

VARIOUS SOURCES FOR PRODUCTION OF BIODISEL

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ABSTRACT: Moreover, biodiesel is produced domestically from a variety of seed oils including soybeans, rapeseed, and corn. Biodiesel can be used in diesel engines (cars, trucks, busses, construction equipment), in jet engines, and, in heating and electricity generating systems. Use of biodiesel reduces nitrogen oxide emissions compared to fuel oil (a form of diesel fuel). This report estimates the net health benefits of using biodiesel. Biodiesel is environmentally safer than petro-diesel. It is nontoxic, produces less skin irritation than soap and water, it degrades four times as fast as petro-diesel, has a flash point significantly higher than that of petro-diesel, thus making it safer to store and handle.

Key Words: Biodiesel, Transesterification, Enzymes, Catalysts.

1. Introduction

Biodiesel is the most promising alternative diesel fuel. It has received considerable attention in recent years due to its biodegradability, renewability, non-toxicity and less emission of gaseous and particulate pollutants with higher cetane number than normal diesel. It meets the currently increasing huge demands of world energy which is dependent on petroleum based fuel resources.

Biodiesel is derived from vegetable oils or animal fats through transesterification. Transesterification is also called alcoholysis, which uses alcohols in the presence of catalyst (e.g., base, acid or enzyme depending on the free fatty acid content of the raw material). The commonly used alcohols for the transesterification include methanol, ethanol, propanol, butanol, and amyl alcohol. Methanol and ethanol are adopted most frequently, due to its low cost.

Commonly used feedstocks (vegetable oil) for transesterification include soybean oil, rapeseed oil, etc. In recent years, there exist active researches on biodiesel production from cottonseed oil (Demirbas, 2008), of which the conversion between 72% and 94% was obtained by enzyme catalyzed transesterification. The application of solid acid catalysts on cottonseed oil transesterification was investigated by them. Their results showed that the yield of methyl ester was above 90% after 8h of reaction. In contrast, transesterifying cottonseed oil by microwave irradiation could produce a biodiesel yield in the range of 89.5-92.7%

2. Feedstock Sources

Various sources of feeds tocks are described here.

Algae oil

Algae are single-celled organisms that, like plants, produce energy through the process of photosynthesis, Algae oil can

be used to produce biodiesel. Extracting the oil leaves behind dried green flakes that can be further reprocessed to create ethanol, another fuel (Clayton, 2006),

Babassu oil

Babassu oil is extracted from the seeds of the babassu palm tree, *Attalea speciosa*. The tree is common in Brazil, Mexico, and Honduras; it grows well in areas typically cultivated for coconut or palm. The kernels contain 60-70% oil (Salunkhe et al. 1992)

Beef Tallow

Crude beef tallow obtained from a commercially available source. Animal tissue is converted to tallow using rendering; a process by which lipid material is separated from meat tissue and water under heat and pressure (Pocket Information Manual, 2003).

Borage Oil

Borage oil, gamma linolenic acid (GLA) content of 20%, Borage oil comes from the plant, *Borago officinalis*, also known as starflower. It has the highest value of γ -linolenic acid in any readily available specialty oil (Borage oil, 2009).

Camelina Oil

Camelina oil comes from the plant, *Camelina sativa*. It is an annual flowering plant that grows well in temperate climates and is also known as gold-of-pleasure and false flax. Some varieties of camelina contain 38-40 % oil. Camelina can be grown in arid conditions and does not require significant amounts of fertilizer (Feedstocks, 2009).

Canola Oil

Crude degummed canola oil was obtained from a commercially available source. Canola is the seed of the species *Brassica napus* or *Brassica campestris*; the oil component contains less than two percent erucic acid and the solid component contains less than 30 micromoles per

gram of glucosinolates(Canola Standards and Regulations, 2009).⁵

Castor Oil

Castor oil comes from the castor bean *Ricinus communis*. Castor is grown in tropical and subtropical regions and prefers a dry climate. The seeds contain about 45-50% oil. Triglycerides of ricinoleic acid constitute 84-90% (Salunkhe et al. 1992).

Choice White Grease

Crude choice white grease (CWG) was obtained from a commercially available source. Choice white grease is a specific grade of mostly pork fat defined by hardness, color, fatty acid content, moisture, insolubles, unsaponifiables and free fatty acids(Choice White Grease, 2009).

Coconut Oil

Refined, bleached, deodorized (RBD) coconut oil obtained from the tree.

Coffee Oil

Refined coffee oil is used. Coffee oil comes from spent coffee grounds; the grounds can contain as much as 11 to 20 percent oil. Currently coffee grounds are disposed of or used as compost. After oil extraction, the grounds could still be used as compost and the oil could be used to make biodiesel (Leighton, 2009).

Corn Oil,

Distiller's Crude, dry distiller's grain (DDG) extracted corn oil was obtained from a commercially available source. The extracted corn oil comes from the DDG stream of the ethanol production process.

Cuphea viscosissima oil

Cuphea viscosissima is also known as blue wax weed, an annual crop. The seeds contain 25-43% oil (Salunkhe et al. 1992).

Evening Primrose Oil

Evening primrose is a wildflower native to North America and used for biodiesel production.

Fish Oil

Fish oil was obtained from a commercially available source.

Hemp Oil

The oil is derived from the plant *Cannabis sativa* and contains significant amounts of α -linolenic acid and γ -linolenic acid. Hemp is legally grown in Canada as a niche crop and is used mainly in the health food market. Hemp seeds have an oil content of 33 percent (Hemp Seed Oil, 2009; Holly, 2007).

Hepar

High Iodine Value and Low Iodine Value (IV) Crude, high IV hepar and crude, low IV hepar are used. Hepar is a byproduct of the heparin manufacturing process. Pharmaceutical grade heparin is derived from the mucosal tissues of animals, such as pig (Heparin Wikipedia, 2009)

Jatropha Oil

Crude jatropha oil was obtained from a commercially available source. Jatropha oil comes from the shrub *Jatropha curcas*, also known as physic nut. The plant is

native to Mexico, Central America, Brazil, Bolivia, Peru, Argentina, and Paraguay and India (Achten, 2008).

Jojoba Oil

Jojoba (*Simmondsia chinensis*) is an evergreen perennial shrub grown in Arizona, Mexico, and neighboring areas. The dehulled seeds of jojoba contain 44% of liquid wax, which is not a triglyceride (Salunkhe et al. 1992).

Karanja Oil

Pure, cold pressed karanja oil obtained from plant. Karanja (*Pongamia pinnata*) is a medium sized evergreen tree that grows in India. The seed contains 27-39% oil. The oil is reddish brown and rich in unsaponifiable matter and oleic acid (Salunkhe et al. 1992).

Lesquerella fendleri Oil

Lesquerella fendleri is also known as Fendler's bladderpod. *Lesquerella* seeds contain 20-28% oil with around 62% lesquerolic acid. *Lesquerella* oil is a source of hydroxyl unsaturated fatty acids, and can be used similarly to castor oil (Salunkhe et al. 1992).

Linseed Oil

Linseed has been traditionally used as a drying oil. It grows in Argentina, India, and Canada. It is an annual herb and contains 37-42% oil. The crude oil contains 0.25% phosphatides, a small amount of crystalline wax, and a water-soluble resinous matter with antioxidant properties (Salunkhe et al. 1992).

Moringa oleifera Oil

Moringa oleifera is a tree that ranges in height from 5 to 10 meters, and is native to India, Africa, Arabia, Southeast Asia, the Pacific and Caribbean islands, South America, and the Philippines. *Moringa* seeds contain between 33 and 41 % oil. It is also known as ben oil, due to its content of behenic (docosanoic) acid (Rashid, 2008).

Mustard Oil

Refined mustard oil was obtained from a commercially available source.

Neem Oil

Neem (*Azadirachta indica*) is a large evergreen tree, 12 to 18 m tall, found in India, Pakistan, Sri Lanka, Burma, Malaya, Indonesia, Japan, and the tropical regions of Australia. The kernels contain 40-50% of an acrid green to brown colored oil (Salunkhe et al. 1992).

Palm Oil

Palm oil was obtained from a commercially available source.

Perilla Seed Oil

Perilla oil comes from the plant *Perilla Ocymoides*, the seeds of which contain 35-45 percent oil. Perilla oil has been cultivated in China, Korea, Japan, and India (Perilla oil, Encyclopædia Britannica, 2009).

Poultry Fat

Crude poultry fat was obtained from a commercially available source.

Rice Bran Oil

Refined, bleached, deodorized, winterized (RBDW) rice bran oil used. Rice bran oil is a non-edible vegetable oil

which is greatly available in rice cultivating countries. Rice bran is a co-product of rice milling, containing about 15-23% oil (Sinha et al. 2008).

Soybean Oil

Refined soybean oil was obtained from a commercially available source.

Stillingia Oil

Stillingia oil comes from the Chinese tallow tree (*Triadica sebifera*). The tree has been used to prevent soil erosion. The tree can be grown on marginal land, and is native to eastern Asia. The seeds contain 45-60 percent oil (Breitenbeck, 2008).

Sunflower Oil

Sunflower oil obtained from plants and flowers.

Tung Oil

Tung oil obtained from natural source.

Used Cooking Oil

Crude used cooking oil was obtained from a commercially available source.

Yellow Grease

Crude yellow grease used. Yellow grease is made up of restaurant greases, which are fats and oils left over from cooking. It can also be from rendering plants producing different quality greases (Pocket Information Manual, 2003).

3. Parameters to be checked for feed stock

Moisture

Moisture can react with the catalyst during transesterification which can lead to soap formation and emulsions (Knothe et al. 2005; ASTM, 2008). It should be less than 0.050 wt %.

Free Fatty Acid (FFA)

The interaction of FFA in the feedstock and sodium methoxide catalyst may form emulsions which make separation of the biodiesel more difficult; possibly leading to yield loss. Emulsions can also increase cost by introducing extra cleaning steps and replacement of filters. To minimize the generation of soaps during the reaction, the target reduction for FFA in the feedstock should be 0.5 wt % or less. (Knothe et al. 2005).

Kinematic Viscosity

Viscosity is defined as the resistance to shear or flow; it is highly dependent on temperature and it describes the behavior of a liquid in motion near a solid boundary like the walls of a pipe.

FAC Color

The Fat Analysis Committee (FAC) color method determines the color of oils and fats by comparing them with color standards.

Saponification Value

The saponification value is defined as the amount of potassium hydroxide (KOH) in milligrams required to saponify one gram of fat or oil under the conditions specified (AOCS, 1998). Saponification value is a measure of the average molecular weight or the chain length of the

fatty acids present. It allows for comparison of the average fatty acid chain length.

Moisture and Volatile Matter

The presence of volatile matter in a feedstock may lead to fatty acid methyl ester yield loss by reacting with the catalyst or by diluting the feedstock

Insoluble Impurities

The insoluble impurities test measures the amount of solids that are insoluble in kerosene and petroleum ether. These solids may consist of sand, dirt, and seed fragments in the case of vegetable oil and small particles of bones and gums in the case of animal fats or used cooking oil (Keith et al. 1954).

Unsaponifiable Matter

Unsaponifiable matter consists of organics which do not react with base to form soaps. These include sterols, higher molecular weight alcohols, pigments, waxes, and hydrocarbons (AOCS, 1998). These are non polar and remain in the biodiesel after the transesterification reaction.

Moisture, Insolubles, and Unsaponifiables (MIU)

MIU represents materials in the oil or fat which cannot be converted to mono alkyl fatty esters by esterification or transesterification.

Oxidation Stability

Oxidation stability is the indicative of the age or prior storage conditions of the oil or fat and can predict if the feedstock is capable of meeting the minimum requirements for biodiesel oxidation stability as specified by ASTM D6751.

Oxidation stability is influenced by two aspects. First the presence of hydrogen atoms next to carbon-carbon double bonds, which act as points where oxidation can occur (McCormick et al. 2007). Second the presence of naturally occurring antioxidants in the feedstock that can prevent oxidation of the triglyceride molecules (AOCS, 1998).

Sulfur

Sulfur content in biodiesel is limited to 15 ppm maximum by ASTM D6751.

Phosphorous, Calcium, and Magnesium

ASTM D6751 requires phosphorous in biodiesel be limited to 10 ppm (0.001 % mass maximum) and the combined amount of calcium and magnesium to be less than 5 ppm. Phosphorous, calcium, and magnesium are minor components typically associated with phospholipids and gums that may act as emulsifiers or cause sediment, lowering yields during the transesterification process (Gerpen et al. 2004).

4. Biodiesel Production by Using Ultrasound

To enhance mixing in production of biodiesel, one can use ultrasound energy that can also produce high shear in the liquid medium. Ultrasound is the process of propagation of the compression (rarefaction) waves with frequencies (20 KHz to 10 MHz), above the range of human hearing (Benitez, 1999). It produces acoustic cavitations. Acoustic cavitation is the formation, growth, and implosive collapse of bubbles in a liquid irradiated with sound or ultrasound.

Bubbles are filled with both solvent and solute vapor and with previously dissolved gases, grow, recompress and implisively collapse. Bubble collapse produces intense local heating, high pressures, and very short lifetime of bubbles, which causes the fast mixing. The collapse of the cavitation bubbles disrupts the phase boundary and causes emulsification, by ultrasonic jets that impinge one liquid to another (Stavarache, 2005).

Ultrasonication provides the mechanical energy for mixing and the required activation energy for initiating the transesterification reaction. Low frequency ultrasonic irradiation is very useful tool for emulsification of immiscible liquids. This was further confirmed by Wu *et al.* (2007), who investigated the effect of ultrasonification on droplet size in biodiesel mixtures. They showed that ultrasonic mixing produced dispersions with average droplet sizes 42% smaller than those generated using standard impellers, leading to larger interfacial area for the transesterification to occur.

Ultrasonic energy can be used to efficiently transesterify fish oil and for the production of EPA and DHA. Researchers (Stavarache *et al.* 2005, 2006; Stavarache *et al.* 2007;) conducted an extensive study concerning the application of ultrasonic energy on the transesterification of commercial edible oil. The reaction time was much shorter than by mechanical stirring and efficiency had increased.

The effects of various parameters like molar ratio, catalyst concentration and temperature on transesterification of triolein were examined and the optimum condition was obtained (Hanh *et al.* 2007; Hanh *et al.* 2008).

Colucci *et al.* (2005) investigated the feasibility of using ultrasonic mixing to produce biodiesel from soybean oil. The authors reported that reaction rate constants were three to five times higher than those reported in the literature for mechanical agitation. Excellent yields were observed in an alkaline catalyzed transesterification of soybean oil in a shorter time at three different levels of temperature and four different levels of alcohol-to-oil ratios.

In one such study, base-catalyzed transesterification of vegetable oil was performed (Starvarache, 2003, 2005) using low frequency ultrasound (28-40 kHz). They reported excellent ester yields (98-99%) with a low amount of catalyst in a much shorter time than with mechanical stirring. The rate constants of this reaction were found to be 3-5 times higher than those reported in the literature for mechanical mixing. This is because of the increase in interfacial area and activity of the microscopic and macroscopic bubbles formed when ultrasonic waves of 20 kHz were applied to a two phase reaction system.

In another experiment (Goldberg, 1966) the continuous alcoholysis of vegetable oils with ultrasonic vibrations (800-1200 cycles/s, irradiation intensity 1-2 W/cm²) resulted in an increased productivity (with or without catalysts) and an improved quality and color of the product without high-

temperature treatment. It was reported that ultrasonic mixing had a significant effect on enzymatic transesterification as well. Ultrasonication showed higher (faster) transesterification rates (Shah, 2005; Wu, 2005) and higher operational stability for the enzymes, without changing the characteristics of the enzymes.

5. Lower-cost Feed stocks for Biodiesel Production

The feed stocks currently used are mainly high quality food-grade vegetable oils, such as soybean oil in United States, rapeseed oil in European, palm oil in Malaysia (Azam *et al.* 2005).

Feed stocks costs are more than 85% of the total cost of biodiesel production (Haas *et al.* 2006; Zhang *et al.* 2003). The biodiesel unit price is 1.5-3.0 times higher than that of petroleum derived diesel fuel depending on feedstock (Zhang *et al.* 2003; Demirbas, 2007). Therefore, many studies have focused on the utilization of lower-cost feedstocks, such as waste cooking oil (WCO), grease, soapstock, *Jatropha*, and algae to produce biodiesel.

The non-edible oils, like *Jatropha*, can also be used to produce biodiesel (Tiwari *et al.* 2007; Tapanes *et al.* 2008). Growing interest arising concerning algae-based biodiesel (Aresta *et al.* 2005).

5.1 Biodiesel Production from Waste Cooking Oil

Waste vegetable oils low in cost and collected from large food processing and service facilities. These oils have very high temperature during food frying process. Chemical reactions such as hydrolysis, polymerization and oxidation occur, which can lead to the increase of free fatty acid (FFA) level. Acid catalysis is preferred since it is insensitive to FFA (Freedman *et al.* 1984).

Zheng *et al.* (2006) studied the reaction kinetics of acid-catalyzed transesterification of waste frying oil. They reported that at the methanol/oil molar ratio of 250:1 at 70°C or in the range 74:1-250:1 at 80°C, the reaction was a pseudo-first-order reaction. High yield of 99±1% could be achieved at both 70°C and 80°C and a stirring rate of 400 rpm, using a feed molar ratio oil:methanol:acid of 1:245:3.8. Wang *et al.* (2006) investigated a two-step catalyzed processes for synthesis of biodiesel by using WCO from Chinese restaurants. In the first step, ferric sulfate-catalyzed methanolysis was carried out, while potassium hydroxide catalysis was performed in the second step. They concluded that compared with one-step sulfur acid catalysis the two-step catalyzed process provided a more simple and economic method to produce biodiesel from WCO.

Issariyakul *et al.* (2007) also used the two-step process to transesterify WCO. Sulfuric acid was selected as acid catalyst and mixtures of methanol and ethanol were used for transesterification. More than 90% ester was obtained by using the two-stage method compared with yield of ~50% ester by using the single stage alkaline catalyst.

The two-step process that was developed by Canakci & Gerpen, (2001). Acid catalyst was first chosen to reduce the FFA to less than 1%, then the pretreated feedstock was transesterified under alkaline catalysis. This had increased the reaction rate by using alkaline catalyst and avoid soap formation by applying acid catalyst.

Chen *et al.* (2006) used immobilized lipase from *Rhizopus oryzae*. Several parameters, including the molar ratio of methanol to waste oils, biocatalyst load, adding method, reaction temperature, and water content were studied. Their results indicated that methanol/oil ratio of 4/1, immobilized lipase/oil of 30 wt.% and 40°C were suitable for waste oils under 1 atm. Under the optimum conditions the yield of methyl esters was around 88–90%.

Heterogeneous catalysts, such as acidic ion-exchange resins, possessed several advantages over homogeneous catalysts, for example, corrosion prevention (Silva & Rodrigues, 2006), easy separation, and high FFA conversions (Lotero *et al.* 2005).

Özbay *et al.* (2008) examined activities of resins in direct FFA esterification in the temperature range of 50–60°C and found all resin catalysts were active. The differences of catalytic activities between resins were concluded to be related to the size of average pore diameters and magnitude of BET surface area. The FFA conversion increased with increasing reaction temperature and catalyst amount.

Çetinkaya *et al.* (2005) investigated the engine performance of biodiesel fuel originated from used cooking oil in a Renault Mégane automobile and four stroke, four cylinder, F9Q732 code and 75 kW Renault Mégane Diesel engine in winter conditions for 7500 km road tests in urban and long distance traffic. The results showed that the torque and brake power output obtained from the used cooking oil biodiesel were 3–5% less than those of No. 2 diesel fuel.

Al- Widyen *et al.* (2002) utilized ethyl ester of waste vegetable oils as fuel in diesel engines and initiated a study to investigate its potential to substitute oil-based diesel fuel. The ester fuel demonstrated a high potential as fuel for diesel engines.

Trend for emission was observed by Dorado *et al.* (2003), who characterized exhaust emissions from a diesel engine fueled with transesterified waste olive oil and found lower emissions of CO, carbon dioxide (CO₂), nitrogen oxide (NO), and SO₂. The particulate emissions from used cooking oil biodiesel were also evaluated by the other research group (Lapuerta *et al.* 2008). The biodiesel fuels were tested in a DI diesel commercial engine either pure or in 30% and 70% v/v blends with a reference diesel fuel. A sharp decrease was observed in both smoke and particulate matter emissions as the biodiesel concentration increased.

Nas & Berkay (2007), presented an overview of energy potential of biodiesel generated from WCO and concluded that biodiesel could reduce nearly all forms of air pollution, especially air toxics and cancer-causing compounds.

5.2 Biodiesel Production from Grease

Greases are one of the less-expensive feed stocks. It contains triglycerides (TG), diglycerides (DG), monoglycerides (MG), and FFA (8–40%). A grease containing 8–12 wt % FFA is categorized as a yellow grease, and a grease containing >35 wt.% FFA is categorized as a brown grease (Kulkarni & Dalai, 2006).

Canakci & Gerpen (2001), extended their two-step process to yellow and brown grease, and was successfully scaled up the process to pilot plant. Significant reductions in particulates, CO, and HC were observed compared with those of the No. 2 diesel.

Ngo *et al.* (2008) developed an efficient procedure in which a series of diarylammonium catalysts were used that are highly effective in catalyzing the esterification of the FFA present in greases (12–40 wt.% FFA). At a catalyst loading of 2–3 mol%, high conversions of FFA to esters (95–99%) were achieved by treating the greases with 5–20 equiv of methanol at 95 °C for 2h. The treated greases had a final FFA content of 0.5–1 wt %.

Cao *et al.* (2008) used a continuous membrane reactor to produce biodiesel from different feedstocks, including yellow and brown grease. The high purity biodiesel produced could meet and exceed the ASTM D 6751 standard.

5.3 Biodiesel Production from Soapstock

Soapstock, known is by-product of the refining of vegetable oils. It contains a substantial amount of water, which can be emulsified with the lipid constituents and is difficult to remove. In addition, the presence of both FFA and acylglycerols makes the transesterification reaction more complicated.

Alkaline catalysis cannot be utilized due to the high FFA level (Canakci & Gerpen, 2001). Haas *et al.* (2000) developed a simple, high-efficiency method for synthesis of biodiesel from soybean oil soapstock. The process involved two steps: the first step, alkaline hydrolysis of all lipid-linked fatty acid ester bonds and the second step, acid-catalyzed esterification of the resulting fatty acid sodium salts. In the first step, all glycerides and phosphoglycerides in the soapstock could be completely saponified. After water removal, the resulting FFA sodium salts were rapidly and quantitatively converted into fatty acid methyl ester (FAME) by incubation with methanol and sulfuric acid at 35°C and ambient pressure in the second step. All variables examined for the ester product, including flash point, water and sediment, carbon residue, sulfated ash, density, kinematic viscosity, sulfur, cetane number, cloud point, copper corrosion, acid number, free glycerin, and total glycerin were within the provisional biodiesel specifications of the ASTM. Density and iodine values were comparable to those of commercial soy-based biodiesel. The emission profile was quite similar to that of biodiesel produced from refined soy oil.

Haas *et al.* (2003) found that though this method could achieve the efficient production of high-purity biodiesel, substantial amounts of solid sodium sulfate were generated as a by-product. The optimal conditions for the maximum esterification were found to be at 65°C, 26h, a molar ratio of total FA/methanol/sulfuric acid of 1:1.5:1.5.

Haas (Haas, 2005) suggested that the production cost of soapstock biodiesel would be approximately US\$ 0.41/l, a 25% reduction relative to the estimated cost of biodiesel produced from soy oil.

Jin *et al.* (2008) developed a three-step process for producing biodiesel from the mixture of oil sediments (OS) and soapstocks (SS), at the same time, phosphatides were obtained. The esterification reaction was carried out with 5:1 methanol/oil (mol/mol) in the presence of 3% sulfuric acid as an acid catalyst at 85°C for 5h. Biodiesel recovery under these conditions was 92.1% of theoretical. Alkaline catalyzed transesterification process was performed in the third step to convert the triglycerides into biodiesel and glycerol. The maximum ester yield of 94% was obtained under the optimal variables: 6/1 methanol/oil (mol/mol), 1% NaOH (wt.%), 65°C, and 1h. Five important fuel properties of biodiesel from the OS-SS mixture, including density (at 15°C), kinematic viscosity (at 40°C), flash point, calorific value, and acid value, were found to be comparable to those of the No. 2 diesel fuel and conforming to both the American and German standards for biodiesel.

Wang *et al.* (2007) pointed out three major disadvantages of the process developed by Haas: (1) High temperature steam is required since conventional acidulation method is taken to recover acid oil from soapstock; (2) Additional process, saponification of the glycerides, is needed to convert them to free fatty acid salts; (3) The esterification reaction time is too long, leading to low productivity. The authors developed an attractive method to produce biodiesel from soybean soapstock.

The optimal esterification conditions were determined to be a weight ratio of 1:1.5:0.1 of acid oil/methanol/sulfuric acid. After distillation, the biodiesel produced by using this method could meet the Biodiesel Specification of Korea.

Usta *et al.* (2005) first used hazelnut soapstock/waste sunflower oil mixture to produce biodiesel. The process involved two steps, including acid (sulfuric acid) and base (sodium hydroxide) catalysis. The hazelnut soapstock/waste sunflower oil mixture was first heated to 100°C to remove the water. Then, the mixture was cooled down to 35°C before the 2nd-step catalysis. Experimental results indicated that the hazelnut soapstock/waste sunflower oil methyl ester could be partially substituted for diesel fuel at most operating conditions without any engine modification and preheating of the blends.

Keskin *et al.* (2008) used cottonseed oil soapstock to produce biodiesel, then the cottonseed oil soapstock biodiesel was blended with diesel fuel. It was reported that high calorific value and cetane number, low sulfur and

aromatic content, and similar characteristics were observed for the blends.

Other studies showed that the reaction duration is significantly shorter than traditional transesterification reaction (Saka & Kusdiana, 2001); The reaction is not sensitive to both FFA and water (Kasteren & Nisworo, 2007). This method requires high molar ratio of alcohol to feedstock (He *et al.* 2007; Demirbas, 2002; Saka & Kusdiana, 2001) and high reaction pressure and temperature, which will cause high operating cost.

5.4 Biodiesel Production from *Jatropha* Oil

Jatropha curcas L. (JCL) is a plant belonging to Euphorbiaceae family. It is a non-edible oil-bearing plant widespread in arid, semi-arid and tropical regions of the world (Chhetri *et al.* 2008). JCL has an estimated annual production potential of 200 thousand metric tones in India and can grow in waste land (Srivastava & Prasad, 2000).

Singh *et al.* (2008) gave detailed information on the use of different components of JCL fruit for energy purposes. It was found that the shell could be for combustion, hull/husk for gasification, cake for production of biogas, spent slurry as manure, oil and biodiesel (made from *Jatropha* oil) for running CI engines. The kernels of JCL have about 50% oil. The oil recovery in mechanical expeller was about 85%, while more than 95% recovery of oil could be achieved when extracted by solvent method.

The biodiesel from JCL oil has a great potential due to its comparable properties to diesel, such as calorific value and cetane number (Sirisomboon *et al.* 2007).

Azam *et al.* (2005) found FAME of *Jatropha curcas* were most suitable for use as biodiesel and it met the major specification of biodiesel standards of USA, Germany and European Standard Organization.

Sarin *et al.* (2007) made an appropriate blends of *Jatropha* and palm biodiesel to improve oxidation stability and low temperature property based on the fact that *Jatropha* biodiesel has good low temperature property and palm biodiesel has good oxidative stability. It was found that antioxidant dosage could be reduced by 80-90% when palm oil biodiesel is blended with *Jatropha* biodiesel at about 20-40%. This techno-economic combination could be an optimum mix for Asian Energy Security.

Tiwari *et al.* (2007) used response surface methodology to optimize three important reaction variables, including methanol quantity, acid concentration, and reaction time. The optimum combination for reducing the FFA of *Jatropha* oil from 14% to less than 1% was found to be 1.43% v/v

sulfuric acid catalyst, 0.28 v/v methanol-to-oil ration and 88 min reaction time at 60°C for producing biodiesel.

Berchmans & Hirata, (2008), developed a two-step pretreatment process in which the high FFA (15%) of *Jatropha curcas* seed oil was reduced to less than 1%. In the first step, the reaction was carried out with 0.60 w/w

methanol-to-oil ratio in the presence of 1 wt.% sulfuric acid as an acid catalyst in 1h at 50°C. In the second step, the transesterification reaction was performed using 0.24 w/w methanol-to-oil ratio and 1.4 wt.% sodium hydroxide as alkaline catalyst to produce biodiesel at 65°C. The final biodiesel yield of 90% in 2h was reported.

In one study, semi-empirical AM1 molecular orbital calculations were used to investigate the reaction pathways of base catalyzed transesterification of glycerides of palmitic, oleic and linoleic acid (Tapanes et al (2008)). The researchers concluded that the reaction mechanism included three steps: Step 1- Nucleophilic attack of the alkoxide anion on the carbonyl group of the glyceride to form a tetrahedral intermediate. Step 2-Breaking of the tetrahedral intermediate to form the alkyl ester and the glyceride anion. Step 3-Regeneration of the active catalyst, which may start another catalytic cycle. This study suggested that the Step 2, decomposition of the tetrahedral intermediate, determined the rate of base-catalyzed transesterification of glycerides.

Preparation of biodiesel from *Jatropha* oil using ultrasonic energy was investigated (Kachhwaha et al. 2006). Low frequency ultrasound (33 kHz) was applied to transesterify *Jatropha* oil with methanol in the presence of base catalyst at 6:1 methanol/oil molar ratio. The reaction time (about 15-30 min) was much shorter than conventional mechanical stirring method.

Moreover, enzyme catalysts were also utilized for biodiesel production from *Jatropha* oil. Shah & Gupta, (2007) evaluated the lipase from *P. cepacia* for conversion of *Jatropha* oil into biodiesel. The best yield of 98% was obtained by using *Pseudomonas cepacia* lipase immobilized on celite at 50°C in the presence of 4-5% (w/w) water in 8h. With respect to economic factor, this enzyme-based process could use commercial grade ethanol instead of expensive grade ethanol. Moreover, the biocatalyst could be used four times without loss of any activity.

Rathore & Madras (2007) used Novozym-435 lipase to synthesize biodiesel from *Jatropha* oil in presence of supercritical carbon dioxide. The optimum conditions were found to be 8h, 45°C, 5:1 molar ratio of alcohol to oil and an enzyme loading of 30% based on the weight of oil. However, conversions of only 60-70% were obtained even after 8h. The authors attributed this to the fact that the enzymatic reaction encountered both substrate and product inhibition.

Synthesis of biodiesel in supercritical alcohols, high conversions (>80%) were obtained within 10 min and nearly complete conversions were obtained within 40 min. Despite of expected high operating cost due to high temperature and pressure associated with supercritical alcohol, it was still considered to be economically feasible since the reaction time was very short (Kasteren & Nisworo, 2007).

Many researchers studied the performance of biodiesel in engines (Singh et al. 2008; Haldar et al. 2008; Kumar et al. 2003).

Haldar *et al.* (2008) found that *Jatropha* oil gave the best results related to the performance and emissions, such as CO, CO₂, HC, smoke and particulates, at high loads and 45° before Top Dead Center (bTDC) injection timing when compared with non-edible straight vegetable oils of *Putranjiva*, *Jatropha* and *Karanja*.

Kumar *et al.* (2003) used *Jatropha* oil and methanol in various methods, such as blending, transesterification and dual fuel operation (methanol/*Jatropha* oil=3:7, v/v) to compare with performance, emission and combustion parameters. Experimental results indicated that *Jatropha* oil and methyl ester showed higher diffusion combustion compared to standard diesel operation.

Similar observation was obtained from other researchers Singh et al(2008), who found that biodiesel from *Jatropha* oil offered higher brake thermal efficiency than blended de-waxed de-gummed *Jatropha* oil or even diesel. *Jatropha* oil biodiesel could be blended with diesel in any proportion or could be used as pure biodiesel successfully in CI engine without any problem.

Higher NO_x level in the *Jatropha* based biodiesel exhaust was reported by several researchers (Sharma, 2003; Chairman, 2003). To solve this, Pradeep & Sharma (2007) effectively employed a low cost technique, hot exhaust gas recirculation (HOT EGR). Compared with COOLED EGR, this method was cost-effective and easy to implement.

Jatropha curcas is still a wild plant which exhibits a lot of variability in yield, oil content and oil quality (Achten et al. 2007). They emphasized the situation-specific interactions between different sustainability dimensions and the consideration of the political and ethical side of bioenergy production.

5.5 Biodiesel Production from Microalgae

Microalgae are grown in such a well-designed system with better access to water, CO₂, and nutrients provided by the aquatic environment. This contributes to its higher average photosynthetic efficiency compared with land crops. Microalgae grow extremely rapidly and commonly double their biomass within 34h. During exponential growth, this time can be shortened as low as 3.5h. The oil content in microalgae is rich, commonly 20-50% (Chisti, 2007). Some microalgae exceeds 80% oil content by weight of dry biomass (Metting, 1996; Spolaore et al. 2006).

Currently the practical methods of large-scale production of microalgae are open ponds, most commonly raceway ponds (Terry & Raymond, 1985), and tubular photobioreactors (Grima et al. 1999).

Unlike open raceways, photobioreactors save water, energy and chemicals. It can provide a controlled environment that can be tailored to the specific demands of highly productive microalgae to attain a consistently good annual yield of oil (Chisti, 2007).

Microalgae possess the following attractive characteristics that are ideal for biodiesel production (Miyamoto, 1997):

(1). Costs associated with the harvesting and transportation of microalgae are relatively low, compared with those of other biomass materials such as conventional crops. (2). Microalgae can be chemically treated. (3). Algae can grow under conditions that are unsuitable for conventional crops. (4). Microalgae are capable of fixing CO₂ in the atmosphere, thereby assisting the reduction of atmospheric CO₂ levels, which are now considered a global problem.

Aresta *et al.* (2005) conducted a research to compare with two different techniques, the thermochemical liquefaction and the supercritical carbon dioxide (sc-CO₂) extraction, for the extraction of oil from microalgae to produce biodiesel. It was found that thermochemical liquefaction was more efficient than the sc-CO₂ method from the quantitative point of view but decomposition of the fatty acid might occur under the operative conditions.

By incorporation of biorefinery concept and utilizing the advances in photobioreactor engineering, the production cost could be further reduced (Chisti, 2007).

6. Conclusions

In summary, WCO, grease, and soapstock are potential feedstocks for biodiesel production, which can lower the cost of biodiesel since they are inexpensive. However, since all these feedstocks contain high FFA, it will cause soap and water formation when using alkaline catalyst, which could decrease the ester yield and make the separation of ester, glycerol, and wash water more difficult. Acid catalysts can convert FFAs into esters, but the reaction rate is too slow. This process requires more alcohol and large reactors and it is corrosive (Canakci & Sanli, 2008).

The two-step process, of which the first step serves as a pretreatment, is usually preferred. This will increase the additional unit cost. Supercritical transesterification process can be an alternative method due to the following advantage: Pretreatment step, soap and catalyst removal are not necessary since catalyst is not required (He *et al.* 2007; Kasteren & Nisworo, 2007).

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