

Available online at www.elixirpublishers.com (Elixir International Journal)

Applied Chemistry

Elixir Appl. Chem. 43 (2012) 6924-6945



Advances in Biodiesel synthesis: from past to present

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ABSTRACT

ARTICLE INFO

Article history: Received: 23 January 2012; Received in revised form: 30 January 2012; Accepted: 14 February 2012;

Keywords

| Biodiesel, |
|-------------|
| Production, |
| Chemistry, |
| Economics, |
| Progress, |
| Challenges. |

The reignited research on biodiesel production has witnessed, in recent decades, so much momentum to lead a great revolution in world energy in the near future. This great resurgence is stimulated in one part by the anxiety of the uncertainty of the supply life span of conventional fuels and in the other by the numerous advantages that biodiesel offer over petroleum diesel fuel. Biodiesel, amongst other benefits, is renewable, biodegradable, environmentally benign, energy efficient, and by far a major role-player in the league of biofuels that will sustain the energy future. Starting from history to present, this work presents a comprehensive review of major advance in biodiesel production. The five basic ways of making biodiesel: direct use and dilution, microemulsions, thermal cracking and transesterification are reviewed with emphasis on heterogeneous catalyst transesterification. Progresses in research into other methods such as enzyme catalysed, non-catalytic supercritical and ultrasound aided transesterification, biox co-solvent and in situ processes as well as production from microalgae are detailed. The factors affecting the yield of the different processes are identified and recommendations are presented for optimum production yield. Evaluation of the economic viability of biodiesel production shows the major challenges as the cost of production and limited availability of fat and oil resources. Microalgae prove to be the economical choice for biodiesel production, because of the availability, high productivity and low cost. Therefore, research should be geared towards the improvement and optimization of biodiesel production from algae.

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Those that experienced the Arab oil embargos of the 1970s remember this period as the first vocal call for a domestic source of renewable energy to counter the rapid escalation in oil prices that has continued through the early 21st century (Songstad et al. 2009). However, the reality is that biofuel was well developed as an alternative fuel before the discovery of petroleum by Edwin Drake in Pennsylvania in the year 1859 (Kovarik 1998). The Lamp fuels developed before petroleum was discovered include all kinds of vegetable oils (castor, rapeseed, peanut); animal oils (especially whale oil and tallow from beef or pork,); refined turpentine from pine trees; and alcohols, especially wood alcohol (methanol or methyl alcohol) and grain alcohol (ethanol or ethyl alcohol). Whale oil which was the preferred of the Lamp oils gradually became expensive following energy crisis. By the late 1830s, alcohol blends had replaced the increasingly expensive whale oil in most parts of the U.S. The most popular fuel in the U.S. before petroleum was a blend of alcohol and turpentine called "camphene" or simply "burning fluid (Kovarik

The roots of what eventually became known as "biodiesel" extend back to the discovery of the diesel engine by Rudolf Diesel (Songstad et al. 2009). Rudolf Diesel's first engine ran on its own power on 10 August 1893 (Shay 1993) and the diesel engine was first demonstrated in the 1900 World Fair in Paris using Peanut oil as the fuel (Nitske, Wilson 1965). However the word biodiesel was first coined in 1898(Wang 1988).

In 1916, Gutierrez tested castor oil as alternative fuel for the first diesel engine imported into Agentina (Gutierrez 1916) and in 1944, also in Argentina, Martinez de Vedia described short duration runs with blends of vegetable oils (such as sunflower,

linseed, groundnut, cottonseed, turnip) and diesel fuel with the vegetable oils comprising 30&70% of the fuel mixture. In an extended run of 420hr with 60:40 diesel-linseed oil as fuel, significant amount of carbon deposits was noted.(Shay 1993, Martinez de Vedia 1944). The use of palm oil as a diesel fuel was reported as early as 1920 (Mayne 1920)and one of the first references to the use of palm oil esters as diesel fuel appears in 1942 (Van den Abeele 1942).

Prompted by shortage of fuel, during the World War II year, export of cottonseed oil was prohibited in Brazil so it could be used as a substitute for diesel (Anonymous 1943) and in China, tung oil and other vegetable oils were used to produce a version of gasoline and kerosene (Cheng 1945, Chang, Wan 1947). During this period research on conversion of a variety of vegetable oils to diesel was conducted in India (Chowhury et al. 1942) and in the USA research was performed to evaluate cottonseed oil as a diesel fuel.(Huguenard 1951). Henry Ford in 1941 built a plastic bodied 'soybean car' which weighed 2000lb, about 1000lb less heavy than the steel car in production. Unfortunately the project was suspended due to the World War II (Young 2003). The Arab petroleum embargo in 1974 reignited interest in alternative liquid fuels, and during the 1970s and 1980s much research was done on a wide variety of oils (Shay 1993)

In the recent decades researches on biodiesel production from agricultural products have witnessed great momentum. New vegetable oils such as jupati (Raphia taedigera Mart) (Da Conceião et al. 2011); Moringa oleifera oil(Da Silva et al. 2010), Jatropha(De Oliveira et al. 2009, Ganapathy, Gakkhar & Murugesan 2009); milkweed (Asclepias) seed oil(Holser, Harry-O'Kuru 2006) ; kusum (*Schleichera triguga*)(Sharma, Bhaskar

Introduction

1998).

2010) and cottonseed oil(Huguenard 1951) have been demonstrated as excellent feedstock for biodiesel production. Also non-edible plant biomass such as algae and seaweeds (Ahmad et al. 2011, Blaine Metting et al. 2010, Demirbas 2011, Tabatabaei et al. 2011) and animal biomass like the tallow (Araújo et al. 2010) have been widely reported. Just to mention but a few and more feedstock are being discovered. The present task will be the optimization of the production of biodiesel from these feedstocks.

This paper reports a critical and wise range survey of the literature on the key aspects of biodiesel production. Emphasis was given to a number of industrial and research successes accomplished and challenges over the decades. Areas requiring further investigations and the ways forward were also discussed. **Feedstocks for biodiesel production**

Biodiesel is composed of long chain monoalkyl (methyl, ethyl, isopropyl or butyl) esters derived from vegetable oils, such as rapeseed oil, soybean, sunflower, cottonseed, canola, or hemp oil, and sometimes from animal fats through a simple transesterification process. It is a non-toxic, biodegradable and renewable fuel which can be used in compression ignition engines with little or no chemical modifications with significantly lower emissions than petroleum-based diesel when it is burned (fig 1).(Koh, Mohd. Ghazi 2011). Biodiesel can be manufactured from recycled oil or fat and can be harnessed from sources like non-edible oil seeds such as Jatropha curcas (De Oliveira et al. 2009), kusum - Schleichera triguga (Sharma, Bhaskar 2010) and tallow from the abattoir(Araújo et al. 2010). In addition, biodiesel is better than petrodiesel in terms of its properties such as sulphur content, flash point, aromatic content and biodegradability etc.(Patil, Deng 2009, Demirbas 2005). Table 1 shows the properties of some methyl esters (biodiesel) from selected vegetable oils compared with those of the petrodiesel. The ASTM standards for diesel and biodiesel are compared in table 2.



Fig. 1. Lower emissions of biodiesel compared with petrodiesel.(Barnwal, Sharma 2005).

Methods of biodiesel production

There are basically four ways of making biofuels from the agricultural feedstocks; namely,

- direct use and dilution/blending,
- microemulsions,
- thermal cracking (pyrolysis) and
- transesterification.

The most commonly used method is transesterification of vegetable oils and animal fats. Table 3 (Leung, Wu & Leung 2010) presents a comparison of the four basic ways of making biodiesel.

Direct use and dilution/blending

Straight vegetable oils have been used to power diesel engines for short runs; however the major disadvantage of the vegetable oil is the high viscosity, lower volatility and the reactivity of unsaturated hydrocarbon chains(Demirbas 2006). Modern diesel engines have fuel-injection systems that are sensitive to viscosity changes. The injection and atomization characteristics of the vegetable oils are significantly different than those of petroleum-derived diesel fuels, mainly as the result of their high viscosities(Balat, Balat 2008, Cigizoglu, Ozaktas & Karaosmanoglu 1997). A way to avoid these problems is to reduce the viscosity of vegetable oil in order to improve its performance(Wang et al. 2006)The known problems, probable cause and potential solutions for using straight vegetable oil in diesel are given in Table 6.

Crude vegetable oils are mixed directly or diluted with diesel fuel to improve the viscosity so as to solve the problems associated with the use of pure vegetable oils with high viscosities in compression ignition engines. (Koh, Mohd. Ghazi 2011) Caterpillar Brazil, in 1980, used a 10% mixture of vegetable oil to maintain total power without any alteration or adjustment to engines. A blend of 20% vegetable oil and 80% diesel fuel was also successfully reported (Singh, Singh 2009). Ziejewski et al(Ziejewski, Goettler & Pratt 1986) conducted a study of 25% of sunflower oil blended with 75% of diesel fuel. The viscosity was 4.88 cSt at 40 °C, while the maximum specified ASTM value is 4.0 cSt at 38 °C. This mixture was not suitable for long-term use in a direct injection engine (Demirbas 2006. Demirbas 2003). However, Further, it was also reported that the viscosity of 25/75 high oleic sunflower oil/diesel fuel blend was 4.92 cSt at 40 °C and has passed the 200 h EMA (Engine Manufacturers' Association) test(Koh, Mohd. Ghazi 2011). A model on vegetable oil atomization showed that blends of No. 2 Diesel fuel with vegetable oil should contain from 0% to 34% vegetable oil if proper atomization was to be achieved (Balat, Balat 2008, Knothe, Dunn & Bagby 1997).

Microemulsions

Another way to reduce the viscosity of vegetable oils is by microemulsion. Microemulsions are isotropic, clear, or translucent thermodynamically stable dispersions of oil, water, surfactant, and often a small amphiphilic molecule, called cosurfactant (Srivastava, Prasad 2000, Fukuda, Kondo & Noda 2001a). The aqueous phase may contain salts or other ingredients, and the oil may consist of a complex mixture of different hydrocarbons and olefins. This ternary phase can improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles.(Koh, Mohd. Ghazi 2011). Some of these microemulsion fuels were tested by the Engine Manufacturers Association (EMA). Shipp non-ionic (SNI) fuel containing 50% No. 2 Diesel fuel, 25% degummed and alkali-refined soybean oil, 5% 190-proof ethanol and 20% 1-butanol was evaluated in the 200 h EMA screening test. The fuel passed the 200 h EMA test, but carbon and lacquer deposits on the injector tips, in-take valves and tops of the cylinder liners were major problems. The SNI fuel performed better than a 25% blend of sunflower oil in diesel oil. The engine performances were the same for a microemulsion of 53% sunflower oil and the 25% blend of sunflower oil in diesel(Balat, Balat 2008, Ma, Hanna 1999). A microemulsion prepared by blending soybean oil, methanol, 2-octanol and cetane improver in the ratio of 52.7:13.3:33.3:1.0 was the cheapest vegetable oil-based alternative diesel fuel ever to pass the 200h EMA test. (Knothe, Dunn & Bagby 1997, Goering 1984)

Thermal cracking or pyrolysis

Pyrolysis is the process of conversion of one substance into another by means of heat or with the aid of catalyst in the absence of air or oxygen(Koh, Mohd. Ghazi 2011). The pyrolysis of fats has been investigated for more than 100 years, especially in those areas of the world that lack deposits of petroleum (Ma, Hanna 1999). A tung oil pyrolysis batch system was used in China as a hydrocarbon supply during World War II. These hydrocarbons were used as raw materials for gasoline and diesel-like fuel production in a cracking system similar to the petroleum process now used(Lima et al. 2004). Thermal decomposition of triglycerides produces the compounds of classes including alkanes, alkenes, alkadienes, aromatics and carboxylic acids. Different types of vegetable oils produce large differences in the composition of the thermally decomposed oil. Figure 1 outlines a schematic that accounts for the formation of alkanes, alkenes, alkadienes, aromatics and carboxylic acids from pyrolysis of triglycerides (Srivastava, Prasad 2000). The main components are alkanes and alkanes, which accounted for approximately 60% of the total feeder weight. Carboxylic acids accounted for another 9.6-16.1%. It is believed that as the reaction progresses the residue becomes less reactive and forms stable chemical structures, and consequently the activation energy increases as the decomposition level of vegetable oil residue increases (Balat, Balat 2008). Soybean oil has been thermally decomposed in air using the standard ASTM method for distillation. The viscosity of the pyrolysed soybean oil distillate is 10.2 cSt at 37.8 °C, which is higher than the ASTM specified range for No. 2 diesel fuel but acceptable as still well below the viscosity of soybean oil(Schwab, Bagby & Freedman 1987)

Recently, the yields of decarboxylation products by pyrolysis from vegetable oil soaps have been investigated by Demirbas and Kara (Demirbaş, Kara 2006). The maximum decarboxylation products of pyrolyses were 96.8%, 97.1%, 97.5%, and 97.8%, respectively, from sunflower oil, corn oil, cottonseed oil, and soybean oil at 610 K (337 °C), respectively. Oxidative pyrolysis of Na-soaps is given as following reaction(Demirbas 2003)

 $4RCOONa+O_2 \rightarrow 2R-R+2Na_2CO_3+2CO_2$

(1)

The soaps obtained from the vegetable oils can be pyrolyzed into hydrocarbon-rich products according to Eq. (1) with higher yields at lower temperatures (Balat, Balat 2008)



Fig. 2. The mechanism of thermal decomposition of triglycerides. (Srivastava, Prasad 2000)

Transesterification

Transesterification is a process where an ester is transformed into another through interchange of the alkoxy moiety (Otera 1993). The transesterification of vegetable oil involves the conversion of the triglycerides (TG) or the free fattyacids (FFA) of the oil to its corresponding alkyl esters when they are reacted with low molecular weight alcohols such as methanol, ethanol, or butanol usually in the presence of catalyst or at high temperature and pressure with the release of glycerol as by product. Transesterification process improved the fuel properties of the oil with respect to density, calorific value, viscosity, flash pint, cloud point and pour point. No hardware modifications of engines are required for the application of this biodiesel which has achieved relatively close fuel property values to that of diesel.(Koh, Mohd. Ghazi 2011) The transesterification of vegetable oils with methanol (also known as methanolysis), in the presence of acid or alkali catalysts such as H_2SO_4 or NaOH, is an important industrial method used in bio-diesel synthesis.

The reaction proceeds in three reversible steps as shown in figure 3a and 3b is the overall reaction. Basically, the first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides, and of monoglycerides to glycerol, yielding one methyl ester molecule per mole of glyceride at each step. (Barnwal, Sharma 2005)

Usually, the alcohol preferred for producing biodiesel is methanol because of its low cost. (Leung, Wu & Leung 2010)And to complete a transesterification stoichiometrically, 1 mol of triglyceride reacts with 3 mol of alcohol to obtain 1 mol of fatty acid ester and 1 mol of glycerol, shown in fig. 1b. In practice, this molar ratio of alcohol to triglyceride is often higher to drive the equilibrium to a maximum ester yield and the reaction can be catalysed by alkalis, acids and enzymes. (Ma, Hanna 1999) The presence of free fatty acids and water always produces negative effects during the transesterification of vegetable oils and fats for biodiesel production, since an alkali catalyst will react with the FFA to form soap and reduce the catalyst effectiveness, which results in lower conversion.



Figure 3. Transesterification reactions of glycerides with methanol:; (a)stepwise consecutive and reversible reactions. (b) Overall reaction R1, R2 and R3 indicate alkyl groups. (Viswanathan, Ramaswamy 2007)

There are four methods of transesterification; namely
Catalytic transesterification which is further divided into homogeneous and heterogenous catalytic transesterification

• Enzymatic transesterification

- Non-catalytic supercritical alcohol(methanol) transesterification
- Utrasound assisted transesterification
- Homogeneous catalyst transesterification

In conventional industrial biodiesel processes, vegetable oil methanolysis is achieved using a homogeneous catalyst system operated in either batch or continuous mode. Homogeneous catalysts transesterification can be divided into two sub groups; the homogeneous acid-catalysed and the homogeneous alkalicatalysed transesterifications.





Also metal complexes of the type M(3-hydroxy-2-methyl-4pyrone)₂(H₂O)₂, where M=Sn, Zn, Pb and Hg, have been reported as active for Soybean oil methanolysis under homogeneous conditions(Abreu et al. 2003). They found that the complexes of Sn and Zn showed great activities for this reaction, achieving a reaction yield of up to 90 and 40%, respectively, in 3 h using molar ratio 400:100:1 (methanol:oil:catalyst), with no emulsion formations at the end. Although, not fully established, these activities are much higher than those observed using the traditional NaOH and H₂SO₄ catalysts under the studied conditions.(Abreu et al. 2004)

Homogeneous Acid Catalysed Transesterification

The commonly employed acid catalysts for transesterification include H₂SO₄, HCl, phosphoric, H₃PO₄, organic sulphuric acids, RSO₃H, Lewis acids (AlCl₃ or ZnCl₂), The simplified flow diagram of acid catalysed etc. transesterification for biodiesel production is shown in figure 5 and the reaction mechanism is given in figure 5. The acidcatalysed transesterification process is not very popular as a base-catalysed process due to the slower reaction rate and the high methanol to oil molar ratio requirement. An acid-catalyst has a lower activity and the transesterification reaction occurs at a higher process temperature than for the base-catalysed reaction.(Georgogianni et al. 2009). In general, acid catalyzed reactions are performed at high alcohol-to-oil molar ratios, lowto-moderate temperatures and pressures, and high acid catalyst concentrations.(Balat, Balat 2008) Acid-catalyzed reactions require the use of high alcohol-to-oil molar ratios in order to obtain good product yields in practical reaction times. However, ester yields do not proportionally increase with molar ratio. For instance, for soybean methanolysis using sulfuric acid, ester formation sharply improved from 77% using a methanol-to-oil ratio of 3.3:1 to 87.8% with a ratio of 6:1. Higher molar ratios showed only moderate improvement until reaching a maximum value at a 30:1 ratio (98.4%)(Lotero et al. 2006). The use of solid acid catalysts still requires a higher temperature and pressure in order to be more effective. Moreover, a long reaction time makes the process impractical and uneconomical. However liquid acid catalysts such as sulphuric acid have a tolerance and less sensitive to FFA and can simultaneously conduct esterification and transesterification by giving a high yield in esters (Miao, Li & Yao 2009). The advantages and disadvantages of the acid catalyst for transesterification is summarised in table 6.



Figure 5 A flow diagram of acid catalysed transesterification for biodiesel production(Lotero et al. 2006). The yellow grease represents the feedstock oil.

The mechanism of acid-catalysed transesterification of vegetable oil, as shown in Fig. 6, proceeds by the protonation of the carbonyl group of the ester, thus, promoting the formation of carbocation, which after a nucleophilic attack of the alcohol produces a tetrahedral intermediate. This intermediate will eliminate glycerol to form a new ester and to regenerate the catalyst (Koh, Mohd. Ghazi 2011)



transesterification of vegetable oils (Meher, Vidya Sagar & Naik 2006)

Homogeneous Alkali Catalysed Transesterification

Base-catalyzed transesterification is the most commonly used technique as it is the most economical process.(Singh et al. 2006) The typical bases employed for alkali catalysed transesterification include NaOH, KOH, Ca(OH)₂, carbonates and alkoxides such as NaOCH₃, NaOC₂H₅, NaOC₃H₇, KOCH₃, etc. The simplified flow diagram of alkali-catalysed transesterification process is shown in Fig 7. The alkalicatalysed transesterification of vegetable oils proceeds faster than the acid-catalysed reaction. Triglycerides are readily transesterified batchwise in the presence of alkaline catalyst at atmospheric pressure and at a temperature of approximately 60– 70 °C with an excess of methanol. (Srivastava, Prasad 2000)

Several studies have been conducted on the operating parameters that affect transesterification reactions. According to the result of the research conducted by Chitra et al (Chitra, Venkatachalam & Sampathrajan 2005), the optimum variables for effective transesterification of Jatropha curcas oil are 20% methanol (by weight of oil), a molar ratio of methanol to oil of 5:1, and 1.0% of NaOH as a catalyst (by weight of oil). A maximum methyl ester yield of 98% was obtained after 90 min with a 60 °C reaction temperature and this biodiesel was found

to be within the specified limits. It was also found that when the concentration of methanol and NaOH were above or below their optimum, there was no significant increase in the yield of biodiesel. After acid pretreatment or acid catalyst esterification to reduce the FFA content in Jatropha curcas oil, subsequent transesterification give an optimum methyl ester yield of 90% in 2 h. and the optimum methanol to oil ratio was 24% w/w and 1.4% w/w NaOH to oil as the alkaline catalyst at a reaction temperature of 65 °C.(Berchmans, Hirata 2008)

Similar results have been obtained by Lu et al (Lu et al. 2009)in their previous work, by using a different type of alkali catalyst. Crude Jatropha oil contains many gums such as phospholipids which can deactivate the alkali catalyst, reducing the yield of methyl ester and giving a bad quality of biodiesel. The phospholipid content was significantly reduced after pretreatment operation. The yield of biodiesel from Jatropha curcas oil was higher than 98% which was obtained in 20 min of reaction time, using 1.3% of KOH (by weight of oil) as a catalyst and a molar ratio of methanol to oil of 6:1 at 64 °C. They also determined that the kinetics of the transesterification reaction of *Jatropha curcas L*. oil and methanol follow a pseudo-second-order mechanism.

The alkaline catalysts show high performance for obtaining vegetable oils with high quality, but a problem arises when the oils contain significant amounts of free fatty acids which cannot be converted into bio-diesels but soap. (Furuta, Matsuhashi & Arata 2004a) These free fatty acids react with the alkaline catalyst to produce soaps that inhibit the separation of the bio-diesel, glycerin, and wash water.(Canakci, Gerpen 2003)

Homogeneous alkali catalysts such as sodium hydroxide and potassium hydroxide , due to the low cost, are most commonly used in processes for the production of biodiesel from vegetable oils. However, the most active catalyst is the alkaline metal alkoxides (e.g CH₃ONa) with very high yield of (>98%) only at low molar concentration (0.5 mol%) even with a short reaction time (30 min).(Koh, Mohd. Ghazi 2011) Potassium carbonate also gives high yields of fatty acid alkyl ester in concentration of 2 or 3 mol% with less soap formation because of the formation of bicarbonate instead of water, in this way the esters formed will be hydrolysed. (Demirbas 2005)

The main concern in adopting alkali catalysts in biodiesel production is the FFA (free fatty acid content) content of feedstocks. A high FFA content of more than 1% w/w will enhance soap formation and the separation of end products will be hard, causing a low yield of biodiesel.(Berchmans, Hirata 2008) Therefore, the pre-treatment of high FFA feedstock is required for effective alkali-catalysed transesterification to occur. A two-stage transesterification process can be used to improve the methyl ester yield. Here the feedstock is first subjected to acid pre-treatment or acid catalyst esterification to reduce the FFA content before the subsequent transesterification to give an optimum methyl ester yield. The merits and demerits of alkali-catalysed transesterification are summarized in Table 7.



Figure 7. The flow diagram of Alkali-catalysed transesterification (Lotero et al. 2006)

The mechanism of this alkali-catalysed transesterification is shown in Fig. 8. The reaction mechanism is formulated in three steps. The first step is the reaction of the carbonyl carbon atom with the anion of the alcohol, forming a tetrahedral intermediate, from which the alkyl ester and corresponding anion of the diglycerides are formed. Another catalytic cycle is started when the catalyst reacts with a second molecule of alcohol. From there, diglycerides and monoglycerides are converted into alkyl esters and glycerol.(Demirbas 2005)

ROH + B = RO' + BH'



Heterogeneous Catalyst Transesterification

The homogeneous alkali and acid catalysed transesterification have been widely studied and established for the transesterification of vegetable oils with short chain alcohol, producing glycerin as sub-product. However, these catalyst systems are associated with various problems. The acid catalyst system is associated with slow reaction and corrosion. And the alkali system is associated with soap formation which emulsifies the biodiesel and glycerine, especially if ethanol is used. (Abreu et al. 2004) Also, both catalytic systems are less active for high molecular weight alcohols.

In order to minimize these problems, attempts to use heterogeneous catalyst systems in alcoholysis of triglycerides have been made (Bournay et al. 2005, Suppes et al. 2001). Some solid metal oxides such as those of tin, magnesium, and zinc are known catalysts but they actually act according to a homogeneous mechanism and end up as metal soaps or metal glycerates (Bournay et al. 2005). Table 8 presents a variety of heterogeneous solid acid and base catalysts reported in the literature and more are discovered continually. These heterogeneous systems are active for high molecular weight alcohols, achieving conversions higher than 95% in systems where neither alkyl nor acid catalysts work (Suppes et al. 2001), and produce neither corrosion nor emulsion, making it easier to separate the products obtained (Abreu et al. 2004). Figure 9 is the typical flow sheet of a heterogenous process. In heterogeneous catalysis, a number of operating parameters such as temperature, extent of catalyst loading, mode of mixing, alcohol/oil molar ratio, presence/absence of impurities in the feed stock and the time of reaction are important (Helwani et al. 2009). Heterogeneous catalyst systems present very low methanolysis and ethanolysis activities when compared with the traditional acid and basic ones (Abreu et al. 2004). The major drawback of heterogeneous catalysts in general lies their preparation and reaction conditions which are energy intensive which will escalate their production cost and their leaching aspect (Sharma, Singh & Korstad 2011). The comparison

between homogeneous catalysts and heterogeneous catalysts in transesterification is given in Table 9.



Fig. 9. Simplified flow sheet of heterogeneous transesterification process, Esterfif-H[™] Solid Acid Catalyst

Solid acid catalysts are more environmental friendly and eliminate the corrosion problem which is one of the major weaknesses of liquid acid catalyst. However, for efficient promotion of transesterification, the solid catalysts require a high porosity with interconnecting pores. In this respect, zeolite has advantage over other oxide catalysts. Also, the surface should possess some hydrophobic character for promoting the preferential adsorption of oily hydrophobic species on the catalyst surface and to avoid deactivation of catalytic sites by strong adsorption of polar by products like glycerol or water (Helwani et al. 2009). The mechanism is similar for homogeneous and heterogeneous Brønsted and Lewis acid catalysts. Brønsted acid is suitably preferred for esterification reaction, whereas Lewis acid gets deactivated due to the water formed in the esterification. In homogeneous and heterogeneous Brønsted and Lewis acid catalysts, the reaction mechanism proceeds by protonation of carbonyl group, thus increasing its electrophilicity. This makes the carbonyl group more susceptible to nucleophilic attack. The rate-determining step is different for Brønsted and Lewis solid acid catalyst. For Nafion, a Brønsted solid acid supported on silica, nucleophilic attack between adsorbed carboxylic acid and unadsorbed alcohol (by Eley-Rideal mechanism) is the rate-determining step. In the case of Lewis acid catalyst, acid strength is the rate-determining step for successful transesterification reaction.(Sharma, Singh & Korstad 2011)

Zeolites

Zeolites of extensive various acidic and textural properties can be synthesized to overcome the diffusional limitations to obtain optimum biodiesel yield. This gives zeolites an edge over other solid acid catalysts. Also, zeolites can be modulated by incorporating suitable organic compounds like the heteropoly acids into the structure to give them hydrophobic characteristics without compromising its acidic sites. However, the predictive capability for the zeolites and the necessary functionalization to alter their hydrophobicity is still not fully established.(Helwani et al. 2009)

Heteropoly acids

Heteropoly acid catalysts appear to be the most water tolerant acid catalysts. Most of these systems have acidity in the range of super acids with the possibility of tailoring the porous architecture as well as solubility in water (like the Cs salt) (Helwani et al. 2009). Chai et al (Chai et al. 2007) have reported that Cs2.5PW heterogeneous acid catalyst shows almost the same activity under optimized reaction conditions as compared to a conventional homogeneous catalyst such as sodium hydroxide or sulphuric acid with the advantages of easy separation and reuse. Although it appears attractive, it is necessary that the activity of this class of catalysts is evaluated and compared with the other hydrophobic solid catalysts from the point of important variables and operating parameters such as methanol to oil molar ratio, reaction temperature and the extent of reusability.(Morin et al. 2007)

Functionalized zirconia and silica

The difficulty of recuperating sulphuric acid from esterification system led to the study of the use of sulphated zirconia catalysts and organo sulphonic acids functionalized silica as the replacement for sulphuric acid in the transesterification system(Omota, Dimian & Bliek 2003, Yadav, Murkute 2004). The main drawback with these systems was that the sulphate ions leached out from the porous support as a result of hydrolysis.(Helwani et al. 2009). As alternatives to sulphated zirconia, sulphated tin oxide and tungstated zirconia-alumina were also experimented(Furuta, Matsuhashi & Arata 2004b). While it was found that the co-existence of amorphous WO₃ and tetragonal ZrO₂ was necessary in order to achieve high activity in biodiesel production, the presence of monoclinic phase of zirconia and crystalline WO₃, however small, carried detrimental effects on the esterification reaction. It was thought that the active sites that fostered notably large catalytic activity were located only at the interface between tetragonal zirconia and amorphous WO₃ (Helwani et al. 2009, Matsuhashi et al. 2001) Solid Base Catalyst

Heterogeneous basic Brønsted and basic Lewis catalysts react similarly with alcohol, forming a homogeneous alkoxide group. The transesterification reaction then occurs between alcohol (usually methanol or ethanol) adsorbed on catalyst and ester of the reactant by the Eley–Rideal mechanism (Sharma, Singh & Korstad 2011)

Oxides and Mixed-oxide Catalysts

The alkaline earth metals (group II elements) have been widely reviewed for their potential for use as heterogeneous catalysts for biodiesel production. They are believed to possess basic sites which are generated by the presence of M^{2+} - O_2^- ion pairs in different coordination environments. The basic strength of the group II oxides and hydroxides increased in the order Mg < Ca < Sr < Ba. Of these Ca-derived bases are the most promising as they are inexpensive, and exhibit low methanol solubility and they are also the least toxic.

Oxides of magnesium and calcium (MgO and CaO) have been tried as solid base catalyst owing to their easy availability, low cost, and non-corrosive nature (Sharma, Singh & Korstad 2011). Recently, a pioneering work on catalytic activity of MgO has been reported by Di Serio et al. where 92% yield has been achieved using 12:1 methanol to oil molar ratio, 5.0 wt.% of the catalyst in 1 h. MgO, when loaded on three different mesoporous silicas (MCM-41, SBA-15, and KIT-6), was found to be quite effective resulting in high conversion of 96%, the reaction conditions (220 $^{\circ}$ for 5 h in batch reactor with continuous stirring with MgO loaded on SBA-15) but they are energy intensive which may incur high cost for biodiesel production(Li, Rudolph 2008).

MgO supported KOH catalyst has shown high conversion (99.36%) and yield (95.05%) of biodiesel from canola oil (Ilgen, Akin 2009). The catalyst with 20 wt % KOH loaded on MgO was found to be the optimum catalyst, which gave the highest basicity of 6.0 mmol/g and the best catalytic activity for the reaction conditions studied (Fig. 10). When the reaction was carried out at reflux of methanol, with a molar ratio of methanol/canola oil of 6:1, and a catalyst amount 3%, the highest conversion of canola oil of 99.36% was obtained after 7

h of reaction time and the highest FAME yield of 95.05% was obtained after 9 h of reaction time. Potassium K interacts with Mg and weakens the Mg-O bond. This facilitates migration of O^{2-} species that react with the CO₂ present in air during calcination. This leads to the formation of K₂CO₃ dispersed over magnesia from KOH loading as determined by Scanning Electron Microscope (SEM) and X-ray Diffraction (XRD) analysis. K₂CO₃ acts as a heterogeneous catalyst(Sharma, Singh & Korstad 2011, Ilgen, Akin 2009). Though the optimum reaction conditions were moderate for molar ratio {i.e. 6:1 (alcohol to oil)} and catalyst amount (3%), a longer reaction time was required (7 h) which will incur high cost of the overall process (Ilgen, Akin 2009). Loading K₂CO₃ on MgO (K₂CO₃/MgO loading ratio 0.7) has shown a high yield of 99.5%. A high base strength of PKa value between 15 and 18.4 (higher than that of K_2CO_3) has been attributed to the decomposition of K₂CO₃ to K₂O by calcinations. Al₂O₃ and CaO, when tried as carriers instead of MgO, have also shown a high yield of 98%. However, K2CO3/CaO was found to be sensitive to water and was converted to hydroxide. K₂CO₃/MgO was resistant to water content; 1% water only reduced the catalytic activity to 95%. The finding is significant in view of the lesser amount of catalyst (1 wt.%) and reaction time (2 h) along with molar ratio {(6:1) alcohol to oil} utilized for transesterification (Sharma, Singh & Korstad 2011)

Although, calcium oxide catalysts require calcinations to avoid H₂O and CO₂ poisoning of the active sites and modification to control its leaching in biodiesel, it has gained increased attention because of its low cost, low toxicity and low methanol solubility. Huaping et al. (Huaping et al. 2006) used CaO as heterogeneous catalyst for biodiesel synthesis from Jatropha curcas oil. The base strength of calcium oxide increased to 26.5 (grouped in the category of super base) on treatment with ammonium carbonate solution and further calcinations at 900 °C resulted in 93% conversion of jatropha oil to biodiesel under optimized conditions (70 °C temperature, 2.5 h reaction time, 1.5% catalyst amount, and 9:1 methanol to oil molar ratio). Kouzu et al. (Kouzu et al. 2008) showed that the active site of the calcium oxide catalyst was calcium diglyceroxide formed by the transesterification reaction of calcium oxide with the by-product glycerol. The active site of the used catalyst was thought to be due to OH groups from calcium diglyceroxide. The mechanism of the reaction is shown in Fig 10 below



Fig. 10.Catalyst, CaO and calcium diglyceroxide (Veljković et al. 2009). Possible mechanism for transesterification of vegetable oil with methanol catalyzed by calcium diglyceroxide. (a) Adsorption of methanol onto catalyst; (b) abstraction of proton by basic sites; and (c) nucleophilic reaction with methoxide anion followed by stabilization of the anion by proton.

Calcium oxide, CaO, have also been wet-impregnated on porous silica (Albuquerque et al. 2008a) such as SBA-15, MCM- 41 and fume silica and tried as catalyst for biodiesel development from castor and sunflower oil. Various alkali compounds (LiNO₃, NaNO₃, and KNO₃) have also been doped on CaO and MgO to foresee their activity in transesterification reactions. A correlation was observed between the base strength and the activity of the catalyst. Calcination of the catalyst resulted in decrease in the surface area of the catalyst from 10 to $1-2 \text{ m}^2/\text{g}$. Higher surface area of the catalyst is not even desired as triglycerides are large molecules and would not be able to diffuse into the pores unless a mesoporous substrate is used (MacLeod et al. 2008). Conversion obtained from uncalcined catalysts (LiNO₃/CaO, KNO₃/CaO, and NaNO₃/CaO) was found to be 85%, 90% and 98%, respectively. When the catalysts were calcined, the conversion of 99-100% was obtained. However, when the alkalis were doped with MgO, only 4-5% conversion was achieved. On calcination, only LiNO₃/MgO gave complete (100%) conversion.(Sharma, Singh & Korstad 2011, MacLeod et al. 2008). Lanthanum have been shown to enhance the basic strength of CaO catalystLanthanum, when added to calcium oxide, has enhanced the basic strength, total basicity, and the surface area prodicing a high yield of 94.3% with 20:1(alcohol to oil) molar ratio, 5% catalyst dose, in 60 min reaction time with refined soybean oil. High yield (96%) was also achieved with crude oil and waste cooking oil having free fatty acid (FFA) and water content in 3 h reaction time(Wei, Xu & Li 2009)

Strontium Oxide, SrO, has also attracted attention as a heterogeneous catalyst owing to its high basicity and insolubility in methanol, vegetable oil and methyl esters. A yield of 95% has been attained at a comparatively moderate temperature of approximately 65 °C within 30 min. The catalyst has been reported to have a longer lifetime and could be reused for 10 runs. SrO has been reported to have the advantage of possessing a basic site stronger than 26.5 and is also insoluble in methanol, vegetable oils and fatty acid methyl esters. The reaction mechanism is similar to that of CaO which involves various steps where initially surface methoxide anion (CH₃O⁻) is formed having high catalytic activity. In the next step, the CH₃O⁻ attached to the surface of SrO is attracted by the carbonyl carbon atom of the triglyceride molecule to form a tetrahedral intermediate. The tetrahedral intermediate formed picks up H⁺ from the surface of SrO. The final step results in the rearrangement of the tetrahedral intermediates to form biodiesel (Liu et al. 2007).

Mixed Oxides

Great research works have been done in developing mixed oxides for application as heterogeneous catalysts for transesterification reaction. A mixed oxide of zinc and aluminum has been synthesized for application as a heterogeneous catalyst resulting in high conversion (98.3%) of biodiesel and glycerol of more than 98% purity. A transparent and colorless glycerol is obtained without any ash or inorganic compound, although, the preparation requires high temperature and pressure which will amount to high cost of biodiesel production.(Bournay et al. 2005).Various metal oxide catalysts such as CaMnO₃, Ca₂Fe₂O₅, CaCeO₃, and CaZrO₃ gave methyl ester yield ranging between 79% and 92% at 60 °C 6:1 (methanol to oil) molar ratio in 10 h: CaTiO₃, with basic strength of $6.8 < H_{-} < 7.2$, gave an average yield of 79% in 10 h; CaTiO₃, when reused, gave biodiesel yield of 79% in the first re-run in 10 h reaction time. Surprisingly, in the second re-run, yield increased to 85%. However, catalytic activity decreased in the third re-run and yield reduced to 68% and almost nil (1%) when used for the fourth time. The reason attributed for the decline in catalytic activity is the obstruction of catalytic activity by glycerin and adsorption of fatty acids to the active sites of the catalyst. Another reason for the decreased catalytic activity is thought to be dissolution of catalytic-active species by the glycerin solution. Similar trends were observed with CaMnO₃ and Ca₂Fe₂O₅. On the other hand, CaZrO₃ and CaCeO₃ were used for 5 and 7 times, respectively, with a methyl ester yield greater than 80%. CaCeO₃ has been reported to be CaOsupported on CeO₃ which imparts a better stability and active basic sites to the compound(Sharma, Singh & Korstad 2011, Kawashima, Matsubara & Honda 2008)

Also, Ca-Zn mixed oxides (CaO·ZnO) prepared by cobeen used catalysts precipitation have as for transesterification(Ngamcharussrivichai, Totarat & Bunyakiat 2008); Mg-Ca mixed oxide was reported to have produced 99% yield with optimized reaction conditions of 12:1 alcohol to oil molar ratio at 60 °C reaction temperature. This result was attributed to the high surface area and presence of strong basic sites on the surface coming from $Ca^{2+}-O^{2-}$ pairs (Albuquerque et al. 2008b); and continuous process for development of biodiesel by porous zirconia, titania and alumina micro particulate for simultaneous esterification and transesterification of fatty acids has been described by McNeff et al. (McNeff et al. 2008). This Mcgyan process (named after the three inventors: McNeff, Gyberg, and Yan) uses supercritical methanol as reactant and does not require surface modification of the catalyst. The process is anticipated to reduce the production cost of biodiesel as feedstock with higher FFA could be converted to fatty acid alkyl esters (Sharma, Singh & Korstad 2011). Titania catalyst was reused effectively up to 115 h of continuous operation without loss of activity. The process has been quite effective for algae as potential and suitable feedstock because algae possesses higher fatty acids and can grow rapidly under controlled conditions (McNeff et al. 2008).

Alumina Loaded with various Compound

Alumina loaded with various compound have been tried as catalyst and have shown varying results (Sharma, Singh & Korstad 2011). Alumina loaded with KNO₃ and Eu₂O₃ have shown conversion less than 90%, whereas alumina loaded KF and KOH has shown high yield of 90–91%. On contrary KI/Al₂O₃ has shown a high conversion of 96% and is near to the specification of EN 96.5%).(Sharma, Singh & Korstad 2011).

Na/NaOH/ γ -Al₂O₃ used as a heterogeneous catalyst along with the co-solvent *n*-hexane has shown activity similar to that of the homogeneous one (i.e. NaOH with a yield of 94% in 2 h reaction time at 60 °C and 9:1 alcohol to oil molar ratio) with moderate rate of stirring (300 rpm). The catalyst was prepared by treatment of γ -Al₂O₃ with sodium hydroxide followed by sodium at 320 °C under controlled nitrogen flow. Loaded sodium has been proposed to be completely ionized and dispersed into the defect sites of γ -Al₂O₃ which was formed during thermal pretreatment (Kim et al. 2004). K₂CO₃ salt loaded with alumina (Al₂O₃) by impregnation method, was investigated for transesterification of triolein and resulted in 94% and 89% yield of ester and glycerol, respectively, at 60 °C in 1 h reaction time. This is significant as moderate temperature conditions and less time are employed for a good yield (94%) of biodiesel. It was observed that basic strength did not necessarily enhance a better conversion. The catalytic activity of K_2CO_3/Al_2O_3 was found to be comparable to that obtained from 0.023 mmol of KOH.(Ebiura et al. 2005)

High conversions of 94.3% and 91.6% were observed with Al_2O_3 supported $Ca(NO_3)_2/Al_2O_3$ and $Li(NO_3)/Al_2O_3$, respectively(Benjapornkulaphong, Ngamcharussrivichai & Bunyakiat 2009) . Alumina loaded on CaO and MgO compounds used as heterogeneous catalyst for transesterification of a microalga, *Nannochloropsis oculata*, as feedstock, in modified single step sol–gel method, was more active than pure CaO and MgO. 97.5% biodiesel yield was achieved with 80 wt.% loading of CaO on Al_2O_3 . (Umdu, Tuncer & Seker 2009) *Basic Zeolite*

Zeolites are microporous aluminosilicate minerals which are commonly used as adsorbents for water and wastewater purification. They have also been used as catalyst for fluid catalytic cracking and hydro-cracking in petrochemical industry. Zeolites as catalyst have the characteristics of acidic sites and shape selectivity. Zeolites vary in pore structure and inner electric fields from crystal and surface properties which result in their varying catalytic properties (Sharma, Singh & Korstad 2011). The base strength of the alkali ion exchanged zeolite increases with increasing electropositive nature of the exchanged cation. The occlusion of alkali metal oxide clusters in zeolite cages through the decomposition of impregnated alkali metal salts results in an increase in the basicity of these materials (Philippou, Anderson 2000). These exchanges can affect the water tolerant behaviour of the basic zeolite system. Systems like ETS-10, a microporous inorganic lithium containing zeolite has been shown to be a new generation solid base catalyst for transesterification. Most of these catalysts contain the basic sites (cation) generated by thermal decomposition of the supported salt. It has been shown that the conversion to methyl ester over NaX faujasite zeolite that was ion exchanged with more electropositive cations was higher than that of the parent zeolite (Helwani et al. 2009, Watanabe et al. 2002).

Hydrotalcites

Hydrotalcite or Layered Double Hydroxide (LDH) is an anionic and basic clay found in nature with the general formula of $([M^{z_{+}}_{(1-x)} M^{3+}(OH)_2]^{b_{+}}(A_b^{n_{-}}/n).xH_2O)$, where $M^{z_{+}}$ is a divalent or monovalent cation and A^{n-} is the interlayer anion (Bejoy 2001). The commonest hydrotalcites is Mg₆Al₂(OH)₁₆CO₃.4H₂O and its conventionally synthesized by co-precipitation, wherein metal nitrates {Mg(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O} and precipitants $\{(NH_4)_2CO_3 \text{ and } NH_4OH\}$ are added slowly and simultaneously at a fixed pH(7.6 - 8) under stirring, followed by a long (about 1 day) ageing time and/or hydrothermal treatment in order to improve the crystallinity (Helwani et al. 2009, Sharma, Singh & Korstad 2011, Cantrell et al. 2005). It presents a positively charged brucite-like layers (Mg(OH)₂) in which some of Mg^{2+} are replaced by AI^{3+} in the octahedral sites of hydroxide sheets. Interstitial layers formed by CO_3^{2-} anions and water molecules compensate the positive charge resulting from this substitution (Othman, Kim 2008). A wide range of compositions containing various combinations of M(II), M(III) and different anions A^{n-} can also be synthesized (Carja et al. 2001).

Decomposition of Mg–Al HT yields a high surface area Mg–Al mixed oxide, which presumably exposes strong Lewis base sites (Corma et al. 2005) . The basic properties of these sites depend on the Mg–Al ratio in the precursor hydrotalcite (Di Cosimo et al. 1998). The reconstruction of decomposed Mg–Al HT by rehydration at room temperature reportedly enhanced the catalytic activity (Rao et al. 1998). During the rehydration, the

brucite-like layers were reformed and the charge-compensating carbonate anions were replaced by hydroxyl anions, thus forming Brønsted base sites. The decomposed–rehydrated Mg–Al HT with Brønsted base sites exhibited higher catalytic activity than the decomposed Mg–Al HT with Lewis base sites for the transesterification of oleic acid methyl ester with glycerol (Corma et al. 2005). A hypothetically simplified model for the reaction is given in Fig. 11 (Helwani et al. 2009).



Fig. 11. A simplified model of hydrotalcite catalyzed transesterification (Helwani et al. 2009).

Xie et al.(Xie, Peng & Chen 2006) had used calcined Mg– Al hydrotalcite { $Mg_6Al_2(OH_{16})CO_3 \cdot 4H_2O$ }, which had earlier been used as a heterogeneous catalyst in various base-catalyzed reactions (Aldol condensations, Michael reaction, cyanoethylation of alcohols, and nitroaldol reaction), for transesterification reaction of soybean oil

The best conversion of soybeen oil to biodiesel obtained using Mg–Al hydrotalcites were below 80% (Helwani et al. 2009, Sharma, Singh & Korstad 2011, Xie, Peng & Chen 2006). For rapeseed oil, 90.5% conversion of biodiesel was obtained with Mg-Al hydrotalcite calcined at 773k for 12h(Sharma, Singh & Korstad 2011, Zeng et al. 2008). The conversion is low as per the EN norm (96.5%). However, the reaction conditions used were moderate, i.e. 6:1 (alcohol to oil) molar ratio, 1.5 wt.% catalyst, and 4 h reaction time at 65 °C and moderate rate of stirring (300 rpm). The catalyst was found to be separable by filtration and was recycled for 3 runs with a minor loss in its activity (>88% conversion) (Zeng et al. 2008).

A1.5% potassium loaded on Mg-Al hydrotalcite was found to enhance the catalytic activity of hydrotalcite and gave a high conversion (96.9%) and yield (86.6%). However, longer duration for calcination (35 h) was required for synthesis of the catalyst which is energy intensive. Biodiesel developed was blended with diesel {to form B10, i.e. 90 part diesel and 10 part biodiesel (v/v)} and its impact on performance of elastomers in the fuel system component were close to that of diesel and established its compatibility(Trakarnpruk, Porntangjitlikit 2008). Also, An 80% (wt/wt) load ratio of KF/hydrotalcite with 12:1 (alcohol to oil) molar ratio gave a yield of 92% in 5 h reaction time at 65 °C (Gao et al. 2008)

Although relatively lower yield was observed, hydrotalcite can still provide large opportunity for improvement in the biodiesel production. This is especially true if the specific surface area of the solid pore is improved, its homogeneity is enhanced and the particle size is greatly reduced. A way to achieve these desirable characteristics is by employing a sol-gel method during hydrotalcite synthesis (Helwani et al. 2009). By way of the sol-gel technique, core-shell nano-particle hydrotalcite and thin films can be prepared (Othman, Rasid & Fernando 2006). By different simple arrangements, sol-gel coatings can be applied at room temperature and pressure (Helwani et al. 2009) and the specific surface area of hydrotalcite obtained from the sol-gel method was up to three times greater than that achieved by co-precipitation(Helwani et al. 2009, Prinetto et al. 2000, Jitianu et al. 2000, Aramendía et al. 2002).`

Other methods of biodiesel synthesis

Enzyme catalysed transesterification

Both extracellular and intracellular lipases are also able to effectively catalyze the transesterification of triglycerides in either aqueous or non-aqueous systems (Balat, Balat 2008, Van Gerpen et al. 2004). For example lipases such as Candida Antarctica (Watanabe et al. 2002, Royon et al. 2007, Reyes-Duarte et al. 2005, Watanabe et al. 2000), Candida rugasa(Linko et al. 1998), Pseudomonas cepacia(Ghanem 2003, Shah, Gupta 2007), *immobilized* lipase (Lipozyme RMIM)(Bernardes et al. 2007, De et al. 2006), Pseudomonas sp.(Lai, Ghazali & Chong 1999), and Rhizomucor miehei(Lai, Ghazali & Chong 1999, Skagerlind et al. 1995) have been used to catalyze transesterification processes.

Bernardes et al.(Bernardes et al. 2007) studied the enzymatic alcoholysis of soybean oil with methanol and ethanol using a commercial, *immobilized lipase* (*Lipozyme RMIM*). The best conditions obtained in that study were in a solvent-free system with ethanol/oil molar ratio of 3.0, temperature of 50 °C, and enzyme concentration of 7.0% (w/w) and the yield was 60% after 1 h of reaction. In a similar investigation Shah and Gupa (Shah, Gupta 2007) obtained a high yield (98%) by using *P. cepacia* lipase immobilized on celite at 50 °C in the presence of 4–5% (w/w) water in 8 h.

Although base catalyzed transesterification reaction is fast, the main disadvantages

include energy intensiveness, difficulty in separating the glycerol from methyl esters.

Alkaline waste water requires treatment and free fatty acid and water interfere with the transesterification reaction. Enzymatic transesterification methods can overcome the problems mentioned above as presented in Table 11 (Fukuda, Kondo & Noda 2001b). However, enzyme-catalyzed system, it requires a much longer reaction time than the base catalyzed systems.(Zhang et al. 2003)

Although, the enzyme-cataysed transesterification reactions are highly specific and chemically clean , the main problem of the lipase-catalyzed process is the high cost of the lipases used as catalyst (Royon et al. 2007). Also, the alcohol can be inhibitory to the enzyme; a typical strategy is to feed the alcohol into the reactor in three steps of 1:1 mole ratio each. The reactions are very slow in nature, with a three step sequence requiring from 4 to 40 h or more to complete. The reaction conditions become modest as temperature is raised, for example, from 35 to 45 °C (Balat, Balat 2008, Helwani et al. 2009, Van Gerpen et al. 2004, Saka, Kusdiana 2001)

Non-catalytic supercritical methanol transesterification

The supercritical methanol transesterification is the synthesis of biodiesel under high conditions of temperature and pressure via catalyst-free reactions. 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 such

conditions, a distinct liquid and vapour phase no longer exist. Instead, a single fluid phase is formed (Van Gerpen et al. 2004). A process for biodiesel production has been developed by a noncatalytic supercritical methanol method (Demirbas 2005, Demirbas 2002). The process provide advantages such as improved phase solubility, overcomes mass transfer limitations, high reaction rate, easy separation and purification of the synthesized products. The process may be carried out even in the presence of moisture and FFA. However, its application in large scale production is limited by high cost involved because of high temperature and pressure, and involving a high alcohol to oil molar ratio (Sharma, Singh & Korstad 2011). Another advantage of the process was thermally decomposition of glycerol to low molecular weight esters, ethers and hydrocarbons on reaction with methanol. Formation of these products enhanced the fuel property such as viscosity and cold flow properties. The process was also observed to be non-reversible (Sharma, Singh & Korstad 2011).

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 (Bunvakiat et al. 2006). Biodiesel have been synthesized in the temperature range (200-400 °C), pressure of 200 bar, and alcohol to oil molar ratio of 40:1 and almost complete conversion was observed in such supercritical conditions in 40 min of reaction time with methanol as well as ethanol(Madras, Kolluru & Kumar 2004). Supercritical carbon dioxide has been tried as an alternate of supercritical alcohol because of non-toxic nature of the former and the maximum conversion obtained was less than 70% even after 5 h of reaction time with supercritical carbon dioxide in comparison to complete conversion obtained by supercritical alcohol (Rathore, Madras 2007). A typical supercritical system is shown in figure 12



Figure 12 Supercritical methanol transesterification system. (1) Autoclave, (2) Electrical furnace, (3) Temperature control monitor, (4) Pressure control monitor, (5) Product exit valve, (6) Condenser, (7) Product collecting vessel.(Demirbas 2003)

Ultrasound aided transesterification

The ultrasonic waves result in an increase of reaction rate if the catalyst is soluble or well dispersed in the liquid phase of the reagents. In this way, the rate of methanolysis would increase as a result of the intensification of the mass exchange process. Gryglewicz's results (Gryglewicz 1999) were supportive of the above hypothesis. In his study of the influence of ultrasound on the rate of transeaterifiction or rapeseed oil using different catalysts, the flask containing the reaction mixture was placed in an ultrasonic water bath with a power of 300 W, and frequency of 25 kHz, every other conditions remaining the same, and the rate of methanolysis of rapeseed oil increased substantially in reactions proceeding in the presence of sodium hydroxide,

barium hydroxide and calcium methoxide (Figure 13). In these three cases, the state of reaction equilibrium had been reached after 30 min of reaction time, which can be regarded as considerable progress. The rate of the reaction decreased in the case of calcium oxide. Magnesium oxide and calcium hydroxide turned out to be inactive in this series of experiments. It is a fact that ultrasonic waves result in an increase of reaction rate if the catalyst is soluble or well dispersed in the liquid phase of the reagents. In the considered cases, sodium and barium hydroxides are well soluble in methanol, and calcium methoxide forms a colloidal suspension. Whereas calcium oxide is a typical heterogeneous catalyst which forms a heavy sediment characterised by a poorly developed surface. For calcium oxide, adsorption of reagents on its surface plays a vital role. In this case, ultrasound probably prevented the adsorption process on the catalyst surface. (Gryglewicz 1999)



Figure 13 Activity of alkaline earth metal compounds in (A) rapeseed oil methanolysis reaction, methanol /oil molar

ratio, 4.5:1.(B) ultrasound aided rapeseed oil methanolysis, methanol/oil molar ratio, 4.5:1.(Gryglewicz 1999)

Biox Co-Solvent Process

The Boocock et al. (Boocock et al. 1996) in 1996 developed the Biox co-solvent process in which, triglycerides are converted to esters through the selection of inert co-solvents that generate a one-phase oil-rich system. This process has the potential to overcome slow reaction times caused by the extremely low solubility of the alcohol in the triglyceride phase (Leung, Wu & Leung 2010). Demirbas(Demirbas 2008) uses tetrahydrofuran (THF) as a co-solvent to make the methanol soluble. After the

completion of the reaction, the biodiesel-glycerol phase separation is clean and both the excess alcohol and the tetrahydrofuran co-solvent can be recovered in a single step (Demirbas 2008). However, because of the possible hazard and toxicity of the co-solvents, they must be completely removed from the glycerol phase as well as the biodiesel phase and the final products should be water-free (Boocock et al. 1996). The unique advantage of the Biox co-solvent process is that it uses inert, reclaimable co-solvents in a single-pass reaction that takes only seconds at ambient temperature and pressure, and no catalyst residues appear in either the biodiesel phase or the glycerol phase (Van Gerpen et al. 2004). This process can handle not only grain-based feedstocks but also waste cooking oils and animal fats. Van Gerpen et al.(Van Gerpen et al. 2004) found, however, that the recovery of excess alcohol is difficult when using this process because the boiling point of the THF cosolvent is very close to that of methanol.(Leung, Wu & Leung 2010)

In Situ Biodiesel Process

The in situ biodiesel production is a novel approach for converting oil to biodiesel which was developed by Harrington and D'Arcy-Evans in 1985 (Harrington, D'Arcy-Evans 1985). In this method, to achieve transesterification of its acyglycerols, the oilseeds are directly treated at ambient temperature and pressure with a methanol solution in which the catalyst has been previously dissolved. That means that the oil in the oilseeds is not isolated prior to transesterification to fatty acid esters(Harrington, D'Arcy-Evans 1985, Haas et al. 2004, Siler-Marinkovic, Tomasevic 1998). To reduce the alcohol requirement for high efficiency during in situ transesterification, the oilseeds need to be dried before the reaction takes place(Haas, Scott 2007). Milled oilseeds are mixed with alcohol in which the catalyst had been dissolved and the mixture is heated under reflux for 1-5 h. Two layers are formed around the time of the completion of the reaction. The lower layer is the alcohol phase and can be recovered. The upper layer, including the crude biodiesel, is washed with water to remove the contaminants until the washing solution is neutral. After the washing step, the upper layer is dried over anhydrous sodium sulfate, then filtered, and the residual product is biodiesel (Qian et al. 2008). Haas and Scott (Haas, Scott 2007) found that the final biodiesel product can conform to the ASTM standard and the conversion of the oilseed is very high (about 98%). Since this method eliminates the need for the isolation of, and possibly for the refining of, the oilseed lipid, the process could reduce biodiesel production costs, reduce the long size of the production system associated with the pre-extraction, degumming, and maximize the yield of the biodiesel production. However, this process cannot handle waste cooking oils and animal fats, which can reduce the cost of feedstock (Qian et al. 2008, Mondala et al. 2009) and (Leung, Wu & Leung 2010)

Biodiesel Production From Algae

Microalgae are prokaryotic or eukaryotic photosynthetic microorganisms that can grow rapidly and live in harsh conditions due to their unicellular or simple multicellular structure. Examples of prokaryotic microorganisms are Cyanobacteria (Cyanophyceae) and eukaryotic microalgae are for example green algae (Chlorophyta) and diatoms (Bacillariophyta)(Li et al. 2008a) and (Li et al. 2008b). As many algal species have been found to grow rapidly and produce substantial amounts of triacylglycerols (oleaginous algae), it has long been postulated that they could be employed to produce oils and other lipids for biofuels (Hu et al. 2008). Microalgae

represent an exceptionally diverse but highly specialized group of micro-organisms adapted to various ecological habitats. Many microalgae have the ability to produce substantial amounts (e.g. 20–50% dry cell weight) of triacylglycerols (TAG) as a storage lipid under photo-oxidative stress or other adverse environmental conditions (Hu et al. 2008). Algae are an economical choice for biodiesel production, because of its availability and low cost. Common species such as *Oedogonium* and *Spirogyra* have been studied (Hossain, Salleh 2008). Algal oil and biodiesel (ester) production was higher in *Oedogonium* than *Spirogyra* sp.

Many microalgae species can be induced to accumulate substantial quantities of lipids thus contributing to a high oil yield (Mata, Martins & Caetano 2010). The average lipid content varies between 1 and 70% but under certain conditions some species can reach 90% of dry weight (Li et al. 2008a). Although the microalgae oil yield is strain-dependent it is generally much greater than other vegetable oil crops {{741 Mata,Teresa M. 2010}} . Table 12 compares the biodiesel production efficiencies and land use of microalgae and other vegetable oil crops, including the amount of oil content in a dry weight basis and the oil yield per hectare, per year.

Table 12 shows that although the oil contents are similar between seed plants and microalgae there are significant variations in the overall biomass productivity and resulting oil yield and biodiesel productivity with a clear advantage for microalgae. In terms of land use, microalgae followed by palm oil biodiesel are clearly advantageous because of their higher biomass productivity and oil yield.(Mata, Martins & Caetano 2010)

Like other higher plant and animal, microalgae are able to biosynthesize triglycerides to store substance and energy. Generally, L-a-phosphoglycerol and acetyl-coA are two major primers in the biosynthesis of triglycerides. The L-aphosphoglycerol mainly derives from phosphodihydroxyacetone which is the product of the glycolysis process. The reaction steps are shown in Figure 14. One of the hydroxyl in L-aphosphoglycerol with reacts acetyl-coA to form Lysophosphatidic acid and later combines with another acetylcoA to form phosphatidic acid. These two reactions are catalyzed by glycerol phosphate acyl-transferase. In the following steps, lysophosphatidic acid is hydrolyzed by phosphatidate phosphatase to form diglyceride which is then combined with the third acetyl-coA to complete the biosynthesis of triglycerides. The last reaction step is catalyzed by glyceryl diester transacylase(Huang et al. 2010).





According to biodiesel standard published by the American Society for Testing Materials (ASTM), biodiesel from microalgal oil is similar in properties to the standard biodiesel, and is also more stable according to their flash point values (Table 13)(Huang et al. 2010).

Main Factors Affecting The Yield Of Biodiesel Alcohol quantity

It has been widely reported that one of the main factors affecting the yield of biodiesel is the molar ratio of alcohol to triglyceride (Ma, Hanna 1999, Zhang et al. 2003, Leung, Guo 2006, Freedman, Butterfield & Pryde 1986). Theoretically, the ratio for transesterification reaction requires 3 mol of alcohol for 1 mol of triglyceride to produce 3 mol of fatty acid ester and 1 mol of glycerol. An excess of alcohol is used in biodiesel production to ensure that the oils or fats will be completely converted to esters and a higher alcohol triglyceride ratio can result in a greater ester conversion in a shorter time. The yield of biodiesel is increased when the alcohol triglyceride ratio is raised beyond 3 and reaches a maximum (Leung, Wu & Leung 2010). Further increasing the alcohol amount beyond the optimal ratio will not increase the yield but will increase cost for alcohol recovery (Leung, Guo 2006). In addition, the molar ratio is associated with the type of catalyst used and the molar ratio of alcohol to triglycerides in most investigations is 6:1, with the use of an alkali catalyst(Zhang et al. 2003, Freedman, Butterfield & Pryde 1986). When the percentage of free fatty acids in the oils or fats is high, such as in the case of waste cooking oil, a molar ratio as high as 15:1 is needed when using acid-catalyzed transesterification(Leung, Wu & Leung 2010, Leung, Guo 2006, Ali, Hanna & Cuppett 1995).

Reaction time

Previous work by Freedman et al. (Freedman, Pryde & Mounts 1984) shows that the conversion rate of fatty acid esters increases with reaction time. At the beginning, the reaction is slow due to the mixing and dispersion of alcohol into the oil. After a while, the reaction proceeds very fast. Normally, the yield reaches a maximum at a reaction time of <90 min, and then remains relatively constant with a further increase in the reaction time (Leung, Guo 2006, Alamu et al. 2007). Moreover, excess reaction time will lead to a reduction in the product yield due to the backward reaction of transesterification, resulting in a loss of esters as well as causing more fatty acids to form soaps(Eevera, Rajendran & Saradha 2009, Ma, Clements & Hanna 1998) and (Leung, Wu & Leung 2010)

Reaction temperature

Temperature clearly influences the reaction and yield of the biodiesel product(Leung, Wu & Leung 2010). A higher reaction temperature can decrease the viscosities of oils and result in an increased reaction rate, and a shortened reaction time(Leung, Wu & Leung 2010). However, Leung and Guo (Leung, Guo 2006) and Eevera et al.(Eevera, Rajendran & Saradha 2009) found that when the reaction temperature increases beyond the optimal level, the yield of the biodiesel product decreases because a higher reaction temperature accelerates the saponification reaction of triglycerides. The reaction temperature must be less than the boiling point of alcohol in order to ensure that the alcohol will not leak out through vaporization. Depending on the oil used, the optimal temperature ranges from 50 °C to 60 °C(Leung, Wu & Leung 2010, Ma, Hanna 1999, Leung, Guo 2006, Freedman, Butterfield & Pryde 1986, Freedman, Pryde & Mounts 1984).

Catalyst concentration

Furthermore, catalyst concentration can affect the yield of the biodiesel product. Freedman et al. (Freedman, Pryde & Mounts 1984) found that sodium methoxide was more effective than sodium hydroxide(the most commonly used catalyst for the reaction) because upon mixing sodium hydroxide with methanol a small amount of water will be produced, which will affect the product yield because of the hydrolysis reaction (Guo 2005). This is the reason why the catalyst should be added into the methanol first and then mixed with the oil. As the catalyst concentration increases the conversion of triglyceride and the vield of biodiesel increase. This is because an insufficient amount of catalysts result in an incomplete conversion of the triglycerides into the fatty acid esters (Leung, Guo 2006, Guo 2005). Usually, the yield reaches an optimal value when the catalyst (NaOH) concentration reaches 1.5 wt.% and then decreases a little with a further increase in catalyst concentration. The reduction of the yield of the biodiesel is due to the addition of excessive alkali catalyst causing more triglycerides to react with the alkali catalyst and form more soap(Leung, Guo 2006, Eevera, Rajendran & Saradha 2009) and (Leung, Wu & Leung 2010)

Economic Viability Of Biodiesel

Biodiesel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources. Below are the key identified advantages of biodiesel.

• Biodiesel is non-toxic: It reduces the emission of harmful pollutants (mainly particulates) but emissions of nitrogen oxides (precursor of ozone) are increased

• Biodiesel degrades four times faster than diesel.

• Pure biodiesel degrades 85-88% in water.

• Blending of biodiesel with diesel fuel increases engine efficiency.

• The higher flash point makes the storage safer.

• Biodiesel is an oxygenated fuel, thus implying that its oxygen content plays a role in making fatty compounds suitable as diesel fuel by "cleaner" burning.

• 90% reduction in cancer risks, according to Ames mutagenicity tests.

• Provides a domestic, renewable energy supply.

• Biodiesel does not produce greenhouse effects, because the balance between the amount of CO_2 emissions and the amount of CO_2 absorbed by the plants producing vegetable oil is equal.

• Biodiesel can be used directly in compression ignition engines with no substantial modifications of the engine.

• Biodiesel contains no sulphur and is generally suitable to match the future European regulations which limit the sulphur content to 0.2% in weight in 1994 and 0.05% in 1996.

• Chemical characteristics revealed lower levels of some toxic and reactive hydrocarbon species when bio-diesel fuels were used.

• The emissions of PAH and nitro PAH compounds were substantially lower with biodiesel are compared to conventional diesel fuel.

• The larger reductions in PAH are not unexpected when considering the biodiesel contains no aromatics and no PAH compounds.

• Biodiesel has a high cetane number (above 100, compared to only 40 for diesel fuel). Cetane number is a measure of a fuel's ignition quality. The high cetane numbers of biodiesel contribute to easy cold starting and low idle noise.

• The use of biodiesel can extend the life of diesel engines because it is more lubricating and, furthermore, power output are relatively unaffected by biodiesel.

• Biodiesel replaces the exhaust odour of petroleum diesel with a more pleasant smell of popcorn or French fries : (Murugesan et al. 2009, Palanisamy, Manoharan 2005, Srinivas, Rathanasamy 2007)

However, the challenges are its cost and limited availability of fat and oil resources (Singh, Singh 2009). The cost of biodiesel, however, is the main obstacle to commercialization of the product.(Demirbas 2003). Table 15 shows the estimated cost of production of biodiesel from palm oil

The cost of Biodiesel can be classified into two aspects, the costs of raw material (fats and oils) and the cost of processing. The cost of raw materials accounts for 60-75% of the total cost of Biodiesel fuel (Sonntag 1979). Most of the biodiesel that is currently made uses edible oils, methanol and an alkaline catalyst. The high value of edible oil as a food product makes production of a cost effective fuel very challenging. With cooking oils used as raw material, the viability of a continuous transesterification process and recovery of high quality glycerol as a biodiesel by-product are primary options to be considered to lower the cost of biodiesel (Demirbas 2003, Ma, Hanna 1999). However, there are large amounts of low cost oils and fats, such as restaurant waste and animal fats that could be converted to biodiesel. The problem with processing these low cost oils and fats is that they often contain large amounts of FFA that cannot be converted to biodiesel using an alkaline catalyst (Canakci, Van Gerpen 2001).

Martin Bender (Martin 1999) conducted a review of 12 economic feasibility studies which showed that the projected costs for biodiesel from oilseed or animal fats have a range of US\$0.30–0.69/l, including the meal and glycerin credits and the assumption of reduced capital investment costs by having the crushing and/or esterification facility added onto an existing grain or tallow facility. Rough projections of the cost of biodiesel from vegetable oil and waste grease are, respectively, US\$0.54–0.62/l and US\$0.34–0.42/l. With pre-tax Diesel priced at US\$0.18/l in the US and US\$0.20–0.24/l in some European countries, biodiesel is, thus, currently not economically feasible, and more research and technological development will be needed (Demirbas 2006, Demirbas 2003, Martin 1999, Balat 2007).

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 Table 1. Fuel properties of methyl ester from selected vegetable oils compared to those of petrodiesel

| Vegetable oil methyl esters (biodiesel) | Kinematic viscosity (mm ² /s) | Cetane no. | Lower heating value (MJ/kg) | Cloud point (°C) | Pour point (°C) | Flash point (°C) | Density (kg/l) |
|--|--|---------------|-----------------------------|---------------------|--------------------|------------------|-------------------|
| Peanut | 4.9 | 54 | 33.6 | 5 | - | 176 | 0.883 |
| Soya bean | 4.5 | 45 | 33.5 | 1 | -7 | 178 | 0.885 |
| Babassu | 3.6 | 63 | 31.8 | 4 | - | 127 | 0.875 |
| Palm | 5.7 | 62 | 33.5 | 13 | - | 164 | 0.880 |
| Sunflower | 4.6 | 49 | 33.5 | 1 | - | 183 | 0.860 |
| Tallow | - | - | - | 12 | 9 | 96 | - |
| Diesel | 3.06 | 50 | 43.8 | - | -16 | 76 | 0.855 |
| 20% biodiesel blend | 3.2 | 51 | 43.2 | - | -16 | 128 | 0.859 |

Source: (Barnwal, Sharma 2005)

| Table 2. Specifications of diesel and biodiesel fu | els |
|--|-----|
|--|-----|

| Fuel property | Diesel | Bio-diesel |
|---|----------------------|----------------------|
| Fuel standard | ASTM D975 | ASTM PS 121 |
| Fuel composition | C10-C21 HC | C12-C22 FAME |
| Lower heating value (MJ/m ³) | 36.6×10^{3} | 32.6×10^{3} |
| Kinematic viscosity at 40 °C (mm ² /s) | 1.3-4.1 | 1.9-6.0 |
| Specific gravity at 15.5 °C | 0.85 | 0.88 |
| Density at 15 °C (kg/m ³) | 848 | 878 |
| Water (ppm by wt.) | 161 | 0.05% max |
| Carbon (wt%) | 87 | 77 |
| Hydrogen (wt%) | 13 | 12 |
| Oxygen (by diff.) (wt%) | 0 | 11 |
| Sulphur (wt%) | 0.05 max | 0.0-0.0024 |
| Boiling point (°C) | 188–343 | 182-338 |
| Flash point (°C) | 60-80 | 100-170 |
| | | |
| Cloud point (°C) | -15 to 5 | -3 to 12 |
| Pour point (°C) | -35 to -15 | -15 to 10 |
| Cetane number | 40–55 | 48-65 |
| Stoichiometric air/fuel ratio (wt./wt.) | 15 | 13.8 |
| | | |

Source: (Joshi, Pegg 2007)

| Methods | Definition | Advantage | Disadvantage | Problems of using in engines | References |
|---------------------------------|---|--|---|--|---|
| Direct use and blending | Direct use as diesel fuel or blend with diesel fuel | Liquid nature- portability | Higher viscosity | Coking and trumpet formation | (Kaya et al. 2009), (Kumar Tiwari, Kumar & Raheman 2007), (Issariyakul et al. |
| | | Heat content (~80% of diesel fuel) | Lower volatility | Carbon deposits | 2008), (Kansedo, Lee & Bhatia 2009) and (Rao et al. 2009) |
| | | Readily available; renewability | Reactivity of unsaturated hydrocarbon chains | Oil ring sticking; thickening and gelling of the lubricating oil | |
| Micro-emulsions | A colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the 1– 150 nm range formed | Better spray patterns during combustion | Lower cetane number | Irregular injector needle sticking; incomplete combustion | (Sahoo, Das 2009) and (Zubr 1997) |
| | spontaneously from two immiscible liquids and one or more ionic or non-ionic amphiphiles | Lower fuel viscosities | Lower energy content | Heavy carbon deposits; increase lubrication oil viscosity | |
| Thermal cracking (pyrolysis) | The conversion of long-chain and saturated substance (biomass basis) to biodiesel by means of heat | Chemically similar to petroleum- derived gasoline and diesel fuel | Energy intensive and hence higher cost | _ | (San José Alonso et al. 2008), (Santos et al. 2010), (Saraf, Thomas 2007), (Singh, Singh 2009), (Srivastava, Prasad 2000) and (Winayanuwattikun et al. 2008) |
| Transesterification | The reaction of a fat or oil with an alcohol in the presence of catalyst to form esters and glycerol | Renewability; higher cetane number; lower emissions; higher combustion efficiency | Disposal of by- product (glycerol and waste water) | _ | (Zubr 1997), (Schinas et al. 2009)and (Goodrum, Geller & Adams 2003) |

Table 3. Comparison of the different methods of biodiesel production

Source: (Leung, Wu & Leung 2010)

Table 4. Known problems, probable cause and potential solutions for using straight vegetable oil in diesels

| Problem | Probable cause | Potential solution | | | | |
|--|---|--|--|--|--|--|
| Short term | Short term | | | | | |
| 1. Cold weather starting | High viscosity, low cetane, and low flash point of vegetable oils | Pre-heat fuel prior to injection. Chemically alter fuel to an ester. Partially refine the oil to remove gums. Filter to 4 μm | | | | |
| 2. Plugging and gumming of filters, lines and injectors | Natural gums (phosphatides) in vegetable oil. Other ash | | | | | |
| 3. Engine knocking | Very low cetane of some oils. Improper injection timing | Adjust injection timing. Use higher compression engines. Pre-heat fuel prior to injection. Chemically alter fuel to an ester | | | | |
| Long term | | | | | | |
| 4. Coking of injectors on piston and head of engine | High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils | Heat fuel prior to injection. Switch engine to diesel fuel when operation at part load. Chemically alter the vegetable oil to an ester | | | | |
| 5. Carbon deposits on piston and head of engine | High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils | Heat fuel prior to injection. Switch engine to diesel fuel when operation at part load. Chemically alter the vegetable oil to an ester | | | | |
| 6. Excessive engine wear | High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils. Possibly free fatty acids in vegetable oil. Dilution of engine lubricating oil due to blow-by of vegetable oil | Heat fuel prior to injection. Switch engine to diesel fuel when operation at part load. Chemically alter the vegetable oil to an ester. Increase motor oil changes. Motor oil additives to inhibit oxidation | | | | |
| 7. Failure of engine lubricating oil due to polymerization | Collection of polyunsaturated vegetable oil blow-by in crankcase to the point where polymerization occurs | Heat fuel prior to injection. Switch engine to diesel fuel when operation at part load. Chemically alter the vegetable oil to an ester. Increase motor oil changes. Motor oil additives to inhibit oxidation | | | | |

| Table 5. | . Yields of | pyrolysis | of vegetable | e oils (percent | t by | weight) |
|----------|-------------|-----------|--------------|-----------------|------|---------|
|----------|-------------|-----------|--------------|-----------------|------|---------|

| | High oleic acid sa | Soybean oil | | |
|------------------------|-----------------------|-------------|-----------------------|------|
| | N ₂ sparge | Air | N ₂ sparge | Air |
| Alkanes | 37.5 | 40.9 | 31.1 | 29.9 |
| Alkanes | 22.2 | 22.0 | 28.3 | 24.9 |
| Alkadienes | 8.1 | 13.0 | 9.4 | 10.9 |
| Carboxylic acids | 11.5 | 176.1 | 12.2 | 9.6 |
| Unresolved unsaturates | 9.7 | 10.1 | 5.5 | 5.1 |
| Aromatics | 2.3 | 2.2 | 2.3 | 1.9 |
| Unidentified | 8.7 | 12.7 | 10.9 | 12.6 |

Sources: (Balat, Balat 2008, Demirbas 2003, Ma, Hanna 1999)

Table 6. Advantages and disadvantages of acid catalysts for transesterification

| Advantages | | Disadvan | tages |
|------------|--|----------|---|
| 1. | Acid catalysts are water-tolerant and less sensitive to high FFAs in | 1. | Reaction is slower than that of alkali- |
| | feedstock. | | catalysed. |
| 2. | Can simultaneously conduct esterification and transesterification by | 2. | Reaction require a higher process temperature |
| | giving a high yield in esters. This avoids the use of pre-extracted seed | | than for the alkali-catalysed reaction |
| | oil | 3. | Require a high alcohol-to-oil molar ratios, and |
| 3. | Acid catalyst is preferred when oil component is low grade material | | high acid catalyst concentrations |
| | like sulphur olive oil. | 4. | Acid system is associated with corrosion |
| Source: (| Helwani et al. 2009) | | |

wani et al. 2009)

Table 7. Summary of the advantages and disadvantages of alkali catalysed transesterification

| Advantages | Disadvantages |
|---|--|
| 1. It is much faster than acid catalysed | 1. Presence of water and FFA leads to saponification, which reduces the catalys |
| transestermeation | enectiveness, results in lower conversion and causes difficulty in separation of |
| 2. Reaction proceeds fast at normal pressure | glycerol. |
| and moderate temperature | 2. Requires a methanol to oil ratio of about 6:1 or higher instead of the |
| Approximately 4000 times faster than acid | stoichiometric 3:1 ratio. |
| catalyzed transesterification | |
| | |

Table 8. Typical solid acid and base catalysts employed for transesterification

| Solid Acid Cataysts | Solid Base Catalysts |
|---|---|
| Sulphonic ion exchanged resin | Hydrotalcites (Mg-Al) |
| Amberlyst -15 | Cs-exchanged sepiolite |
| Nafion | Oxides like MgO, CaO, La2O3, ZnO |
| Unstated Zironia-alumina | Quanidine anchored cellulose/polymer |
| Sulphated tin oxide | NN'N" tricyclohexyl quinidine encapsulated in Y zeolite |
| Sulphated zirconia/alumina | Metal salts of amino acids |
| Zeolites (H-Y) H-Beta, H-ZSM-5, ETS-4,10 | CaCO3, Ba(OH)2 |
| MCM family | Cs exchanged faujasites |
| Heteropoly acids | Li-promoted CaO |
| H3PW12O40, H4SiW12O40 | KxX/Al2O3 (X-halide ion or other |
| Cs2.5H0.5PW12O40 | mono/di-valent anion) |
| Zinc acetate on silica | Zinc aluminates |
| Organosulphonic acid on mesoporous silica | |
| Mesoporous unstated zirconium phosphate | |

Source: (Viswanathan, Ramaswamy 2007)

Table 9. The comparison between homogeneous catalysts and heterogeneous catalyzed transesterification (Viswanathan, Ramaswamy 2007)

| Factors | Homogeneous catalysts | Heterogeneous catalysts |
|------------------------|---|---------------------------|
| Reaction Rate | Fast and high conversion | Moderate conversion |
| | | Not sensitive |
| After treatment | Catalyst cannot be | Catalyst can be recovered |
| | recovered, must be | |
| | neutralized leading to waste production | |
| Processing methodology | Limited use of continuous | Continuous fix bed |
| | methodology | operation possible |
| Presence of water/free | Sensitive | Not Sensitive |
| fatty acids | | |
| Catalyst reuse | Not possible | Possible |
| Cost | Comparatively costly | Potentially cheaper |

Table 11. Comparison between alkali-catalysis and lipase-catalysis methods for bio-diesel fuel

| | ^ | |
|-----------------------------------|--------------------------------|--------------------------|
| | Alkali-catalysis process | Lipase-catalysis process |
| Reaction temperature (°C) | 60–70 | 30-40 |
| Free fatty acids in raw materials | Saponified products | Methyl esters |
| Water in raw materials | Interference with the reaction | No influence |
| Yield of methyl esters | Normal | Higher |
| Recovery of glycerol | Difficult | Easy |
| Purification of methyl esters | Repeated washing | None |
| Production of catalyst | Cheap | Relatively expensive |
| | | |

Source: Ref. (Balat, Balat 2008, Fukuda, Kondo & Noda 2001a, Helwani et al. 2009).

Table 12. Comparison of microalgae with other biodiesel feedstocks

| Plant source | Seed oil content (% oil by wt in biomass) | Oil yield (L oil/ha year) | Land use (m ² year/kg biodiesel) | Biodiesel productivity (kg biodiesel/ha year) |
|--|---|---------------------------|---|--|
| Corn/Maize (Zea mays L.) | 44 | 172 | 66 | 152 |
| Hemp (Cannabis sativa L.) | 33 | 363 | 31 | 321 |
| Soybean (Glycine max L.) | 18 | 636 | 18 | 562 |
| Jatropha (Jatropha curcas L.) | 28 | 741 | 15 | 656 |
| Camelina (Camelina sativa L.) | 42 | 915 | 12 | 809 |
| Canola/Rapeseed (Brassica napus L.) | 41 | 974 | 12 | 862 |
| Sunflower (<i>Helianthus annuus</i> L.) | 40 | 1070 | 11 | 946 |
| Castor (Ricinus communis) | 48 | 1307 | 9 | 1156 |
| Palm oil (Elaeis guineensis) | 36 | 5366 | 2 | 4747 |
| Microalgae (low oil content) | 30 | 58,700 | 0.2 | 51,927 |
| Microalgae (medium oil content) | 50 | 97,800 | 0.1 | 86,515 |
| Microalgae (high oil content) | 70 | 136,900 | 0.1 | 121,104 |

Table 13. Comparison of properties of microalgal oil, conventional diesel fuel, and ASTM biodiesel standard

| Properties | Biodiesel from microalgal oil | Diesel fuel | ASTM biodiesel standard |
|--|-------------------------------|-----------------|-------------------------|
| Density (kg L ⁻¹) | 0.864 | 0.838 | 0.84–0.90 |
| Viscosity (mm ² s ⁻¹ , cSt at 40 °C) | 5.2 | 1.9-4.1 | 3.5-5.0 |
| Flash point (°C) | 115 | 75 | Min 100 |
| Solidifying point (°C) | -12 | -50 to 10 | _ |
| Cold filter plugging point (°C) | -11 | -3.0 (max -6.7) | Summer max 0 |
| | | | Winter max <-15 |
| Acid value (mg KOH g ⁻¹) | 0.374 | Max 0.5 | Max 0.5 |
| Heating value (MJ kg ⁻¹) | 41 | 40-45 | - |
| H/C ratio | 1.81 | 1.81 | |

Source: (Huang et al. 2010, Xu, Miao & Wu 2006)(Xu, Miao & Wu 2006)

| Plant | size | Capital costs | Feedstock | Methanol | Other | Total | Glycerol credit | Net | Distribution and blending | Total |
|-------|---------------------|---------------|-----------|----------|-------|-------|-----------------|------|---------------------------|-------|
| ktpa | Million liters | | | | | | | | | |
| Tallo | Tallow-based (\$/1) | | | | | | | | | |
| 5 | 6 | 0.33 | 0.40 | 0.05 | 0.11 | 0.89 | 0.12 | 0.77 | 0.08 | 0.85 |
| 20 | 23 | 0.15 | 0.40 | 0.05 | 0.10 | 0.70 | 0.12 | 0.58 | 0.08 | 0.66 |
| 40 | 46 | 0.11 | 0.40 | 0.05 | 0.09 | 0.64 | 0.12 | 0.52 | 0.09 | 0.61 |
| 60 | 69 | 0.08 | 0.40 | 0.05 | 0.08 | 0.61 | 0.12 | 0.49 | 0.15 | 0.64 |
| 120 | 137 | 0.06 | 0.40 | 0.05 | 0.06 | 0.56 | 0.12 | 0.44 | 0.15 | 0.60 |
| | | | | | | | | | | |
| Palm | Palm oil (\$/) | | | | | | | | | |
| 50 | 60 | 0.09 | 0.73 | 0.05 | 0.08 | 0.95 | 0.12 | 0.83 | 0.04 | 0.88 |
| 60 | 71 | 0.08 | 0.73 | 0.05 | 0.08 | 0.94 | 0.12 | 0.82 | 0.04 | 0.86 |
| 120 | 143 | 0.06 | 0.73 | 0.05 | 0.06 | 0.89 | 0.12 | 0.78 | 0.04 | 0.82 |

Table 14. Costs of bio-diesel production