Biodiesel Feedstock and Production Technologies: Successes, Challenges and Prospects

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Additional information is available at the end of the chapter

1. Introduction

In order to achieve the biodiesel central policy of protecting the environment, replacing petroleum diesel and protecting and/or creating jobs, a good understanding of biodiesel history is essential. This is because consumers always tend to buy cheap rather than "green" fuels. Moreover, it is more difficult for a new technology to dislodge one that has reached societal standard. The more the popular technology is used, the more it improves; becoming less expensive due to wider market potentials. Petrodiesel has become the "life-blood" of our economy. It would be almost impossible to find a commercial product today that does not consume diesel fuel during its production and distribution [1-4]. Therefore, the aim of this chapter is to provide an overview on the history and motivation, successes, challenges and prospects of biodiesel as source of energy. This will provide a global outlook in making biodiesel an economical and eco-friendly alternative to petroleum diesel.

The historical developments of the biofuel industry in general and biodiesel in particular, is unlike many industries. This is because the driving factors for its advances are more of economics and politics than technological [5]. As early as 1853, transesterification was conducted on vegetable oil in the search for a cheap method to produce glycerine for producing explosives during World War II by E. Duffy and J. Patrick [6-8]. In 1937, G. Chavanne, Belgian scientist patented the "Procedure for the transformation of vegetable oils for their uses as fuels". ''Biodiesel" as a concept was thus established [9]. It is a simple process where alkoxy group of an ester compound (oil or fat) is exchanged with an alcohol. However, it was not until 1977 that first patent on commercial biodiesel production process was applied for by Expedito Parente; a Brazilian scientist [10].

Prior to the discovery of and boom in fossil fuels, power was mainly generated from steam. However, the use of hydro-energy consumes large resources coupled with the inefficiencies

of the steam engine where only about 10 to 12% efficiency is derived from new power generation plant. A patent for an efficient thermal engine which was to be operated on peanut oil was filed in 1892 by Rudolph Diesel in Germany. By 1893, Diesel's invention was demonstrated in an exhibition in Paris. Within five years of its invention, Diesel's engine ran on its own power with 75% efficiency against its initial 26% efficiency [11]. In 1912, Diesel published two articles [12,13] in which he reflected:

"The fact that fat oils from vegetable sources can be used may seem insignificant to-day, but such oils may perhaps become in course

of time of the same importance as some natural mineral oils and the tar products are now. (…) In any case, they make it certain that

motor power can still be produced from the heat of the sun, which is always available for agricultural purposes, even when all our

natural stores of solid and liquid fuels are exhausted."

The demand for biofuels began to increase in America from the 1890's to 1920's. These were attributed to the pioneering efforts on the diesel engine by Adolphus Busch and Clessie L. Cummins along with other engine manufacturers. However, the biofuel industry was faced with a major challenge of cheap and readily available feedstock. Unfortunately for the biofuel industry, at this same period, the petroleum industries found out more advanced technologies for improving the properties of the "black gold". The discoveries of large reservoirs and developments created new markets for this "black gold". Therefore, by 1940, diesel engines were altered to enable them use petroleum-based fuels which have lower viscosities. Thereafter, the sales of biodiesel were weakened and the production structure was pushed to the background. Therefore, no significant efforts were made to increase the public awareness on its potentials. This period witnessed increased demands for automobiles which were propelled by petroleum fuels. The availability of public funds, and new transportation infrastructure such as interstate and highway systems helped in this regard [14].

The early post-WWII fossil fuel demand and supply was influenced by the commencement of offshore oil and gas production in 1945 at the Gulf of Mexico and the invention of jet aircraft [14]. However in the 1970s, speculations regarding the finite nature of the fossil oil reserves became an issue worth pondering over. In 1973 and 1978, OPEC reduced oil supplies and increased the prices to meet with the shortages of the petroleum crisis of that time. This marked the reemergence of the potentials of biofuels in the public consciousness. Thus in 1979, South Africa started the commercial development of biodiesel. Sunflower oil was transesterified and refined to a standard similar to petroleum diesel fuel [15]. The outcome was the discovery of several sources and technologies that improved engine performance with reduced environmental impacts. Experiences from past were used in achieving improved efficiencies, while reducing costs by developing the renewable energy marketing advantage.

The procedure for the production, quality and engine-testing for biodiesel was finalized and published internationally in 1983. The South African technology was obtained by Gaskoks; an Austrian company. Gaskos established the first pilot plant for biodiesel production in 1987.

By April of 1989, the firm set up the first commercial-scale plant producing 20 million gallon per year (MGPY). However during this period, biodiesel was only being produced on a noncommercial scale in the United States. The growth in producing biodiesel in Europe began in 1991 because of the need to reduce environmental impacts from emissions of greenhouse gases (GHG). Three years later, the first commercial biodiesel production was started in America. By 2000, the Commodity Credit Corporation started subsidizing value-added agriculture towards biodiesel production. The past decade (2002 to 2012) witnessed an unprecedented production of biodiesel. Incentives from policy makers such as tax exemptions, tax credits and renewable fuel standards aided the biodiesel growth. However, some properties of biodiesel also contributed to the unprecedented growth we are witnessing in the biodiesel industry [16-18].

The increasing interests on biodiesel is fueled by the need to find a sustainable diesel fuel alternative. This is mainly because of environmental issues, apprehensions over energy independence and skyrocketing prices. Several processing options are available for the biodiesel production. The various feedstocks and processing conditions provide several processing technologies. The choice of a particular technology is dependent on catalyst and the source, type and quality of feedstock. Others include postproduction steps such as product separation and purification and catalyst and alcohol recovery. The dominant factor in the production process is the cost of feedstock while capital costs contribute only about 7%. It is therefore essential to utilize cheap feedstock to reduce the overall production costs. In the same regards, some technologies are designed to handle variety of feedstocks.

2. Past achievments

Non-fossil fuel alternatives are favored because of their common availability, renewability, sustainability, biodegrablability, job creation, regional development and reduced environmental impacts. Table 1 summarizes some of the major successes of biodiesel.

2.1. Feedstocks

Numerous feedstocks have been experimented in biodiesel production. Advancements from such experimentations led to establishment of waste-to-wealth biodiesel production. Cheap and readily available raw materials such as used cooking oil and yellow grease are used for producing biodiesel. These efforts helped in reducing the environmental impacts associated with dumping in landfills as well as saves the cost of paying for such dumping. Another notable success is the use of Jatropha or the "miracle plant" in many developing countries. The fact that it can be cultivated almost anywhere with minimal irrigation and less intensive care, made it suitable for peasant farmers. Sustained high yields were obtained throughout its average life cycle of 30–50 years. Castor plantation are also intercropped with jatropha to improve the econmic viability of jatropha within the first 2 to 3 years [19]. Another oil crop that is used to improve soil quality is the nitrogen-fixing *Pongamia pinnata*. It produces seeds with significant oil contents.

2.2. Technologies

Biodiesel is one of the most thoroughly tested alternative fuel in the market today. Studies by many researchers have confirmed similar engine performance of biodiesel to petroleum diesel. Transesterification produce oil with similar brake power as obtained with diesel fuel. Minimal carbon deposits were noticed inside the engine except the intake valve deposits which were slightly higher. The level of injector coking was also reduced significantly lower than that observed with D2 fuel [7,17]. An important breakthrough in transesterification is the Mcgyan Process®, which can utilize various inexpensive, non-food-grade and free fatty acids (FFAs) containing feedstocks (Figure 1). The process can be small in physical size and it utilizes heterogeneous catalysts to produce biodiesel within 4 s [20,21]. The easy fatty acid removal or EFAR system ensures that no wastes are produced from the process. It eliminates post production costs such as the washing and neutralization steps. To achieve 100% conversion, it recycles all unreacted feedstock and excess alcohol back into the reactor. Energy efficiency is also achieved through heat transfer mechanism; in-coming cold reactants are preheated by the out-going hot products [20,21].
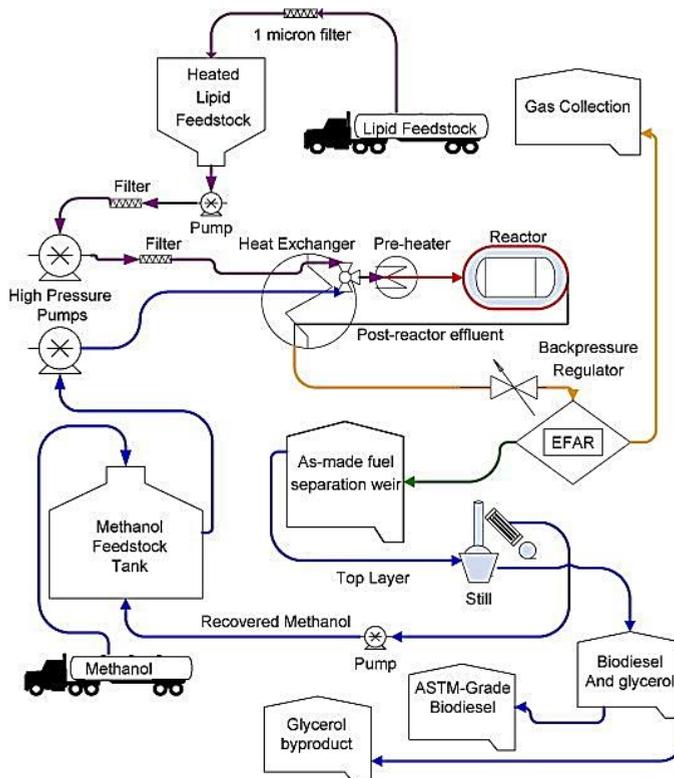

Figure 1. Process flow diafram of a biodiesel plant based on the Mcgyan proces[21].

Economic & social impact	Environment impact	Energy security
Sustainability; made from agricultural or waste resources	Reduced 78% GHG emissions	Reduced dependence on fossil fuels
Fuel diversity & improved fuel efficiency & economy	Reduced air pollution	Domestic targets
Improved rural economy	Biodegradability	Supply reliability
Increased income tax & trade balances	Improved land & water use	Readily available
International competitiveness	Carbon sequestration	Renewability
Increased investments on feedstocks & equipment	Lower sulfur content	Domestic distribution
Technological developments (R & D)	Lower aromatic content	Improved fuel economy
Higher cetane number (52 vs. 48), lubricity & flash point	Lesser toxicity	Comparable energy content (92.19%)
Knowledge development & diffusion	Safer handling & storage	Strict quality requirements are met
Strong growth in demand & market formation		Viscosity 1.3 to 1.6 times that of D2 fuel
Improved engine performance		Good energy balance (3.24:1 vs. 0.88:1)
Reduces the need for maintenance & prolongs engine life		
Compatible with all conventional diesel engines		
Offers the same engine durability & performance		
Has the potential of displacing petroleum diesel fuel		
Comparable start-up, torque range & haulage rates		

Table 1. Major achievements of biodiesel [16,23-27]

2.3. Environmental impacts and health effects

A 78% reduction in GHG emission was reported by the U.S. Departments of Agriculture and Energy with biodiesel usage. Essentially, biodiesel is non-aromatic and sulphur-free as compared with petrodiesel which contains 20 to 40 wt.% aromatic compounds and 500 ppm

SO_2 [7]. The potential of pure biodiesel to form ozone (smog) from hydrocarbons is 50% less. Also, sulfates and oxides of sulfur (major constituents of acid rain) are essentially eliminated from the exhaust emissions compared to petrodiesel. These help in curbing the increasing global warming problems. Average decrease of 22.5% for smoke density, 17.1% for CO and 14% for CO_2 have been reported when biodiesel was used [22]. Human life expectancy is thereby enhanced because of improved air quality.

2.3.1. Energy independence

Biodiesel reduces the excessive reliance on fossil fuels. This enhances the global energy security [17]. It also has the potential to replace oil importation since it is produced domestically, thereby providing additional market for agricultural products. It supports the rural communities where it is cultivated by protecting and generating jobs. Producing biofuels equivalent to 1% of automobile fuel consumption in the EU protected and/or created approximately 75,000 jobs [16]. Approximately, for every unit of fossil energy used in biodiesel production, 4.5 units of energy is gained. Moreover, lesser energy is required for biodiesel production than the energy derived from the final product [16].

3. Different feedstocks used in the production of biodiesel

More than 350 oil-bearing crops have been identified as potential sources for producing biodiesel. However, only palm, jatropha, rapeseed, soybean, sunflower, cottonseed, safflower, and peanut oils are considered as viable feedstocks for commercial production [28].

3.1. Edible feedstocks

Depending on availability, different edible oils are utilized as feedstocks for biodiesel production by different countries. Palm oil and coconut oil are commonly used in Malaysia and Indonesia. Soybean oil is majorly used in U.S. [30].

3.2. Non-edible feedstocks

In order to reduce production costs and to avoid the *food-for-fuel* conflict, inedible oils are used as the major sources for biodiesel production. Compared to edible oils, inedible oils are affordable and readily available. They are obtained from *Jatropha curcas* (jatropha or ratanjyote or seemaikattamankku), *Pongamia pinnata* (karanja or honge), *Calophyllum inophyllum* (nagchampa), *Hevca brasiliensis* (rubber seed tree), *Azadirachta indica* (neem), *Madhuca indica and Madhuca longifolia* (mahua), *Ceiba pentandra* (silk cotton tree), *Simmondsia chinensis* (jojoba), *Euphorbia tirucalli,* babassu tree, microalgae, *etc*. [31]. Among the 75 plant species which have more than 29% oil in their seed/kernel; palm, *Jatropha curcas*, and *Pongamia pinnata* (Karanja) were found to be the most suitable for biodiesel production [32]. Many European countries utilize rapeseed [29]. During World War II, oil from *Jatropha* seeds was used as blends with and substituted for diesel [33,34]. It has been reported that biodiesel produced from palm and

Jatropha have physical properties in the right balance; conferring it with adequate oxidation stability and cold performance [35]. Most of the strict requirements set by the American and European biodiesel standards for biodiesel have been achieved [36]. The major oils used for producing biodiesel are presented in Table 2.

Group	Source of oil
Major oils	Coconut (copra), corn (maize), cottonseed, canola (a variety of rapeseed), olive, peanut (groundnut), safflower, sesame, soybean, and sunflower.
Nut oils	Almond, cashew, hazelnut, macadamia, pecan, pistachio and walnut.
Other edible oils	Amaranth, apricot, argan, artichoke, avocado, babassu, bay laurel, beech nut, ben, Borneo tallow nut, carob pod (algaroba), cohune, coriander seed, false flax, grape seed, hemp, kapok seed, lallemantia, lemon seed, macauba fruit (Acrocomia sclerocarpa), meadowfoam seed, mustard, okra seed (hibiscus seed), perilla seed, pequi, (Caryocar brasiliensis seed), pine nut, poppy seed, prune kernel, quinoa, ramtil (Guizotia abyssinica seed or Niger pea), rice bran, tallow, tea (camellia), thistle (Silybum marianum seed), and wheat germ.
Inedible oils	Algae, babassu tree, copaiba, honge, jatropha or ratanjyote, jojoba, karanja or honge, mahua, milk bush, nagchampa, neem, petroleum nut, rubber seed tree, silk cotton tree, and tall.
Other oils	Castor, radish, and tung.

Table 2. Major oil species for biodiesel production [37]

3.2.1. Algae oil

Currently, algae-based biodiesel is the focus of many research interests because they have the potential to provide sufficient oil for global consumption. It has the potential to produce biodiesel yields >100 times those attainable per hectare from plant feedstock (Table 3). Besides their high lipid contents and fast growth rate, microalgae have the potential to mitigate the competitions for land-use and food-for-fuel conflicts. They are also able to reduce the GHG effect via CO_2 sequestration [38]. Microalgae can be cultivated in habitats which are not favorable for energy crops. Compared with oilseeds, the harvesting and transportation costs of microalgae are relatively low. *Nannochloropsis*, members of the marine green algae are considered the most suitable candidates for biodiesel production. These strains have shown high lipid content and biomass productivity. However, research in this area especially algal oil extraction is still limited and in early stages.

3.2.2. Other feedstocks

Used vegetable oils (UCO), yellow grease (8-12 wt% FFA), brown grease (>35 wt% FFA), and soapstock (by-product of refining vegetable oils) are potential feedstocks for biodiesel production. Their low costs and availability make them suitable for reducing the production

costs of biodiesel. To achieve this however, the problems associated with high FFA which are common to these feedstocks, particularly when alkaline catalysts are employed need attention. Solid acid catalysts are currently receiving great attention because they are suitable for feedstocks containing FFAs [39-41]. Another process that has the potential of processing these feedstocks is supercritical transesterification. The pretreatment step, soap and catalyst removal common to alkaline catalysis are eliminated since the process requires no catalyst [42,43]. The process has fast reaction rate which significantly reduces the reaction time [44]. The process is insensitive to water and FFAs [43,45]. However, this method is not economical because it requires high reaction temperature, pressure and higher molar ratio of alcohol to feedstock [42,43,46]. Another interesting feedstock is *Salicornia bigelovii* (Halophytessuch). It can produce equal biodiesel yields obtained from soybeans and other oilseeds. They grow in saltwater of coastal areas unsuitable for energy crops.

Microalgae/Plant	Oil yield (L/ha/year)	Oil content (% wt in biomass)	Required land (M ha $^{-1a}$)	Biodiesel productivity (kg biodiesel/ha/year)
Microalgae[b] (high oil content)	136 900	70	2	121 104
Microalgae[c] (low to low oil content)	58 700 to 97 800	30 to 50	4.5	51 927-85 515
Oil palm (*Elaeis guineensis*)	5 950	30 to 60	45	4747
Jatropha (*Jatropha curcas* L.)	1 892	Kernel: 50 to 60 Seed: 35 to 40	140	656
Canola/Rapeseed (*Brassica napus* L.)	1 190	38 to 46	223	862
Soybean (*Glycine max* L.)	446	15 to 20	594	562
Corn/Maize (Germ) (*Zea mays* L.)	172	44 to 48	1540	152

Table 3. Estimated oil content, yields and land requirement for various biodiesel feedstocks.[36,47,48]

4. Methods of oil extraction

The three common methods used in extracting oil are: (i) Mechanical extraction, (ii) solvent extraction and (iii) enzymatic extraction.

4.1. Mechanical extraction method

This method is used by smaller production firms for processing less than 100,000 kg/day. Usually, an engine driven screw press or a manual ram press is used to extract 68–80% or 60–65% of the available oil respectively. Pretreatment such as dehulling and cooking increase oil yields to 89% and 91% after single and dual pass respectively [48,49]. However, most of the mechanical presses are designed for particular seeds which affect yields with other seeds. Also, extra treatments such as degumming and filtration are required for oil extracted by this technique.

4.2. Chemical (solvent) extraction method

The commonly used chemical methods are: (1) soxhlet extraction, (2) Ultrasonication technique and (3) hot water extraction [48,49]. Solvent extraction (or leaching) is typically used for processing more than 300,000 kg/day [50]. Yields are affected by particle size, solvent type and concentration, temperature and agitation. To increase the exposure of the oil to the solvent, the oilseeds are usually flaked. After extraction, the oil-solvent mixture or *miscella*, is filtered while heat is used to vaporize the solvent from the miscella. Steam is injected to remove any solvent remaining from the oil. The immiscibility of the solvent and steam vapors is used to separate them in a settling tank after condensation. The highest oil yields are obtained with n-hexane. However, the process requires higher energy and longer time compared to other methods. Furthermore, the human health and environmental impacts associated with toxic solvents, waste water generation and emissions of volatile organic compounds are challenges facing this method.

4.3. Enzymatic extraction method

Oilseeds are reduced to small particles and the oil is extracted by suitable enzymes. Volatile organic compounds are not produced by this method which makes it environmentally friendly when compared to the other methods. However, it has the disadvantage of long processing time and high cost of purchasing enzymes [51].

5. Technologies used in biodiesel production

Several researches were carried out to overcome or minimize the problems associated with producing biodiesel. The methods that have been used for minimizing the viscosity of vegetable oils for practical application in internal combustion engines include: pyrolysis, microemulsification, blending (diluting) and transesterification. Dilution and microemulsification are not production processes and are therefore not discussed in this chapter. A summary of vegetable oils and animal fats and the major biodiesel production technologies are presented in Table 4.

5.1. Pyrolysis or catalytic cracking

Pyrolysis is the heating of organic matter in the absence of air to produce gas, a liquid and a solid [52]. Heat or a combination of heat and catalyst is used to break vegetable oils or animal fats into smaller constituents. Olefins and paraffins are thus obtained with similar properties to petrodiesel where such products derived the name *"diesel-like-fuel"* [53]. Studies on effects of rapeseed particle size showed that the product yield is independent of the oilseed particle size [52]. The maximum temperature range for conversion of bio-oil is 400°C to 450°C [54]. Rapid devolatilization of cellulose and hemicellulose occur at this temperature. Heating rate and temperature have significant effects on bio-oil yields, char and gas released from olive [55]. The viscosity, flash and pour points and equivalent calorific values of the oil are lower than diesel fuel. Though the pyrolyzate has increased cetane number, it is however lower than that of diesel oil. Apart from reducing the viscosity of the vegetable oil, pyrolysis enables de-coupling of the unit operation equipment in shorter time, place and scale. It produces clean liquids which needs no additional washing, drying or filtering. Product of pyrolysis consists of heterogeneous molecules such as water, particulate matter, sulfur, alkanes, alkenes and carboxylic acids [39,56]. Consequently, it is difficult to characterize fuel obtained from pyrolysis [52]. This process is energy consuming and needs expensive distillation unit. Moreover, the sulfur and ash contents make it less eco-friendly [57].

5.2. Transesterification (alcoholysis)

Transesterification is the most widely employed process for commercial production of biodiesel. It involves heating the oil to a designated temperature with alcohol and a catalyst, thereby restructuring its chemical structure. This conversion reduces the high viscosity of the oils and fats. For the transesterification of triglyceride (TG) molecule, three consecutive reactions are needed. In these reactions, FFA is neutralized by the TG from the alcohol. One mole of glycerol and three moles of alkyl esters are produced (for each mole of TG converted) at the completion of the net reaction. These separate into three layers, with glycerol at the bottom, a middle layer of soapy substance, and biodiesel on top [57]. Transesterification is a reversible reaction. To obtain reasonable conversion rates therefore, it requires a catalyst. The reaction conditions, feedstock compositional limits and post-separation requirements are predetermined by the nature of the catalyst. Table 5 presents a genaral overview of the several transesterification techniques for biodiesel production.

5.2.1. Homogeneous alkali-catalyzed transesterification

Alkali catalysts such as NaOH and KOH were preferred over other catalysts because of their ability to enhance faster reaction rates [63]. This is because they are readily available at affordable prices and enable fast reaction rates [24]. Detailed review on base-catalyzed transesterification of vegetable oils can be found in ref [64]. However, homogeneous catalysis has been faced with the been faced with the problems saponification, highly sensitive to FFAs, expensive separation requirement, waste water generation and high energy consumption.

5.2.2. Homogeneous acid-catalyzed transesterification

Though the performance of this method is not strongly affected by FFAs in the feedstock, the process is not as popular as the base-catalyzed process. This is because the use of strong acids such as H_2SO_4 [65,66], HCl, BF_3, H_3PO_4, and organic sulfonic acids [67], is associated with higher costs and environmental impacts. Moreover, the technique is about 4000 times slower than the homogeneous base-catalyzed reaction. The mechanism of the acid-catalyzed transesterification can be found in ref [68].

5.2.3. Heterogeneous acid and base-catalyzed transesterification

Solid acid can simultaneously catalyze the esterification and transesterification without the need for pretreating feedstocks with high FFAs. Thus, this technique has the potential of reducing the high cost of biodiesel production by directly producing biodiesel from readily available and low-cost feedstocks [67].
Solid basic catalysts also have the potential of reducing the cost of biodiesel production because of lesser catalyst consumption, reuse and regeneration. However, these catalysts have some disadvantages which hinder their wide acceptability. These include mass transfer (diffusion) problem which reduces the rate of reaction as a result of the formation of three phases with alcohol and oil. Other problems associated with base catalyzed transesterification are loss of catalyst activity in the presence of water and post-production costs such as product separation, purification and polishing.

5.2.4. Enzymatic transesterification

Some of the problems associated with homogeneous catalysts such as expensive product separation, wastewater generation, and the presence of side reactions are avoided with enzymatic transesterification [69]. Enzyme immobilization is usually done to enhance the product quality, increase the number of times the catalyst is reused and to reduce cost [28,70]. However, several technical difficulties such as high cost of purchasing enzymes, product contamination, and residual enzymatic activity are limiting the applicability of this technique.

5.2.5. Supercritical alcohol transesterification

Unlike the conventional transesterification of two heterogeneous liquid phases involving alcohol (polar molecule) and non-polar molecules (TGs), supercritical transesterification is done in single homogeneous phase. Subjecting solvents containing hydroxyl groups (such as water and alcohol) to conditions in excess of their critical points make them to act as superacids. Under supercritical conditions, alcohol serves a dual purpose of acid catalyst and a reactant [46,71]. The absence of interphase solves the mass transfer limitations which gives the possibility of completing the reaction in minutes rather than several hours. In fact, the Mcgyan Process® was used to produce biodiesel under 4 s [19,20]. However, this process is not economical especially for commercial production as it requires expensive reacting equipment due to high temperature and pressure [72]. Studies are currently being undertaken in order to reduce these high reacting conditions.

Direct use	Dilution with vegetable oils	Microemulsion of oils	Pyrolysis and catalytic cracking	Transesterification of oils and fats	
Advantages	Advantages	Advantages	Advantages	Catalytic	Non-catalytic
Simple process	Simple process and non-polluting	Simple process and non-polluting	Simple process & non-polluting no additional washing, drying or filtering required		
Disadvantages	Disadvantages	Disadvantages	Disadvantages	Acid-catalyzed	BIOX cosolvent process
Highly viscous	Highly viscous	Incomplete combustion	Contains heterogeneous molecules	Alkali catalytic	Supercritical alcohol
Highly unstable	Highly unstable	Injector needle sticking	Low purity	Enzyme-catalyzed	Microwave and ultrasound assisted
Low volatility	Low volatility	Carbon deposits	Requires high temperature	Catalytic supercritical alcohol	
Not suitable for commercial production	Not suitable for commercial production	Not suitable for commercial production	Requires expensive equipment	See Table 5 for advantages and disadvantages	

Table 4. Use of vegetable oils and animal fats and major biodiesel production processes.

5.3. Technologies

5.3.1. Microwave assisted transesterification

The microwave irradiation as energy stimulant has been attracting the attention of many researchers. This is because the reaction process fast (within minutes), it employs a lower alcohol-oil ratio and it reduces by-products quantities. It uses a continuously changing electrical and magnetic fields to activate the smallest degree of variance of the reacting molecules. These rapidly rotating charged ions interact easily with minimal diffusion limitation [73]. However, this process also has commercial scale-up problem because of high operating conditions and safety aspects [74]. An even more daunting challenge is in increasing the irradiation penetration depth beyond a few centimeters into the reacting molecules.

5.3.2. Ultrasound assisted transesterification

This process utilizes sound energy at a frequency beyond human hearing. It stretches and compresses the reacting molecules in an alternating manner. Application of high negative

pressure gradient beyond the critical molecular distance forms cavitation bubbles. Some of the bubbles expand suddenly to unstable sizes and collapse violently. This causes emulsification and fast reaction rates with high yields since the phase boundary has been disrupted [75-77].

	Chemical catalysed				Chemical catalysed (Modified)			Biochemical catalysed	Noncatalysed
Homogeneous acid	Homogeneous base	Heterogeneous acid	Heterogeneous base	Microwave irradiation	Ultrasound (sonication)	Oscillatory flow reactor	Enzyme	Supercritical methanol
Merits	Merits	Merits	Merits	Merits	Merits	Merits	Merits	Merits
Employs feedstocks with high FFAs ("/>2 wt %)	Reaction is 4000 times faster than homogeneous acid catalysed reactions	High possibility of reusing and regenerating catalyst many times	High possibility of reusing and regenerating catalyst many times	Speeds up rate of reaction (from hours to minutes)	Increases FAME production from seedcakes	Increases mixing of reactants	Operates at milder reaction conditions	Simultaneous transesterification of TGs and esterification of FA
No pretreatment required	Operates at mild temperature (50 to 80 °C)	Simultaneous transesterification of TGs and esterification of FA	Saves cost of purchasing catalyst	Improves catalyst activity and selectivity	*In situ* extraction transesterification	Efficient heat and mass transfer	Cleaner biodiesel and glycerol are produced	High biodiesel yield
	Lower alcohol-to-oil (5:1) molar ratio	Simpler and less energy intensive	Simpler and less energy intensive	Minimizes energy consumption	High FAME yields	Higher yield in shorter time compared to batch-type	Energy consumption is minimized	Simultaneous transesterification of TGs and esterification of FA
	High biodiesel yield	Does not require feedstock pretreatment	Easy separation of products		Eliminates of saponification	Reduces reactor length-to-diameter ratio	Waste generation is minimized	Requires no catalyst
	Catalysts are cheap and readily available	Mild reaction conditions & less prone to leaching	Mild reaction conditions		Low reaction time	Reduces costs		Relatively fast reaction rate
		Waste generation is minimized			Mild reaction conditions			Short reaction time (<30 minutes)
		Relatively fast reaction rates			Enhances mass transfer			
		Easy product separation						
		Saves cost of purchasing catalysts						
		Minimizes solvation of active sites by action of water						
		Eliminates of saponification						

Chemical catalysed				Chemical catalysed (Modified)			Biochemical catalysed	Noncatalysed
Homogeneous acid	Homogeneous base	Heterogeneous acid	Heterogeneous base	Microwave irradiation	Ultrasound (sonication)	Oscillatory flow reactor	Enzyme	Supercritical methanol
	Reduces size & cost of reaction vessel							
	Very attractive commercially							
Challenges	*Challenges*	*Challenges*	*Challenges*	*Challenges*	*Challenges*	*Challenges*	*Challenges*	*Challenges*
Very slow reaction rate & mineral acids used are corrosive to the equipment	Highly sensitive to water and FFAs in the oil	Availability of specific catalysts at low cost. Researches are ongoing to find low cost precursors.	Requires feedstock pretreatment & catalyst get poisoned with prolong exposure to ambient air	Difficulties in process scale-up from laboratory scale to large-scale	Difficulties in process scale-up from laboratory scale to large-scale	Difficulties in process scale-up from laboratory scale to large-scale	High cost of enzymes	Energy intensive
Catalyst required in large quantities	Requires refined feedstock (0.5 % FFA; 0.06% H$_2$O)	Limitation due to diffusion problems. This is solved by designing catalysts with large interconnected pores with high concentration of acid sites	High cost of reacting vessels	Depth of radiation is limited to a few cm.	Requires advanced technology	Requires advanced technology	High production cost	Very expensive
Requires high alcohol-to-oil molar ratio	Water saponifies the esters and FFAs reacts with the catalyst		Two-step reaction of esterification and transesterification	Requires advanced technology	Safety issues in equipment handling	Safety issues in equipment handling	Enzymes easily denatured	Not commercially profitable
Higher temperature	Requires methanol-to-oil of 6:1 (or higher) molar ratio instead of the stoichiometric 3:1 ratio		Product contamination from leaching of active catalytic sites	Safety issues in equipment handling.			Not commercially profitable	Safety issues
Undesirable etherification reaction (dialkyl or glycerol ethers)	Soap formation (FFA"/>2%)		Water saponifies the esters and FFAs reacts with the catalyst making purification difficult				Very slow reaction rates (slower than homogeneous acid catalysed)	High temperature and pressure

Chemical catalysed				Chemical catalysed (Modified)			Biochemical catalysed	Noncatalysed
Homogeneous acid	Homogeneous base	Heterogeneous acid	Heterogeneous base	Microwave irradiation	Ultrasound (sonication)	Oscillatory flow reactor	Enzyme	Supercritical methanol
Separation and purification of glycerol	Loss of catalyst		Catalyst leaching leads to product contamination				Sensitive to methanol	Energy intensive
Not commercially profitable	Reduces biodiesel yield & generates wastewater		Purification decreases biodiesel yield					

Table 5. Merits and challenges surrounding transesterification processes[78]

6. Current challenges and future prospects

In order to make biodiesel profitable, several technical challenges need to be resolved. The most important challenge is in reducing the high cost of feedstock. Low-cost feedstocks such as algal oils, used cooking oils and animal fats are utilized to increase biodiesel profitability. However, presence of higher amounts of water and FFAs in these feedstocks poses the problems of saponification and extra pretreatment and purification costs with alkali catalysts. The challenge facing researchers currently is developing efficient heterogeneous acid catalysts that would alleviate these problems. Also, diversifying the by-product of biodiesel production processes is critical to ensuring its economic, social and environmental sustainability.

6.1. Vegatable oil as feedstock for biodiesel

Currently, biodiesel production costs are higher than those of petroleum diesel. Subsidies such as tax exempt and excise duty reductions are essential to make biodiesel price-competitive. It is not certain whether these political supports will be sustained in the future. It is therefore crucial for the biofuel industry to establish readily available and affordable feedstocks and efficient production systems to sustain its market growth.

6.2. Non-food crops

Early studies have indicated relative differences in the cultivation patterns and oil production management of the non-food feedstocks compared to food crops. These are still under investigation [79]. Therefore, more data is needed to evaluate the sustainability index to estimate the real global impact of these feedstocks. Microalgae are promising in solving most of the problems associated with energy crops. However, the cultivation and extraction technologies are still at their infancy and need major advancements for sustainable commercial production [1]. The oil extraction methods currently in use for algal

oil are expensive. Efficient mixing from pumps or motionless mixers is required to en-sure homogeneity and to reduce mass transfer limitations. However, this increases the dispersion of glycerol into the FAME phase and the time required for separation. Techniques that utilize motionless mixing requires higher temperature and pressure to achieve shorter residence time. This increases energy consumption and cost implications. This aspects of biodiesel production technology is still being developed.

6.3. Effects of moisture and FFA

The key parameters that determine the viability of most feedstocks is FFA and moisture content. Pretreatments to less than 0.05% FFA is required for homogeneous alkali catalysts [80,81]. Prolonged storage in the presence of water and air leads to microbial growth and fuel degradation. This contributes to deposit formation on fuel injectors and engine damage. Heterogeneous acid catalysts are utilized to avoid the pretreatment and post production costs and storage problems.

6.4. Pyrolysis

Pyrolysis generates aromatic toxins. The bio-oil produced is corrosive due to high acidity, water content and other impurities such as solids and salts. These and other problems such as variable viscosity make it unstable and unsuitable for direct use [82]. It has 40% less energy density compared to diesel fuel because of the high oxygen content [83]. Depending on the feedstock and reacting conditions used, bio-oil is 10 to 100% more expensive than petroleum diesel. There is also the need to establish standards for product quality, use and distribution [1]. In order to stabilize the composition of the bio-oil and reduce water and oxygen content, processes such as steam reforming, hydro-treatment, hydro-cracking and emulsification with mineral diesel for direct use are employed [84-87].

6.5. Alcohol

Methanol is toxic, highly flammable and contributes to global warming. Gaskets and rubber seals made from natural rubber get easily deteriorated when biodiesel containing a high level of alcohol is used [80]. Therefore, control or replacement of the alcohol content is required. The biodiesel produced with methanol from fossil sources has approximately 94 to 96% biogenic content. In order to produce a 100% renewable biodiesel (fatty acid ethyl ester; FAEE), bioethanol is currently experimented as a substitute for methanol [88]. However, it is expensive to purify and recover ethanol because it forms an *azeotrope* with water. Additionally, chemical grade ethanol is usually denatured with poisonous substances to prevent it from being abused. Therefore, it is difficult to obtain pure chemical grade ethanol.

6.6. Supercritical alcohol process

The residence time for this process is within 4 s to 10 min because of efficient mixing [71,72]. However, due to higher reacting conditions of temperature and pressure, the process is faced with some limitations. Process scale-up for commercial production is the major one amongst

them. The process requires more energy at extra cost and higher molar ratio of alcohol-to-oil (42:1). Also, there is the need to quench the reaction in a rapid manner. This prevents the biodiesel from decomposing as a result of the high temperature and pressure. To reduce the high operating conditions and increase product yield, some researchers employ co-solvents, such as hexane, CO_2, and CaO [72]. Oil and alcohol are sparingly soluble in each other. However, small amount of hexane (2.5 wt%) added increased the biodiesel yield from 67.7% to 85.5% under supercritical conditions [72]. This was made possible because the co-solvent increased the homogeneity of the reactants. Supercritical CO_2 is a facile substance that can obtained at affordable cost. It is also environmentally friendly and can effectively used in the reaction and safely recovered via depressurization. A process that combines co-solvents in superctical conditions is promising in increasing product yield, reducing process time and overall production costs.

6.7. Biodiesel/glycerol separation and FAME quality

The slightly soluble nature of FAMEs and glycerol makes product separation a necessary step. The product is usually allowed to settle for some hours into the different phases. However, the solubility of glycerol in ester and vice versa is increased in the presence of excess unreacted methanol which acts as solvent. This solvent action by the methanol increases the post production costs. Besides, it is also essential to remove all traces of TGs which form emulsion layer between the two phases. The presence of this layer further makes separation difficult and expensive. On the other hand, the storage, transportation, distribution and retail infrastructure used for petroleum diesel can be used for biodiesel even in its neat form. This will reduce construction costs for establishing new insfrasctures for biodiesel. However, biodiesel degrades after long period of storage. In order to prevent this from occuring, advances in storage and distribution logistics have to be developed. Also, similar logistics employed by the petroleum industry could be adapted.

6.8. Use of cosolvents

A technique developed to overcome mass transfer limitations and to increase the rate of reaction is the use of cosolvents such as methyl tert-butyl ether (MTBE) and tetrahydrofuran (THF). High quality FAMEs is obtained at moderate conditions (30 °C) within 10 minutes. However, the process requires larger and special "leak proof" reacting vessels and complete removal of the cosolvent from the product.

6.9. NO_x emissions

Despite the favorable environmental impacts in terms of overall reduced GHG emissions, biodiesel has the potential to increase NO_x emissions. Approximately 3 to 4%, 4 to 6% and 6 to 9% over petroleum diesel is emitted from B20, B40 and B100 respectively [89]. Adjustments in combustion temperatures and injection timing [90], use of antioxidants [91] and catalytic conversion techniques were successful in reducing these emissions [90].

6.10. Economic analysis

As discussed in the introductory section, vegetable oils have other important uses. Recently, dielectric oils and synthetic lubricants used for electric transformers have joined the market competition for these raw materials. This will impact negatively towards the cost of raw materials for the biodiesel industry [92]. About 15% of lubricants used in vehicles in some European countries are from vegetable oil derivatives [93]. Additionally, the heating value of biodiesel is 10% lower than that of petroleum diesel. This is because of the substantial amount of oxygen in the fuel. Moreover, it also has a higher specific gravity of 0.88 when compared to 0.85 of petroleum diesel. Therefore, its overall energy content per unit volume is having an impact which is approximately 5% lower than that obtained from petroluem diesel [94]. This results in higher specific fuel consumption values of the biodiesel. Another problem encountered when switching from petroleum diesel to biodiesel in the same fuel system is the clogging of the fuel filters. This is because biodiesel acts as a solvent which dissolves sediments in diesel fuel tanks [95]. On a positive note, sales of purified glycerol (glycerine) saved 6.5% of the operational cost [97-99] while 25% saving was reported in ref [96] from the utilization of waste soapstock with respect to virgin soybean oil. However, it is necessary to compensate the negative cost implications from commercial production of biodiesel from such low value feedstocks before valid conclusions can be derived.

7. Conclusions

Some of the major challenges faced by the biodiesel industry include readily available and affordable feedstocks, competition from a popular and cheaper energy source, technological advancements and acceptability. Those challenges requiring immediate attention are product stability under long storage, lower energy content, cold flow properties, catalyst leaching, microalgal oil extraction and NOx emissions. Despite these challenges however, the historical development of biodiesel is intriguing. Biodiesel has successfully remained an energy source to be reckoned with even after being relegated to the background for so many years. Concerns over diminishing oil reserves, increasing crude oil prices and associated environmental impacts aided the reemergence of biodiesel; making it the fastest growing industry worldwide. Several technologies were developed while more advances are in the process of being established. Other successes associated with the biodiesel industry include reduction in environmental impacts, job creation, energy security and waste-utilization. Biodiesel is regarded as a viable alternative or additive to petrodiesel because of its good properties such as nontoxicity, clean-burning, renewability and acceptability. Consequently, the prospects of the biodiesel industry are numerous. The biodiesel production process is shifting from other sources to algal oil and heterogeneous acid catalysts. Algal oil is a more reliable and efficient source. It has the potential of producing yields of more than 100 times those attainable per hectare from oilseeds. Affordable and readily available non-food feedstocks such as microalgae have been produced in commercial scale without competing with arable land or causing deforestation. Additionally, the use of heterogeneous acid catalyst produces cleaner and higher yields.

It employs cheaper and readily available feedstocks and minimizes pre- and post-product costs. These and other factors such as waste-utilization and cleaner emissions will help ensure biodiesel as a cheaper energy source with greater economic benefits and healthier environments.

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References

[1] Haung, D, Zhou, H, & Lin, L. Biodiesel: an alternative to conventional fuel. Energy Procedia (2012). , 1-1874.

[2] James, M. Utterback. Mastering the Dynamics of Innovation. Boston: Harvard Business School Press, (1994).

[3] Arthur, W. Competing Technologies, Increasing Returns, and Lock-In By Historical Events. Economic Journal (1989). , 99(394), 116-131.

[4] Hughes, T. P. The evolution of large technological systems. In: Bijker W.E., Hughes TP and Pinch T. The social construction of technological systems. Cambridge, Massachusetts: MIT Press. (1989). , 51-82.

[5] Luque, R, Herrero-davila, L, Campelo, J. M, Clark, J. H, Hidalgo, J. M, Luna, D, Marinas, J. M, & Romero, A. A. Biofuels: a technological perspective. Energy Environ. Sci. (2008). , 1-542.

[6] Lin, L, Cunshan, Z, Vittayapadung, S, Xiangqian, S, & Mingdong, D. Opportunities and challenges for biodiesel fuel. Applied Energy (2011). , 88-1020.

[7] Demirbas, A. Biofuels, in: Green Energy and Technology, (2009). Springer London, , 103-230.

[8] Shay, E. G. Diesel fuel from vegetable oils: status and opportunities. Biomass Bioenergy (1993). , 4-227.

[9] Knothe, G. Historical perspectives on vegetable oil-based diesel fuels. Inform (2001). , 11-1103.

[10]   Parente, E. Lipofuels: biodiesel and biokerosene. National Institute of Standards and Technology. (2007).

[11]   Lappe, P. The Biodiesel Industry: Past, Present and Future, GEAPS: Proceedings Sessions. http://www.geaps.com/knowledge/proceedings/article.cfm?id=15.Assessed 07 May (2012).

[12]   Diesel, R. The Diesel oil-engine. Engineering (1912). , 93-395.

[13]   Diesel, R. The Diesel oil-engine and its industrial importance particularly for Great Britain. Proc Inst Mech Eng. (1912). , 179-280.

[14]   Jones, J. C. Energy Resources for the Past, Present and Future. The Open Thermodynamics Journal (2010). , 4-72.

[15]   SAE technical paper series noSAE international of highway meeting, Milwaukee, Wisconsin, USA; (1983).

[16]   Demirbas, A. Biofuels securing the planet's future energy needs. Energy Conversion and Management (2009). , 50-2239.

[17]   Soy Biodiesel Supplier and User Guidehttp://www.mdsoy.com/consumer/biodiesel-guide.pdf,accessed 08 May (2012).

[18]   Yusuf NNANKamarudin SK and Yaakob Z. Overview on the production of biodiesel from Jatropha curcas L. by using heterogeneous catalysts. Biofuels, Bioprod. Bioref. (2012). , 6-319.

[19]   Gui, M. M, Lee, K. T, & Bhatia, S. Feasibility of edible oil vs. non-edible oil vs. waste edible oil as biodiesel feedstock. Energy (2008). , 33-1646.

[20]   Mcneff, C. V, Mcneff, L. C, Yan, B, Nowlan, D. T, Rasmussen, M, Gyberg, A. E, Krohn, B. J, Fedie, R. L, & Hoye, T. R. A continuous catalytic system for biodiesel production. Appl. Catal. A: Gen. (2008). , 343, 39-48.

[21]   Krohn, B. J, Mcneff, C. V, Yan, B, & Nowlan, D. Bioresourc. Production of algae-based biodiesel using the continuous catalytic Mcgyan® process. Technol. (2011). , 102, 94-100.

[22]   Utlu, Z. Evaluation of biodiesel fuel obtained from waste cooking oil. Energy Sources Part A (2007). , 29-1295.

[23]   Ban-weiss, G. A, Chen, J. Y, Buchholz, B. A, & Dibble, R. W. A numerical investigation into the anomalous slight NOx increase when burning biodiesel: A new (old) theory. Fuel Process. Technol. (2007). , 88-659.

[24]   Vicente, G, Martinez, M, & Aracil, J. Integrated biodiesel production: a comparison of different homogeneous catalysts systems. Bioresourc. Technol. (2004). , 92-297.

[25]   Nas, B, & Berktay, A. Energy potential of biodiesel generated from waste cooking oil: an environmental approach. Energy Sources Part B (2007). , 2-63.

[26] Wardle, D. A. Global sale of green air travel supported using biodiesel. Renew. Sustain. Energy Rev (2003). , 7-1.

[27] Chand, N. Plant oils-fuel of the future. J Sci Ind Res (2002). , 61-7.

[28] Al-zuhair, S. Production of biodiesel: possibilities and challenges, Biofuels, Bioprod. Bioref. (2007). , 1-57.

[29] Goering, E, Schwab, W, Daugherty, J, Pryde, H, & Heakin, J. Fuel properties of eleven vegetable oils. Trans ASAE (1982). , 25-1472.

[30] Demirbas, A. (2003). Fuel conversional aspects of palm oil and sunflower oil. Energy Sources , 25, 457-466.

[31] Karmee, S. K, & Chadha, A. Preparation of biodiesel from crude oil of Pongamia pinnata. Biores Technol (2005). , 96-1425.

[32] Azam, M. M, Waris, A, & Nahar, N. M. Prospects and potential of fatty acid methyl esters of some non-traditional seed oils for use as biodiesel in India. Biomass Bioenergy (2005). , 29-293.

[33] Foidl, N, Foidl, G, Sanchez, M, Mittelbach, M, & Hackel, S. Jatropha curcas L. As a source for the production of biofuel in nicaragua. Biores Technol (1996). , 58-77.

[34] Gubitz, G. M, Mittelbach, M, & Trabi, M. Exploitation of the tropical seed plant Jatropha Curcas L. Biores Technol (1999). , 67-73.

[35] Sarin, R, Sharma, M, Sinharay, S, & Malhotra, R. K. Jatropha-palm biodiesel blends: An optimum mix for Asia. Fuel (2007). , 86-1365.

[36] Berchmans, H. J, & Hirata, S. Biodiesel production from crude Jatropha curcas L. seed oil with a high content of free fatty acids. Bioresour. Technol., (2008). , 99-1716.

[37] Demirbas, A. Progress and recent trends in biodiesel fuels. Energ Convers Manage (2009). , 50-14.

[38] Christi, Y. Biodiesel from microalgae. Biotechnol Adv. (2007). , 25-294.

[39] Fan, X, & Burton, R. Recent Development of Biodiesel Feedstocks and the Applications of Glycerol: A Review, The Open Fuels & Energy Science Journal (2009). , 2-100.

[40] Canakci, M, & Sanli, H. Biodiesel production from various feedstocks and their effects on the fuel properties. J. Ind. Microbiol. Biotechnol. (2008). , 35-431.

[41] Kulkarni, M. G, & Dalai, A. K. Waste cooking oil-An economical source for biodiesel: A review. Ind. Eng. Chem. Res. (2006). , 45-2901.

[42] He, H. Y, Wang, T, & Zhu, S. L. Continuous production of biodiesel fuel from vegetable oil using supercritical methanol process. Fuel (2007). , 86-442.

[43] Demirbas, A. Biodiesel from vegetable oils via transesterification in supercritical methanol. Energy Convers. Manage., (2002).

[44] Saka, S, & Kusdiana, D. Biodiesel fuel from rapeseed oil as prepared in supercritical methanol. Fuel (2001). , 80-225.

[45] Van Kasteren JMN and Nisworo APA process model to estimate the cost of industrial scale biodiesel production from waste cooking oil by supercritical transesterification. Resour. Conserv. Recy. (2007). , 50-442.

[46] Kusdiana, D, & Saka, S. Effects of water on biodiesel fuel production by supercritical methanol treatment. Bioresource Technol. (2004). , 91-289.

[47] Mata, T. M, Martins, A. A, & Caetano, A. S. Renew. Sustain. Energy Rev. (2010). , 14-217.

[48] Atabani, A. E, Silitonga, A. S, & Badruddin, I. A. Mahlia TMI, Masjuki HH and Mekhilef S. Renew. Sustain. Energy Rev. (2012). , 16-2070.

[49] Achten WMJVerchit L, Mathijs Franken YJ, Singh E, Aerts VP and Muys RB. Jatropha bio-diesel production and use. Biomass Bioenergy (2008). , 32(12), 1063-1084.

[50] Williams, M. A. Extraction of Lipids from Natural Sources, Chapter 5 in: Lipid Technologies and Applications, Edited by Gunstone FD and Padley FB, Marcel Dekker, New York, (1997). , 113.

[51] Mahanta, P, & Shrivastava, A. Technology development of bio-diesel as an energy alternative. Department of Mechanical Engineering Indian Institute of Technology. http://www.newagepublishers.com/samplechapter/001305.pdf;(2011). accessed 11 August 2012).

[52] Pramanik, K. Properties and use of Jatropha curcas oil and diesel fuel blends in compression ignition engine Renew. Energy. (2003). , 28-239.

[53] Narayan CM In: Proceedings on recent trends in automotive fuelsNagpur, India. (2002).

[54] Ramadhas, A. S. Jayaraj Sand Muraleedharan C. Use of Vegetable Oil as I.C. Engine Fuels: A Review. Int. J. Renew. Energy (2004). , 29-727.

[55] Ma, F, & Hanna, M. Biodiesel production: A review. Bioresourc. Technol. (1999). , 70-1.

[56] Ranganathan, S. V, Narasimhan, S. L, & Muthukumar, K. An overview of enzymatic production of biodiesel. Bioresourc. Technol. (2008). , 99-3975.

[57] Fukuda, H, Kondo, A, & Noda, H. Biodiesel Fuel Production by Transesterification of Oils. J. Biosci. Bioeng. (2001). , 92-405.

[58] Uzun, B. B, Putun, A. E, & Putun, E. Fast pyrolysis of soybean cake: Product yields and compositions. Bioresourc. Technol. (2006). , 97(4), 569-576.

[59] Sonntag NOVReactions of fats and fatty acids. Bailey's industrial oil and fat products, th edition, Edited by Swern D., John Wiley & Sons, New York, , 1, 99.

[60] Sharma, Y. C, Singh, B, & Upadhyay, S. N. Advancements in development and characterization of biodiesel: A review. Fuel (2008). , 87(12), 2355-2373.

[61] Sensoz, S, Angin, D, & Yorgun, S. Influence of particle size on the pyrolysis of rapeseed (Brassica napus L.): fuel properties of bio-oil. Biomass and Bioenerg. (2000). , 19-271.

[62] Sensoz, S, Demiral, I, & Gercüel, H. F. Olive bagasse (Olea europea L.) pyrolysis. Bioresourc. Technol. (2006). , 97(3), 429-436.

[63] Freedman, B, Pryde, E. H, & Mounts, T. L. Variables affecting the yields of fatty esters from transesterified vegetable oils. JAOCS (1984). , 61-1638.

[64] Demirbas, A. Biodiesel production from vegetable oils via catalytic and non-catalytic supercritical methanol transesterification methods. Prog Energy Combust Sci (2005). , 31-466.

[65] Al-widyan, M. I, & Al-shyoukh, A. O. Experimental evaluation of the transesterification of waste palm oil into biodiesel. Bioresour Technol (2002). , 85-253.

[66] Yong, W, Shiyi, O, Pengzhan, L, Feng, X, & Shuze, T. Comparison of two different processes to synthesize biodiesel by waste cooking oil. J Mol Catal A: Chem (2006). , 252-107.

[67] Lotero, E, Liu, Y, Lopez, D. E, Suwannakarn, K, Bruce, D. A, & Goodwin, J. G. Synthesis of biodiesel via acid catalysis. Ind Eng Chem Res (2005). , 44-5353.

[68] Ulf, S, Ricardo, S, & Matheus, V. R. Transesterification of vegetable oils: a review. J Braz Chem Soc (1998). , 9(1), 199-210.

[69] Raman, J. K, Sariah, A, Denis, P, Seng, C. E, & Pogaku, R. Production of biodiesel using immobilized lipase- a critical review. Crit Rev Biotechnol (2008). , 28-253.

[70] Nielsen, P. M, Brask, J, & Fjerbaek, L. Enzymatic biodiesel production: technical and economical considerations. Eur J Lipid Sci Technol (2008). , 110-692.

[71] Pinnarat, T, & Savage, P. E. Assessment of noncatalytic biodiesel synthesis using supercritical reaction conditions. Ind Eng Chem Res (2008). , 47-6801.

[72] Yin, J-Z, Xiao, M, & Song, J-B. Biodiesel from soybean oil in supercritical methanol with co-solvent. Energy Convers Manage (2008). , 49-908.

[73] Azcan, N, & Danisman, A. Alkali catalyzed transesterification of cottonseed oil by microwave irradiation. Fuel (2007). , 86-2639.

[74] Yoni, G, & Aharon, G. Continuous flow, circulating microwave system and its application in nanoparticle fabrication and biodiesel synthesis. J Phys Chem C (2008). , 112-8802.

[75] Thompson, L. H, & Doraiswamy, L. K. Sonochemistry: science and engineering. Ind Eng Chem Res (1999). , 38-1215.

[76] Colucci, J. A, Borrero, E. E, & Alape, F. Biodiesel from an alkaline transesterification reaction of soybean oil using ultrasonic mixing. JAOCS (2005). , 82(7), 525-530.

[77] Carmen, S, Vinatoru, M, Nishimura, R, & Maeda, Y. Fatty acids methyl esters from vegetable oil by means of ultrasonic energy. Ultrason Sonochem (2005). , 12-367.

[78] Sani, Y. M. Daud WMAW and Abdul Aziz AR. Solid acid-catalysed biodiesel production from algal oil- The Dual Advantage. Submitted.

[79] Van Eijcka, J, & Romijnk, H. Energy Policy, (2008). , 2008(36), 311-325.

[80] Meher, L. C, Sagar, D. V, & Naik, S. N. Technical aspects of biodiesel production by transesterification-A review. Renew. & Sust. Energy Rev. (2006). , 10-248.

[81] Demirbas, A, & Karsliöglu, S. Biodiesel production facilities from vegetable oils and animal fats. Energy Sources, Part A (2007). , 29-133.

[82] Qi, Z, Jie, C, Tiejun, W, & Ying, X. Review of biomass pyrolysis oil properties and upgrading research. Energy Conv. Manage., (2007). , 48-87.

[83] Maher, K. D, & Bressler, D. C. Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals. Bioresour. Technol., (2007). , 98-2351.

[84] Chiaramonti, D, Bonini, D, & Fratini, E. Tondi, Gartner K, Bridgwater AV, Grimm HP, Soldaini I, Webster A and Baglioni P. Development of emulsions from biomass pyrolysis liquid and diesel and their use in engines-Part 1: emulsion production. Biomass Bioenerg, (2003). , 25, 85-99.

[85] Czernik, S, French, R, Feik, C, & Chornet, E. Hydrogen by catalytic steam reforming of liquid byproducts from biomass thermoconversion processes. Ind. Eng. Chem. Res. (2002). , 41-4209.

[86] Pindoria, R. V, Megaritis, A, Herod, A. A, & Kandiyoti, R. A two-stage fixed-bed reactor for direct hydrotreatment of volatiles from the hydropyrolysis of biomass: effect of catalyst temperature, pressure and catalyst ageing time on product characteristics. Fuel, (1998). , 77-1715.

[87] Pindoria, R. V, Lim, J. Y, Hawkes, J. E, Lazaro, M. J, Herod, A. A, & Kandiyoti, R. Structural characterization of biomass pyrolysis tars/oils from eucalyptus wood waste: effect of H-2 pressure and sample configuration. Fuel, (1997). , 1997(76), 1013-1023.

[88] Isayama, Y, & Saka, S. Biodiesel production by supercritical process with crude bio-methanol prepared by wood gasification. Bioresour. Technol., (2008). , 99-4775.

[89] Szybist, J. P, Kirby, S. R, & Boehman, A. L. NO$_x$ emissions of alternative diesel fuels: A comparative analysis of biodiesel and FT diesel. Energy Fuels (2005). , 19-1484.

[90] Walker, K. Biodiesel from rapeseed. J. R. Agric. Soc. Engl. (1994). , 155-43.

[91] Hess, M. A, Haas, M. J, Foglia, T. A, & Marmer, W. N. Effect of antioxidant addition on NOx emissions from biodiesel. Energy Fuels (2005). , 19-1749.

[92] Carioca JOBBiofuels: Problems, challenges and perspectives. Biotechnol. J. (2010). , 5-260.

[93] Mcshane, P. C. Vegetable-oil based dielectric coolants, IEEE Industry Applications Magazine (2002). , 8-34.

[94] Agarwal, A. K. Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines Prog. Energy Combust. Sci. (2007). , 33-233.

[95] Abdullah, A. Z, Razali, N, Mootabadi, H, & Salamatinia, B. Critical technical areas for future improvement in biodiesel technologies. Environ. Res. Lett. (2007).

[96] Haas, M. J. Improving the economics of biodiesel production through the use of low value lipids as feedstocks: vegetable oil soapstock. Fuel Process. Technol., (2005). , 86, 1087-1096.

[97] Wang, Y, Ou, S, Liu, P, Xue, F, & Tang, S. Comparison of two different processes to synthesize biodiesel by waste cooking oil. J. Mol. Catal. A: Chem. (2006). , 252-107.

[98] Dorado, M. P, Cruz, F, Palomar, J. M, & Lopez, F. J. An approach to the economics of two vegetable oil-based biofuels in Spain. Renewable Energy (2006). , 31-1231.

[99] Zang, Y, Dube, M. A, Mclean, D. D, & Kates, M. Biodiesel production from waste cooking oil: 1. Process design and technological assessment. Bioresour. Technol., (2003). , 2003(90), 229-240.