

Chapter 2

Bio-fuels: A Blessing in Disguise

O. Surriya, Syeda Sarah Saleem, K. Waqar, A. Gul Kazi and M. Öztürk

Abstract Biofuels are part of the bio energy family that can be transformed into fuels for both mobile as well as stationary incentives. Bio-fuels obtained from various forms of bio-mass are considered environmentally safe and economically efficient candidates for complete replacement of natural oil in the twenty-first century. Depending on their future accessibility, geologists categorize bio-fuels into three generations, namely; first, second and third. According to research analysts, energy demand will increase with alarming celerity until late 2020–2030, up to more than 50%. Because of the emerging economies of the developing countries in recent years, energy consumption will directly enhance the demand for renewable, cost effective energy generation sources. The depleting life expectancy of natural fossil fuels in the world market has led research institutes, policy makers and enterprises to discover alternative means of generating transportation fuel. One such prominent and promising alternative is “Biofuels” which not only contributes to diminishing the increasing bubble of global warming but also generates substantial amount of energy in a less cumbersome manner.

Keywords Biofuel · Biodiesel · Bioethanol · Biomethanol · Biohydrogen · Algae biofuels

1 Introduction

Biofuels refer to combustible materials which are directly or indirectly derived from biomass. Most common biomass includes wood, agricultural crops, aquatic plants, forestry products and animal wastes (Keck 2001; Öztürk et al. 2006, 2007, 2010; Öztürk 2010; Abideen et al. 2011). Biofuels are part of the bio energy family that can be transformed into fuels for both mobile as well as stationary incentives. These

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Table 2.1 Detailed classification and characteristics of biofuels on generation basis

Biofuels	Basic technology	Feedstock
<i>First generation</i>		
1. Bio-diesel	Transesterification of fats and oils	Rapeseed, sunflower oil soya
2. Plant oils	Transesterification, pyrolysis, micro emulsification	Coconut oil, jojoba oil, sunflower oil, rapeseed oil
3. Bio-gas	Microbial metabolism via fermentation	Energy crops, waste material, proteins, carbohydrates, cellulose, fats
<i>Second generation</i>		
1. Bio-alcohols	Breakdown of cellulosic biomass in several steps including fermentation and hydrolysis	Wheat, wood, sugar cane and bagasse
2. Wood diesel	Fischer tropesch process, gasification	Woody biomass
3. DMF	Conversion of carbohydrates to DMF via acid catalyzed dehydration process reaction	Lignocellulosic biomass, waste biomass carbohydrates
<i>Third generation</i>		
1. Algal fuel	Use of bioreactors, pyrolysis, transesterification	Marine or fresh water micro algae

can be in the form of solid, liquid or gases. Wood, charcoal and bagasse (sugar cane after juice extraction) are some useful examples of solid biofuels which are extensively consumed for domestic purposes such as cooking in rural areas of most third world countries. Waste bagasse; the fibrous material obtained from the processing of sugar cane is widely used for power generation in raw sugar mills. Liquid biofuels like ethanol, methanol, plant oils and methyl esters produced from these oils are biodiesel, whereas methane and producer gas are forms of gaseous biofuels. According to the research analysts, energy demand will increase with alarming celerity up to more than 50% between 2020 and 2030. Because of the emerging economies of the developing countries in recent years, energy consumption will directly enhance the demand for renewable, cost effective energy generation sources.

The depleting life expectancy of natural fossil fuels in the world market has led research institutes, policy makers and enterprises to discover alternative means of generating transportation fuel. One such prominent and promising alternative is “Biofuels” which not only contribute to diminishing the increasing bubble of “Global Warming” but also generates substantial amount of energy in a less cumbersome manner. Biofuels are categorized according to their current and future availability as first, second or third generation biofuels as shown in Table 2.1. First generation biofuels are manufactured using conventional technology. Starch, sugar and vegetable oils are the main substrates used to provide the synthesis of first generation bio-fuels. Some common examples of first generation biofuels include bio-diesel, biogas and vegetable oils. Second generation biofuels are considered more preferable over the first generation biofuels, since they are obtained from biomasses produced by non-food crops, cellulosic materials like wood and waste materials of animals. Wood diesel, dimethyl ether and bio-alcohol are a few examples of second generation biofuels.

Third generation biofuels are relatively the cheapest and most energy producing of all the three types of biofuels. Algal oil obtained from algae is utilized for the synthesis of third generation biofuels. They may also be called as oilgae.

2 Historical Perspective

The use of biofuels dates back to the early sixteenth–seventeenth century. Humans have consumed ethyl alcohol since before it was chemically discovered. In prewar America the same alcohol was utilized as fuel for lightening a lamp. In the World Fair of 1900 in Paris, biofuel in the form of peanut was used for the very first time as engine fuel by Rudolf Diesel; since then the French government has been exploring the possibilities of bio oils for the generation of transportation fuel.

Henry Ford, an American industrialist and the founder of Ford Motor Company, made his first automobile using ethanol in 1916. America, one of the earliest growing economies of the world began working on promoting bio-alcohols during mid-nineteenth century. Later towards World War II, when scarcity of fuel hit the military camps, ethanol was considered as a viable alternative. But it was not until 1970 that bio fuels successfully captured the lime light for being the second most preferable source of engine fuel after diesel. American Congress passed the Energy Tax Act of 1978 that enforced incentives and economic subsidies for the development of ethanol. Much to automobile industries amazement, The Clean Air Act Amendments of 1990 and Energy Policy Act of 1992 issued a compulsive authorization for the use of ethanol fuel in trucks and bus fleets. These laws were the catapult force behind expanding the popularity of biofuels.

3 First Generation Biofuels

3.1 *Bio Diesel (FAME)*

Bio diesel is a fuel encompassed with mono alkyl esters derived from vegetable or animal fats, of long chain fatty acids. It is a renewable transportation fuel consisting of fatty acid methyl esters (FAME), mainly produced by trans-esterification of vegetable oils and animal fats (Wang et al. 2006). Engine carbon monoxide emission is reduced when biodiesel proportion in diesel fuel is increased. For example using the blend B50, the carbon monoxide emission is lessened to 31 % compared to the neat diesel fuel (Wang et al. 2006).

The interest in biodiesel production increased because of some important reasons:

1. Concerns to reduce greenhouse gas emission for maintaining a stable climate.
2. A desire for renewable energy source.
3. Interest in developing domestic and more secure food supplies (Vyas et al. 2010).

Table 2.2 The feed stock types with their examples used for biodiesel production

Feed stock type	Examples
Plant oils	Cottonseed, jatropha oil, soya bean
Animal fats	Tallow, lard, grease

Some of the advantages of biodiesel are that it is a renewable energy source, can decompose easily under natural conditions, has high combustible value, is safe, easily transportable and less toxic as it has less sulphur compounds in it.

The disadvantages include high viscosity, high surface stress, easily subjected to oxidation and expensive raw material used for its production (Wang et al. 2006).

3.1.1 Feed Stocks Used for Bio-diesel Production

Biodiesel can be produced by using various feed stocks. The main biodiesel feed stocks are classified into three types; plant oils, animal fats and waste cooking oils with industrial wastes. Table 2.2 presents some examples of plant oils and animal fats used in this connection. Each country develops feed stock for biodiesel production in accordance with their geographical conditions. The United States generally uses soya bean which is genetically modified while Canada and other European countries use rapeseed to produce biodiesel. Indonesia and Malaysia own plentiful palm oil so they use it for biodiesel formation (Vyas et al. 2010).

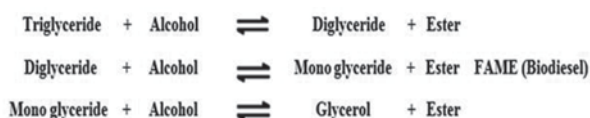
China is a big agricultural country because of which it faces a lot of problems regarding food supply. In order to produce biodiesel they use a principle by which they never get to compete with food grains as they use waste cooking oil for biodiesel production.

3.1.2 Bio-diesel Production via Trans-esterification

The main chemical composition of animal fats along with vegetable oils is triglycerides. The industrial method used for the production of biodiesel is trans esterification also called alcoholysis (Wang et al. 2006). Trans esterification is a process which involves a reaction of an oil or fat with an alcohol (with or without using a catalyst) to produce esters and glycerol. This reaction is extremely reversible so additional amount of alcohol is used to shift equilibrium towards the product production side (Fukuda et al. 2001). *Jatropha* is a good source of biodiesel formation as it grows on waste land with really less amount of water and minimum need of fertilizer. This oil is non-edible because of toxic phorbol esters (Tan et al. 2010).

This reaction takes place in three steps. These three steps are shown in Fig. 2.1. It involves the alteration of triglycerides as a result of which diglycerides are formed, which is trailed by transformation of glycerol through various high glycerides. The whole process yields one methyl ester molecule from each glyceride at every stage. This reaction proceeds by mixing the reactant and it may accelerate with the presence of a catalyst (Fukuda et al. 2001).

Fig. 2.1 The three main steps of trans esterification



There are various types of trans-esterification reactions. Some of these are:

i. **Homogeneous alkali catalyzed trans-esterification:**

Trans-esterification can be catalyzed by using homogeneous and heterogeneous catalyst. This is carried out in the same three steps. The alkali catalyzed reactions for trans-esterification are faster than acid catalyzed reactions (Vicente et al. 2004)

ii. **Homogeneous acid catalyzed trans-esterification:**

The liquid acid catalyzed reaction of trans esterification is not popular as compared to base catalyzed reaction. This process is about four thousand times slower as compared to base catalyzed reaction. The performance of this process isn't affected much due to the presence of free fatty acids in feed stock. It can catalyze both esterification and trans esterification. The great advantage of using this process is direct formation of biodiesel from low cost lipids feedstocks, having high free fatty acid concentration which is greater than 6%. The common catalysts for acid catalyzed reactions are hydrochloric acid, sulphuric acid, phosphoric acid, boron tri fluoride and organic sulphonic acid (Lotero et al. 2005).

iii. **Heterogeneous acid and base catalyzed transesterification:**

The former reaction has greater performance for trans-esterification to gain bio diesel but they consume high amount of energy. Heterogeneous catalyst in comparison utilizes less energy, can be separated from the product more easily, avoids undesired saponification reactions and can use high free fatty acid feed stocks. Biodiesel synthesis by using solid catalyst can lead to a cheap manufacture cost because the catalyst can be re-used and esterification can be carried out along with trans esterification simultaneously (Di Serio et al. 2007; Garcia et al. 2008).

iv. **Enzymatic trans esterification:**

Enzymatic trans esterification using lipase has promising outcomes such as ease in product separation, negligible water surplus requirements, ease in glycerol regaining and nonexistence of side responses. It also faces some difficulties like infectivity of product due to left over enzyme action and market price. To fix these problems enzyme is used in immobilized condition hence allowing to be used numerous times to decrease the cost and improve the quality of product formed. When free enzymes are used in this process the enzyme activity is incompletely recovered but the built up of glycerol also limits the number of uses of free and immobilized enzymes (Nielsen et al. 2008).

v. **Supercritical and subcritical alcohol trans esterification:**

Trans-esterification of vegetable oils by super critical without the use of catalyst offers a novel way of making bio-diesel. By using this process the trans esterification is finished in minutes while other catalytic processes take several

hours (He et al. 2007). In this process the blend converts into a single uniform phase which quickens the reaction as there is no intermediate phase in mass transfer to limit the reaction rate. The benefit of using this procedure is that alcohol is a reactant and an acid catalyst. The main drawback of the process is great charge of apparatus due to the usage of high pressure and temperature (Yin et al. 2008).

vi. **Microwave assisted trans esterification:**

Micro wave irradiation can be used for biodiesel formation. This process activates polar molecules and ions to alcohol with fast modification in magnetic field, due to which it cooperates with dipoles and charged ions. The preparation of biodiesel using this method offers fast, easy, small response time, little oil to methanol ratio, decrease in amount of by products and cheap energy consumption (Azcan and Danisman 2007).

vii. **Ultra sound assisted trans esterification:**

Ultra sound delivers the power-driven energy for mingling and trans-esterification reaction. This process maximizes the chemical speed and harvest of the entire procedure of trans esterification of oil and fats into bio diesel. The main advantages of this process are less time, less energy consumption especially in mechanical stirring and simplicity of the process. The trans esterification of 1 kg soya bean oil using ultra-sonic and conventional stirring method consume 250 and 500 W/kg energy respectively (Singh et al. 2007).

3.2 Vegetable Oil

In the colossal network of biological entities that can render the replacement of fossil fuels with immense appositeness, oils obtained from plants are surfacing the list with great celerity. According to the experts on environmental sciences, vegetable oils are evaluated for production of biofuel for the following two reasons:

1. Vegetables oils render sustainability in relation to factors like viscosity, energy content and combustion product.
2. Capital, labor and yield of biodiesel production from vegetable oil are favorable.

Some edible oils listed in Table 2.3 below have also been considered for the use of biofuels. Though due to food population ratio crisis elevating higher and higher, not much effort has been poured into this idea.

3.2.1 Plant Oils Used for Biodiesel

The main plants whose oils have been employed for the use of bio-diesel include:

Table 2.3 List of edible oils suitable for biofuel production. (After Vijayalakshmi et al. 2007)

Edible oil for biofuel	Property and uses
<i>Corn oil</i>	Abundance of crop
<i>Coconut oil</i>	Favorable for locations harvesting coconut
<i>Castor oil</i>	Lower cost than other oils. But has viscosity issues
<i>Hemp oil</i>	Has a high flash point but low emissions
<i>Mustard oil</i>	Satisfactory for biofuel
<i>Palm oil</i>	Very promising for a biofuel
<i>Peanut oil</i>	Been used in the very first demonstration for diesel engine in 1900
<i>Radish oil</i>	Crop contains 48 % oil, making it very desirable for a fuel
<i>Safflower oil</i>	Relatively new discovered
<i>Soybean oil</i>	Not very economical for use as biofuels

i. **Artichoke**

Its seed is used to extract edible oil. The oil composition constitutes of 3 % stearic, 12 % palmitic, 25 % oleic and 60 % linoleic acids. Presently continuous experiments and analysis of the crop are in full swing and deduce vast potential for producing biodiesel (Vijayalakshmi et al. 2007).

ii. **Canola Oil**

Canola seeds are rich in oil content (40 %). During the last few years, canola oil has started coming under the lime light of bio-fuels. In Australia a small group of farmers have begun producing bio-diesel from canola oil. Not much is known about its commercial success. Other countries too have started producing it (Vijayalakshmi et al. 2007).

iii. **Castor Oil**

Castor oil is one of the few vegetable oils that bears the 100 % viscosity as that of diesel fuel. It is one characteristic that has dismantled the environmentalists parallel to attracting their attention with its other few noteworthy characteristics.

iv. **Coconut Oil**

Least viscous oil and thus appears to be a good candidate for biodiesel. As opposed to castor oil, coconut oil has the largest oil content, of about 70 % (Vijayalakshmi et al. 2007).

v. **Corn Oil**

Corn has been over many decades under constant experimentation as a feed-stock for biodiesel. But it was never favored, because primitive extraction methods did not favor production of wide quantity of oil suitable for processing of bio-diesel (Vijayalakshmi et al. 2007).

vi. **Cottonseed Oil**

So far USA is in function of producing bio-diesel from cotton seed but the production volumes are quite low (Vijayalakshmi et al. 2007).

vii. **Jatropha Oil**

The *Jatropha* tree has been used as a significant fuel source for a lot of years especially in Southeast Asia and India. The tree has convenient harvesting condition that allows it to grow in arid conditions and gives a significantly large oil yield (Vijayalakshmi et al. 2007).

viii. **Jojoba Oil**

Jojoba oil is a new candidate in vege oils as bio-fuel. Easy growth in saline soils and on desert lands has landed jojoba oil under the spotlight of researchers. Given the small amounts of cultivation, studies across the globe have shown that jojoba oil will make scanty impact on the production of bio-diesel (Vijayalakshmi et al. 2007).

ix. **Karanj Plant**

Native plant found in India, appears to be a good candidate for biodiesel production. It is considered less toxic and cheap as well. However there is a large room for studies and more research is needed on Karanj plant (Vijayalakshmi et al. 2007).

x. **Peanut Oil**

From the beginning in diesel shortages, peanut oil was used frequently since Rudolf ran his first diesel engine on peanut oil. But gradually its usage decreased, mostly because of economic reasons (Vijayalakshmi et al. 2007).

3.2.2 Production of Diesel oil from Vegetable Oil

Vegetable oils fulfill the parameters of being economical and environment friendly. However characteristics like high viscosity, low volatilities and polysaturatedness act as tangible obstacles in replacing diesel fuels with triglycerides. Methods that produce vegetable oil derivatives have been developed to circumvent this hindrance: Pyrolysis, Micro emulsification, Dilution, Transesterification.

a. **Pyrolysis**

Pyrolysis harbors the decomposition of vegetable oil via thermal energy in the absence of air. The resultant vegetable oil product is referred to as pyrolyzate and has been shown to have less viscosity, pour point and flash point but equal calorific values. Even the cetane number of the vegetable oil pyrolyzate turned out to be low. The sulphur water and sediment of the pyrolyzate remain under acceptable range alongside acceptable copper corrosion (Vijayalakshmi et al. 2007).

b. **Micro emulsification**

The formation of micro emulsification of liquids has potentially added to the lessening of vegetable oil viscosity. These are colloidal dispersions that are thermodynamically stable ranging from 100 to 1,000 Å (Vijayalakshmi et al. 2007).

c. Transesterification

The most popular technology employed for the production of bio diesel from vegetable oils is the transesterification of triglycerides to methyl esters of glycerin and fatty acids. It is a relatively simple method than others cited here. Duy and Patrick first discovered it in 1853 (Vijayalakshmi et al. 2007). In the transesterification of vegetable oils, a triglyceride is made to react with an alcohol alongside strong acid or base accompanying the reaction, forming a mixture of fatty acids, alkyl esters and glycerol. Various factors such as temperature, molar ratio, type of catalyst, free fatty acid content and clarity of the reactants have an impact on the course of the transesterification. The various processes involved are given below:

i. Acid catalyzed process

Transesterification is usually carried out using this process, with preference for sulphonic or sulphuric acids. These catalysts have high yielding capacities of alkyl esters but the reactions are relatively slow, demanding temperatures above 100 °C with cumbersome time consuming durations to reach complete conversion. For example lysis of methane in soybean oil, in the presence of 1 mol percent of H_2SO_4 at 650 °C takes 50 h to reach whole transformation (Vijayalakshmi et al. 2007).

The most influential factor acting on transesterification is alcohol vegetable-oil molar ratio. Copious amounts of alcohol favor the synthesis of product. But excess alcohol creates the retrieval of glycerol problems (Vijayalakshmi et al. 2007). The transesterification catalyzed by acid must be performed in the absence of water so that the competitive formation of carboxylic acid can be avoided which reduces the amount of alkyl esters produced (Payawan et al. 2010).

ii. Base catalyzed process

Base catalyzed reaction, on the other hand, is employed for a large scale production particularly because of its celerity and reduced corrosive troubles. The process commences with the first step mainly consisting of a reaction of the base with alcohol which results in the formation of a protonated catalyst and an alkoxide. The next step proceeds to be a nucleophilic reaction in which the alkoxide reacts with the carbonyl group of the triglyceride producing a tetrahedral intermediate that later gives an alkyl ester and diglyceride anion. The alkyl ester product deprotonates the catalyst in the end to re-initiate the cycle (Payawan et al. 2010). However a few disadvantages are associated with the base catalyzed reaction. Chief among these are the condition of the presence of water in the reaction that may react with the alkyl ester to give rise to Free Fatty acids (FFA). High content of FFA may perturb the separation, purification and washing stages of glycerol and ester. Hence modifications in the base catalyzed method have been introduced.

In a recent study by Payawan et al. (2010) on the characteristics of *Jatropha* oil as a convenient and one of the leading candidates for biodiesel is seen to contain 14% FFA content. An amount that is largely beyond the 1% FFA level can

be transformed into biodiesel via transesterification process through an alkaline catalyst. Alterations in the process were administered to achieve a higher FFA content in the biodiesel. Heterogeneous catalysts have been produced which can lead to higher efficiency and convenient removal of glycerol and aqueous base catalyst. Not much is discovered about the deleterious emission of biodiesel made from vegetable oils. Much needs to be experimented on its clinical and economical attributes.

3.3 Bio-gas

With the rising population and urban development towards the millennium, air pollution issues have touched the peak. As the number of vehicles on roads multiplied, so did the harmful emission in the atmosphere. The urgent need to reduce the menacing emission for minimizing global warming was therefore the first catapult objective behind the idea of biogas.

Biogas is by far the most versatile renewable resource that cannot only replace fossil fuels for the use of vehicle engines but also for the use of heat and power production (Fehrenbach et al. 2008). The production mechanism of biogas via anaerobic digestion provides environmental and energy-efficient advantages over other energy sources. Methane gas is the first viable candidate for the major composition of biogas since its early production.

3.3.1 Biochemical Process

Methane gas is fermented for obtaining it in colossal amounts. Its fermentation is a perplex process, composing of distinct steps, namely, hydrolysis, dehydrogenation and methanation (Angelidaki et al. 1999). The first step is hydrolysis using hydrolyzing microorganisms. These secrete hydrolyzing enzymes: cellulose, amylase and lipase to breakdown the added monomers and polymers (Bagi et al. 2007). This breakdown of polymers or monomers results in the production of acetate and hydrogen and some fatty acid derivatives like butyrate and propionate.

An exclusive nexus of microorganisms are added into the culture medium for the production of methane gas. Of this consortium of microorganisms, mostly anaerobes are employed, such as *Bacterioides*, *Bifidobacteria* and *Clostridia*. Some facultative anaerobes can also be employed such as *Streptococci* and *Enterobacteriaceae* (Bagi et al. 2007). Subsequent to hydrolysis of polymers, the methanogenic bacteria produce methane gas using acetate and hydrogen molecules. When using methanogenic bacteria, hydrogen production is easily achieved in two stages only (Schink 1997).

The neighboring degradation steps of the anaerobic fermentation have to occur in an equilibrium proportion, if it occurs at a faster rate, the pH will fall below 7, putting the survival of the methanogenic bacteria in trouble. If the second step out

runs the first one, methane yield will suffer. Therefore special care has to be taken while designing the process to achieve minimal loss (Karakashev et al. 2005).

The next step, digestion, takes place under both mesophilic and thermophilic conditions. A constant temperature throughout the entire process is necessary for a fruitful yield of biogas. Numerous studies have shown that methanogenic bacteria work best at thermophilic temperatures and tolerate a temperature change of $\pm 3^{\circ}\text{C}$ (Karakashev et al. 2005). In terms of pH, methane gas is released most efficiently at pH between 6–8. However if the pH goes down below 6 or rises above 8, the production of methane gas is severely inhibited. The pH alters or reaches above 8 mostly due to accumulation of ammonia gas released upon degradation of protein substrates (Abdoun and Weiland 2009).

3.3.2 Growth Parameters for Microorganisms

All living microorganisms require certain macro and micronutrients for growth and reproduction. Carbon, phosphorus and sulphur are added as macronutrients for the culture medium. Micronutrients are added in considerably lower amounts (0.05–0.06 mg/l), since their need is not particularly essential (Bischoff 2009). Trace metals are added in significant amounts, as they are needed as co-factor for enzyme functions. Nickel, cobalt, selenium, molybdenum, tungsten and iron are the common trace metals added (Bischoff 2009). Nickel is utilized by the methanogenic bacteria for the synthesis of an essential cell component called F_{430} , involved in the formation of methane. Iron is normally added in the concentration ranging from 1 to 10 mg/l.

3.3.3 Feedstock

The criteria for use of biomass as substrates for biogas production is the presence of carbohydrates, cellulose, proteins, lipids, fats and hemicelluloses as main components. According to researchers, the biogas yield depends upon the content of carbon, proteins and fats. Wood, a strong lignified organic biomass is not encouraged for use as substrates in biogas production mainly because its anaerobic decomposition is extremely slow. Different biomasses produce different amounts of biogas concentrations, depending on the content of their organic substances. For instance fats yield the most biogas amount but require long retention time, whereas proteins and carbohydrates have faster rates of conversion but low amount of gas yields.

Crop plants are the most paramount, biogas producing substrate candidates. Figure 2.2 shows the potential of crop plants and organic wastes for usage as biomass for biogas production in Germany. About 50 % of biogas energy is synthesized from using crop plants as co-substrates. The net energy yield per hectare of crop plants is phenomenal. Maize, forage beets, perennial grass and cereal crops provide high gross energy per hectare. Certain parameters of crop plants such as harvesting and the frequency of harvesting are to be kept in consideration while choosing the

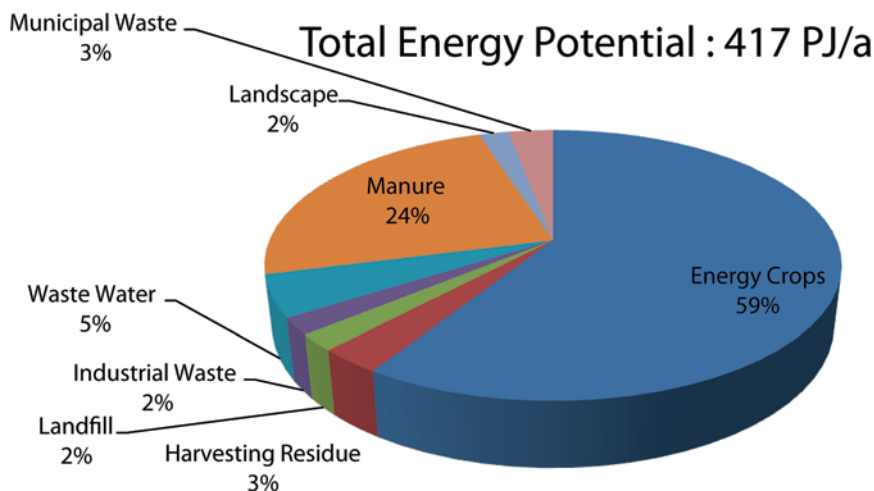


Fig. 2.2 Usable biomass potential for biogas production in Germany

variety of crop as biomass. Forage crops are thus mostly suitable for biogas production because of small harvesting periods (Weinberg et al. 2003).

The crop residues and the crops themselves are stored via a process called ensiling. In the biochemical process of ensiling, the soluble carbohydrates in plant crops are converted into butyrate, acetate, lactic acid and propionate. The production of these organic compounds inhibits the growth of contagious pathogens by lowering the pH to 3–4 (Banemann and Nelles 2009). However one downfall of energy losses of up to 8–20% accompanies the process of ensiling. To minimize the energy loss by biomass degradation, the energy crops are put in silos and wrapped in plastic wraps (Weiland 2006).

4 Second Generation Biofuels

4.1 Bio Alcohols

Alcohol is a very important source of energy because it can be produced chemically and biologically. Alcohol produced by the traditional chemical methods is now being replaced by the bio alcohols produced by microorganisms and enzymes using renewable energy sources (Weber et al. 2010). Out of all the other biofuels, bio alcohol fuels proposes the most verified and attainable substitute for the gasoline, which is three fourth of on-road fuel practice, over one-half of all transportation energy use especially in the USA (Weber et al. 2010). Main bio alcohols used for the production of energy are methanol, ethanol, propanol and butanol. The main reason why bio alcohol based fuels are essential is their advantage to hold a high

octane number which is very important for efficiency and balancing the low energy density of the fuel. Out of all bio alcohols, bio methanol and bio ethanol are most important (Agarwal 2007).

4.1.1 Bio Methanol

Bio methanol is an emerging biofuel. Some of the properties which make bio methanol really attractive as a biofuel are that it is a liquid fuel which can be combined with gasoline and ethanol and used with vehicle equipment at minimal expenses. It is a high octane fuel having combustion properties that permit engines specifically designed for methanol fuel to work at the best efficiencies and regulating pollutant release. It can be produced from renewable biomass, is a safe fuel though toxic but the toxicity is comparable to or better than gasoline, and biodegrades quickly in case of a spill and doesn't persist in surface waters. Bio methanol is a greenhouse gas reduction fuel as the fuel just returns the carbon back into the surroundings when formed from a renewable resource (Agarwal 2007).

The Partial Oxidation and Gasification Using Water and Oxygen The main method used for the making of bio methanol via biomass is by its partial oxidation and gasification. The plant comprises of two chief parts in which the process is carried out. First is a biomass gasifier in order to transform the feedstock to synthesis gas (syngas) and second one is a methanol production plant. Biomass resources usually used are wood components including wood wastes. The oxygen required for the conversion of biomass into gas is obtained from electrolysis of water by consuming electricity. About 10.32 kt of oxygen gasifies 10.1 kt of biomass yearly. The complete output of biomass derived methanol can be improved by more electrolytic oxygen supply. The fume from the gasifier consists of elements like tar, alkali, sulphur and chloride complexes. These particles can lead to poisoning of the catalysts and cause corrosion of the equipment being used. Hence the minor particles using the gas are formed, which are its principal investments, compulsory for the treatment of the syngas (Demirbas 2009a, b).

The presence of nickel based catalyst reforms natural gas, tar and additional hydrocarbon compounds into carbon monoxide and hydrogen gas at extreme temperature. The addition of hydrogen helps to regulate the appropriate hydrogen:carbon monoxide percentage for methanol production. 1.29 kt amount of hydrogen is used for the manufacture of 12.2 kt of methanol annually (Cifre and Badr 2007).

Methanol processor uses catalytic conversion of syngas for methanol manufacture. The key benefits of this technology are low production cost and improved working reliability. The unpolished methanol is treated in a distillation chamber to attain good quality. The gas turbine can be used in order to consume the residual gas for electricity production (Cifre and Badr 2007).

Bio methanol manufactured using this process is at least 2–3 times extra costly than methanol formed by fossil fuel. Methanol competes with the fossil fuels only under a green assessment based on pollutant released, mainly involving carbon dioxide, which favors the manufacture of methanol using biomass. Some new

Fig. 2.3 Methanol production using Bio-MCN process, the crude glycerin processing leads to bio methanol production



methods propose the usage of renewable hydrogen for methanol production. Methanol production using biomass is inexpensive and more effective compared with that formed from carbon dioxide. Methanol production from carbon dioxide reduces the emission of this greenhouse gas. Numerous choices are being examined for utilization of carbon dioxide taken from flue gases of power stations (Cifre and Badr 2007).

i. Flue gas carbon dioxide

The methanol can also be formed using carbon dioxide. This process increases the yield of methanol, controls the greenhouse effect and recycles carbon dioxide emitted from various sources as a hydrogen carrier. Once carbon dioxide is obtained, it is converted into liquid phase and is taken to the hydrogen manufacture unit. The water electrolysis is done using electricity. The manufacture of methanol using reprocessed carbon dioxide along with hydrogen gas comprises of two stages: methanol production using a catalyst and methanol decontamination (Cifre and Badr 2007). Methanol manufactured using biomass and flue gases is about 428.26 and 576.42 €/t respectively, while natural gas source produces least amount of methanol which is 101.91 €/t (Cifre and Badr 2007).

ii. Bio-MCN method

Another method for the production of biomethane is using crude glycerin. Bio-MCN is the first corporation in the whole globe to manufacture and sell large amount of bio methanol having extraordinary quality. The Fig. 2.3 shows the flow diagram of the process of methanol production by Bio-MCN process (Van Bennekom et al. 2012). In this process, the crude glycerin as a byproduct from biodiesel manufacture is converted into bio methanol, which is disinfected and converted into gaseous phase. Its purification is done by vacuum distillation unit, where it is evaporated and the contaminations are removed. The glycerin vapors are introduced into the steam to remove water, alkanes and heavy fractions. The resultant methanol formed via this process is 99.85 %, having the same purity as from methane (Van Bennekom et al. 2012). The low amount of greenhouse gases using Bio-MCN process for methanol production is seen when compared to gasoline. The Fig. 2.4 tells that gasoline causes about 80 % of greenhouse gases emission all around the globe. In comparison Bio-MCN bio methanol resulted in 50 % greenhouse gases emission in 2011.

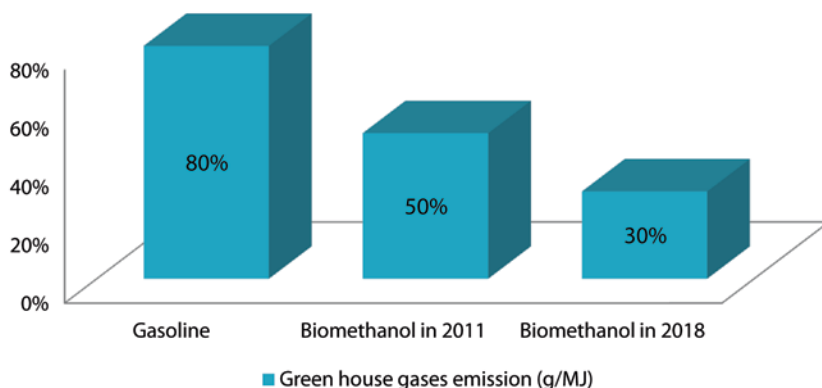


Fig. 2.4 The estimated greenhouse gas emission by gasoline production and bio methanol synthesis using BioMCN process

It is estimated that by 2018, the emission of greenhouse gases will be reduced to 30%. This is because the reuse of the byproduct of biodiesel production (glycerin) reduces the amount of carbon dioxide in the atmosphere (Van Bennekom et al. 2012), thereby reducing the greenhouse effect and global warming by controlling the over production of carbon dioxide in the atmosphere. This process is environmental friendly. Bio-methanol is used as a chemical building block for a range of future-oriented products, including bio-methyl, tertiary-butyl ether, bio-dimethyl ether, bio-hydrogen, and synthetic biofuels etc. Bio-methanol is environment friendly and helps limit global warming by reducing carbon dioxide emission by about 70% in comparison with conventional methanol production technologies (Cifre and Badr 2007; Van Bennekom et al. 2012). The Nobel Laureate George Olah suggested whole methanol budget instead of hydrogen economy because using bio methanol only, slight changes will be required in filling stations and car engines, unlike hydrogen gas which would require an entirely novel setup (Cifre and Badr 2007).

4.1.2 Bio Ethanol

Fossil fuels produce about 73% of the CO_2 and release it into the environment. Production of bio-ethanol using biomass reduces the use of crude oil along with environmental pollution. Bio-ethanol is used in the car engine because of its great octane and cetane ratings, which delays self-ignition in an engine (Lokhorst and Wildenborg 2005). Some drawbacks of bio ethanol include low energy density compared to gasoline, corrosive nature, little flame radiance, low vapor pressure that make cold starts challenging, miscibility and harmfulness to environment (Luque et al. 2010). It can be produced from cellulosic feedstocks; but the main issue with it is the handiness of raw materials. The accessibility of feedstock for this can vary greatly from one season to another and is dependent on geographical localities. For planning bioethanol manufacture procedures, evaluation of consump-

Table 2.4 Various feed stocks used for ethanol formation and their relative production value. (Luque et al. 2010)

Soure used	Ethanol obtained (l/ton)
Sugar cane	70
Sugar beet	110
Sweet potato	125
Potato	110
Cassava	180
Maize	360
Rice	430
Barley	225
Wheat	340

tion of various feedstocks is required as they hold big share in bioethanol costs (Dien et al. 2003).

i. Feedstocks of bioethanol manufacture

There are many types of feedstock for the production of bioethanol, some of which are shown in Table 2.4.

The bioethanol feedstock can be mostly classified into three kinds: sucrose, starch and lignocellulosic biomass. These are discussed below:

a. Sucrose containing feedstock

This includes sugar cane, sugar beet, sweet sorghum etc. but bioethanol is chiefly formed from sugar beet and sugar cane (Dhavalala et al. 2006). About 2/3 sucrose is made from sugar cane while 1/3 from sugar beet. Brazil is the chief manufacturer of sugar cane having worldwide manufacture of about 27% (Kim and Dale 2004). Bioethanol formation by sugar cane is very cost-effective especially in Brazil; since Brazil lowered the sugar cane prices in order to support the bioethanol industry. This significantly dropped the price of the feedstock and generated a petition for the maintained worth of bioethanol (Cardona and Sanchez 2007). In European countries, sugar beet molasses is the best used feedstock. The benefits of using sugar beet include: minimum rotation of crop production, greater harvest, and great resistance towards climatic variations, less water and fertilizer necessity. Sugar beet requires 35–40% less amount of water and fertilizer as compared to sugar cane (Dhavalala et al. 2006; Luque et al. 2010).

b. Starch containing feedstock:

Starch is a biopolymer. In order to obtain bioethanol from this feed stock it is necessary to break it down, which can then further be transformed into bio ethanol by yeasts. This process is mostly followed for bioethanol production in Europe and North America (Luque et al. 2010). Wheat and corn are largely engaged for these procedures (Balat et al. 2008). USA owns a large corn bioethanol industry producing over 15 billion tons per year. The single factor increasing the cost of the manufacture of bioethanol from corn is the rate of the corn itself. Corn prices vary from 1 year to another. The price previously ranged between 1.94 and 3.24 \$ per bushel (De Oliveira et al. 2005). The value of corn now is four

dollars per bushel, which is extremely high (Luque et al. 2010). The prices of corn will also vary in various places due to shipping expenses. USA bioethanol manufacture is 1.1, which is visibly less than the percentage of 3.7 for bioethanol produced in Brazil using sugar cane (De Oliveira et al. 2005). Other reasons for the high cost of starch based bioethanol are that the yeast *Saccharomyces cerevisiae* is not able to utilize starch, so large amount of amylolytic enzymes are needed and the starchy material is essentially cooked at a quite high temperature to acquire a great bioethanol harvest. The two-step enzymatic hydrolysis of corn meal at a lower temperature yields bioethanol of more than 80% just after 4 h (Mojovic et al. 2006).

c. **Ligno cellulosic biomass**

The chief structure of all lignocellulosic biomass is: cellulose, hemicelluloses and lignin. This feedstock is used for bioethanol fuel production since it is the most abundant resource all around the globe (Luque et al. 2010). Lignocellulosic biomass could go up to 442 billion/year. The entire possible bioethanol making from crop left over and crop wastes is 491 billion/year, which is 16 times greater than the present world bioethanol production (Karimi et al. 2006). The highly overflowing lignocellulosic waste material in the world is rice straw. It has the potential to produce about 205 billion bio-ethanol (Hamelinck et al. 2005). Lignocellulosic perennial crops are a good feedstock as they give excessive yield, least expenses, worthy suitability for low quality land, and great environmental resistance. Pine has the highest collective sugar content, involving the extreme potential of bioethanol production. The lignin content is about 27% for most feed stock while grasses contain visibly lesser amount and thus result in less electricity production (Hamelinck et al. 2005). The bioethanol formed using lignocellulosic materials has a moderately greater cost, based on the chief encounters and at hand technologies, such as high price of the hydrolysis process (Dhavalala et al. 2006). The feedstock can signify 440% of all process charges; a money-making biomass-to-bioethanol process analytically relies on the fast and effective transformation of the sugars into both cellulose and hemicellulose portions (Hamelinck et al. 2005). Lignin fermentation, which is coproduced in bioethanol prepared from lignocellulose, can actually produce 458 terra-watt-hours of current and 2.6 EJ of steam unit (Weber et al. 2010).

ii. **Thermochemical method of bioethanol production:**

Two leading methods for bioethanol production, which use thermochemical reactions in their processes are:

a. **Hybrid biological and thermochemical system**

In this process cellulosic biomass is first thermochemically converted in gas phase and the synthesis is bubbled through specifically aimed fermenters (Dhavalala et al. 2006). Also a microorganism with the ability of converting syn-gas is present in the fermentation containers thus permitting bioethanol to get fermented (Jansson et al. 2009).

b. Bioethanol production thermochemically without microorganisms

Biomass is mainly thermochemically converted into gas and then the syngas is passed through a unit comprising of catalysts, which allow the gas to be converted into bioethanol. Bioethanol yields up to 50% have been achieved using syngas—bioethanol way. The quest for an economical thermochemical process has been problematic (Dhavala et al. 2006). Thermochemical is encouraging than biological selection for the transformation of lignin of cellulosic biomass, which can have an unfavorable consequence on enzymatic hydrolysis but also helps in processing energy and formation of possible byproducts with significant profits (Jansson et al. 2009).

iii. Lignocelluloses to bioethanol:

There are numerous choices for bioethanol production using this feed stock irrespective of which one is selected. The following points need evaluation in contrast with various well-known feed stocks for bioethanol making (Luque et al. 2010): effective de-polymerization of cellulose and hemicellulose; effective fermentation of a mixed-sugar hydrolysate; innovative method used in order to lower procedure energy claim, less lignin content of feedstock which reduces the price of bioethanol.

The benefits of using lignocelluloses are the chances to create a bio plant, generating byproducts along with the fuel, bioethanol. For example, sugars when exposed to bacterial fermentation in the absence or presence of oxygen produce a variation of products like lactic acid, which may be managed into plastics and other products (Dhavala et al. 2006). The treatment of lignocelluloses to bioethanol comprises of four leading units: pretreatment, hydrolysis, fermentation and separation/distillation of product (Luque et al. 2010).

a. Pre-treatment:

Pretreatment and size reduction is the first step in lignocellulose to ethanol bio-conversion. The purpose of pretreatment is to change and eliminate mechanical and compositional obstructions to hydrolysis so that rate of enzyme hydrolysis increases leading to more fermentable sugar from cellulose and hemicellulose. A popular pretreatment should fulfill the requirements like; increase sugar formation, allow least degradation of carbohydrate, evade the production of hydrolysis and fermentation inhibitory byproducts and should be cost effective (Luque et al. 2010).

b. Hydrolysis:

When pre-treatment is complete, the cellulose undergoes hydrolysis. This includes acid hydrolysis and enzymatic hydrolysis. Acid hydrolysis can be of two types, dilute and concentrated. The dilute acid hydrolysis is for transforming cellulose biomass to bioethanol. The hemicellulosic part is depolymerized at lower temperature than cellulose. Usually dilute acid procedures are restricted to 50% regaining of sugar. The current task is to raise sugar recovery to as high as 70% in a favorable industrial use (Luque et al. 2010). Enzymes are naturally occurring in nature used for several chemical reactions and both bacteria and

fungi can be evaluated in this direction. In this procedure two technologies are used: (1) direct microbial transformation method and (2) enzymatic transformation method. It has numerous advantages like less cost, insignificant conditions needed and improved yields (Luque et al. 2010).

c. Fermentation:

The process of fermentation comprises of microbes which consume sugar as food and in the process lead to the production of bioethanol and other varieties of products. The microbes are termed as the ethanologens, as these convert a portion of sugar to ethanol. The microorganisms used are compatible with the fermentation conditions i.e. pH, temperature, growth rate, tolerance to inhibitory compounds, output result, osmotic tolerance, specificity, yield, stability etc (Luque et al. 2010). The fermentation can be done in batch, fed batch and continuous process. The selection of the method depends on properties of microbes and nature of lignocellulosic hydrolysate other than economic aspects. Fed batch containers are extensively used on the industrial level since they have both the benefits of batch and continuous process. The key benefit when compared to batch is, ability to increase the cell viable concentration, longer culture life and more product accumulation (Luque et al. 2010).

d. Product and Solid recovery:

Fermentation products are unstable, so distillation is widely used equipment for the recovery of the bioethanol and other products from a number of impurities. The distillation separates bioethanol from water; the virgin ethanol has 80% water in it. Large amount of energy is needed for the concentration of bioethanol to 95.6% (Luque et al. 2010). At first bioethanol is recovered from water which has high moisture content. The bioethanol (37%) is concentrated in the rectifying column and is adjusted below a zeotrope, reaching 95%. The residual product is fed to stripping column for the removal of extra water (Luque et al. 2010). Bioethanol is recovered in the distillation unit which is stabilized to be about 99.6% to lessen the bioethanol loss (Garcia et al. 2008). Solids are dispersed by centrifuge and dried over rotary dryer. About 25% waste is reprocessed to fermentation while the remaining is sent to evaporator. The concentrated solution comprises of 15–20% weight of total solid (Luque et al. 2010).

4.2 DMF (2, 5-Dimethylfuran)

Until recently scientists perfectly were confident on “Bio-ethanol” as the only satisfying bio-fuel in the energy market across the globe. The advent of advancement in methods like catalytic systems for the production of 2,5 Dimethylfuran from biomass opened a new window of research and hope in the world of biofuels. With its infallible chemical characteristics fulfilling particularly all requirements as an ideal candidate for biofuels, DMF was largely considered an auspicious bio-fuel for the future of power generation and internal combustion engines.

i. Structural Chemistry of DMF

Dimethylformamide is a colorless, polar, high boiling point liquid with a distinctive odor having a molecular formula of C_3H_7NO . It is immune to decomposition upon distillation procedures and even at elevated temperatures. It is freely miscible in water, ketones, esters, alcohols and ethers. However its rate of hydrolysis increases in the vicinity of acids and alkalis. DMF is one of the rare liquids that has a high dielectric constant and low volatility which qualifies DMF as an excellent universal solvent, particularly for chemical reactions that require a high solvency power.

Physical Properties: Density -0.949 g/cm^3 ; Distillation Range- 760 mmHg ; Temperature— 347°C ; Boiling Point- 153°C

a. Production of DMF from Biomass: Carbohydrates

Previously, DMF was widely employed in a number of industries but at a high cost and low production yield. In 2007, biochemists from University of Wisconsin (USA) developed a new technique for the convenient conversion of carbohydrates to DMF. Earlier, carbohydrates were enzymatically broken down to fructose which was then deoxygenated to DMF. It was proposed that the production of bio-fuel with high yield and low energy consumption from biomass is possible if 5 oxygen atoms are removed from hexose for the production of DMF. This step can be carried out in two steps. The first step maneuvers the removal of 3 oxygen atoms via the process of acid catalyzed dehydration reaction with a solvent having low boiling point to produce 5-hydroxymethylfuran, following it butanol solvent is used for quick extraction of DMF, the quicker the extraction, the bigger the yield. The second step includes removal of two oxygen atoms via copper catalyzed hydrogenolysis involving the production of two intermediates: 2 methyl furan and 2-methyl,5-hydroxymethylfuran (Leshkov et al. 2007). These methods were modified later on by rendering the need of acid based catalysts as non-imperative. This led to an augmented interest towards DMF as a prospective gasoline alternative biofuel. Engineers from the automotive community began paying attention to DMF as an alternate automotive fuel. The first study on the capability of DMF as a fuel, focusing on its emission and combustion performance commenced in Birmingham University of UK. The factors under observation viable for required performance of a fuel were spray characteristics, laminar burning velocity and unregulated engine emission (Leshkov et al. 2007).

b. Fuel Spray Characteristics

A desired engine performance fuel spray characteristics tremendously influence the fuel-air mixture generation and combustion manner. A number of comparative studies between spray characteristics of ethanol, gasoline and DMF have been conducted through use of Optical methods such as Phase Doppler Particle Analyzer. Results of the studies have shown that spray characteristics of DMF are preferably favorable over those of ethanol and gasoline. The spray pattern of DMF was not very different from that of gasoline. DMF spray velocity turned out to be greater than that of ethanol and DMF spray droplet size very small than the large ones of ethanol. These findings rendered DMF a considerably suitable engine fuel given its extreme similarity to gasoline behavior.

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