available for reaction, increase the effective local concentration of reactive species, and enhance the mass-transfer in interfacial region. Therefore it leads to a remarkable increase in reaction rate under phase-transfer conditions transesterification with solid catalyst. Ultrasonication could reduce the transesterification reaction time to around 10 min compared with over 6 h for conventional processing.

4.3 Ionic liquids

Ionic liquids (ILs) are defined as salts that are in the state of liquid at low temperatures (below 100 °C). They are composed solely of cations and anions, and were used as solvents/catalysts for reactions. ILs are nonvolatile and thermal stable, hence they are excellent alternatives to traditional solvents. Some ILs are Lewis and Franklin acids. Acidic ILs are new-type of catalysts with high-density active sites as liquid acids but non-volatilization as solid acids. Furthermore, cations and anions of ILs can be designed to bind a series of groups with specific properties, so as to achieve the purpose of regulating the acidity. Recently, they have been used to replace traditional liquid acids such as sulfuric acid and hydrochloric acid for biomass conversion (Qi et al., 2010).

ILs were originally used as solvents for biodiesel synthesis with high biodiesel yield in short reaction time, by forming an effective biphasic catalytic system for the transesterification reaction. Neto et al. (2007) introduced a complex $[\text{Sn}(3\text{-hydroxy-2-methyl-4-pyrone})_2(\text{H}_2\text{O})_2]$ immobilized in BMI-InCl₄ with high price metal salts, and a maximum biodiesel yield of 83% was achieved. Later, biodiesel synthesis from vegetable oils using imidazolium-based ionic liquids under multiphase acidic and basic conditions was reported (Lapis et al., 2008). It is found that the acid is almost completely retained in ionic liquid phase, and ILs could be reused at least six times without any significant loss in the biodiesel yield or selectivity. However, the ILs is expensive and was only used for neutral vegetable oils. Brønsted acidic ILs were highly efficient catalysts for biodiesel synthesis from vegetable oils. Sulfuric acid groups in these ILs are the active sites for transesterification. Dicationic ILs exhibited better stability than the traditional ones. The acidic dicationic ILs with an alkane sulfuric acid group gave a superior catalytic performance in esterification reaction. Neto et al. (2007) assumed that the use of ILs with inherent Lewis acidity may constitute a more stable and robust catalytic system for the transesterification reaction. Guo et al. (2011) used 7 low-cost commercial ILs as both catalysts and solvents for the direct production of biodiesel from un-pretreated *Jatropha* oil. It was found that [BMIm][CH₃SO₃] had the highest catalytic activity with 93% of oleic acid being converted into ethyl oleate. When FeCl₃ was added to [BMIm][CH₃SO₃], a maximum biodiesel yield of 99.7% was achieved from un-pretreated *Jatropha* oil. However, it is complicated to synthesize these functional ILs and their cost is too high for industrial applications. Therefore, further investigation is necessary to synthesize inexpensive, stable and highly-active ILs.

5. Conclusions and future perspectives

Currently, homogeneous catalysis is a predominant method for transesterification reaction. Separating the catalyst from a mixture of reactants and product is technically difficult. Compared with liquid acid catalysts, solid acid catalysts have distinct advantages in recycling, separation, and environmental friendliness. Solid acid catalysts are easily separated from the products mixture for reuse after reaction. Both Lewis acid-base sites and Brønsted acid-base sites have the ability to catalyze oil transesterification reaction. Besides specific surface area, pore size and pore volume, the active site concentration and acidic type are important factors for solid acid performance. Moreover, types of active precursor have significant effect on the catalyst activity of supported catalysts. However active site concentration was found to be the most important factor for solid catalyst performance. Solid acids with a large potential for synthesis of biodiesel should have a large number of Brønsted acid sites and good thermal stability. A good solid catalyst with sufficient catalytic

activity combined with appropriate reactor design should make it possible to realize biodiesel production on a practical scale.

Among solid catalysts introduced in this chapter, Solid acid (i.e. ion-exchange resins, HPAs and supported acid catalysts) and Solid base (i.e. hydrotalcites, metallic salts and supported base catalysts) are promising material for study. Low-cost catalysts that still retain the advantages of a supported base catalyst should be developed to simplify the preparation process. Design of solid catalysts with higher activity is an important step for clean production of biodiesel. Innovation and breakthrough in hydrolysis process is a key for commercialization of solid acid catalysts. In the near future, through the combination of green solvents, chemical process, biotechnology and catalysis, it can be expected that novel solid catalysts will replace the current-used homogeneous catalysts in biodiesel production.

6. References

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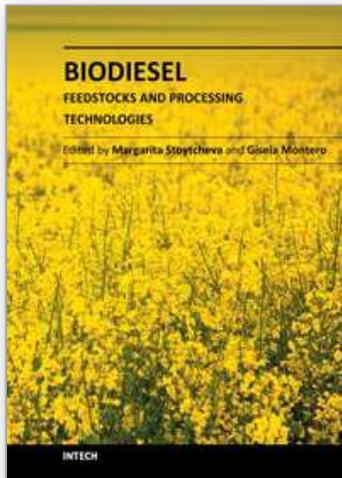
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The book "Biodiesel: Feedstocks and Processing Technologies" is intended to provide a professional look on the recent achievements and emerging trends in biodiesel production. It includes 22 chapters, organized in two sections. The first book section: "Feedstocks for Biodiesel Production" covers issues associated with the utilization of cost effective non-edible raw materials and wastes, and the development of biomass feedstock with physical and chemical properties that facilitate its processing to biodiesel. These include Brassicaceae spp., cooking oils, animal fat wastes, oleaginous fungi, and algae. The second book section: "Biodiesel Production Methods" is devoted to the advanced techniques for biodiesel synthesis: supercritical transesterification, microwaves, radio frequency and ultrasound techniques, reactive distillation, and optimized transesterification processes making use of solid catalysts and immobilized enzymes. The adequate and up-to-date information provided in this book should be of interest for research scientist, students, and technologists, involved in biodiesel production.

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