CHAPTER 2

2.1 Introduction

Introduction to green technology has been focused from last two decades but the real boost in its use and research was in this decade with many alternatives to petroleum-based fuels which will be environmentally friendly, economically viable, technologically feasible and readily available. At present, the technology mainly concentrated on green fuels such as hydrogen and other biofuels. Biofuels are generally produced from biomass conversion like production of bio-methane from cellulose [Markou et al., 2013], bioethanol from starch [Bai et al., 2008], conversion of plant oils [Naik et al., 2008] and animal fats [Al-Zuhair et al., 2012] into biodiesel.

2.1.1 First generation biofuels (FGBs):

For production of FGBs, the feedstock are commonly vegetable oils, animal fats, starch or sugar with the help of conventional technology. Starch which is obtain from wheat grain, is fermented in bioethanol and pressing the sunflower seed to yield vegetable oil that can be used in the production of biodiesel. The first generation biofuels have created many drawbacks as they are products that are generally considered as part of a food chain; thus there is diversion of food products to energy feedstock for production of these fuels which results in increase of prices of crops due to rise in demand for non-food feedstock production, which overall hampers economic stability.

2.1.2 Second generation biofuels (SGBs):

In the wake of this second generation or advanced bio fuels are being manufactured from non-food sources. Second generation biofuels also prepared from waste like cellulosic feedstock and non-food oilseeds and plants, agricultural residues and wastes. Cellulose-based ethanol fermentation is the best example; how does it make use of waste products like bagasse, which is made possible by refined techniques and new scientific discoveries.

2.1.3 Third generation biofuels (TGBs):

(TGBs) is also called algal oil or algal fuel. (TGBs) is made from algae using more innovative and advanced technology. This third generation biofuel research is undergoing to locate more potential energy sources than the existing ones, its myriad uses and sustain the existing techniques used for present biofuels.

2.1.4 Fourth generation biofuels:

Fourth generation fuel is coming to attention in recent times. In this generation, biodiesel and vegetable oil is converted into bio-gasoline using the most advanced technology. Biodiesel is emerging more considerable which can prove to be an alternative of diesel. Biodiesel is obtained from vegetable sources, especially non-edible which can be generated locally. As compared with diesel fuel, there is net reduction in exhaust gases such as particulate matter, hydrocarbons and carbon monoxide. Only NO_x emission has been reported in biodiesel emission [Mueller et al., 2009] and oxygen present in the biodiesel is inclined to supply extra oxygen for NO_x formation [Canakci, 2007]. Biodiesel called as “carbon neutral” because of biodiesel producing plant utilize more carbon dioxide from the air during the mechanism of photosynthesis. Many types of vegetable oils are used in the production of biodiesel in different countries. Soybean oil is used as a raw material in the United State for biodiesel production. In European countries, rape seed oil is used for biodiesel production and coconut oil or palm oil is used in tropical countries like Malaysia for the same purpose [Demirbas, 2006].

2.2 Production of biodiesel from different feedstocks

Application of non-edible feedstocks (jatropha , karanja , etc.) could be more commercially viable and more sustainable for biodiesel production in India [Joshi et al., 2015] and non-edible oils such as *Pongamia pinnata*, *Jatropha curcas*, *Madhuca longifolia*, *Azadirachta indica*, *Simarouba glauca,* etc. Table 1.1 depicts some of the feedstocks (edible, non-edible, waste and algae) for the synthesis of biodiesel. Raw oil is obtained by crushing the seeds followed by solvent extraction [Madhu et al., 2016]. Biodiesel synthesis from these non-edible oils required huge land but in India, agriculture land is limited because of tropical region and due this, waste generated from fish industry as raw material has been used in present work to extract oil for biodiesel production. Calorific value of vegetable oil is high due to its high viscosity and low volatility. High viscosity and low volatility inhibits it to burn entirely and forms storage in the fuel injector of diesel engine. Along with these properties, the vegetable oil has limitation in its direct application as fuel. There are many ways to reduce viscosity: embrace microemulsions, catalytic cracking, dilution, pyrolysis and transesterification. Among these processes transesterification is more preferable over other because of easy process and glycerol obtain as by-product, which is a commercial and valuable product [Ramadhas et al., 2005].

2.3 *Pongamia pinnata* oil

Several non-edible plants such as *Jatropha curcas*, *Pongamia pinnata*, *Castor*, *Mohua*, and *Neem* were examined for the synthesis of biodiesel. Among these *Pongamia pinnata* has potential to survive in poor soil circumstances starting from stony to sandy, to clayey, as well as verticals with little fertilizer. *Pongamia pinnata* has ability to grow fast in a short period of time [Sangwan et al., 2010] and can tolerate with minimum rain fall. *Pongamia pinnata* seeds contain 27 % to 39 % oil [Rahman et al., 2011] content which is effortlessly extractable for the production of biodiesel. Annual production of *Pongamia* in India in the year 2011 was 55,000 tonnes [Dwivedi et al., 2011], and increasing year by year but only 6 % *Pongamia pinnata* oil is utilized out of total annual production in each year [Bobade and Khyade, 2012]. Biodiesel synthesis from *Pongamia pinnata* oil via esterification followed by transesterification [Verma et al., 2016b] reactions or simultaneously by both esterification as well as transesterification reactions has been reported [Devi et al., 2014]. Biodiesel yield depends upon the amount of mass transfer during the reaction but in the case of *Pongamia pinnata* oil, the amount of mass transfer for the progress of reaction is high to get high biodiesel yield [Aniya et al., 2015]. Biodiesel has been produced from *Pongamia pinnata* oil with acid [Karmee and Chadha, 2005] or base [Kumar et al., 2011] catalyst as well without catalyst through supercritical methanolysis [Goembira and Saka, 2015; Ortiz-Martínez et al., 2016]. High biodiesel

Table 2.1 Synthesis of biodiesel from different feedstocks

Type of feedstock	Name of feedstock	References
Edible oil	Palm oil	[Indarti, 2016; Verma et al., 2016a].
	Coconut	[Qiu et al., 2016; Woo et al., 2016]
	Sunflower	[Saydut et al., 2016; Vahid and Haghighi, 2016]
	Canola	[Rustandi and Wu, 2010; Yang et al., 2016]
	Peanut	[Likozar and Levec, 2014; Moser, 2012]
	Soybean	[Bashiri and Pourbeiram, 2016; Dai et al., 2014]
	Rapeseed	[Kouzu et al., 2016; Mazanov et al., 2016]
	Rice bran	[Einloft et al., 2007; El Boulifi et al., 2013]
Non edible oil	Castor	[Baskar and Soumiya, 2016; Román-Figueroa et al., 2016]
	Linseed	[Cazarolli et al., 2014; Dixit and Rehman, 2012]
	Jatropha curcas	[Kuo et al., 2015; Nitièma-Yefanova et al., 2016]
	Tobacco	[Usta et al., 2011; Veljković et al., 2006]
	Karanja	[Aniya et al., 2015; Verma and Sharma, 2016]
	Mahua	[Ghadge and Raheman, 2006; Senthil et al., 2016]
	Rubber	[Morshed et al., 2011; Onoji et al., 2016]
	Neem	[Gurunathan and Ravi, 2015; Maran and Priya, 2015]
Waste oil	Used frying oil	[Corro et al., 2016; Singh et al., 2016]
	Fish oil	[de Almeida et al., 2015; García-Moreno et al., 2014]
	Trap Grease	[Aguilar-Garnica et al., 2014; Thompson et al., 2012]
	Tallow	[Adewale et al., 2015; Öner and Altun, 2009]
	Lard	[Sarantopoulos et al., 2014; Stojković et al., 2016]
Algae	Microalgae	[Cho et al., 2016; Mathimani and Nair, 2015]

conversion can be obtain using *Pongamia pinnata* oil [Syamsuddin et al., 2016]. Synthesis of biodiesel from *Pongamia pinnata* oil is environmentally viable and environmentally friendly.

2.4 Waste fish oil

Vegetable oils for biodiesel synthesis do not fit as suitable feedstock due to their expensive and inadequate absence. There is resilient concern to lower the total cost of biodiesel since use of these vegetable oils increase total cost of biodiesel. Food processing industries, especially fish industry generates huge amount fish wastes (fish wastes include, anal fin, pelvic fin, operculum, dorsal fin, caudal fin, overlapping scales, eyes, etc.). It is estimated that one third of world food production is considered as waste which is ultimately discarded [Gustavsson et al., 2011] but according to Food and Agriculture Organization of the United Nations (FAO), stated that 795 million people went undernourished in the year 2014 -2015. This undernourished states of the people may nullified by converting waste produced from total food production into another form of raw material. According FAO, world fisheries and aquaculture production in the year 2014-2015 was 167.2 million tons. Waste generated during the processing of fish is found to be nearly 20% to 50% of the total amount of fish processed and this waste contains nearly 40 % to 60% oil [Arruda et al., 2007]. Fish oil can be extracted from fish waste which is generated from fish industry and used as low cost feedstock for the synthesis of biodiesel [Yahyaee et al., 2013]. Waste fish oil has been used as renewable energy resource for the production of biodiesel since waste fish oil fulfils the same calorific values obtain from the conventional petrodiesel products [Godiganur et al., 2010]. Fish oil can be converted into biodiesel and used as green fuel in diesel engines [Aryee et al., 2009; Blythe, 1996; Lin and Li, 2009b; Preto et al., 2008; Steigers, 2002]. Biodiesel from fish oil in diesel engines reduces the amount of CO emissions compared to other diesel fuels since biodiesel from fish oil contains 11% of oxygen which will help in complete combustion of fuel in diesel engines [Behçet, 2011]. Fish oil extracted from waste parts of fish is environmentally friendly [Lin and Li, 2009a] because it reduces the waste generated from fish industry. Cost of biodiesel is the most important parameter for manufacturer as correlated to other conventional diesel fuels in the market. Cost of biodiesel mainly depends upon the cost of feedstock but use of vegetable oils especially edible oils, increase total cost of biodiesel due to their high price. Use of waste parts of fish from the fish industry as raw material for the fish oil will certainly decrease the total cost of biodiesel and also results in decreased emissions.

2.5 Homogenous and heterogeneous catalyst

In biodiesel production from vegetable oil and animal fat, homogenous as well as heterogeneous catalysts are being used in the transesterification of triglycerides (Table 1.2), short chain alcohol such as methanol and ethanol, both strong acid and strong base can be used as homogenous catalyst. Liquid bases are more commonly used because of their low corrosive nature than liquid acid catalyst, such as sulphuric and sulphonic acid [Tang et al., 2013]. NaOH, KOH and $NaOCH_3$ are commonly used as base homogenous catalysts. These catalyst have many drawback like non-eco-friendly, non-recyclable and ionized form of sodium or potassium contaminates both biodiesel as well as glycerol [Joshi et al., 2015]. Large amount of water is also produce by using homogenous catalyst [Ma and Hanna, 1999]. Therefore, refined feedstock for biodiesel production can be used in case of homogenous catalyst which is uneconomical. To overcome the difficulty with homogenous catalyst, heterogeneous catalyst have better potential especially transestrification of triglyceride for biodiesel production. Heterogeneous catalyst caters more easy separation, no demand of product neutralization and purification, and obtained product is free from catalyst [Semwal et al., 2011; Witoon et al., 2014]. In comparison to homogenous catalysts, heterogeneous catalysts make the biodiesel production more economical due to reusability and less consumption [Di Serio et al., 2007; Dossin et al., 2006]. Significant number of heterogeneous solid acid and base catalyst have been studied for biodiesel production which comprise of zeolites, sodium aluminates, heteropolyacid ion exchange resins and metal catalyst, alkali impregnated alumina, alkali earth metal oxide, hydrotalcites, Al_2O_3-supported alkali metal oxide catalyst, KF/γ-Al_2O_3 [Shahraki et al., 2015], etc. Presently, calcium oxide based heterogeneous catalysts have received attention because of their non-toxicity, high basicity, lower leaching properties, mild reaction condition, less impact on environment, sterling yield of biodiesel production and its very low solubility in biodiesel [Joshi et al., 2015; Witoon et al., 2014]. Research has been flourished towards the biodiesel production employing economic and natural calcium carbonate sources like Meretrix venus , waste shells of egg [Correia et al., 2014; Sharma et al., 2010; Wei et al., 2009], oyster shell [Nakatani et al., 2009], mud crab [Boey et al., 2009] and golden apple snail [Agrawal et al., 2012]. Calcium oxide is generally prepared from different 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 [Boey et al., 2009; Boey et al., 2011b; Madhu et al., 2016] and coral sand [Chou et al., 2007], which are rich in calcium carbonate ($CaCO_3$). It was reported that the calcium oxide used as solid base catalyst for the synthesis of biodiesel [Kouzu et al., 2009] is economically viable since the raw materials as well as reusability of catalyst can reduce the total cost of biodiesel production. High biodiesel yield was obtained at optimum reaction conditions by using calcium oxide catalyst [Kouzu et al., 2008]. β-Tri calcium phosphate ($Ca_3(PO_4)_2$ catalyst was synthesized from fish waste [Boutinguiza et al., 2012] through thermal decomposition. β-tri calcium phosphate ($Ca_3(PO_4)_2$ catalyst has shown a high-performance and reusability for synthesis of biodiesel [Chakraborty et al., 2015]. It is basic in nature and previous studies reported that the β-Tri calcium phosphate ($Ca_3(PO_4)_2$ is thermally stable at high temperatures and retains catalytic activity for six consecutive 5-hour runs [Chakraborty et al., 2011]. It was reported that the low-cost β-tri calcium phosphate catalyst produced high biodiesel yield at moderately or lower catalyst concentration and alcohol to oil molar ratio [Farooq et al., 2015; Madhu et al., 2014].