

CHAPTER 2
Literature Review

2.1 Biodiesel

Biodiesel is mixture of fatty acid methyl esters (FAME) which is derived from either plant oils or animal fats [Lin et al., 2011]. Biodiesel is relatively non-toxic as well as biodegradable fuel obtained from various edible oils, non-edible oils and fats [Syazwani et al., 2015] and has quality to be applied as a substitute to diesel fuel [Liaquat et al., 2010]. It possesses many superior qualities such as more efficacies in burning as well as more oxygenated fuel which results in reduction in emissions of carbon dioxide, carbon monoxide, hydrocarbons, GHG and particulate matters [Silitonga et al., 2013] over petroleum diesel. Moreover, it also shows advancement in form of high cetane number, high flash point, high lubricity and low viscosity. Oils or fats derived from plants and animals cannot be utilized directly as a fuel in diesel engine due to its high viscosity and density hence, require chemical treatment to reduce the viscosity, of these materials [Dupont et al., 2009].

2.2 Distant feedstock for biodiesel production

Feedstock used for biodiesel production has been categorized mainly into three categories: first generation, second generation and third generation feedstock which are discussed in this chapter as follows:

2.2.1 First generation feedstock

For low cost production of biodiesel, selection of feedstock is an important criterion. Crops viz. soy beans, sunflower, palm, rapeseed, etc. which were used for the production of biodiesel were included in first generation feedstock. There are many problems arising due to usage of first generation feedstocks for biodiesel production as it

has adverse effects on food security causing crisis for food and with this, cost of biodiesel will automatically be amplified. Fertilized land requirement for cultivation of first generation crops is also one of the considerable issues.

2.2.2 Second generation feedstock

To overcome on the problems due to usage of first generation feedstocks; non-edible feedstock such as Karanja, Jatropha, Jojoba, Waste frying oil, Animal fats, etc. have been developed to reduce dependency on first generation feedstocks. These are known as second generation feedstocks. They reduce the competition between food and fuel. They are more eco-friendly, pose less land requirement and by-products obtained can be used in various processes. They do not affect on food supply and are used for their cultivation in wastelands.

2.2.3 Third generation feedstock

Third generation feedstock is under consideration in recent years, when algae and microalgae have significant concern in biodiesel production. They can be easily cultivated and their reproduction is fast, their yield is more as compared to other feedstocks. Third generation feedstocks generate some valuable by-products and they are capable to fix carbon dioxide in atmosphere, hence, CO₂ levels of atmosphere decrease which are responsible for global distress. However, the processing cost and chances of contamination are the major downsides regarding the use of third generation feedstocks. The details of all these feedstocks have been presented in Table 2.1.

2.3 Selection of feedstock

Biodiesel can be synthesized from edible and non-edible vegetable oils, animal fats and waste cooking oils as discussed above. Selection of feedstock plays a constitutive role

in deciding the cost of biodiesel production. Cost of feedstocks is the major obstacle in commercialization of biodiesel production, since it affects up to 70–95% of total production cost. Appliance of edible oil for biodiesel production raises energy security issues for developing countries and hence, non-edible oil has gained attention in recent years as it lowers production cost up to 60-70% and is environmentally acceptable [Sahoo and Das, 2009].

2.3.1 Waste vegetable oil (WVO)

In recent times, waste vegetable oil (WVO) has also been reported as a potential feedstock material over the other vegetable oil sources [Shu et al., 2010] which improves economic viability of biodiesel. Farooq et al. [2013] reported that cost of biodiesel might be decreased up to 60-70% by utilizing waste vegetable oil as a feedstock which diminishes its disposal problem as well. Many researchers have reported waste vegetable oil as a convenient feedstock for biodiesel production and with this performance, combustion and emission characteristics were also considered [Almeida et al., 2015]. Expenditure of this WVO not only avoids contest of same resource for both food and fuel, but also resolves the problem regarding disposal of WVO.

Waste vegetable oils could be collected from household, food manufacturers and industrial deep fryers, for example, potato processing plants by fast-food establishments, snack food factories, catering industries and restaurants. This large amount of waste vegetable oils will continue to increase with growing rate related to the population growth rate. If recycling is not executed properly, oil wastes lead to clogged drains and rancid odours. In addition to this, extra cost is posed on wastewater treatment facilities. Recycling of this waste vegetable oil is crucial from the environmental perspective to avoid contamination of soil and water resources [Gude et al., 2013]. Hence; utilization of

WVO for biodiesel production avoids these problems.

2.3.2 *Pongamia pinnata* (Karanja) oil

Pongamia pinnata has annual global production of 200 million tons [Kamath et al., 2011]. According to current records, in India 467 lakh hectares wasteland has been recognised by central Govt. throughout the country. On the basis of data obtained from satellite, the ministry has estimated that approximately 3,166 lakh hectares wasteland is available in India. Across the country, overall 57% of total wasteland is available in Tamil Nadu alone [Baka, 2014]. After studying state-wise distribution of wastelands in India, it is observed that in the Jammu and Kashmir state, wasteland availability is up to ~72.75% (percentage of total geographical area). Contribution of remaining states is less than 50%. The state of Himachal Pradesh and Sikkim contributes ~40-50% and other states have inferior wasteland distribution [Source, Dept. of Land resources (GOI)]. This data suggests that these states have ample scope to establish projects based on non-edible oil biodiesel production. Some non-edible plants such as *Jatropha curcas*, *Pongamia pinnata*, Castor, Mahua, Neem, etc. cultivated in those wastelands was used as feedstock for biodiesel production. Among these *Pongamia pinnata* has ability to survive in poor soil conditions as in stony, sandy, clayey and verticals with slight fertilizer. Some parts of this wasteland (10%) can be utilized to cultivate Karanja trees. *Pongamia pinnata* has capability to develop in a short period of time [Sangwan et al., 2010] and with this, it can be grown in minimum rain fall. A *Pongamia pinnata* seed comprises of 27% to 39% oil [Rahman et al., 2011] content which can be easily extractable for biodiesel production. Annual production of *Pongamia pinnata* in India was 55,000 tonnes in the year 2011 and is rising every year, however, only 6% oil is utilized out of total annual production every year [Bobade and Khyade, 2012]. The constituents of Karanja oil viz. furanoflavonols,

furanoflavones, flavones, chromenoflavone, and furanodiketones make the oil non-edible and hence the oil is underutilized. But, occurrence of these constituents makes the oil antifungal and expands its application in medicinal ointments.

There are numerous studies on biodiesel production from Karanja oil as a feedstock. Biodiesel production from *Pongamia pinnata* oil is conducted via esterification followed by transesterification reactions [Verma and Sharma, 2016] or simultaneous esterification and transesterification reactions have been performed [Devi et al., 2014]. Biodiesel Synthesized from *Pongamia pinnata* oil is environmentally feasible and eco-friendly.

2.4 Catalyst selection

There are mainly three types of catalysts; acid, alkali and enzymes which take part in transesterification (Table 2.2) to enhance the rate of reaction [Rawat et al., 2011]. Oil which contains high free fatty acids requires acid catalyst for transesterification process and in this case reaction rate is slow. Usually sulphuric acid, hydrochloric acid and sulphonic acids are used as acid catalyst in transesterification reaction. Use of alkaline catalysts depends on free fatty acid concentration obtained in oil. High free fatty acids in the feedstock are responsible for saponification during alkaline transesterification; hence require pre-treatment of oil or acid esterification. Conversion rate of alkali catalysed transesterification method is high [Ma and Hanna, 1999]. Enzymatic catalysts are also known as biological catalyst [Ghaley et al., 2010]. These are naturally occurring catalysts such as lipase which could be utilised in transesterification process but due to high cost and denaturation at high temperature, appliance of enzyme was not preferred.

2.4.1. Homogenous and heterogeneous catalyst

Generally, homogeneous catalysts (acid/base) are used for biodiesel production via transesterification reaction because of their better catalytic activity [Sharma et al., 2008]. However, separation of homogeneous catalysts from synthesized biodiesel needs washing with large amount of water which also results in the loss of fatty acid methyl esters (FAME), more energy accumulation and produces huge amount of waste water and this increases overall production cost of biodiesel [Lam et al., 2010]. Hence, heterogeneous catalysts are superior since they can be purged by filtration and can be reinvigorated and reused. Numerous studies have been reported on application of supporting materials for biodiesel production in recent years such as oxides [Balsamo et al., 2017], hydrotalcites [Georgogianni et al., 2009], zeolites [Suppes et al., 2004], alumina [Kulkarni et al., 2006; Laosiripojana et al., 2010], silica [Kulkarni et al., 2006; Laosiripojana et al., 2010], zirconia [Singh et al., 2016; Singh et al., 2016] etc. were used efficiently as supporting material in catalyst synthesis. Zeolites have high surface area, unique pore volume as well as high stability which attracted researchers in recent years, but in microporous materials, mass transfer limitation is major drawback [Taguchi and Schutch, 2005] and their high cost makes it unfeasible for biodiesel production. Hence, more efficient, easier preparation, cheaper and environmentally benign heterogeneous catalyst should be used for large scale biodiesel production. In this perspective, zirconia and alumina seem to be the most appropriate substitutes to be used as support for production of biodiesel. There are several zirconia supported catalysts that have been recognised due to their redox properties and amphoteric nature [Wang et al., 2000]. Alkali zirconates have wide applications in carbon dioxide adsorption but still have very petite attention for catalytic use in biodiesel production [Ding et al., 2011]. Application of zirconia as a support material ensued unique interface between support and active

material which may yield superior activity of the synthesized catalyst [Mercera et al., 1991]. Alumina has been most commonly used as adsorbent, catalyst and catalyst support due to its high specific surface area (above $100 \text{ m}^2/\text{g}$). In addition to this, calcium oxide based heterogeneous catalysts have received attention due to their properties such as high basicity, non-toxicity, mild reaction conditions and less impact on environment [Joshi et al., 2015]. Calcium oxide is usually synthesized from raw materials such as limestone and calcite. Calcium oxide (CaO) can be prepared through thermal decomposition of naturally occurring sources such as eggshells [Witoon, 2011], crab shells [Madhu et al., 2016] and waste animal bones [Obadiah et al., 2012], which are rich in calcium carbonate (CaCO_3). It was reported that the use of calcium oxide is economically feasible since the raw materials and reusability of catalyst can decrease the total cost of biodiesel production.

2.5 Production of biodiesel

There are five primary production methodologies for synthesis of biodiesel: direct use or blending method; micro-emulsion; pyrolysis; supercritical methanol and transesterification. Among all these methods, transesterification is advantageous over others due to high viscosity, heavy carbon deposit, incomplete combustion of resultant fuel and expensive equipment used in rest of the methods [Ma and Hanna, 1999]. In transesterification reaction, glycerol obtained as a by-product has numerous applications in industries. A comparison of all techniques was illustrated in Table 2.3. In case of direct use or blending, though vegetable oils are easily available but due to high viscosity of oils, carbon deposition and coking occurs in the reaction. Micro-emulsion also causes carbon deposition and with this, thermal cracking is expensive as compared to other techniques. Supercritical methanol extraction is the method which does not require any kind of catalyst but the method has many problems including expensive equipment and

operating cost etc. [Lin et al., 2011]. Hence transesterification is a preferable technique.

Table 2.3 Comparison of different techniques for biodiesel production. Source: [Ma and Hanna, 1999; Lin et al., 2011].

Direct use and Blending	Availability, portability, heat content and renewability; these are some advantages of using vegetable oil as feedstock; there are some limitations such as high viscosity, deposition of carbon, coking formation and thickening of lubricating oil.
Micro-emulsion	To overcome the difficulty due to viscosity of oil, micro-emulsion is one of the techniques which have been used with solvents like methanol, ethanol, 1-butanol; this is simple process. Deposition of carbon and liquor on the tip of injector is a considerable problem during micro-emulsion. Micro-emulsion is expensive due to high temperature requirement.
Thermal cracking	Thermal cracking or pyrolysis includes simply heating in lack of oxygen supply; with this breaking of chemical bonds is also observed to obtain small molecules. This technique is cost effective and also possibility of production of low value product because less purity of materials.
Supercritical methanol	Without using any kind of catalyst possibility of high conversion in less reaction time; but cost of equipment is more because of high temperature, pressure and energy consumption.
Trans-esterification reaction	Transesterification is also known as alcoholysis, in this oil or fat react with an alcohol to convert into ester and glycerol as a by-product. This process has high efficiency of conversion and low cost.

2.5.1 Trans-esterification reaction

The most frequent method used for biodiesel production is transesterification of the feedstock in presence of alcohol and catalyst (homogeneous or heterogeneous). Transesterification is a facile reaction probably used to reduce viscosity of bio-oils. Feedstocks derived from non-edible oils have high viscosity and are needed to be converted into fatty acid alkyl esters (low molecular weight) compounds [Rawat et al., 2011]. Transesterification is the process which involves multiple step reaction. There are three reversible steps in this process. Conversion takes place from triglycerides into diglycerides and then converted into monoglycerides, finally result into the fatty acid alkyl ester with glycerol as a by-product [Banerjee et al., 2002]. Each step provides one fatty acid alkyl ester which forms three molecules of fatty acid alkyl ester per triglyceride molecules.

Transesterification has been illustrated as simple and efficient method for large scale production of biodiesel [Ghaley et al., 2010]. More supply of alcohol is to be needed to shift equilibrium towards the product side and to enhance the rate of reaction [Singh and Singh, 2010]. Usually methanol and ethanol are used for this chemical reaction but methanol is superior due to its cost as well as chemical and physical advantages over the other [Bisen et al., 2010]. Otherwise also, ethanol itself is a fuel and is not preferred for transesterification.

Table 2.1 Various feedstocks used for biodiesel production

	Examples	Advantages	Disadvantages	References
First generation feedstock	Soyabean Palm, Sunflower, rapeseed, etc.	<ul style="list-style-type: none"> • Synthesis of biodiesel. 	<ul style="list-style-type: none"> • Crises in food market. • Rise in cost of edible oil as well as biodiesel. • Land requirements for cultivation of plant are in large proportion. 	[Celikten et al., 2010; Sumathi et al., 2008; Siler-Marinkovic et al., 1998]
Second generation feedstock	Karanja, Jatropha, Jojoba, Waste frying oil, Animal fat, etc.	<ul style="list-style-type: none"> • Decrease dependency on first generation feedstocks which are edible oil since alternative source of biodiesel. • Wastelands can be used which are not preferred for food crop. 	<ul style="list-style-type: none"> • Not liberal to retribute our total transportation. • Impecunious performance in the frosty temperature. 	[Pramanik, 2003; Canoira et al., 2006; Canakci, 2007; Singh and Singh, 2010]
Third generation feedstock	Microalgae of different species such as Botryococcus Braunii, Chlorella species, Nanochloro-opsis species, etc.	<ul style="list-style-type: none"> • Superior over first and second generation feedstock. • Due to its expeditive reproduction, cultivation is facile, extensive productivity and oil yield. • Does not require specific land for production. It can be grown in salt water, fresh water and in bioreactor which is inappropriate for above two feedstocks. 	<ul style="list-style-type: none"> • Cost for processing is expensive. • There are chances of contamination from bacteria so proper sterile conditions required. • Most algal lipid has lower fuel value than diesel fuel and biodiesel with many poly-unsaturates. 	[Mata et al., 2010; Chisti, 2007]

Table 2.2 Various Homogeneous and heterogeneous catalyst for biodiesel production

Catalyst	Feedstock	Catalyst wt%	Oil: alcohol molar ratio	Reaction temperature	Time (min)	Conversion	References
Homogeneous Acid catalyst							
H ₂ SO ₄	Sunflower oil and Soybean oil	2.5	1:6	60	60	96.6	[Frag et al., 2011]
HCl	Sunflower oil and Soybean oil	2.5	1:6	60	120	87.9	[Frag et al., 2011]
AlCl ₃	Sunflower oil and Soybean oil	2.5	1:6	60	120	87.98	[Frag et al., 2011]
CH ₃ SO ₃ H	Palm fatty acid	0.1	1:3	130	60	91	[Aranda et al., 2007]
H ₃ PO ₄	Palm fatty acid	0.1	1:3	130	60	50	[Aranda et al., 2007]
CH ₃ SO ₃ H	Palm fatty acid	0.1	1:3	130	60	80	[Aranda et al., 2007]
C ₂ HF ₃ O ₂	Soybean oil	2.0	1:20	80	360	98.40	[Miao et al., 2009]
PTSA	Corn oil	4.0	1:10	80	120	97.10	[Guan et al., 2009]
BSA	Corn oil	4.0	1:10	60	480	82	[Guan et al., 2009]
Homogeneous Base catalyst							
NaOH	<i>Pongamia pinnata</i>	0.5	1:9	60	45	89.5	[Sharma and Singh,

							2008]
NaOH	Waste frying oil	0.8	1:6	60	60	95	[Dias et al., 2008]
NaOCH ₃	Duck tallow	1.0	1:6	65	180	83.60	[Chung et al., 2009]
KOH	Sunflower oil	1.0	1:6	60	60	95	[Dias et al., 2008]
TMAH	Cotton seed oil	2.0	1:6	65	120	98	[Karavalakis et al., 2010]
TMG	Waste frying oil	3	1:12	65	90	93.80	[Karavalakis et al., 2011]
TEA	Cotton seed oil	6	1:9	190	180	55.3	[Yao et al., 2010]
Heterogeneous Acid catalyst							
Propyl-SO ₃ H-SBA-15	Palm oil	6	1:20	140	120	72	[Melero et al., 2010]
Amberlyst-36	Palm oil	6	1:20	140	120	32	[Melero et al., 2010]
Sulfated zirconia	Oleic acid	0.50 gm	1:40	60	720	90	[Patel et al., 2013]
Chlorosulfonic zirconia	Oleic acid	3	1:8	100	720	100	[Zhang et al., 2014]
30% WO ₃ /AlPO ₄	Soybean oil	5	1:30	180	300	72.5	[Xie et al., 2012]
Ce/HUSY zeolite	Soybean oil	0.001 mol	1:30	200	1440	99.80	[Borges et al., 2013]
Fe(HSO ₄) ₃	Waste oil	1	1:15	205	240	94.5	[Alhassan et al., 2013]
30% Tungstosilicic acid/zeoliteH β	Oleic acid	100 mg	1:20	60	600	86	[Narkhede and Patel, 2013]

Heterogeneous Base catalyst							
CaO	Rapeseed oil	1	1:26	60	180	90	[Kawashima et al., 2009]
MgO	Canola oil	3	3:20	190	120	82.8	[Jeon et al., 2013]
SrO	Olive oil	5	1:6	65	15	82	[Chen et al., 2012]
K ₃ PO ₄	Fried oil	5	1:6	65	180	78	[Viola et al., 2012]
Li/CaO	Karanja oil	5	1:6	65	60	99	[Kaur and Ali, 2011]
Na/Al ₂ O ₃	Soybean oil	1	1:32	120	360	97.1	[Tonetto and Marchetti, 2010]
Cs/SiO ₂	Canola oil	100 mg	1:40	135	300	25.35	[Kazemian et al., 2013]
MgAlFe hydrotalcite	Soybean oil	3	1:21	65	240	81	[Wang et al., 2012]
β - Ca ₃ (PO ₄) ₂	Soybean oil	1.01	1:6.27	70	300	97.73	[Chakraborty et al., 2011]
Enzyme catalyst							
Immobilized lipase on crystalline PVA	Soybean oil	4	1:6	37	-	66.3	[Bergamasco et al., 2013]