

# First Generation Biodiesel

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## 1. Introduction

Recent years, with the fossil oil crisis, biodiesel is no longer a new word for everyone. The internationally generally accepted definition is according to ASTM biodiesel standard D6751, which biodiesel is defined as a "fuel comprised of mono-alkyl esters of long-chain fatty acids derived from vegetable oils or animal fats, designated B100."

### 1.1 History

Using vegetable oil to make diesel is not a new idea, which can date back to 1853 by E. Duffy and J. Patrick (Feofilova et al., 2010). At the Paris International Exhibition in 1900, R. Diesel demonstrated a test engine sample working on peanuts oil. In 1912, Rudolf Diesel said, "The use of vegetable oils for engine fuels may seem insignificant today. But such oils may become in course of time as important as petroleum and the coal tar products of the present time" (Murugesan et al., 2009). During the following decades, because of fossil diesel's low price, the demands and research on biodiesel was not that much required. On 31 August 1937, G. Chavanne of the University of Brussels (Belgium) was granted a patent for a "Procedure for the transformation of vegetable oils for their uses as fuels" (Belgian Patent 422,877). This patent described the alcoholysis (often be called as transesterification) of vegetable oils using ethanol (and mentions methanol) in order to separate the fatty acids from the glycerol by replacing the glycerol with short linear alcohols. This appears to be the first account of the production of what is known as "biodiesel" today (Knothe, 2001).

The 1970s' energy crisis and people's more attention in environment re-sparked the study of biodiesel and boomed it rapidly. In the period 2001 - 2009, the production of biodiesel in the world increased by more than 16 times (from 9.57 billion tons to 157.6 billion tons). Except the traditional biodiesel production countries - the EU and US, a significant increase of market has been expected in developing countries as China, Brazil, Japan, Indonesia, and Malaysia.

### 1.2 Properties of biodiesel

Biodiesel is a mixture of monoalkyl (mostly methyl or ethyl) esters of fatty acids obtained from renewable resources, such as plant oils or animals fats.

Many industrial devices to produce biodiesel had been set up in Europe and USA, and certain standard of biodiesel had been formulated. EU and ASTM Standards on biodiesel listed in Table 1.

Properties	EN14214	ASTM D6751
FAME content	≥96.5% (m/m)	-
Density at 15°C	≥ 860, ≤ 900 (kg/m) <sup>3</sup>	-
Viscosity at 40°C	≥ 3.5, ≤ 5.0 (mm <sup>2</sup> /s)	≥ 1.9, ≤ 6.0 (mm <sup>2</sup> /s)
Flash point	≥ 101°C	≥ 130°C
Sulfur content	≤ 10 mg/kg	≤ 50 mg/kg
Carbon residue remnant (at 10% distillation remnant)	≤0.3% (m/m)	≤0.05% (m/m)
Cetane number	≥51.0	≥47
Sulfated ash content	- ≤ 0.02% (m/m)	- ≤ 0.02% (m/m)
Water content	≤ 500 mg/kg	≤ 0.05% (v/v)
Total contamination	≤ 24 mg/kg	-
Copper band corrosion (3 hours at 50 °C)	Class 1 max	No. 3 max
Oxidation stability, 110°C	≥6 hours	≥3 hours
Acid value	≤ 0.5	≤ 0.8
Iodine value	≤ 120	-
Linolenic Acid Methylene ester	≤ 12% (m/m)	-
Polyunsaturated (≥4 Double bonds) Methylene ester	≤1% (m/m)	-
Methanol content	≤0.2% (m/m)	-
Monoglyceride content	≤0.8% (m/m)	-
Diglyceride content	≤0.2% (m/m)	-
Triglyceride content	≤0.2% (m/m)	-
Free Glycerine	≤0.02% (m/m)	≤ 0.02
Total Glycerine	≤0.25% (m/m)	≤ 0.25
Group I metals (Na+K)	≤ 5 mg/kg	≤ 5
Group II metals (Ca+Mg)	≤ 5 mg/kg	-
Phosphorus content	≤ 4 mg/kg	≤ 0.001% (m/m)

Table 1. Biodiesel standards of EU and US

### 1.3 Advantages & disadvantages of biodiesel

Compared with fossil diesel, biodiesel has the following advantages (Feofilova et al., 2010; Murugesan et al., 2009) :

1. Biodiesel is a renewable energy source as opposed to oil, the reserves of which are finite as the reserves of other fossil fuels.
2. Biodiesel can decompose easily under natural conditions, and over 90% pure biodiesel can be degraded in a few weeks.
3. Compared with common diesel and petrol, biodiesel has higher combustibility value that makes it relatively safe to be stored and transported.
4. Biodiesel contains much less sulfur which not only provides lower share of toxic substances in the exhaust but also enables to provide the lubrication of movable parts during the work of the engine (Knothe & Steidley, 2005). The decrease of other harmful

compounds like PAHs and NO<sub>x</sub> occurs due to a big percentage of oxygen and more complete combustion of fuel. And pure or blend biodiesel also could suppress the net production of carbon dioxide.

Although biodiesel is "greener" than fossil fuels, it still has a number of disadvantages:

1. High viscosity and surface stress would lead to bigger drops which may cause problems with the system of fuel injection.
2. Vegetable oil contains much more unsaturated compounds than diesel, so biodiesel from it is much easier subjected to oxidation. This parameter correlates with the iodine number.
3. More expensive due to the raw material. Nowadays, the raw material of biodiesel usually soybean oil in US and peanuts oil in EU.

## 2. Transesterification

Generally, the main contents of vegetable oil and animal fats were triglycerides. The common and industrial method to produce biodiesel is chemically described as the transesterification of oil with short chain alcohol. The overall reaction equation is listed in Fig. 1. And this transesterification of triglycerides with alcohol is a three steps reversible reaction (Fig. 2). This reaction proceeds essentially by mixing the reactants, however, it may accelerate with the presence of a catalyst.

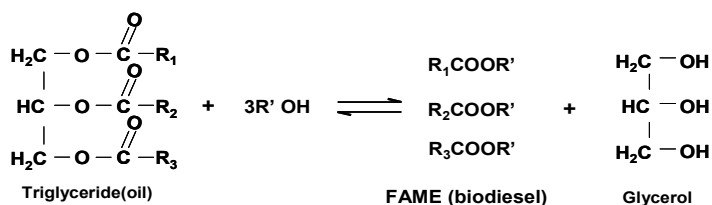


Fig. 1. The overall transesterification reaction of oil with alcohol (left)

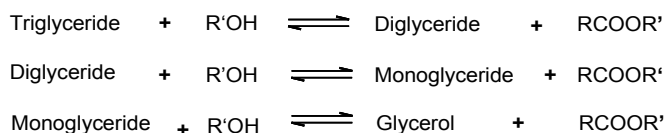


Fig. 2. Chemistry of transesterification process

Methanol is most frequently used, mainly because the reaction rate is higher and the price is cheaper than any other commercial alcohols. The fuel qualities of alkyl esters have received varying evaluations in terms of alcohol used. Methyl ester was better than ethyl ester from the standpoint of engine performance: higher power and torque were achieved from the engine when methyl ester was used as fuel (Knothe, 2005).

### 2.1 Mechanism

The mechanism of alkali-catalyzed transesterification is described in Fig.3 (Ma & Hanna, 1999). The first step is an attack on the carbonyl carbon atom of the triglyceride molecule by

the anion of methoxide ion to form a tetrahedral intermediate. In the second step, the tetrahedral intermediate reacts with a methanol to regenerate the anion of the alcohol methoxide ion. In the last step, rearrangement of the tetrahedral intermediate results in the formation of a fatty acid ester and a diglyceride.

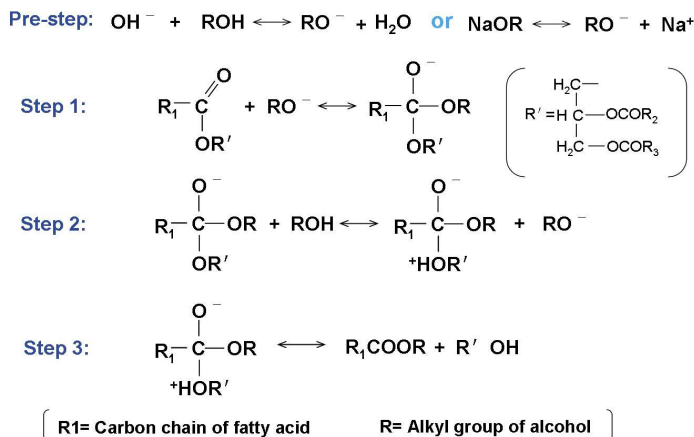


Fig. 3. The mechanism of alkali-catalyzed transesterification of triglycerides with alcohol (Ma & Hanna, 1999, as cited in Scridharan & Mathai, 1974)

Transesterification can also be catalyzed by Brønsted-Lowry acids. These catalysts give very high yields in alkyl esters but reactions are slow, requiring typically temperature above 100 °C and hours to complete the conversion (Schuchardt et al., 1998). The mechanism of acid catalyzed transesterification of vegetable oil (for a monoglyceride) is shown in Fig. 4 (Meher et al., 2006). However, it can be extended to di- and tri-glycerides. The protonation of carbonyl group of the ester leads to the carbocation, which after a nucleophilic attack of the alcohol produces a tetrahedral intermediate. This intermediate eliminates glycerol to form a new ester and to regenerate the catalyst.

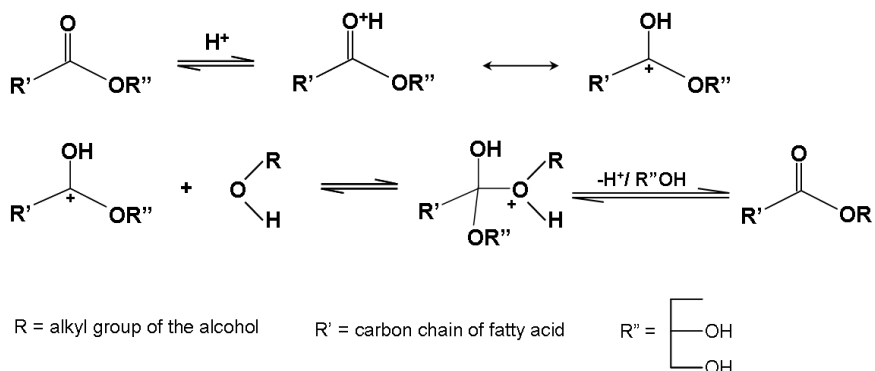


Fig. 4. The mechanism of acid-catalyzed transesterification of triglycerides with alcohol (Meher et al., 2006)

## 2.2 Main factors affecting the transesterification reaction

Except the effect of different catalysts, the process of transesterification is affected mainly by the following factors: temperature, molar ratio of methanol to oil, reaction time, mixing condition, amount of free fatty acid and moisture in the raw oil.

### 2.2.1 Molar ratio of methanol to oil

The methanol/oil molar ratio is one of the most important variables affecting the ester yield. The stoichiometric ratio for transesterification is 3:1 (methanol/oil). Since this is an equilibrium reaction, an excess of methanol will increase the oil conversion by shifting this equilibrium to producing FAME. An acid catalyzed reaction usually needs much more alcohol than an alkali catalyzed one.

### 2.2.2 Temperature & reaction time

Transesterification can occur in different temperatures depending on the type of oil employed (Ma & Hanna, 1999). A few works reported the reaction at room temperature (Encinar et al., 2002; Graboski & McCormick, 1998). With sodium and potassium hydroxides as catalysts, the transesterification reaction between *Cynara cardunculus L.* oils and ethanol could obtain a conversion of 91.6% at room temperature (Encinar et al., 2002). Being an equilibrium reaction, the equilibrium constant is influenced by temperature and pressure. High temperature and pressure is benefit for the conversion of oil, however, as usually this reaction occurs under atmosphere and the oil has a relatively higher boiling point, the boiling point of alcohol used in transesterification is considered as the best reaction temperature (Bo et al., 2007; Cui et al., 2007; Gao et al., 2008).

The conversion rate increases with reaction time. Ma et al. (Ma et al., 1999) studied the effect of reaction time on transesterification of beef tallow with methanol. The reaction was very slow during the first minute due to mixing and dispersion of methanol into beef tallow. From one to 5 min, the reaction proceeds very fast. The production of beef tallow methyl esters reached the maximum value at about 15 min.

### 2.2.3 Mixing condition

The transesterification reaction employing methanol commences as two immiscible phases as a result of the very low solubility of TAG in methanol (Boocock et al., 1996a; Boocock et al., 1996b; Zhou & Boocock, 2006a, 2006b), which is about only 7.5 g of soybean oil soluble in 1 L of methanol at 30°C (Boocock et al., 1996b). Sufficient magnitude Stirring can make TAG transport into small drops which contact the methanol phase more effectively, and then convert into FAME and glycerin (Moser, 2009). The rate at which FAME are produced during the transesterification reaction is thus controlled by mass-transfer limitations, which results in a lag time before conversion to FAME begins (Boocock et al., 1998; Doell et al., 2008; Zhou & Boocock, 2006b). This condition is more obvious when the reaction is catalyzed by solid catalysts. In order to omit the mass transferring resistance between oil phase and alcohol phase, cosolvents like tetrahydrofuran (THF), 1, 4-dioxane, isopropyl ether and diethyl ether were added into the reaction system to obtain a one phase reaction (Meher et al., 2006).

### 2.2.4 Free fatty acid and moisture

The free fatty acid and moisture content are key parameters for determining the viability of the vegetable oil transesterification process. The starting materials used for base catalyzed

alcoholysis should meet certain specification which is that a free fatty acid (FFA) value lower than 3% is needed to carry the base catalyzed reaction to completion (Meher et al., 2006). If the reaction conditions do not meet the above requirements, ester yields are significantly reduced. When catalyzed by NaOH, without adding FFA and water, the apparent yield of beef tallow methyl esters (BTME) was highest, and when only 0.6% of FFA was added, the apparent yield of BTME got to the lowest, less than 5% (Ma et al., 1998). When 0.9% of water was added, without addition of FFA, the apparent yield was about 17% (Ma et al., 1998).

### 2.2.5 Catalyst concentration

Catalyst concentration can affect the yield of the biodiesel product (Leung et al., 2010). Usually, the conversion of triglycerides and the yield of biodiesel increase with the catalyst concentration increasing. This is because an insufficient amount of catalysts result in an incomplete conversion of the triglycerides into the fatty acid esters (Leung & Guo, 2006). However, if the catalyst amount over the optimal concentration, the biodiesel yield would decrease a little with a further increase, which is due to the excess alkali catalyst causing more triglycerides to react with the alkali catalyst and form more soap (Dorado et al., 2002).

### 2.2.6 Case study: Effect of reaction parameters in the transesterification of palm oil with methanol by KF/ hydrotalcite

The following part describe the main parameters effect of the transesterification reaction between palm oil and methanol, which catalyzed by a solid base KF/hydrotalcite. In this case, it is clearly shown the effect of methanol/oil molar ratio, temperature, catalyst amount, and reaction time.

Figure 5 a) showed the influence of methanol to oil molar ratio on FAME yields. The ester yields increased as the amount of methanol increased, and reach the maximum value of 85 % with a molar ratio of 12:1. The increased ester yield with increasing methanol amount below 12:1 can be explained by the pushing effect of excess methanol on the reaction balance. And the decreasing of yield should be due to the large amount of methanol diluting the oil and reducing the reaction rate.

Figure 5 b) showed the yields of FAME obtained over various amount of catalyst. As can be observed, the best results were reached with a concentration of 3 %. The excess catalyst over 3 % did not raise the FAME yield but caused a little decrease. This can be explained by the theory that the catalyst only changes the reaction rate and do not affect the balance of an equilibrium reaction. Therefore, in a fixed reaction time, sufficient amount catalyst is necessary to obtain a reaction rate fast enough. In this case, with 3 % catalyst, reacting 3h is enough to reach the balance, and the more catalyst could not shifting the balance to get higher FAME yield.

In Figure 5 c), as indicated, reaction temperature was varied between 318 ~ 348 K. For the same final reaction time, yield of FAME increased with the increasing of reaction temperature. The equilibrium constant of a reaction is influenced by temperature and pressure. And in this case, which carried out under atmospheric pressure, the former factor, reaction temperature, affected the equilibrium constant much. Therefore, as the temperature rose, the conversion of the oil went up. Moreover, mass-transfer effect was another factor which hinders the transesterification. High temperature is benefit to the mass transfer.

Based on the two reasons above, higher temperature could get higher yield. However, from the results in Figure 5 c), when the temperature exceeded 338 K, the FAME yield dropped obviously. That voluminous methanol gasified and reduced the amount of it in the liquid, when the temperature rose over 338 K (the boiling point of methanol), might be the reason of lower yield.

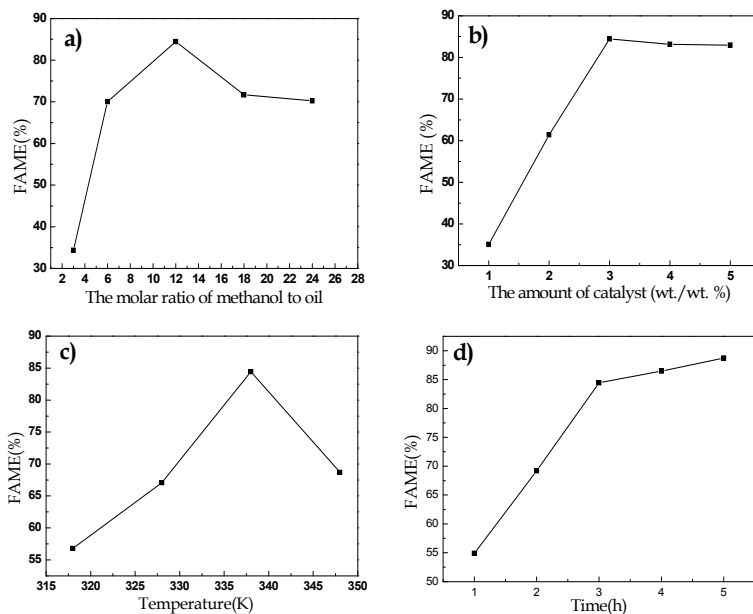


Fig. 5. a) Effect of the molar ratio of methanol/oil on the FAME yield; b) Effect of catalyst amount used on the FAME yield; c) Effect of reaction temperature on the FAME yield; d) Effect of reaction time on the FAME yield. (The mass ratio of KF/HT is 80 %). (Gao et al., 2008)

In Figure 5 d), the influence of reaction time has also been studied. The FAME yield increased with the prolonging of reaction time. From this figure, 3 h is the proper contact time, and longer time didn't enhance the yields obviously.

### 3. Catalysts in transesterification

Both base and acid can catalyze the transesterification reaction between oil and alcohol. Generally, the reaction catalyzed by base is faster than the one by acid. On the other hand, base catalysts have much more demands on the raw materials, especially the amount of free fatty acid and water, while acid catalyst don't need. Hundreds of researches have been done on each kind of catalyst.

#### 3.1 Homogeneous catalyst

Industrially, Biodiesel is commonly produced using homogenous basic catalysts such as sodium (or potassium) hydroxide or methoxide because the transesterification reaction is

generally faster, less expensive, and more complete with these materials than with acid catalysts (Boocock et al., 1996a). The biodiesel industry currently uses sodium methoxide, because methoxide cannot form water upon reaction with alcohol such as with hydroxides, which influence the reaction and the quality of the production biodiesel (Zhou & Boocock, 2006a). Furthermore, base-catalyzed reactions are performed at generally lower temperatures, pressures, and reaction times and are less corrosive to industrial equipment than acid-catalyzed methods (Moser, 2009). Therefore, fewer capital and operating costs are incurred by biodiesel production facilities in the case of the base-catalyzed transesterification method (Demirbas & Dincer, 2008; Freedman et al., 1986).

The liquid acid-catalyzed transesterification process is not much popular as the base-catalyzed process. Homogeneous acid catalyzed reaction is about 4000 times slower than the homogeneous base-catalyzed reaction (Srivastava & Prasad, 2000). However, the performance of the acid catalyst is not strongly affected by the presence of FFAs in the feedstock. Actually, acid catalysts simultaneously catalyze both esterification of FFAs with alcohol and transesterification of oil with alcohol. Thus, acid catalysts can directly produce bio-diesel from low-cost lipid feedstocks, generally associated with high FFA concentrations, which expands the raw materials to low-cost feedstocks, such as used cooking oil and greases, commonly have FFAs levels of >6% (Lotero et al., 2005). For acid-catalyzed systems, sulfuric acid (Al-Widyan & Al-Shyoukh, 2002; Wang et al., 2006), HCl, BF<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, and organic sulfonic acids, have been used by different researchers (Lotero et al., 2005).

### 3.2 Heterogeneous catalysts

Although homogeneous catalysts are cheap and showed great performance toward transesterification, the drawbacks of them are evident. The first is corrosion of the reactor and pipelines by dissolved acid/base species, which inevitably raises the material cost for process construction. The second is the impossibility of catalyst recovery from the reactant-product mixture, which also causes the problems of product separation. A third drawback of homogeneously catalyzed transesterification is the limitation in establishing a continuous process. The heterogeneous catalysts were introduced and studied to solve the drawbacks that homogeneous catalysts caused (Lotero et al., 2005). Heterogeneous catalysts can be separated more easily from reaction products (Di Serio et al., 2008). Saponification reactions can also be avoided by using heterogeneous acid catalysts, which expand the raw materials to vegetable oils or animal fats with high contents of FFAs, such as deep-frying oils from restaurants and food processing (Garcia et al., 2008). Bio-diesel synthesis using solid catalysts could potentially lead to cheaper production costs because of reuse of the catalyst and the possibility for carrying out both transesterification and esterification simultaneously (Lopez et al., 2005).

#### 3.2.1 Solid base

##### i. Metal oxides

The early studies on heterogeneously catalyzed transesterification were focused on the catalysis by single metal oxides. The structure of metal oxides is made up of positive metal ions (cations) which possess Lewis acid and negative oxygen ions (anions) which possess Bronsted base. In methanolysis of oils, it provides sufficient adsorptive sites for methanol, in which the O-H bonds readily break into methoxide anions and hydrogen cations. And



methoxide anions then react with triglyceride molecules to form corresponding FAMES (Zabeti et al., 2009). Bancquart compared the activities of  $\text{La}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CaO}$ , and  $\text{ZnO}$  (Bancquart et al., 2001), for the transesterification of glycerol with fatty acid methyl esters (FAME) at 220 °C. The author concluded that the reaction rates by single metal oxides directly depend on the basicity of the oxide, especially of the strong basic sites. The order of activity followed that of the intrinsic basicity of oxides is  $\text{La}_2\text{O}_3 > \text{MgO} \gg \text{ZnO}$ . Magnesium oxide which is produced by direct heating of magnesium carbonate or magnesium hydroxide has the weakest basic strength and solubility in methanol among group II oxides and has been rarely used for biodiesel production. This catalyst showed activity at high temperature and pressure. Under supercritical temperature of 523 °C and high pressure of 24 MPa, Nano magnesium oxide catalyzed transesterification of soybean oil and yields of 99% were obtained in 10 min (Wang & Yang, 2007).

Calcium oxide is the single metal oxide catalyst catches more attention for biodiesel synthesis, due to its cheap price, minor toxicity and relatively high availability. Gryglewicz (Gryglewicz, 1999) compared heterogeneous catalysis by  $\text{CaO}$  with typical homogeneous catalysts like alkaline-earth metal hydroxides and alkoxides for the transesterification of rapeseed oil by methanol at the boiling point of methanol. The reaction rate over the heterogeneous catalysts, however, was much lower than that of the homogeneous catalysts such as  $\text{NaOH}$ . The rate of  $\text{CaO}$  catalysis is accelerated in the presence of water, because methoxide ions, which are thought to be the true catalytic agent for transesterification, are increased through the hydrolysis of monoglyceride molecules (Liu et al., 2008). However, if too much water (more than 2.8% by weight of soybean oil) is added to methanol, the FAME will hydrolyze under basic conditions to generate fatty acid, which can react with  $\text{CaO}$  to form soap (Lee et al., 2009). Demirbas believes that the calcium oxide catalytic performance is quite weak at low temperatures since only 5% methyl ester yields were obtained at 60 °C after 3 h (Demirbas, 2007). However, the active surface sites of  $\text{CaO}$  were easily poisoned with  $\text{CO}_2$  and covered with  $\text{H}_2\text{O}$  (Granados et al., 2007). Therefore, some careful handling is required in order to use  $\text{CaO}$  as a base catalyst. Increasing the surface basicity of  $\text{CaO}$  by chemical treatment is a method to increase its catalytic activity (Zhu et al., 2006). Immersed  $\text{CaO}$  into ammonium carbonate solution and calcined the catalyst at high temperature of 900 °C. With this catalyst, a FAME yield of 94% was obtained for the transesterification of *jatropha curcas* oil with a relatively lower methanol/oil ratio (9:1) and catalyst amount (1.5 wt%) at a reaction temperature of 70 °C (Zhu et al., 2006).

#### ii. Layered Double Hydroxides (LDHs) & mixed Metal Oxides

Layered double hydroxides (LDHs), which also be called as hydrotalcite or hydrotalcite-like compound, is a kind of based upon layered double hydroxides with brucite ( $\text{Mg}(\text{OH})_2$ ) like hydroxide layers containing octahedrally coordinated  $\text{M}^{2+}$  and  $\text{M}^{3+}$  cations (Roelofs et al., 2002). The general formula of LDHs is  $[\text{M}^{2+}_{(1-x)}\text{M}^{3+}_x(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n} \cdot y\text{H}_2\text{O}$ , and its idealized layered structure is shown in Fig. 6. In this formula,  $\text{M}^{2+}$  ( $\text{M} = \text{Mg}, \text{Ca}, \text{Fe}, \text{Co}, \text{Cu}, \text{Ni}, \text{or Zn}$ ) and  $\text{M}^{3+}$  ( $\text{M} = \text{Al}, \text{Cr}, \text{Ga}, \text{Mn or Fe}$ ) are di- and trivalent cations, respectively, the value of  $x$  is equal to the molar ratio of  $\text{M}^{2+}/(\text{M}^{2+} + \text{M}^{3+})$  and is generally in the range 0.2-0.33;  $\text{A}^{n-}$  is an anion to balance the charge. As a result, a large class of isostructural materials with versatile physical and chemical properties can be obtained by changing the nature of the metal cations, the molar ratios of  $\text{M}^{2+}/\text{M}^{3+}$ , as well as the types of interlayer anions.

Conventionally, HT is synthesized by co-precipitation, wherein metal nitrates and precipitants are added slowly and simultaneously at a fixed pH under stirring, followed by a long (about 1 day) ageing time and/or hydrothermal treatment in order to improve the

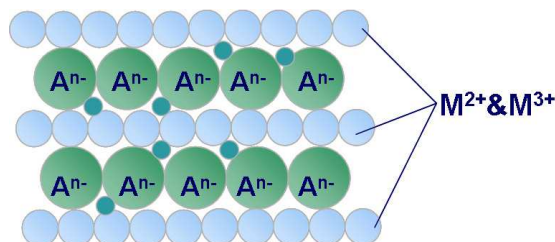


Fig. 6. The structure of LDHs

crystallinity. A particular chemical composition and the method of synthesis, i.e., temperature, solution pH, and ageing time of the gels, have a strong influence on the final basicity of the mixed oxides (Morato et al., 2001; Schulze et al., 2001). The change of the Mg/Al ratio in Mg–Al hydrotalcite leads to the variation of the basic property that is induced by the redistribution of acid-base sites, change of structure and transformation of the cation environment (Diez et al., 2003). Increasing Al content, the relative abundance of low and medium strength basic sites increased. For the Mg–Al hydrotalcites featuring Al contents of  $1 < \text{Mg}/\text{Al} < 5$ , the basic site density increased because the  $\text{Al}^{3+}$  cations within the MgO lattice created a defect in order to compensate for the positive charge generated, and the adjacent oxygen anions became coordinatively unsaturated (Di Cosimo et al., 1998). In the biodiesel synthesis process, the Mg/Al molar ratio of hydrotalcites is usually set from 2 to 4, with the ratio 3 being chosen as the best in terms of basic activity by many authors (Cantrell et al., 2005; Fishel & Davis, 1994; Xie et al., 2006a; Zeng et al., 2008). However, the transesterification catalyzed with Mg–Al HT catalysts prepared by coprecipitation, the best ester conversions from soybean oil and triglycerides were below 80% (Barakos et al., 2008; Cantrell et al., 2005; Xie et al., 2006a). But, if the transesterification reaction occurs under high temperature and pressure, the uncalcined hydrotalcite could show higher activity (Barakos et al., 2008).

Calcining hydrotalcite materials at high temperature, the interlayer water is lost first, followed by dehydroxylation and decomposition of interlayer carbonate to  $\text{CO}_2$ , which generate an interactive, high surface (ranging from 150 to 300  $\text{m}^2/\text{g}$ ) area and well-dispersed mixed oxides that completely destroyed the layered structure (Corma et al., 2005; McKenzie et al., 1992). These effects combine to make the catalyst quite competitive as a heterogeneous basic catalyst. The basic properties of these sites depend on the Mg–Al ratio in the precursor hydrotalcite (Di Cosimo et al., 1998). These mixed metal-oxides show higher activity in the transesterification reaction than LDHs. The Calcined Li–Al and Mg–Al LDHs (Corma et al., 1998) are able to catalyze the glycerolysis of fatty acid methyl esters to monoglycerides (the reverse of biodiesel synthesis). Shumaker (Shumaker et al., 2007; Shumaker et al., 2008) also used calcined Li–Al LDHs to catalyze soybean oil with methanol, and Liu et al. (Liu et al., 2007) used calcined Mg–Al hydrotalcite to catalyze poultry fat with methanol. All of these studies showed that LDHs, except the Li–Al LDHs, performed low activities at the lower temperature, and when the reaction was performed in autoclave at high temperature, the conversion of soybean oil or acid cotton oil could reach 90% (Barakos et al., 2008; Di Serio et al., 2006).

If the mixed oxides obtained by calcined under certain temperature (generally below 550  $^\circ\text{C}$ ) encounter water, the typical layered structure of hydrotalcite would represent. This is the well known “memory” property of hydrotalcite (Corma et al., 2005). The

reconstruction of decomposed Mg–Al HT by rehydration at room temperature reportedly enhanced the catalytic activity (Rao et al., 1998). And during this reformed process, some other cations or anions could be introduced into the structure. Therefore, based on the hydrotalcite properties, loading some active substance can improve the activity of the HT.  $\text{KNO}_3/\text{HT}$  (Sun et al., 2006) showed stronger alkalinity and more active in methylation of cyclopentadiene than  $\text{KNO}_3/\text{Al}_2\text{O}_3$ . Catalyzed by the hydrotalcite loaded with  $\text{CH}_3\text{COOK}$  (Trakarnpruk & Porntangjitlikit, 2008), at the condition of a 30:1 methanol to oil molar ratio at 373 K for 6 h and 7 wt.% catalyst, the FAMES content could get to 96.9 %. Gao et al. studied KF loaded hydrotalcites KF/Mg–Al hydrotalcite (Gao et al., 2008), KF/Ca–Al hydrotalcite (Gao et al., 2010b) and KF/Ca–Mg–Al hydrotalcite (Gao et al., 2010a), found that different kinds and ratio of cations in LDHs led different catalytic activities. And they obtained a FAMES highest yield over 99% (by KF/Ca–Mg–Al hydrotalcite) in 10 mins in the transesterification reaction between palm oil and methanol at 65 °C.  $\text{K}_2\text{CO}_3/\text{Mg}$ –Al hydrotalcite also showed very encouraged activity in biodiesel synthesis (Teng et al., 2010).

### iii. Metal salt on porous support

Loading alkali metal or alkali-earth metal salt is the most familiar way to synthesis solid base catalysts. Na, K, Li, Ba, and Mg are frequently used in the metallic form or as various ionic forms of halide, carbonate, hydroxide and nitrate. The metal ion-supported catalysts are usually calcined at 400– 600 °C to obtain active sites. The catalysts generally exhibit the preferential dependence of activity on the surface basicity, rather than on the other properties such as specific surface area and pore volume (Lee et al., 2009). All researchers believe that the different activities of these catalysts were all mainly attributed to the difference in impregnated metal amount (Bo et al., 2007; Cui et al., 2007). Another key factor determining the surface basicity of alkali metal salt-supported catalysts is the calcination temperature. The support for alkali metal species could be diversified from alumina (Bo et al., 2007; Cui et al., 2007; Teng et al., 2009; Xie & Li, 2006; Xie et al., 2006b) to basic oxides such as ZnO (MacLeod et al., 2008; Xie & Huang, 2006), CaO (MacLeod et al., 2008; Watkins et al., 2004) and MgO (MacLeod et al., 2008). In every case, supported alkali metals on alkaline earth oxides are partly dissolved into the liquid phase and the catalysis section invariably becomes homogeneous, regardless of whether the calcination step was included in the preparation procedure of the catalysts or not.

### 3.2.2 Solid acid

Researches on the direct transesterification of lipid feedstocks into biodiesel by solid acid catalysts are not examined extensively. Among the catalysts reported, sulfuric acid prepared by impregnation method has shown the highest activity. Impregnation method prepared solid acid catalysts showed higher activities. However, leaching of sulfate species restricted the reusability of the catalyst, and on another hand, the use of solid acids still need high temperatures and high methanol-to-oil molar ratio (60:1) for a feasible process (Jothiramalingam & Wang, 2009).

Zirconium oxide, titanium oxide and zinc oxide can all be used as solid acid catalyst in biodiesel production. In transesterification reaction of palm kernel oil at supercritical methanol, zinc oxide and zirconium oxide both showed activity as solid acid catalysts. After 1 h of reaction time, using 3 wt.% catalyst and 6:1 molar ratio of alcohol/oil, 86.1% FAMES yields were obtained for zinc oxide while only 64.5% for zirconium oxide (Jitputti et

al., 2006). However, using sulfated zirconia ( $\text{SO}_4^{2-}/\text{ZrO}_2$ ), the yields considerably increased to 90.3%.

$\text{SO}_4^{2-}/\text{ZrO}_2$  and  $\text{WO}_3^{2-}/\text{ZrO}_2$  was considered as super acid catalysts in the methanolysis of triacetin was compared (Lopez et al., 2005). The results indicate that  $\text{SO}_4^{2-}/\text{ZrO}_2$  showed more activity (conversion of 57%) than  $\text{WO}_3^{2-}/\text{ZrO}_2$  (conversion of 10%) under the same conditions of 60 °C and 8 h of reaction time. The activity of  $\text{WO}_3^{2-}/\text{ZrO}_2$  was attributed to the formation of tetragonal phase of  $\text{ZrO}_2$ . Beyond 500 °C the tetragonal phase transferred to the monoclinic phase which caused a decrease in the activity (Ramu et al., 2004). However, the transesterification reaction catalyzed by  $\text{SO}_4^{2-}/\text{ZrO}_2$  at low temperature is very slow. It was taken over 8h to obtain a FAMES yield over 80% at 65 °C, while only 2h at 120 °C (Fu et al., 2009).

Fe–Zn double metal cyanide complex has been studied as a solid acid catalyst for methanolysis of sunflower oil (Sreeprasanth et al., 2006). The specific surface area of the catalyst was 51.6m<sup>2</sup>/g. When the transesterification reaction was performed at 170 °C, with oil/alcohol molar ratio of 1:15 and 3 wt.% of catalyst, the oil conversion reached 97% after 8 h of reaction. The catalyst activity was attributed to the Lewis acid active sites of probably  $\text{Zn}^{2+}$  on the surface of catalyst. Moreover, the catalyst converted the oil with up to 20% of water content which implies the surface hydrophobicity of the catalyst. The activity of catalyst was successfully tested for esterification of high amount of FFA in the oil. In addition, the catalyst was stable after many cycles since no significant loss of activity was detected.

#### 4. Other transesterification methods

Except traditional chemical catalyzed method (base and acid), new methods has been introduced into biodiesel synthesis process. These new method mostly focus on the following goals. First, “greener”, means causing less pollution as waste water. Second, “faster”, indicate obtaining high FAMES yield in relatively short time.

##### 4.1 Enzyme

Enzymatic transesterification catches attentions for reasons of easy product separation, minimal wastewater treatment needs, easy glycerol recovery and the absence of side reactions (Jegannathan et al., 2008). The transesterification is typically catalyzed by lipases such as *Candida antarctica* (Watanabe et al., 2002), *Candida rugosa* (Linko et al., 1998), *Pseudomonas cepacia* (Shah & Gupta, 2007), *Pseudomonas spp.* (Lai et al., 1999) or *Rhizomucor miehei* (Lai et al., 1999). The yield of biodiesel from this process can vary depending on the type of enzyme used. The enzyme-catalyzed system normally requires a much longer reaction time than the base catalyzed systems.

While enzyme reactions are highly specific and chemically clean, the main problem of the lipase-catalyzed process is the high cost of the lipases. Du et al. reported that 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 improve/extend the operational life of the lipase, and this can be achieved through enzyme immobilization, alcoholysis reaction optimization, etc. (Du et al., 2008).

## 4.2 Supercritical & subcritical alcohol

Mass transfer between oil and alcohol phases inhibits the transesterification. As is known, when a fluid or gas is subjected to temperatures and pressures in excess of its critical point, a number of unusual properties are exhibited. Under the 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 (Pinnarat & Savage, 2008). Another positive effect of using supercritical conditions is that the alcohol is not only a reactant but also an acid catalyst (Alenezi et al., 2010).

Supercritical transesterification is carried out in a high pressure reactor, with heat supplied from an external heater. Reaction occurs during the heating period. After the reaction is complete, the gas is vented and the product in the reactor is poured into a collecting vessel. The remaining contents are removed from the reactor by washing it with methanol (Bunyakiat et al., 2006). During the whole process, several variables (i.e. reaction pressure and temperature) affect the yield of the biodiesel product and the highest yield can be obtained under the optimal conditions.

Synthesis of bio-diesel by supercritical methanol has a drawback with the high cost of apparatus due to the high temperature and pressure, which are not viable in the large scale practice in industry. So, researches have focused on how to decrease the severity of the reaction conditions. Co-solvents and subcritical alcohol with small amount of catalyst, can decrease the operating temperature, pressure and the amount of alcohol (Vyas et al., 2010).

## 5. Biodiesel Industry: Opportunity & challenge

Sooner or later, petroleum will become the huge barrier to human development. Searching substitute is an extremely urgent thing. Although hydrogen energy or solar energy has the chance to use as main energy resource, the day of their wide application is still far away. Biodiesel is the most ideal substitute for fossil oil in a relatively short time. The primary market for biodiesel in the near to long-term future is likely to be as a blend component in petrodiesel.

Despite its many advantages as a renewable alternative fuel, biodiesel presents a number of technical problems that must be resolved before it will be more attractive as an alternative to petrodiesel. These problems include improving the relatively poor low-temperature properties of biodiesel as well as monitoring and maintaining biodiesel quality against degradation during long-term storage. The raw material of biodiesel is also a restraining factor. The 70% cost of biodiesel is coming from its raw material oil. Therefore, development of alternative feedstocks is another important area research. Additionally, genetic modification oil plants may provide a solution of this problem.

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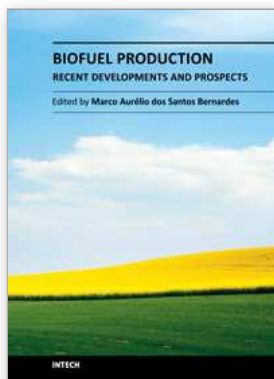


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## **Biofuel Production-Recent Developments and Prospects**

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This book aspires to be a comprehensive summary of current biofuels issues and thereby contribute to the understanding of this important topic. Readers will find themes including biofuels development efforts, their implications for the food industry, current and future biofuels crops, the successful Brazilian ethanol program, insights of the first, second, third and fourth biofuel generations, advanced biofuel production techniques, related waste treatment, emissions and environmental impacts, water consumption, produced allergens and toxins. Additionally, the biofuel policy discussion is expected to be continuing in the foreseeable future and the reading of the biofuels features dealt with in this book, are recommended for anyone interested in understanding this diverse and developing theme.

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