An Overview of Biofuel

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Chapter 1
An Overview of Biofuel

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Abstract Fossil fuels applications are linked with current widely held environmental issues. The decline of these fuels resources with environmental penalties has compelled for substitutes and usage of renewable biofuel as energy sources; has gained a significant importance in last two decades. Production of biodiesel, biogas and bioethanol from various feedstock, several kinds of wastes, many types of biomass and agricultural residues, is ecological viable and sustainable option. The involvement of biofuel in worldwide transportation fuels seems to be revolving about 5% over the next decade. But, many studies put forward that biofuel may share up to a one fourth of transport fuel supplies by 2050. In the first part of the chapter, advantages and applications of mostly used biofuel is presented. The second part of the chapter keeps concepts about biodiesel. Biogas production and composition has been addressed in third portion. Finally, the production of bioethanol from different feedstock has been discussed. Instability of fossil fuels prices in last decade and environment concerns has increased biofuel production many folds. Such a fast growth has been resulted controversial and raised some concerns over potential water use in production of biofuel.

Keywords Global warming · Biofuel · Bioethanol · Biodiesel · Biogas

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1.1 Introduction

Presently, three major issues are in front of human beings: hunger, the lack of energy and the deterioration of the environment (Popp et al. 2014). It is obligatory to fight with all the three vehemence simultaneously, because any one of these is capable to extinct out our civilization (Escobar et al. 2009). The ease of access to energy is the basic driving force behind the socio-economic progress and the vital element to sustain human's current elevated standard of living (Walker et al. 2016; Arshad and Ahmed 2016). Globally consumption of energy has been almost doubled up in recent times (Bentley 2016) and fossil fuels share more than 80% (Pfenninger and Keirstead 2015). When we talk about energy, it is clear to each and every person that its saving is the best attitude to be privileged by minimizing irrational use and enhancing the utilization efficiency (Abdmouleh et al. 2015) as fossil fuel reservoirs are depleting fast (Hook et al. 2014). Up till now human's energy requirements has been met by the fossil fuels (coal; oil; gas) since many decades. Alternative cheap and environment friendly energy is the hot issue in today's world. Fossil fuels account for over 80.3% of the primary energy consumed in the world, and 57.7% of that amount is used in the transport sector (Escobar et al. 2009). Burning of conventional fuels results in the harmful emissions of greenhouse gases such as carbon dioxide (CO_2), nitrogen oxide (NO_x), volatile organic compounds (VOC) and hydrocarbons (HC); incremental for the climate changes (Chavez-Baeza and Sheinbaum-Pardo 2014; Friedlingstein et al. 2014; Reuter et al. 2014). Although such fuels give the best cost/benefit ratio; but at the same damage the environment. Fossil based diesel is an essential fuel for running vehicles, power plants and motor engines in the transportation, agricultural and industrial sectors (Emanuel and Gomes 2014; Orsi et al. 2016) and remained the most merchandising commodity among primary products trade in 2010 (Janaun and Ellis 2010). Transportation sector spent more than 30% of the energy supply globally, in which above 80% is by the road transport (Holmberg and Erdemir 2015). Worldwide almost 60% oil supply is consumed by this sector (Bilgen 2014), practically operating on gasoline, diesel oil almost 97.6%, with a small amount from liquid natural gas (Ramadhas et al. 2004; Murphy et al. 2013).

Now the world has been challenged by global warming problem (IPCC 2014). The release of Carbon dioxide from the combustion of fossil fuels, the key contributor to the process has generated the interest in promoting biofuel as one of the leading renewable energy sources (Kumar et al. 2013). Table 1.1 shows the major benefits of the biofuel. The sustainable production of biofuel is a valuable tool in stemming climate change (Creutzig et al. 2015), boosting local economies, particularly in lesser-developed parts of the world (van Eijck et al. 2014a; van Eijck et al. 2014b), and enhancing energy security for all (Jatrofuels 2012; Hughes et al. 2014). Advancement in renewable biofuel sources; cling to solution key of the dual difficulties, running down the fossil fuel reservoirs and environmental pollution (Smith 2013). Therefore, exploration of novel, renewable, environment friendly, clean, reliable and economically feasible energy resources is serious requisite of the

Table 1.1 Major benefits of biofuels (Balat 2011a, b)

Commercial value	Variety in fuel mix More sustainable Ability to create many rural jobs Can increased the government revenue through taxes Industrial investments (plant and equipment) will be increased Farming/agricultural sector can be developed Less international competition Independence from imported petroleum
Climate change effects	Reduction in release of greenhouse gases Air pollution can be minimized Easy for biodegradation Better combustion efficiency Better carbon sequestration
Indigenous impacts	To achieve the domestic targets More reliability in supply Reduced utilization of fossil oils Ready availability Indigenous distribution

day (Dale et al. 2014). The discharge of greenhouse gases through the burning of fossil fuels in transport sector alters the natural equilibrium of environment. The world has now started to realize the problem and syndromes created by conventional fuels (Karwat et al. 2014). To minimize the fossil fuels role, the exploration of renewable substitutes, the biofuel like bioethanol, biogas and biodiesel are on rise (Ho et al. 2014). Biofuel, biodiesel, biogas and bioethanol are currently available in the market, already being used for various types of engines (Prasad et al. 2007; Demirbas 2008; Janaun and Ellis 2010; Shahid and Jamal 2011; Geczi et al. 2015; Malakhova et al. 2015; Choudhary et al. 2017).

The "bio" in biofuel refers to crop and wood-based raw materials such as molasses, rice husks, corn and wood waste, which are processed into fuel. For developed countries, biofuel offer prospects for meeting their emission reduction commitments under the Kyoto Protocol (de Alegría et al. 2016). For developing countries, biofuel present a means to both reduce energy import bills as well as earn precious foreign exchange (Khan 2007). Biofuel are produced from bio-origin resources by thermochemical processes (Liu et al. 2008; Balat et al. 2009; De Kam et al. 2009; Alonso et al. 2010; Sims et al. 2010; Ertas and Alma 2011) and biochemical process (Amin 2009; Uddin et al. 2016; Shukla et al. 2017). Biomass is reformed in thermo-chemical catalytic and non-catalytic processes such as pyrolysis, gasification, liquefaction, supercritical fluid extraction, supercritical water liquefaction to produce maximum energetic exploitable liquid and gaseous products. Biofuel include bioethanol, biodiesel and biogas produced through biochemical path ways such as, alcoholic fermentation, anaerobic fermentation and trans-esterification (Balat 2011a). Trans-esterification of vegetable oils, animal fats, waste oils/fats, used oils/fats and microbial oils with methanol and to some extent with ethanol/butanol results in biodiesel production (Hoekman et al. 2012; Arshad et al. 2014a). In spite of the constant requirement of biodiesel production, the lack of oil's feedstock have become problematic and decrease the production of first generation biodiesel as there was an almost two-fold increase in the price of conventional plant oils (Choi et al. 2010). The reply was production of biodiesel from "non-conventional oils" and with the aid of microorganisms capable of producing intracellular lipids (Koberg et al. 2011) called as second generation biodiesel. The third generation biodiesel is derived through atmospheric CO_2 sequestration (Thiyagarajan et al. 2017; Bhola et al. 2014).

Worldwide ethanol production is based upon petrochemical and biochemical methods (Van Uytvanck et al. 2014). In the petrochemical method ethylene is hydrated in the presence of mineral acids (Ren et al. 2015). The process is much attractive, if the price of raw material remains low. But price comparison between ethanol and ethylene, has displaced the method almost completely by the processes depending on the treatment of biomass (Haro et al. 2013). Ethanol fermentation of the glucose is the oldest technique and also used to produce alcoholic beverages (Majchrowicz 2013). Agricultural based stuffs containing sugar, starch, and cellulose are employed as raw material (Rothman et al. 2015). Normally the fermentation process by the yeasts occurs at room temperature, anaerobically (Mielenz 2014). The general equation of the process is represented as,

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$

There arise two molecules of CO_2 and ethanol for each molecule of the glucose fermented (Sarris and Papanikolaou 2016). Industrial alcoholic fermentation process normally halts as ethanol concentration approaches at 9–10% (Dai et al. 2014) participating yeasts can be used in subsequent cycles of fermentation (Stanbury et al. 2013). The ethanol yield from glucose is 88–95% (Luterbacher et al. 2014) with some byproducts such as glycerin (3–5%) and acetic acid etc. (Onuki et al. 2016). Fermented mash is distilled (Borse and Sheth 2017) to increase the ethanol concentration up to 94% (Mayer et al. 2015), bring it to the required marketability (Duffield et al. 2015). Resultant bioethanol can be further purified through dehydration process (Vázquez-Ojeda et al. 2013). Bioethanol in both forms hydrated and dehydrated (also called absolute alcohol) is used as fuel in pure or blended with gasoline (Foong et al. 2014). The production of bioethanol is accompanied by serious economic and environmental benefits (Maroun and La Rovere 2014), since ethanol as a fuel presents a high octane number (Leone et al. 2014), while even small amounts of ethanol added into the gasoline can significantly increase the octane number of the blend (Foong et al. 2014). Moreover, the higher oxygen content improves the efficiency of the combustion (Rakopoulos et al. 2014). Also green house gas emissions are generally considered to be reduced as ethanol burns results in lower emission of carbon monoxide (CO), volatile organic compounds, sulfur oxides, etc. in comparison with the burn of the typical fossil fuels (Dwivedi et al. 2015).

Biogas is another mostly used fuel and its significance as renewal biofuel is well recognized (Lee et al. 2014). It is produced during anaerobic digestion of biodegradable organic materials (Ariunbaatar et al. 2014) and typically keeps approximately 60–65% methane (Divya et al. 2015). It can be used to offset part of the energy requirement (Rahman et al. 2014). Biogas production, collection and utilization methods have been gradually competent to improve the quality (Havukainen et al. 2014). Energy recovery from biogas is developing into a successful “waste/residues to bioenergy” technology (Gonzalez-Salazar et al. 2016). Biogas is commonly used as fuel in the boilers, employed in combined heat and power applications to electricity generation and to make steam (Wellinger et al. 2013; Poschl et al. 2010). Overall efficiency of biogas use can approach 80% if all the recovered heat is used. The quantity and quality of gas produced during anaerobic digestion depends on the feed characteristics. Several methods are available to estimate methane generation from a waste stream during anaerobic digestion. Knowing the chemical composition of the waste stream, the methane production can be estimated (El-Mashad and Zhang 2010).

1.2 Global Interest in Biofuel

Biofuel have been well thought-out as supplement to fossil fuels for transportation since the oil crises of 1973 and 1979 (Kalam and Masjuki 2002). Attention toward biofuel has been resurged in the early 2000s due to heavy distresses about climate change, depleting fossil oil reserves with fluctuations in price (Fogel 2007). More than 40 countries have formulated their national policies to sustenance the biofuel (Timilsina 2014). Table 1.2 shows the list of the countries that have set their targets for the biofuel. Current fascinating biofuel production has burst an aggressive talk, whether to support the policies and programs about biofuel production or not. Because at one end the biofuel are promoted as a solution to climate change issues and setting up better energy supply globally (Headey and Fan 2008; Tilman et al. 2009; Lynd and Woods 2011) while, at the other end, it is indicated that these are a risk to food supply with stress on water supply on earth (Diouf 2007; Pimentel et al. 2009; Borras et al. 2010). Claims for reduction in green house gases discharge, (the basic argue to support biofuel) have also been challenged (Searchinger et al. 2008; Danielsen et al. 2009). Such discussions have lessened the earlier enthusiastic support to biofuel.

1.2.1 Different Types of Biofuel Today

From a long list of biofuel only biodiesel, bioethanol and biogas are presently produced as a fuel on an industrial scale (Antoni et al. 2007). These fuels make up to more than 90% of the biofuel market (Demirbas 2009c, d). All biofuel have to exhibit defined chemical and physical properties, meeting the demands of engine application such as stability and predictable combustion at high pressures as well as the demands of transportation such as safety and energy density. Table 1.3 shows

Table 1.2 Liquid biofuels mandates and targets of selected countries globally (Arshad 2010)

Country	Ethanol	Biodiesel
Australia	E6	B2
Argentina	E5	B7
Belgium	E4	B4
Bolivia	E10	B20 by 2015
Brazil	E18-E25	B5
Canada	E5	B2
China	E10	
Colombia	E10	B20
Costa Rica	E7	B20
Dominican Republic	E15	B2
EU	10% renewable in transport (2020)	
Ethiopia	E10	
Finland	E5.75	B5.75
Germany	E10	
India	E5; E20 (2017)	B20 (2017)
Indonesia	E15	B20
Italy	E5	B5
Jamaica	E10	B5
Malaysia		B5
Malawi	E20	
Mozambique	E10	B5
Te Netherland	E4	B4
Norway		B3.5
Pakistan		B5
Panama	E10	
Paraguay	E18-E24	B5
Peru	E7.8	B5
Philippines	E10	B2
South Africa	2% of transport energy	
South Korea		B2.5
Thailand	E10	B3

various gaseous and liquid biofuel. Liquid biofuel can be stored, distributed, carried and used as an energy source in cars, trucks, trains and planes without any difficulty (Nigam and Singh 2011). Biogas is gaseous in nature and somewhat difficult to transport. It requires a separate distribution infrastructure to be developed.

Liquid biofuel have to remain in a liquid state and pumpable at all temperatures encountered. Further requirements on liquid biofuel are a high heat of combustion value to reduce energy losses and costs during transportation and stability during storage. Some longer chain alcohols like butanol have a heat of combustion sufficiently high to allow for their use in high thrust-to-weight applications such as

Table 1.3 The biofuels with possible production route, their use and the applications to engines (Antoni et al. 2007)

Biofuel	Process	Status	Engine application
Biomethanol	Thermochemical/microbial	Pilot plant	[pure/blend] MTBE/biodiesel
Bioethanol	Microbial	Industrial	Pure/blend
Biobutanol	Microbial	Pilot plant/Industrial	Pure/blend
ETBE	Chemical/Microbial	Industrial	blend
Biomethane	Microbial	Industrial	Pure/blend
Biohydrogen	Microbial	Laboratory	Pure/blend
Pure biodiesel	Physical/chemical (enzymatic)	Industrial (laboratory)	Pure/blend

airplanes (Yanai et al. 2015). Safe and environment friendly storage, vapour pressure and ignition temperature are important factors.

1.2.2 *Economics of Biofuel*

The economics of biofuel is majorly determined by the value of the feedstock used for their production (Elbehri et al. 2013). For first-generation biofuel raw material price accounts approximately between 60 and 90% of the total production (Ho et al. 2014; Tan et al. 2013). The price competitiveness of biofuel to petroleum counterparts varies between countries and with the feedstock used (Wesseler and Drabik 2016). The “factory gate” price of Brazilian ethanol remained lesser than the “refinery gate” price of gasoline in last decade (Onal and Nunez 2014). Both Brazilian and US ethanol remains expensive than gasoline on an energy equivalent basis. Sugarcane derived Brazilian ethanol is better competitive than US ethanol, but is still usually more expensive than gasoline. In case of biodiesel, it is more expensive than diesel, even though a liter of biodiesel provides around 14% less mileage than diesel. While the biogas is much completive due to unavailability of natural gas everywhere (Alam and Hasan 2017).

Brazilian ethanol production cost remains lower than for US corn or European wheat ethanol, due to use of sugarcane bagasse in boilers; to come across on site steam and power demand. Moreover the production of biogas and its utilization in electricity can further lower the production cost. Ethanol production cost from wheat grains can be lowered if the impact value of by-products is considered. Likewise, biodiesel production cost will be fall, if main byproduct, glycerin can fetch a market value, which is utilized in the beverages, food and pharmaceuticals industries (Jonker et al. 2015; Losordo et al. 2016). To produce ethanol from sugarcane molasses is cheaper than from sugarcane itself (Castañeda-Ayarza and

Cortez 2016). Biodiesel from non-food seeds like jatropha largess an interesting, alternative if yields can be improved to commercial level sand if sufficient low-cost labour can be assembled for the highly labour intensive seed collection process (Carriquiry et al. 2011). The capital costs of second-generation biofuel account for a higher portion, while the feedstock costs are significantly lower as compared to first-generation biofuel (van Eijck et al. 2014). Overall production costs from micro-algae appear to be higher presently, but could fall in the future as well as technology improves and production expands (Kern et al. 2017).

Biofuel, like fossil fuels, come in a number of forms and meet a number of different energy needs. The present book chapter is an introduction of the major globally used biofuel, biodiesel, bioethanol and biogas. Each type of the biofuel has been explained well.

1.3 Biodiesel

Biodiesel is a mono-alkyl ester of fatty acids from vegetable oil and is presently produced by catalytically trans-esterification process with petro-chemically derived methanol (Ma and Hanna 1999). The glycerol produced during trans-esterification creates a deposit problem in some areas. It could be fermented, e.g. to 1,3-propanediol and possibly to other products by metabolically engineered bacteria (Calero et al. 2015) or to methane in biogas plants where it can be added in low concentrations as co-substrate. Instead of using vegetable oil, microalgae could be grown in photo-bioreactors for the production of suitable oil. Because of their high oil productivity, the specific demand of land area needed is strongly reduced by this concept in contrast to oil from plants (Chisti 2007). Mono-alkyl esters of long chain fatty acids originated from renewable lipid sources such as plant oils, animal fats or algal sources for use in compression ignition (diesel) engines" are called as biodiesel (Kafuku and Mbarawa 2010; Satyanarayana and Muraleedharan 2011; Shahid and Jamal 2011; Ghazali et al. 2015). Biodiesel can be superior replacer of conventional diesel as it based on oxygenated esters of long chain fatty (Ong et al. 2011; Hoekman et al. 2012).

Global warming issue can be well managed with the use of biodiesel in transportation sector. Biodiesel is highly biodegradable (Hossain and AlEissa 2016) and has minimal toxicity and its ignition in diesel engines can withdraws the total unburned hydrocarbons (HC) and polycyclic aromatic hydrocarbons (PAHs) (Hoekman and Robbins 2012). İt can replace diesel fuel use in boilers and internal combustion engines without major modifications (Bergthorson and Thomson 2015) and can significantly reduce the particulate matter and carbon monoxide emission (Basha et al. 2009). Emissions of sulphates, aromatic compounds and other chemical substances, that are destructive to the environment are almost zero (Popovicheva et al. 2015). High flash point, better lubrication, and high Ocetane number with very close physical and chemical characteristics to those of fossil diesel (Rashedul et al. 2015) allow its application as pure biodiesel, B100 or may be blended with fossil diesel fuel with minute technical adjustments (Basumatary 2015). Wolrdwide many countries such as Malaysia, United States of America, Brazil, Germany and many other European states are using it due to its potential for better safeguard the environment from hazards emissions and protect the human health from potential or probable threats (Canakci et al. 2009; Cremonez et al. 2015; Johari et al. 2015; Knothe et al. 2015; Eryilmaz et al. 2016; Tsoutsos et al. 2016).

1.3.1 Biodiesel Feedstock

The wide range of feedstock for biodiesel production is available to sustain newly emerging biodiesel industry. The availability of feedstock depends upon some factors such as climate of the region, geographical locations, soil conditions and agricultural practices of a country. Worldwide, more than 350 oil crops have been identified as potential sources of biodiesel production (Bart et al. 2010). Presence of oil percent and the yield per hectare are important parameters in feestock selection. (Atabani et al. 2012; Tabatabaei et al. 2015) have reported estimated oil content and yields of many biodiesel feedstock. Oil composition, type and ratio of fatty acids present impact the fitness of oil as a raw material for biodiesel production (Basumatary 2015). Alone feedstock denote 75% of the overall biodiesel production cost (Ahmad et al. 2011; Atabaniet al. 2012). So, selection of the cheapest feedstock is vital to reduce cost of biodiesel production cost. Generally, feedstock of biodiesel production are classified into four major categories (Satyanarayana and Muraleedharan 2011):

A. Edible plant oils
B. Non-edible plant oils
C. Waste or recycled oils
D. Animal and poultry fats

Some non-edible and edible oil sources used for biodiesel production have been shown in Table 1.4. Applications of edible oils have generated lots of concerns such as food versus fuel debate, creation of serious environmental problems such as grave destruction to soils, deforestation and consumption of arable land/water (Balat and Balat 2010; Balat 2011b; Deng et al. 2011). Edible oils become un-feasible in the long term because of the expected growing gap between supply and demand of such oils (Chapagain et al. 2009).

Non-edible oils can reduce the utilization of the edible oil for biodiesel production. Non-edible oil resources are easily available in many parts of the world especially wastelands that are not suitable for food crops, eliminate competition for food, reduce deforestation rate, more environmentally friend, produce useful by-products and they are very economical as compared to edible oils (Sarma et al. 2005; Chhetri et al. 2008; Gui et al. 2008; Murugesan et al. 2009; Sarin et al. 2009;

Table 1.4 Some non-edible and edible oil sources used for biodiesel production

Source	Oil yield (kg oil/ha)	Oil yield (wt%)	References
Non-edible oil			
Jatropha	1590	Seed: 35–40 Kernel: 50–60	Gui et al. (2008)
Rubber seed	80–120	40–50	Ramadhas et al. (2005)
Castor	1188	53	Saka (2005)
Pongamiapinnata	225–2250	30–40	Karmee and Chadha (2005)
Edible oil			
Soybean	375	20	Gui et al. (2008)
Palm	5000	20	Berchmans and Hirata (2008)
Rapeseed	1000	37–50	Westbrook et al. (2011)

Table 1.5 Some animal sources of fat and their fatty acid compositions

% (By weight)	Beef tallow[a]	Chicken fat[b]	Pork lard[c]	Mutton fat[d]
Lauric acid (C12:0)	–	–	–	0.2
Myristic acid (C14:0)	2.72	0.5	1.7	3
Palmitic acid (C16:0)	25.3	24	23.2	27
Palmitoleic acid (C16:1)	2.02	5.8	2.7	2
Stearic acid (C18:0)	34.7	5.8	10.4	24.1
Oleic acid (C18:1)	29.87	38.2	42.8	40.7
Linoleic acid (C18:2)	0.75	23.8	19.1	2
Linolenic acid (C18:3)	–	1.9	64.7	–

[a]Ma and Hanna (1999), [b]Wyatt et al. (2005), [c]Dias et al. (2008), [d]Mutreja et al. (2011)

Saravanan et al. 2010; Falasca et al. 2010; Kumar and Sharma 2011; Atabani et al. 2012; Banković-Ilić et al. 2012; Mofijur et al. 2013; Shirazi, et al. 2014; Haile 2014; Zhang et al. 2015). Table 1.5 shows some fat sources of animal origion with relevant fatty acid composition.

Microalgae have emerged as third generation biodiesel feedstock. These are photosynthetic microbes capable to convert sunlight, water and CO_2 to algal biomass, more efficiently as compared to conventional crops. High oil content, better growth rates and productivity as compared to edible and non-edible feedstock make microalgae as promising feedstock. Table 1.6 shows micro algal strains keeping various quantities of oils that can be further processed to produce biodiesel. Up to 25 times higher yields than oil palm and 250 times than soybeans is achieved through the algal cultivations (Sharma and Singh 2009; Singh and Singh 2010; Ahmad et al. 2011).

Table 1.6 Some microalgal strains capable for biodiesel production keeping oil contents (% dry wt)

Microalga	Oil content	References
Botryococcus braunii	25–75	Metzger and Largeau (2005)
Chlorella sp.	28–32	Li et al. (2015)
Crypthecodiniumcohnii	20	Brennan and Owende (2010)
Cylindrotheca sp.	16–37	Meng et al. (2009)
Isochrysis sp.	25–33	Renaud et al. (1991)
Monallanthussalina N	20	Mata et al. (2010)
Nannochloris sp.	25–35	Gouveia and Oliveira (2009)
Nannochloropsis sp.	31–68	Brown et al. (2010)
Neochlorisoleoabundans	35–54	Popovich et al. (2012)
Nitzschia sp.	45–47	Demirbas and Demirbas (2011)
Schizochytrium sp.	50–77	Ratledge (2004)

1.3.2 Biodiesel Production Technologies

In last decade, biodiesel production is gone through fast technological improvements in industries and academia. Higher production cost is the major drawback in its commercialization. Various studies on the economic improvement of technologies and methods have been conducted in search of optimal conditions of biodiesel production. The primary methods to make biodiesel are direct use and blending of vegetable oils, micro-emulsions, thermal cracking (pyrolysis) and trans-esterification (Ma and Hanna 1999). Trans-esterification process is the most common method used in the biodiesel industry, in which vegetable oil or animal fat and an alcohol (methanol, ethanol) react in the presence of a catalyst or without the use of catalysts (Demirbas 2009a).

1.3.2.1 Direct Use and Blending of Oils

Application of vegetable oils as fuels stems around since 1900 when Dr. Rudolph Diesel, firstly experienced Peanuts oil in his newly invented compression engine. The direct applications of vegetable oils as fuel are problematic and have many weak spots in diesel engines. Although it's being researched comprehensively for the previous few decades, but experimentation started for about hundred years. Vegetable oils may be blended with diesel fuels to better the viscosity so as to make solution of the problems linked with the use of pure vegetable oils (Koh and Ghazi 2011). Blending ratios of 1:10 to 2:10 vegetable oil to diesel fuel have been found to be better rather than direct use of vegetable oils. Increased thickness due to high viscosity, presence of acid components, higher free fatty acids ratio, with the gum formation are some apparent teething troubles (Ma and Hanna 1999).

1.3.2.2 Micro-Emulsion of Oils

The formation of microemulsions is a potential solution for resolving the problematic high vegetable oil viscosity issue. A colloidal equilibrium dispersion that is clear, stable with three components: an oil phase, an aqueous phase and a surfactant, of optically isotropic fluid microstructures with dimensions generally in the 1–150 nm range formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphiles (Fernandes et al. 2012) is called micro-emulsion. Such fuels are also called "hybrid fuels" (Satyanarayana and Muraleedharan 2009).

The solvents like methanol, ethanol and 1-butanol have been studied and micro-emulsions with butanol, hexanol and octanol can meet the maximum viscosity limitation for diesel engines (Oner and Altun 2009).

1.3.2.3 Pyrolysis of Oils

Conversion of one organic compound into some other substance using heat with or without presence of a catalyst is called pyrolysis. Vegetable oil, animal fats, natural fatty acids or methyl esters of fatty acids can be subjected to pyrolysis (Yusuf et al. 2011). Thermal cracking of triacylglycerol's is much promising method for biodiesel production as it is very similar to petroleum refining (Maher and Bressler 2007). Liquid product fractions resulted through thermal decomposition of vegetable oils are closely approaching to characteristics of fossil diesel oil and reported as suitable for diesel engines. Pyrolysis process can further divided into catalytic and non-catalytic processes (Leung et al. 2010). Equipment/machinery used for pyrolysis and thermal cracking is much expensive (Ma and Hanna 1999).

1.3.2.4 Trans-Esterification of Oils

The most used method for biodiesel production is trans-esterification of oils with alcohol (methanol or butanol). Glycerin is major byproduct of this reaction. In the first step, the triglycerides are changed into diglycerides, and diglycerides are converted to monoglycerides and glycerol, yielding one methyl ester molecule from each glyceride at each step (Ma and Hanna 1999). Most important process variables are temperature, time, proportion of alcohol to oil, catalyst concentration, mixing force (RPM) and type of feedstock used (Marchetti et al. 2007). As alcohols and triglycerides are immiscible to generate a mixture of single phase, therefore surface contact between these two reactants remains very low and causes the trans-esterification reaction to proceed relatively slow. Presence of a catalysts makes the surface contact better among the reactants; thus speed-up the reaction. Henceforth, the researchers have been exploring alternatives that can solve the problems (Demirbas 2009b).

Catalytic biodiesel production The oils are transesterified by warming them with an alcohol and a catalyst. If the catalyst remains in the same phase in which reactants (liquid phase) throughout trans-esterification process, it is called as homogeneous catalyst. When the catalyst remains in different phase to that of the reactants, then it is called as heterogeneous catalyst (Zabeti et al. 2009). Application of the appropriate catalyst is the vital to lower the biodiesel production cost. Presently, commercial biodiesel is prepared by using homogenous catalyst. (Ragit et al. 2011).

Homogeneous catalytic transestrification The homogenous catalysts used in transesterification reactions are classified into basic and acidic catalysts. Basic type catalysts used transestrification processes needs a very high purity of raw materials with post reaction separation of catalyst, byproduct, and product. These conditions increase the cost of biodiesel.

Heterogeneous catalytic trans-esterification Heterogeneous catalysts act in a different phase from the reaction mixture in such type of trans-esterification. The catalysts can be easily separate and reuse. Moreover use of heterogeneous catalyst does not yield soap (Leu 2013). The heterogeneous catalytic systems of trans-esterification put forward the exclusion of different steps like washing, separation of biodiesel and catalyst. Higher efficiency with better profitability is the key features of the process.

Non-catalytic biodiesel production There are only two trans-esterification processes in which no catalyst is employed. These are supercritical alcohol process and BIOX process.

Supercritical alcohol trans-esterification In supercritical alcohol method, instead of using catalysts, high pressure and temperature are applied to do the trans-esterification reaction. Reaction becomes faster and conversion just occurs in (50–95%) the first 10 min. The required temperature ranges from 250 to 400 °C (Meher et al. 2006; Teo et al. 2014).

BIOX co-solvent trans-esterification As the oils are not well soluble in alcohols, so the rate of trans-esterification remains very slow. To solve the issue, another tactic is being used in form of co-solvent which can solve both. Tetrahydrofuran, has a boiling point much closer to methanol can solve the issue (Kusdiana and Saka 2004).

1.3.3 Microdiesel

E. coli cells were metabolically engineered by introducing the pyruvate decarboxylase and alcohol dehydrogenase genes pdc and adhB, respectively, from *Zymomonas mobilis* for abundant ethanol production. The gene atfA for an unspecific acyltransferase from *Acinetobacter baylyi* was introduced to esterify ethanol with the acyl moieties of CoA thioesters of fatty acids. If the cells are grown aerobically in the presence of glucose as an energy and carbon source and of oleic acid, ethyl oleate was the major product. However, de novo synthesized fatty acids were not used by the acyl transferase, which made the external addition of fatty acids necessary. This indicates that considerable further development is needed. However, a new concept of the microbiological production of biodiesel has been shown with these experiments (Barney 2014).

Conversion of plant oil to biodiesel is a mature technology. However, microbial contribution to the production process is close to zero at present. Inclusion of biologically fermented ethanol and butanol will not pose technical problems. The use of enzymes or biological systems in trans-esterification is to be developed. Most diesel cars are now licensed to use a biodiesel diesel blend of up to 5% (v/v). The conversion of a conventional diesel engine for pure biodiesel use is offered by many companies and costs in Germany up to 1,500€ per car. The modified engine, however, requires more frequent engine oil changes.

1.4 Biogas

The world is progressively more looking for the imperative nature of sustainable development due to environmental concerns caused by the burning of fossil fuels. Therefore joint research on energy and environment is growing day by day, in both R&D and technology implementation level. Microbes convert organic matter into biogas through a natural process called anaerobic digestion. The process naturally occurs in marshes, landfills, wetlands, and also in the digestive tract of ruminants. It is quite possible to collect biogas and can easily be utilized as an energy resource. It can also yield valuable industrial products or byproducts. The value of biogas has been risen up due to two causes: (i) for the reason that its liberation into the atmosphere contributes principally to increase greenhouse gas volume (ii) its energetic contents are high, so those make it valuable.

Biogas plants produce methane gas sustainably along with carbon dioxide from plant biomass, which may come from organic household or industrial waste or from specially grown energy plants (Divya et al. 2015; Mao et al. 2015). The general composition of biogas and value of its components has been shown in Table 1.7. The advantage of the biogas process is the option to use the polysaccharide constituents of plant material to produce energy, such as electrical power and heat, in relatively easy-to-manage and small industrial units. Alternatively, the gas can be compressed after purification and enrichment and then fed to the gas grid or used as a fuel in combustion engines or cars.

Its greatest advantage is the environmentally friend aspect of the technology, which includes the potential for complete recycling of minerals, nutrients (phosphate etc.) and fiber material (for humification), which come from the fields and return to the soil, playing a functional role by sustaining the soil's vitality for future plantation. The technology is currently mature, but there is plenty of room for optimization, which will result in large high-tech production plants with integrated utilization of by-products.

Table 1.7 General characteristics of the biogas produced through anaerobic digestion

Characteristics	Corresponding values	References
Composition	55–70% methane (CH_4) 30–45% carbon dioxide (CO_2) Traces of other gases	Rasi et al. (2007)
Energy content	6.0–6.5 kWh m^{-3}	Rao et al. (2010)
Explosion limits	6–12% biogas in air	Kapdi et al. (2005)
Ignition temperature	650–750 °C	Kolbitsch et al. (2008)
Critical pressure	75–89 bar	Kapdi et al. (2005)
Critical temperature	−82.5 °C	Kapdi et al. (2005)
Normal density	1.2 kg m^{-3}	Esteves et al. (2008)
Smell	Rotten eggs smell	Rasi et al. (2007)
Molar mass	16.043 kg $kmol^{-1}$	Esteves et al. (2008)

1.4.1 Substrates for Biogas Production

Generally, biomass of any kind containing carbohydrates (Starch, cellulose and hemicellulose), proteins and fats as core components can be employed for biogas production. Following points are important for the selection of biomass for biogas production (De Francisci et al. 2014).

- The composition of organic matter has to carefully chosen for fermentation process.
- The potential of the organic matter for biogas formation should be as high as possible.
- Selected substrate must be free from pathogens and other microbes which can harm the fermentation process.
- Biogas composition has to be examined proper for further use.
- The fermentation residues may keep the suitable content to be applied it as fertilizer.

A lot of substrates have been used for biogas production and reported in the literature. In Table 1.8 a comprehensive list of different substrates utilized for biogas production has been provided.

Cow manure is better substrate and is also useful for inoculation, manure from other farm animals such as pigs, chickens and horses, fat from slaughter waste or frying oil, organic household or garden waste, municipal solid waste and rotten foodstuff is equally applicable for anaerobic digestion. Even organic waste from hospitals containing paper and cotton, municipal sewage sludge, waste from agriculture or food production, organic-rich industrial waste water etc. can be used as consumable substrate. Often, energy crops such as maize (whole plant including the corn), clover, grass, young poplar and willow are especially grown for biogas production and added purely or in mixture. To ensure a homogeneous substrate quality throughout the year, the green plant material is usually stored as silage,

Table 1.8 Different feed stocks used for biogas production reported in literature

Substrate for biogas production	References
Residuals from beverage production	
Spent grain, fresh or ensilaged	Malakhova et al. (2015), Wolters et al. (2016)
Spent grain, dry	
Apples pulp	Géczi et al. (2015)
Apple mash	Kafle and Kim (2013)
From fruits and vegetable waste	Sagagi et al. (2009)
Animal waste	
Slaughterhouse waste	Ware and Power (2016), Fathya et al. (2014)
Meat and bone meal	Zarkadas et al. (2015)
Fat from the separator used ingelatine production	Moeller and Görsch (2015)
Animal fat	Martínez et al. (2016)
Blood	Abdeshahian et al.(2016)
Greens, grass, cereals, vegetable wastes	
Vegetable wastes	Scano et al. (2014), Janczak et al. (2016)
Grass	Rodriguez et al. (2017)
Hay	Zhu et al. (2014)
Meadow grass, clover	Kristensen et al. (2016)
Market wastes	Sridevi et al. (2015)
Leaves of sugar beet	Ohuchi et al. (2015)
Wheat bran	Wolters et al. (2016)
Soybean	Zhu et al. (2014)
Giant cane, cornsilages and pig slurry	Luca et al. (2015)
Sugar beet cossettes and pig manure	Aboudi et al. (2015)
Olivepomace and milk whey	Battista et al. (2015)
Food waste and rice husk	Haider et al. (2015)
Many flower, silvergrass and microalgae	Li et al. (2015)
Sugar beet pulp silage and vinasse	Zieminski and Kowalska-Wentel (2015)
Cow slurry, apple pulp and olive pomace	Riggio et al. (2015)
Food waste and cattle manure	Zarkadas et al. (2015)
Rice straw and cow manure	Li et al. (2015a)
Rice straw and pig manure	Li et al. (2015b)
Biodiesel waste glycerin and municipal wastewater sludge	Razaviarani and Buchanan (2015)
Olive mill wastewater and liquid poultry manure	Khoufi et al. (2015)
Sewage sludge and sugar beet pulp	Montanes et al. (2015)
Pig manure and algae	Astals et al. (2015)
Forage radish and dairy manure	Belle et al. (2015)

preferably by a process favoring homo fermentative lactobacilli to minimize carbon loss (Gassen 2005). Biogas formation from plant fibres is generally a three-stage process involving a different set of anaerobic and facultative anaerobic microorganisms in each stage:

A. Hydrolysis of biomolecules
B. Acetogenesis: the production of acetic acid and carbon dioxide.
C. Methanogenesis with up to 70% (v/v) CH_4 and 30% CO_2 and the by-products NH_3 and H_2S by slow-growing archaea, which are sensitive to acidification, ammonia accumulation, low amounts of oxygen and other factors.

The bacterial community engaged in these three stages may be similar to those in cows rumen (Einspanier et al. 2004) or wastewater treatment plants (Ariesyady et al. 2007).

Further development of biogas technology is expected to increase production efficiency. Presently, only up to a maximum of about 70% of the organic matter in biomass is converted to CH_4 and CO_2. In order for this to increase, the hydrolysis stage must be enhanced. The separation of the processes for hydrolysis and for acetogenesis/methanogenesis allows for the application of different optimized conditions in the two stages, such as pH and temperature adjustment. Aside from the traditional mesophilic processes, thermophilic processes are being used more frequently to speed up the reactions and especially to optimize biomass hydrolysis. However, whereas in many industrial biogas plants the separation of the hydrolysis stage has already been carried out, most agricultural biogas plants use the single-stage technology.

Dried and desulfurized biogas is usually fuelled without CO_2 separation into stationary block heat and power plants connected to the biogas plants. Utilization of the excess heat is rarely possible because farms are usually located far away from residential or industrial areas where it could be used for domestic heating or manufacturing processes. This is not a problem if biogas is compressed like compressed natural gas stored in high-pressure cylinders and used in the engines of urban co-generation plants. In addition, direct use in car combustion engines is possible.

1.4.2 Composition of Biogas

Methane and carbon dioxide are major constituents of biogas with several impurities. Its general characteristics have been listed in Table 1.7 already. Biogas containing methane ratio above 45% is flammable. Influence of biogas components on its quality has been shown in Table 1.9. It gives general idea about usual gas constituents and their impact on the burning capacity of the biogas.

Table 1.9 Typical components and impurities in biogas

Component	Content (volume)	Effect	References
CO_2	25–50%	Lowers the calorific value Increases the methane number and the anti-knock properties of engines Causes corrosion (low concentrated carbon acid). If the gas is wet	Rasi et al. (2007)
H_2S	0–0.5%	Damages alkali fuel cells Corrosive effect in equipment and piping systems (stress corrosion); many manufacturers of engines therefore set an upper limit of 0.05 by vol.%; SO_2 emissions after burners or H_2S emissions with imperfect combustion—upper limit 0.1 by vol.% Spoils catalysts	Soroushian et al. (2006)
NH_3	0–0.05%	NO_x emissions after burners damage fuel cells Increases the anti-knock properties of engines	Burch and Southward (2000)
Water vapors	1–5%	Causes corrosion of equipment and piping systems Condensates damage instruments and plants Risk of freezing of piping systems and nozzles	Kapdi et al. (2005)
Siloxanes	0–50 mg/m^3	Act like an abrasive and damages engines	Dewil et al. (2006)

1.4.2.1 Methane and Carbon Dioxide

Methane to carbon dioxide ratio in the biogas can be managed to some extent. Following factors majorly effect:

- The presence of material rich in long chain hydrocarbon compounds having fat, can enhance the biogas quality
- More liquid in the bioreactor can decrease the CO_2 concentration in biogas as the water keep dissolving the CO_2, so reducing in the gas phase.
- Higher temperature during process of fermentation leads to low concentration of CO_2 dissolved in water.
- More CO_2 is dissolved in water at higher pressures.

The content of hydrogen sulfide in biogas mostly depends on the process and the type of waste used. Without a desulfurizing step, the concentration of H_2S would often exceeds 0.2% by volume.

1.4.3 Paybacks from Biogas Production

Biogas is a renewable energy source and has many applications. Several profits have to be derived from the conversion of various substrates in a biogas plant:

- In many countries, governments subsidize the erection of biogas plants to give the farmers an additional fuel source.
- Production of biogas from agricultural crops may maintain the structure of the landscape.
- Left over agricultural residues that are no more wanted are frequently prone to decomposition, but bioenergy can be generated.
- Landfill area can be minimized with the protection of the groundwater.
- Throwing away expenses of organic materials are reduced.
- Using plants as co-substrates increase the chances for recycling of the mineral fertilizer.
- CO_2 neutral production of energy is achieved.

1.5 Bioethanol

As the world population is increasing, the typical calorie consumption is on rise; thus enhancing the pressure on production from rare arable land but simultaneously, the energy requirement by developing nations is also increasing and the additional fuel most likely will be demanded from alternative renewable sources such as biofuel (Graham-Rowe 2011; Dutta et al. 2014).

In first generation ethanol production processes, readily available sugars or starch are utilized. The ethanol produced is readily used in today's engines. During the process, CO_2 is extracted from carbohydrates, which have a C/H/O ratio of 1:2:1 (Arshad et al. 2017). Ethanol, with its high (C + H) to O ratio, retains most of the original energy content. Because cell can produce much less energy from this anaerobic reaction than from oxidative respiration, it has to consume about ten times the amount of substrate to gain the same amount of energy; 2–3 ATP compared to 26–38 ATP in oxidative respiration, depending on the organism. This higher turnover of substrate is an advantage for biotechnology. This anaerobic fermentation also helps to avoid energy intensive aeration during industrial production (Antoni et al. 2007).

1.5.1 Ethanol as Fuel in History

Since the humanity exists, the biofuel are in use over the history. Mankind had relied on renewable energy resources like wood, windmills, water wheels and animals such as horses and oxen. Exploration of new energy resources was a major driving force behind technological revolution. In the start of nineteenth century, alcohols were over and over again reported as biofuel with the invention of ignition engines using biofuel. Nikolaus August Otto used ethanol for his spark ignition engine in the 1860s. Henry Ford also marketed his Model T, totally operating on 100% ethanol (Kovarik 1998). Ethanol production was widely abolished due to the unbeatably low price of gasoline in the USA. Ethanol as a fuel was revived in the 1970s in Brazil where one of the largest bioethanol industries is located today. Like modern crude oil refinery, the bio-industry for biofuel has a dual purpose in the economy, as it is used as a supply of energy as well as basic chemicals (Zaborsky 1982). The upcoming "bio refinery" revitalizes the old tradition of a careful thrifty economy and intends to make use of all energy and carbon stored in biomass, feeding byproducts into secondary conversion process or refining them as fuel.

1.5.2 Ethanol Fermentation

Glycolysis is the series of reactions taking place entirely in the cytosol, is the process of intracellular transformation of hexoses (glucose and fructose) into pyruvate with the formation of ATP and NADH (Zamora 2009). In the beginning, sugars are shifted inside the cell through facilitated diffusion (Weusthuis et al. 1994). Yeast cells keep many glucose transporters such as Gal2, Hxt1, Hxt2, Hxt3, Hxt4, Hxt6 and Hxt7 (Maier et al. 2002). Firstly, the glucose is converted to fructose 1,6-biphosphate. The reaction requires 2 ATP molecules, comprising three steps (Ratledge 1991; Bellou et al. 2014). In the second phase, glyceraldehyde-3-phosphate and dihydroxyacetone phosphate are made (Aggelis 2007). Then, glyceraldehyde-3-phosphate is transferred to 1,3-biphosphoglycerate.

The reaction catalyzed by glyceraldehyde 3-phosphate dehydrogenase, involves the synthesis of one mole of NADH. Afterward,1,3-Biphospho Glycerate is transferred into 3-phosphoglycerate, reaction catalyzed by phosphoglycerate kinase, with simultaneous release of one mole of ATP. In the end 3-phosphoglycerate is converted into pyruvate which is the final product of glycolysis, with immediate formation of another mole of ATP (Aggelis 2007; Festel 2008; Arshad et al. 2014b). So in this way, one mole of glucose in glycolysis creates two moles of pyruvic acid and NADH with four moles of ATP. As two moles of ATP are consumed to activate a mole of hexose molecule, balanced energy gain in glycolysis for the cell is remains only two ATP per hexose metabolized. Now pyruvate formed through glycolysis can be utilized by yeasts in different metabolic pathways.

Obviously, the microbes have to regenerate NAD^+ from the NADH to restore the oxidation-reduction potential of the cell and done through fermentation or respiration. Here the common trunk of glycolysis ends. Further, to proceed through alcoholic fermentation, glycerol-pyruvic fermentation or respiration depends upon various conditions (Rib´ereau-Gayon et al. 2006; Zamora 2009). In anaerobic conditions, the reducing power of NADH produced through glycolysis must be transferred to an electron acceptor to regenerate NAD^+ consumed by glycolysis. The process is called alcoholic fermentation and occurs in the cytoplasm, where acetaldehyde accepts the electrons (Ratledge 1991).

In addition to glycolysis, two additional enzymatic reactions occur in alcoholic fermentation. Pyruvate decarboxylase performs decarboxylation of pyruvate into acetaldehyde, using cofactors thiamine pyrophosphate and magnesium. In the end acetaldehyde is reduced into ethanol recycling NADH to NAD^+ by the alcohol dehydrogenase enzyme using zinc as cofactor. The final products of alcoholic fermentation, carbon dioxide and ethanol, are simply diffused out of the cell (Arshad et al. 2011).

1.5.3 Substrates Utilized for Bioethanol Production

Bioethanol fermentation is considerably the largest scale microbial process. Regardless of the simple or complex substrates utilized as microbial carbon sources acquiescent for conversion to ethanol, all types of substrates firstly result in the formation of hexoses, pentoses or glycerol (after the enzymatic, physical, chemical or mechanical pretreatment) that will be fermented by the relevant microorganisms in order to be converted into bioethanol. Major types of feedstock used in fuel ethanol production are presented in Table 1.10. In industrial ethanol production sugars present in sugar cane molasses or from enzymatically hydrolysed starch (from corn or other grains) and batch fermentation with yeast *Saccharomyces cerevisiae* is employed to produce ethanol.

Byproducts of the process include CO_2 with low amounts of methanol, glycerol, higher alcohols and acetic acid (Arshad et al. 2008). Ethanol does not need to be rectified to high purity if it is to be used as a fuel. Alcoholic fermentation process of sugars to ethanol has been well progressed in recent years. Alcoholic fermentation biochemistry includes substrate degradation pathways (glycolysis, alcoholic fermentation, glycerol-pyruvic fermentation and respiration for the case of the utilization of hexoses, xylose catabolic pathways for the case of utilization of pentoses and glycerol assimilation and glycolysis for the case of glycerol-converting

Table 1.10 Major feedstock used for fuel ethanol production

Feedstock	References
Sugar cane juice	Moreira and Goldemberg (1999)
Caasava	Agrocadenas (2006)
Sugarbeet	Poitrat (1999)
Wheat	Agrocadenas (2006)
Corn	Shapouri et al. (2003)
Sugarcane bagasse	Moreira (2000)
Corn stover	Kim and Dale (2004)
Wheat straw	Kim and Dale (2004)
Biomass	Berg (2001)

microorganisms) and regulation between fermentation and respiration (Pasteur effect, Crabtree effect, Kluyver effect and Custers effect).

Inhibitor sensitivity, product tolerance, ethanol yield and specific ethanol productivity have been improved in modern industrial strains to the degree that up to 20% (v/v) of ethanol are produced in present-day industrial yeast fermentation vessels from starch derived glucose. Substrates used for bioethanol production can be categorized into three major types:

1.5.3.1 Feedstock Containing Sucrose

Major feed stocks containing sucrose are sugarcane and sugar beet. Approximately 70 and 110 L/ton ethanol is produced from sugar cane and sugar beet respectively. Brazil alone produces 40% of world sugarcane. Sugar beet is the major feedstock for bioethanol production in European countries.

1.5.3.2 Starch Containing Feedstock

In Europe and North America, ethanol is majorly produced from starch containing feedstock such as corn, wheat and barley. In starch, D-glucose is linked through α-1,4 linkage with specific branches of 1-6 bonds. Conversion of starch into its monomer glucose is must require for ethanol fermentation. Corn is fermented into ethanol, starting by either dry- or wet-milling.

1.5.3.3 Lignocellulose Biomass

Present corn-based ethanol production may not be socio economically sustainable due to its impact on agricultural land usage and water shortage. The potential alternative substrate is lignocellulose biomass for ethanol production. Advantages and disadvantages about different methods for pretreatment of lignocellulose materials have been presented in Table 1.11. The lignocellulose biomass includes wood, straw, grasses, crop residues and other agricultural wastes, available in much higher quantities as compare to starch and sucrose containing substrates. Glucose yield is although much lower in cellulosic biomass as compared to sugar or starch crops, but easily accessible vast mass makes it better option for fuel ethanol production. Estimated potential of bioethanol production from agricultural residues is about 491 billion L/year.

Important difference between sugar and lignocellulosic material is the readily availability of substrate for fermentation. The technical process using lignocellulosic hydrolysates (Gray et al. 2006) is going to be better day by day. However, as the enzymatic hydrolysis reaction of cellulose is about two orders of magnitude slower than the average ethanol fermentation rate with yeast, there is a theoretical gap in simultaneous scarification of cellulosic biomass and ethanol fermentation

Table 1.11 Advantages and disadvantages about different methods for pretreatment of lignocellulose materials (Harmsen et al. 2010)

Pretreatment process	Benefits	Drawbacks
Biological	Lignin and hemicellulose can be decomposed easily Least energy needed	Hydrolysis reaction is much sluggish
Milling	Crystal structure of cellulose can be relaxed	Additional power required
Steam explosion	Lignin can be converted to its components easily Better release of glucose molecules	Discharge of toxic compounds Partial degradation of hemicellulose
CO_2 explosion	Much surface area exposed Better in terms of cost No toxic compounds generation	High pressure needed
Wet oxidation	Better abstraction of lignin Reduced formation of inhibitors	High cost
Organosolv	Efficient decomposition of lignin and hemicellulose	Drainage can cause environmental issues
Diluted acid	Lesser corrosion issues as compared to concentrated acid	Byproducts are formed
Concentrated acid	Much better glucose production	Acid recovery is essential

Table 1.12 Various fermentation processes for ethanol production

Mode of fermentation	Ethanol (g/L) in fermentation broth	Productivity, g/(L h)	Maximum yield (%)	References
Batch	80–100	1–3	85–90	Claassen et al. (1999)
Fed batch	53.7–98.1	9–31	81	Echegaray et al. (2000)
Repeated batch	89.3–92	2.7–5.25	80.5	Hojo et al. (1999)
Continuous	70–80	7–8	94.5	Costa et al. (2001)

(SSF). This must be addressed if total biomass is to be fermented, not only glucose syrups, for example from starch. Table 1.12 shows various fermentation processes for ethanol production. The fermentation of pentose sugar with industrial yeast strains is a difficult task and still under development (Hahn-Hagerdahl et al. 2007), although some pilot plants are already running.

Biological ethanol fermentation from molasses and starch is basically a mature technology. The utilization of non-food substrates such as cellulose-containing waste material is in the pilot stage. The hydrolysis of cellulosic material by the cellulase enzymes is very slow due to less porosity, crystal structure and presence of lignin and hemicellulose (Karim et al. 2017). More over the process also needs utilization of C_5 sugars to be economical. There are several approaches for the pretreatment of such biomass to release the required sugars. Physical, chemical and enzymatic treatments are availed. Availability of feedstock is not uniform throughout the year and also varies from region to region. Production cost of bioethanol is depended on the price of feedstock (Ray et al. 2017).

1.5.4 Ethanol Purification

Many yeast strains and their varieties are employed for industrial ethanol production. Certain strains lead over others, in specific rate of fermentation, better yield, efficient sugar utilization and higher tolerance of ethanol (Choudhary et al. 2017). But the byproducts are unavoidable in each and every strain. Formation of byproduct also depends on the purity of the substrate used. Acetaldehyde is one of the major byproduct of this process. Some higher alcohols as isoamyle alcohol are also produced as byproducts.

1.5.5 Ethanol as Fuel

Unlike petroleum, ethanol comes from renewable resources. It keeps cleaner burning characteristics (Prasad et al. 2007) as compared to gasoline; thus produces less greenhouse gases (McMillan 1997; Alzate and Toro 2006; Marchetti et al. 2007). Use of agro-industrial residues as raw material for ethanol fermentation, not only provides alternative substrates but also reduces carbon dioxide emissions with solution of their disposal problems. As ethanol is a biodegradable and comparatively highly soluble in water, has low toxicity risk. In case of any large spilling, far less danger for the environment than those associated with conventional oils (McMillan 1997). The potential of bioethanol production in totally non-aseptic environment (Roukas 1995; Kopsahelis et al. 2012; Sarris et al. 2013; Sarris et al. 2014) makes the process easier to apply at industrial scale. The use of Ethanol in place of petroleum could, provided that a renewable energy resource was used to produce crops required to obtain ethanol and to distil fermented ethanol.

Ethanol is the compound of carbon and hydrogen atoms, with a hydroxyl group have chemical formula C_2H_5OH, also known as ethyl alcohol or hydroxyl ethane. Its molecule is small and light, as compared to most gasoline components. The electrochemistry of the ethanol molecule is slightly exceptional being polar at one end and non-polar at the other. It participates in hydrogen linkage with other ethanol molecules or other polar substances due to presence of hydroxyl group. The polar end help ethanol to be miscible in water or other polar compounds and the non-polar end is advantageous in mixing with non-polar substances, such as gasoline. Generally ethanol is produced in two forms: anhydrous, keeping water content less than 1%, or hydrous, having water content up to 10%. Purity of ethanol above 96% cannot be achieved through conventional distillation. To convert hydrous ethanol into anhydrous, separate technique as azeotropic distillation using 20–25% extra energy is used.

Generally ethanol in blended with gasoline in percentages from 5 to 85% (Kim and Dale 2006) and diesel for its use as fuel. Above half of the fuel ethanol used worldwide is blended with gasoline. Globally most prevalent blends are E_{85}, E_{20} and E_{10} (Festel 2008). Primary reason for using ethanol as an additive to gasoline is reduction in CO_2 emissions. Ethanol addition also raises the octane number of the fuel blend thus it can replace more costly octane-boosting components such as alkylate. Ethanol keeps oxygen, so gasoline burns more cleanly and reduces the amount of harmful emissions of carbon monoxide (CO), particulates and unburned gasoline components. Ethanol can be used in the trans-esterification of vegetable oils for the production of fatty acid ethyl esters (Marchetti et al. 2007).

1.6 Conclusion

Owing to rapid growth of biofuel production in last decades biofuel are fulfilling almost 3% of transport fuel needs worldwide. Such a rapid increase has given rise to many concerns. World has faced increased in food prices worldwide and an alarm to food security. Major advantage of biofuel in climate change mitigation has been also facing questions. As the per energy equivalence, factory gate prices of ethanol and biodiesel were almost higher as compared to refinery gate prices of fossil based gasoline and diesel. Production costs of biofuel needs substantial reduction to make these products completive. The technological breakthroughs can do the best in future. Present production ways and techniques has been comprehensively discussed above.

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