Chapter 3
Biofuels from Renewable Biomass Resources: An Overview of Technologies for Production, Environmental and Economic Impacts

J. Thangaraja, Akella Sivaramakrishna and Rajagopal Desikan

Abstract In recent years, there is a great deal of social obligation involve with scientists to common people that a sustainable chemical processes having industrial importance which is associated with greener concept and environmentally benign methodology is the need of the hour. This trends of technology driven greener process will continues to roll on for next few decades. With this aspects in mind, biomass, a sustainable alternative feedstock, can be processed into liquid and solid fuels via thermal, light-induced, catalytic and bio-based techniques. Conversion of biomass materials into value added products and energy can address environmental sustainability and recycling of waste materials. Utilization of bio-based energy has not been explored fully. We continue to rely on fossil fuels, nuclear energy and hydroelectricity to meet our energy demands. Alcohols and its derivatives are the important source of bioenergy that are hidden in biomass. In this context, the production of alcohols or esters is an extremely important industrial process as they are useful as precursors, reagents, solvents or additives in perfumes, essential oils, food flavorings, cosmetics, etc. Even though there have been numerous methods available for the production of alcohols and esters, designing non-hazardous methods to generate chemical products that limit the usage of hazardous substances is highly required. The present chapter aims at the analysis of various green methods reported for the production of alcohols and esters from renewable energy sources. Also provide a broad overview of the environmental and economic impacts of biofuels. The major environmental impacts are conceived under two headings, viz. direct emissions those that are expelled during the biofuels production and consumption and indirect emissions those that are associated with their land use.

J. Thangaraja (✉)
Department of Mechanical Engineering, Vellore Institute of Technology, Vellore,
Tamil Nadu 632014, India
e-mail: thangaraja.j@vit.ac.in

A. Sivaramakrishna · R. Desikan
Department of Chemistry, School of Advanced Sciences, Vellore Institute
of Technology, Vellore, Tamil Nadu 632014, India

© Springer Nature Singapore Pte Ltd. 2020

A. P. Singh et al. (eds.), *Alternative Fuels and Their Utilization Strategies in Internal Combustion Engines*, Energy, Environment, and Sustainability,
https://doi.org/10.1007/978-981-15-0418-1_3

Keywords Bioenergy · Alcohols · Esters · Thermochemical · Sustainability · Greenhouse gases

3.1 Introduction

Evaluation of data from various quarters indicate that USA can sustainably generate roughly one billion tons of biomass from non-edible biomass per year. Bio-based fuels can substitute roughly 1/3 of the conventional fuels which are chiefly used in automobile sector. Currently about 2 million barrels per day vehicular fuels are generated from biomass. By 2030, it is expected to increase nearly 6 million barrels per day. This is roughly six percent increase in fuel consumption. Hence, it is convincing that there is a trend toward decreasing the reliance on conventional source of fuels and meeting the future requirements for transportation fuels by an amalgamation of non-conventional source of electricity and bio-based fuels. To exemplify the inspiration for sustainable strategy in the bio-energy creation, it is important to look into the property parameters of biomass and those of the fuels one would like to generate. Bio-fuels can be generated from edible and non-edible sources as shown in Table 3.1. Predominantly, edible source mainly comes from corn crops. On the other hand, non-edible source is mainly from lignocellulosic biomass.

Lignin, hemicellulose and cellulose are the important ingredients of lignocellulosic biomass. Within this, hemicellulose and cellulose are carbohydrate based polymers having five and six carbon sugars. Carbohydrates, monosaccharides nor disaccharides, produced from enzymatic or acid catalyzed hydrolysis of bio-mass are not considered as appropriate fuels. This is mainly due to elevated level of oxygen content and reduced energy density (15–20 MJ/kg versus 42 MJ/kg for hydrocarbon fuels). Figure 3.1 describes the types of bioenergy.

Furthermore, fuels that are routinely used in automobile sector need low volatility and appropriate combustion properties, viz. octane number, cetane number and lubricity. Thus, generation of fuels from biomass should exclude most, if not all, oxygen content level and generation of carbon molecular framework with five to twenty two carbon atoms holding branched network of carbon skeleton for gasoline fuels and linear carbon backbone for diesel. An additional limitation on any procedure for

Table 3.1 Biomass feedstock based on edible and non-edible source

First generation biomass feedstock	Second generation biomass feedstock
Based on the food crops	Based on the non-food crops
Bioethanol and vegetable oil from corn crop and sugar cane	Lignocellulosic materials
	Homogeneous—wood chips Quasi homogeneous—agriculture and forest residue Non-homogeneous—municipal and industrial solid waste

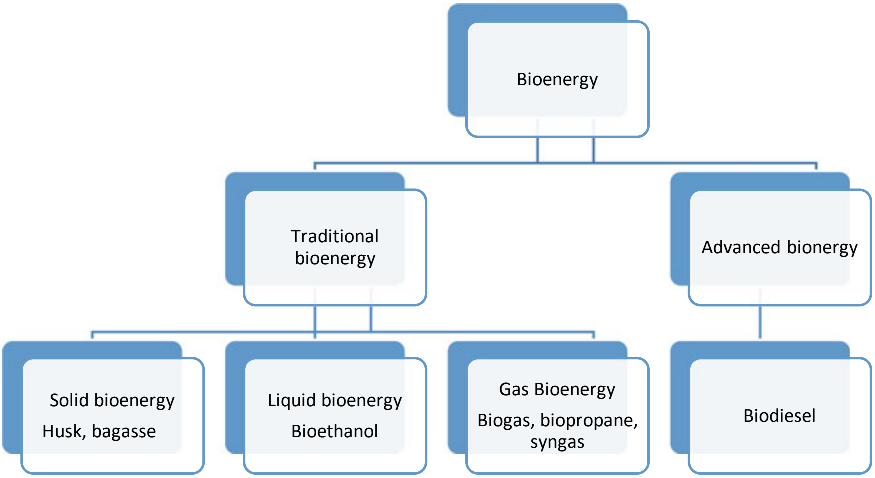

Fig. 3.1 Classification of bioenergy

the conversion of biomass to fuels is the entire hydrogen demand for oxygen conversion. By adopting steam reforming method of methane, industrial methods of fuel generation is achieved for a fossil fuel for generation of hydrogen, and while every carbon dioxide generated in the reforming reaction produces four moles of hydrogen. The endothermicity of the chemical transformation and the elevated pressure at which reduction processes (hydrogenation) are normally carried out to facilitate additional energy inputs from fossil sources.

3.1.1 Biomass to Bio-chemicals—An Alternate Source of Bioenergy Additive

Annually, twenty five billion gallons of bioethanol is manufactured from biomass. It is the most versatile chemical method adopted to generate alcohol. Despite the fact most of the bioethanol is mixed with gasoline, it is construed as an important feedstock for generating multiple chemicals like unsaturated non-aromatics, aromatic hydrocarbons and oxygenates. For example, annually about one hundred and forty million tons of ethane is produced by adopting chemical dehydration of ethanol. On the other hand, new and more sustainable pathways utilizing ethanol and other three-carbon to five-carbon alcohols as feedstocks can be utilized to generate different kinds of aldehydes, treasured chemical intermediates to be useful as plasticizers and detergents. Aldehydes can be synthesized by hydroformylation reaction of alkene as well as dehydrogenation of alcohols by non-oxidative pathways. Later method is specifically fascinating because it produces hydrogen as a byproduct. It was also revealed that nanoparticles from gold can act as acid-base supports such as hydrotalcite (Au/HT) and hydroxyapatite (Au/HAP) initiate this reaction very efficiently. By taking ethyl alcohol or three-carbon to five-carbon alcohols, the corresponding carbonyl compounds (aldehydes or ketones) are generated at 473 K with an excellent selectivity of more than 90%.

Generation of alkenes and ethers from alcohols can be achieved by utilizing powerful acidic supports like silica-alumina (Si–Al), which can catalyze the dehydration of two carbon to five carbon structures. Similarly, basic supports, such as magnesium oxide, generate substantial yields of Guerbet products.

Globally, organic chemicals are produced from bio-based sources like cellulose, hemicellulose, lignin and pectin which covers roughly 10% of world production. These chemicals are highly useful in various sectors. These hydrocarbons are highly diverse in nature. Moreover, these chemicals require low technological utility. Many of these hydrocarbons are important intermediates valuable in multi-step process. Eventually, these chemical intermediates are believed integrate with ultimate consumer utility products.

From a commercial point of view, chemicals that are derived from biomass are extremely valuable in international market as a result of greener methods involved in the production. Generation of optically active highly pure amino acids from natural sugar components or demonstrated cost-competitive with their conventional counterparts.

With regard to market potential of high utility chemical products, specifically, this sector is well recognized due to its importance. These products include functionalized high-value but low volume chemicals cosmetics, therapeutic agents and extremely useful polymers. Basic chemicals derived from biological sources have the limitation of reaching out broader market utility. This is primarily due to higher price range which are consistently well-adjusted to exceptional market prices. Chiefly motivated by consumer expectations, a rapidly expanding growth market for bio-based polymeric material has to supersede a market share of three percent in 2020. Nevertheless, the learning curve in fuel-bio refineries in blend with the creation of improved catalytic components derived from biological sources would enhance the price component for sustainable chemicals as well and hence a constant exponential growth to a bio-based share of twenty two percent by sales in 2020. The production volume of bio-based chemicals is smaller than bio-based fuels, the more market for bio-based chemicals are not popularized by government subsidies.

3.1.2 Features of Bioenergy

Combination of several large varieties of numerous hydrocarbons constitutes petroleum based fuels. Bio-based fuels chemically consist of pure single component substances such as H_2, CH_4 and CH_3CH_2OH. On the other hand, chemical constituent of biofuels are chiefly consist of a mixture of typically 5–6 esters of fatty acids. The relative ingredients of which may vary depending upon the source of raw materials. This comparatively fixed number of fatty acid esters in bio-based diesel divergences with the much wider and more intricate varieties of hydrocarbons that occurs in petroleum. Apart from this, fossil fuels are mixed with bio-based fuels. The existence of oxygen content within the hydrocarbon molecular framework can differentiate alcohol fuels from bio-based diesel and petroleum-based fuels. This is important parameter that discriminates the types of fuels that are available for day to day use.

By utilizing multidimensional spray technique and combustion modelling, a recent investigation demonstrated the changing the fuel's properties on the spray and combustion specific of diesel-engines when fuels are functioned by multiple bio-diesel fuels. The normal properties of biodiesel fuel that are used in the investigations and the simulation studies outcome, are correlated with those of traditional diesel fuels.

The sensitivity of the computational outcomes to selected physical properties is also studied by varying one parameter at a time. Taking advantage of selected studies outcome, it offers a standard on the acceptable properties of combined fuels. The analyzed properties are; (i) density measurement of liquid; (ii) vapor pressure; (iii) surface tension; (iv) fluid viscosity; (v) thermal conductivity of liquid sample; (vi) liquid specific heat; (vii) latent heat; (viii) vapor specific heat; (ix) vapor diffusion coefficient; (x) vapor viscosity; and (xi) vapor thermal conductivity. The outcomes of the studies advocate that the intrinsic physical properties of each of these fuels ominously effect spray structure, ignition delay and combustion rates in a broad range of engine specific to functional parameters.

Furthermore, the interpretation that substantiates the prediction that ignition delay between diesel and bio-based fuels is not governed by single physical properties. Nevertheless, liquid fuel density, vapor pressure and surface tension properties have profound effects on fuel. There is a strong correlation exists on the atomization, spray and mixture preparation methods of fuels which contributed to the prominence of aforementioned properties.

With regard to cold weather conditions, diesel fuel has the capabilities hold liquid characteristics. This is very significant characteristics of diesel fuels. However, when optimal temperatures are low enough, a few hydrocarbons in diesel fuel start to become solid, thus, preventing the flow of fuel from the storage tank to the fuel injection pump through the filter system. This parameter is characterized by the cloud point and cold filter plugging point (CFPP), for which bio-based diesel fuels normally have elevated temperatures; this keeps them vulnerable to obstruction of the fuel system and hindering the engine being started when cold. The presence of relative levels of saturated and unsaturated fatty acids in bio-based fuels has direct correlation with liquid characteristics of fuels. Higher the level of the saturated component, the greater the cloud point and CFPP temperature. Chemical additives such as malan-styrene esters and polymethacrylate can effectively address these limitations.

Energy density is a degree of quantum of energy a fuel holds; this property has a straight effect on quantity of energy an engine generates by burning this specific fuel. The energy content for wider varieties of fuels is attributed to the lower heating values. Ethyl alcohol has about thirty percent reduced energy content than gasoline on a per unit volume basis; this transforms into a reduced distance travelled per tank of fuel compared to gasoline. By the same token, biodiesel shows an energy content that is roughly nine percent lower than that of conventional fossil-based diesel. One important chemical behavior of ethyl alcohol is its resistance to auto-ignition, as echoed by its elevated octane number. The octane number of a fuel is a vital property to reveal whether the given fuel will knock the engine under given operating conditions. In order for a fuel to resist knocking, it is preferred to have fuel with higher octane number. To improve the fuel properties, ethyl alcohol is added as an enhancer for gasoline. The reason for this property variation is due to ethyl alcohol is relatively having high heat of vaporization. The elevated level of heat of vaporization results in cooler fuel-air composition, which in turn slows down the burning and offers a higher resistance to knocking. Further, the significance of increased octane number can burn ethyl alcohol at a higher compression ratio. In a similar way, the cetane number offers a degree of compression ignition. The greater the centane number is, the higher the ignition parameter of a fuel and reduced ignition delay. This is a critical parameter since extended ignition delay results in most of the fuel being injected before ignition happens. In turn, this results in rapid combustion rates and very high rates of pressure rise once ignition starts such that, in some cases, diesel knock can happen. This article covers in detail the thermochemical, biochemical, and chemical routes for biofuel production. Further, this study highlights the environmental and economic impacts of biofuels. Thus the chapter outlines on the efforts to progress for sustainably transforming biomass-based materials to additive fuels (alcohol and ester) to selected useful chemicals mainly used in the transportation sector.

3.2 Overview of Transformation Methods

Numerous biomass resources (Owusu and Asumadu-Sarkodie 2016) have been used to convert them to fuels (liquid, solid, and gaseous) with the help of chemical, thermochemical, biochemical routes (refer Fig. 3.2). Other processes related to biomass conversion reported are physical extraction, electrochemical, direct liquefaction and indirect liquefaction.

3.2.1 Thermochemical Conversion Process

Thermochemical conversion can be classified into three subcategories: pyrolysis, gasification, and liquefaction as shown in Fig. 3.3 (Appell et al. 1971).

The conversion of biomass materials into fuels having physico-chemical characteristics facilitates the transferability through pumping routes and economic storage. In general, gasification at the first stage is partial combustion of biomass to yield gas and char and subsequent reduction of the gases produced CO_2 and water; useful CO and H_2 as major products and CH_4 and other hydrocarbon fractions as minor

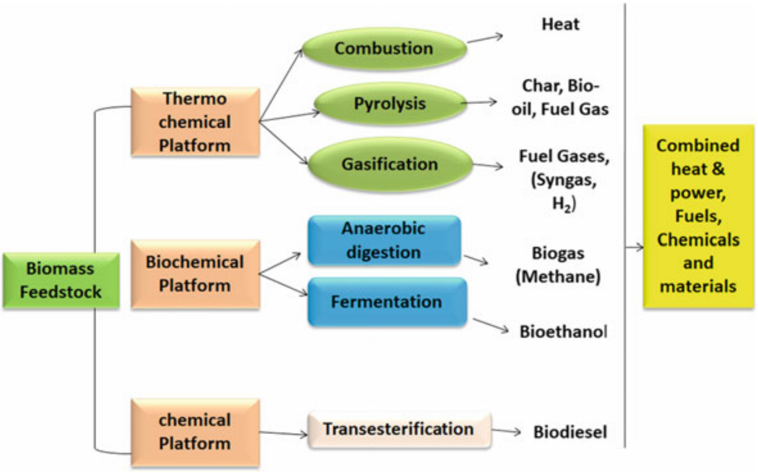

Fig. 3.2 Various routes for the production of value added products from biomass

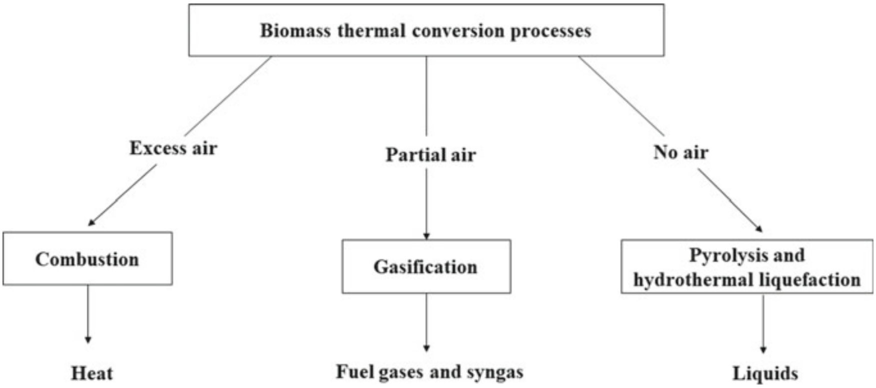

Fig. 3.3 Thermal conversion processes reported for biomass conversion

products by charcoal. The conversion efficiency in this process is affected by the design of the reactor and operating conditions (Balat 2008).

Pyrolysis is an incomplete gasification process with the source of both gasification and combustion of solid fuels, by facilitating the chemical changes of a material at elevated temperatures in the absence of oxygen. The flash pyrolysis of biomass directly converts small dried biomass particles in the absence of oxygen into a liquid fuel. The vapor phase of char catalyzes the secondary cracking. Plasma arc processes provide very high heat from electricity to produce a discharge converting the surrounding gases to an ionized gas. But the mechanistic aspects in the formation of various products have been regarded as complex systems. Thermochemical conversion is known for their faster rate of reactions under the extreme conditions. The rate of conversion is influenced by the strength of oxidizing or reducing media, process temperature, and pressure.

Various fluids have been employed including water for the biomass conversion processes: hydrothermal upgrading (HTU) and supercritical water gasification (SCWG). In order to design the efficient biomass conversion processes, both phase equilibria and phase behavior in the reactor and separators are extremely important (Feng et al. 2004). HTU (or direct liquefaction) is a favorable technology to treat waste from various sources and to produce valuable bio-products such as bio-crudes.

Mechanistic aspects of thermal decomposition of biomass

Liquefaction takes place through the systematic structural and chemical changes of carbonaceous materials, which involve any one or more following steps (Chornet and Overend 1985; Demirbas 2000).

1. Cracking/reduction of polymers (*e.g.* lignin and lipids)
2. Conversion of cellulose and hemicelluloses by hydrolysis to glucose
3. Hydrogenolysis of the matter in the presence of hydrogen gas
4. Reduction of amino acids
5. Dehydration and decarboxylation reactions for molecular rearrangements
6. Hydrogenation of active functional groups.

As per the studies, the reactions in biomass de-polymerization process are remarkably complex.

Hydrothermal Liquefaction of Bio-renewable Feedstocks

Direct hydrothermal liquefaction and further rapid pyrolysis produce condensable organic vapors, oils and tars in liquid form (Goudriaan and Peferoen 1990). The catalysts are used in indirect liquefaction to convert the non-condensable products of gasification or pyrolysis into liquified products. Figure 3.4 shows the block scheme of commercial HTU plant.

Hydrothermal reaction is one of the effective methods for the treatment of organic wastes under supercritical or subcritical reaction conditions (Jomaa 2001). This is classified into two broad categories: (a) oxidative process in the presence of oxidants, and (b) non-oxidative process in the absence of oxidants. Subcritical temperatures provide the production of huge quantities of dissolved organic matter along with volatile fatty acid including acetic acid. In general, the efficiency of combustion is based on the temperature of flue gas and the air (Jomaa et al. 2003).

The calculations on combustion efficiency assuming the complete fuel combustion mainly depend on three following factors:

(1) the properties and chemistry of the fuels
(2) the net temperature of the corresponding stack gases and
(3) the volume percentage of oxygen/CO_2 after the combustion

The efficiency of combustion remarkably increases with increasing contact time and the temperature of the reactants which leads to enhanced vapor pressures, improved surface areas, and increasing stored chemical energy. The liquid ethanol is called as

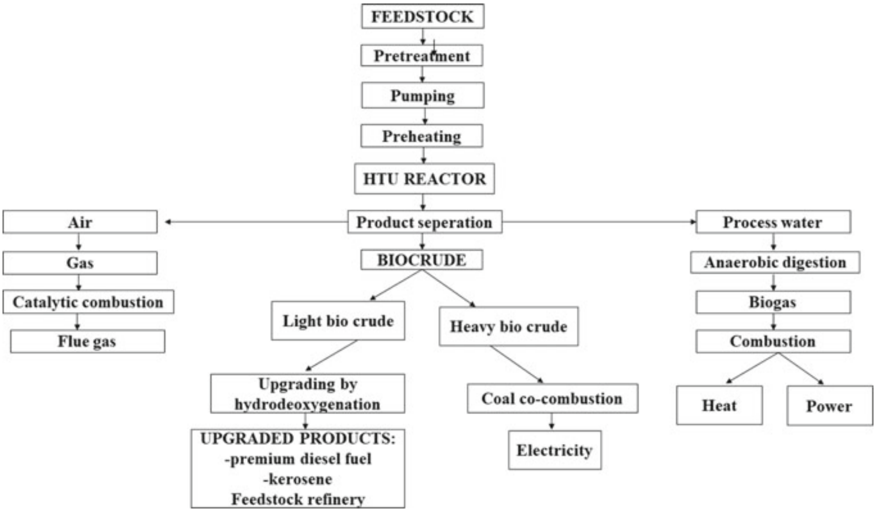

Fig. 3.4 Block diagram of a commercial HTU plant

oxygenated fuel and it has significantly low combustion heat than those of petroleum-based fuels. Figure 3.5 shows the procedures for isolation of aqueous liquefaction products. Direct liquefaction involves hydrothermal route to produce liquid tars and oils including condensable organic vapors (Demirbas 2007). Indirect liquefaction can have successive production of synthesis gas or ethylene intermediates, and the

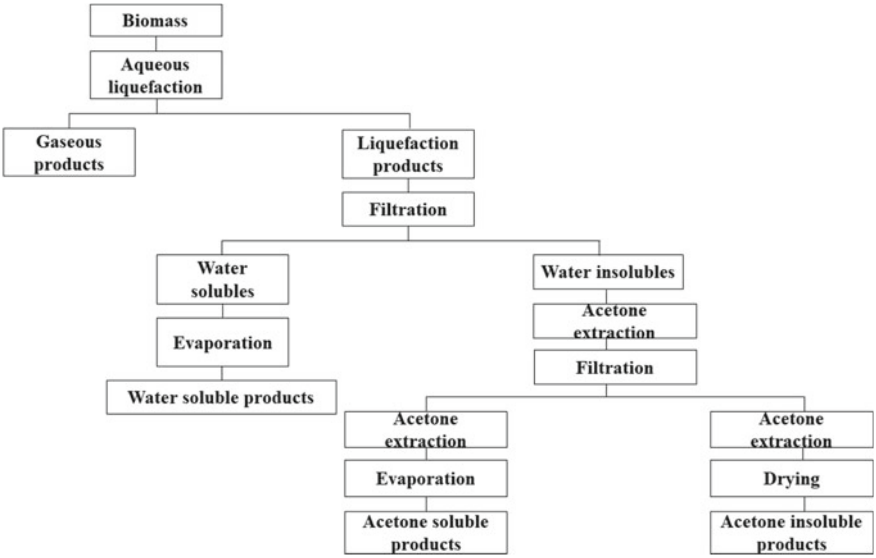

Fig. 3.5 Procedures for separation of aqueous liquefaction products (Demirbas 2009a, b)

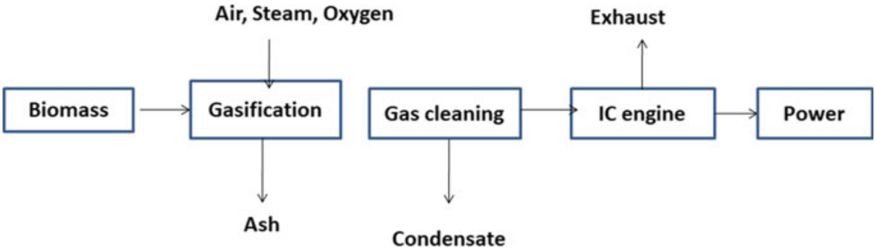

Fig. 3.6 Flow-chart for biomass gasification process

formation of liquid fuels through Fischer–Tropsch processes in the presence of catalysts. In this context, the degradation of biomass proceeds through depolymerization and deoxygenation to produce smaller products.

Biomass gasification technologies are based upon the partial oxidation or partial combustion principles, resulting in the production of hot, dirty, low heating value containing gaseous products (Chen et al. 2004; Warnecke 2000). Biomass integrated gasification combined cycle cogeneration technology is not yet commercially available as this process has several limitations including the source of insufficient energy and release of unwanted gaseous products into the atmosphere (Stevens 2001). The system for power production by means of biomass gasification is given in Fig. 3.6 (Demirbas 2009a, b).

3.2.2 *Catalytic Conversion Processes of Biomass to Bioenergy*

There has been significant interest continuously to produce sustainable energy, fuels for transportation, and valuable chemicals from renewable resources (Hao et al. 2005). This interest stems from the sincere efforts of researchers to address the problems associated with climate change, job creation, sustainability, energy independence and national security. Among the processes those are envisioned for the conversion of biomass into value added products are strongly dependent upon nature of catalysts. The stability, activity, and selectivity of the catalysts play a critical role in the process economics of biomass conversion methodologies.

In general, there are three types of feedstocks recognized from biomass that are suitable for the generation of renewable fuels (Yung 2016): (i) starch related (including sugars), (ii) triglycerides, and (iii) lignocellulosic materials. As shown in Fig. 3.7, the representative chemical structures for triglycerides and starches are compared to that of cellulose (lignocellulosic biomass). Starchy feedstocks contain glucose polysaccharides linked by aglycosidiclinkages (amylaseandamylopectin). Trigylderide feedstock consist of fatty acids and glycerol derived from the sources of both plants and animals, various vegetable oils, waste oil products, and algal

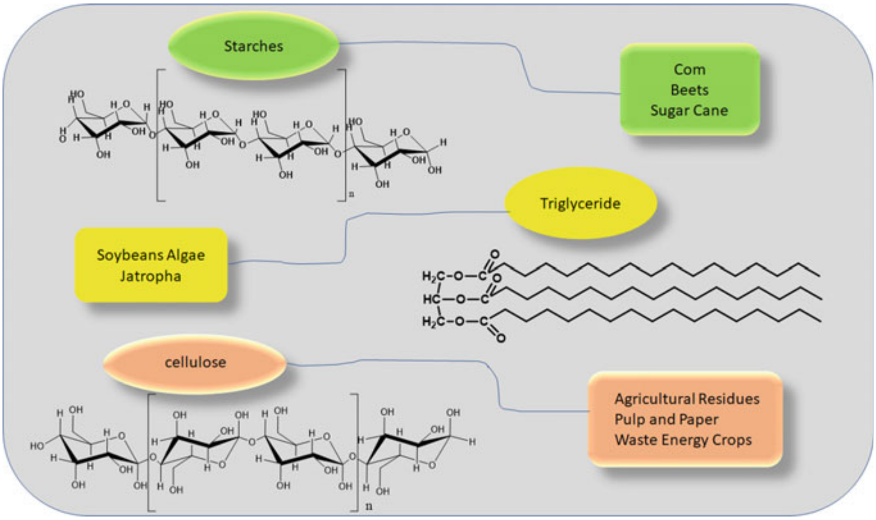

Fig. 3.7 Chemical structure of biomass feedstocks

sources. The most abundant lignocellulosic biomass is a combination of three different fractions: lignin, hemicellulose, and cellulose (Alonso et al. 2012).

First generation biofuels (i.e. alcohols-bioethanol and oils-biodiesel) are readily available and can be derived from the well-refined conventional technologies using food crops. The main challenge in current research for the generation of biofuels is the optimization of processes to reduce cost, but not the development of new technologies. The production of bioethanol begins with the pre-treatment of biomass to produce sugar monomers, such as glucose, that can be converted into ethanol by fermentation using various microorganisms (e.g., yeast, bacteria etc.). The purification of ethanol obtained is done by distillation for the further use as an additive or a direct fuel. The second generation bioethanol is derived from the feedstocks of lignocellulosic biomass. The limitation in the utilization of lignocellulosic biomass is pre-treatment and hydrolysis for the production of sugars. These steps are regarded as the greatest disorder to economic feasibility of various strategies involved in the production of sugars from lignocellulosic biomass. Algae crops have been considered as third generation biofuels as they possess a sustainable source of feedstocks for bioethanol and biodiesel. The second most abundant renewable liquid fuel is biodiesel prepared by using a variety of basic (Kim et al. 2004; Di Serio et al. 2006; Granados et al. 2007) or acidic catalysts (Lotero et al. 2005; Melero et al. 2009), and has been used in current engines with a wide range of blends the preparation is outlined schematically in Fig. 3.8. Normally canola. sunflower, palm, soybean and rapeseed oils are useful as food oils, but they are expensive. Currently the biodiesel research is mainly focused on the development of new catalytic processes that makes the use of low quality or waste oils (used oils), such that biodiesel production becomes less expensive and does not directly involve with the food supply (Liu and Zhang 2016).

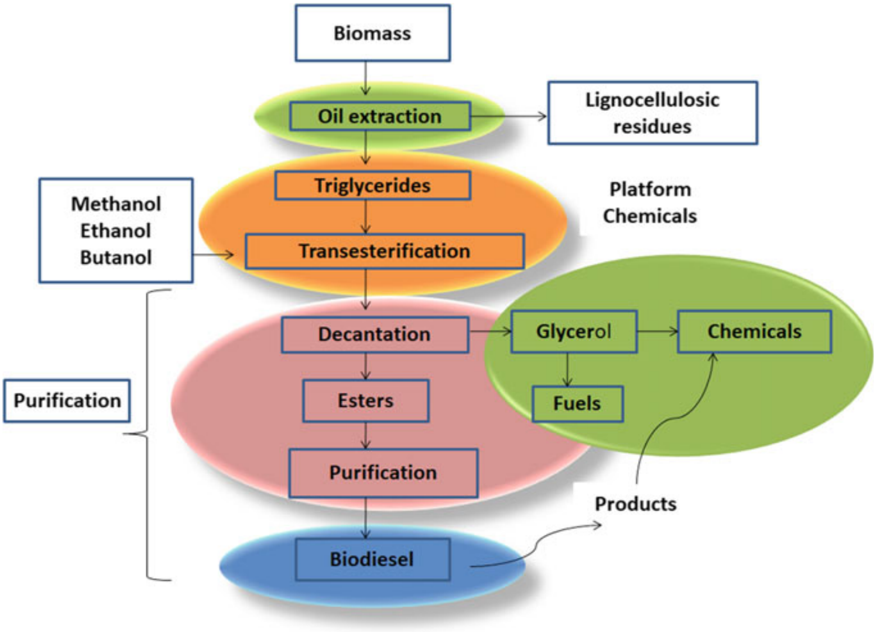

Fig. 3.8 Process schematic: biodiesel production

3.2.3 *Biochemical Processes*

It is well-known that micro-organisms are regarded as biochemical "factories" and can convert the biomass to ethanol. Further, the microbial technology has been developed different fermentation processes (aerobic and anaerobic) to produce biogas and fertilizers (Bisio et al. 1997). The production of methane from manure (human and animal) can be achieved by anaerobic reactors and the crop residues by employing mixed methanogenic bacterial cultures at optimal temperature ranges for the appropriate growth. Under the suitable conditions, about 90% of the feedstock energy content can be converted by the bacteria into biogas (around 55% of methane) and the sludge produced is absolutely non-toxic and odourless. Anaerobic digesters of various types were widely used in the form of biogas plants as ideal candidates for rural villages. The efficiency of bio-conversion processes strongly depends on construction defects, the rate of bacterial growth, the digesters requirements for water, mixed nature of the bacterial population and maintaining the optimum nitrogen ratio of the medium. Modern designs in the recent past have solved many of these problems associated with the digesters. Methane gas can be produced through anaerobic digestion in landfills by the microbial decomposition of the organic matter in refuse. Landfill-generated gas is on average half methane and half carbon dioxide and the production does not require high pressure.

The production of ethanol by well-developed fermentation technologies has been remarkable as a petroleum substitute and fuel enhancer, and beneficial in view of both economic and environmental fronts. The most common feedstock is sugarcane by "Biostil" process in developing countries, due to its high production value. The following section comprehends the techno-economics of biofuels and is further categorized into three sub sections, wherein the first section comprises the effect of biofuels on direct emission followed by the second section bears the impact on greenhouse gases and the last section outlines the economics of biofuel market.

3.3 Environmental and Economic Impacts of Biofuels

In 1997, an international summit held in Kyoto, Japan identified combustion of hydrocarbon fuels as the dominant factor enhancing the concentration of Greenhouse gases (GHG) which induces global warming. Till date numerous measures have been taken by various governments and protection agencies to control emissions. However, the environmental impacts of biofuels have been a growing concern around the world. For these reasons, it is important to clearly understand the environmental and also the economic impact of biofuels. The direct emissions, which are incurred due to the production and consumption of the biofuels, would be discussed here.

3.3.1 Direct Emissions

In last three decades, there have been extensive investigations carried out to evaluate the emission characteristics of biodiesel fuel in different types of compression ignition engines vis-a-vis fossil diesel. Usage of biodiesel in a conventional diesel engine substantially reduces the emissions of unburned hydrocarbons (UBHC), carbon monoxide (CO), and smoke emission. However, biodiesel generally tends to increase the oxides of nitrogen (NO_x) emissions. Similar trends are reported by McCormick et al. (2001) and Anand et al. (2009) in their investigations. Biodiesel operated diesel engines significantly lowers the soot/particulate emissions due to the presence of fuel bound oxygen and absence of sulfur and aromatic constituents. Table 3.2 provides the detail of investigations concerning the variety of neat biodiesel and/or their blends with fossil diesel using single and multi-cylinder engines.

Graboski and McCormick (1998) identified the following important causes for biodiesel-NO_x formation, changes in spray and ignition characteristics, absence of soot particles and variation in fuel chemistry. It can be summarized that the NO_x emission with neat biodiesel remains higher than fossil diesel, and composition of biodiesel plays a significant role in altering fuel property characteristics affecting the NO_x emission. Various strategies such as optimization of the injection parameters, recirculation of exhaust gases, blending methanol/ethanol in biodiesel, water-in-oil emulsions, hydrogenating biodiesel, etc. are used for mitigating the biodiesel-NO_x

Table 3.2 Impact of biodiesel and their blends on diesel emissions

Investigator(s)	Fuels	Engine type	Remarks
Ali et al. (1995)	Soybean, 10, 20, 30, 50 and 75% blends	Detroit 206 kW and Cummins 298 kW diesel engine	Exhaust emissions except NO_x reduced with increase in biodiesel blend percent for both the engines
Monyem and Van Gerpen (2001)	Soybean and 20% blend	Four cylinder, DI, turbocharged	Exhaust emission such as HC, CO and smoke reduced, NO_x increased up to 14%
Dorado et al. (2003)	Waste olive oil	Three cylinder, DI, 34 kW @ 2250 rpm	8.5% lower fuel consumption with 58.9% lower CO, 37.5% lower NO
Silva et al. (2003)	5 and 30% blends of oleic sunflower	Six cylinder, turbocharged, 180 kW @ 2200 rpm	Decrease in CO at full load and idle condition, a slight increase in NO_x and lower smoke opacity
Canakci (2005)	Soybean and 20% blend	Four cylinder, DI, turbocharged, 57.1 kW @ 2100 rpm	Neat soybean resulted in 42.5% lower HC, 18.3% lower CO, 11.2% higher NO_x, 61.5% lower smoke
Haas (2005)	Neat Soybean oil soap-stock and 20% blend	Six cylinder, turbocharged, DI, 257 kW @ 1800 rpm	50% lower HC, 45% lower CO, 10% higher NO_x, 70% lower PM for neat biodiesel, 20% blend results in similar HC, CO, 20% lower PM, 1.5% higher NO_x
Usta (2005)	10, 17.5 and 25% Tobacco seed oil blends	Four cylinder, IDI, turbocharged	Lower CO emissions and slightly higher NO_x at full load
Lin and Lin (2006)	Soybean	Four cylinder, NA, DI	Lower CO and higher NO_x emissions
Szybist et al. (2007)	Soybean, 20% blend, 10% methyl oleate and 80% diesel	Single cylinder, naturally aspirated, DI	Biodiesel-NO_x penalty is attributed to the inadvertent advance in injection timing (0.9 deg.CA)

(continued)

Table 3.2 (continued)

Investigator(s)	Fuels	Engine type	Remarks
Dudaa et al. (2018)	swine lard and turkey lard with mixtures of rapeseed oil/diesel	Turbocharged, CRDI engine with Euro 4 complaint	A significant reduction in exhaust gas emissions such as CO and HC was observed with an increase in NO_x emission (~7%) for both the animal origin biofuels
How et al. (2018)	B20 and B50 of coconut oil biodiesel blends	Four cylinder, turbocharger CRDI diesel engine	Significantly lower NO_x level (<100 ppm) is claimed by retarded start of injection (SOI) for both the fuel blends with triple injection strategy
Rajkumar and Thangaraja (2019)	Diesel, karanja, coconut biodiesel and their blends, hydrogenated karanja samples	Four-cylinder, turbocharged diesel engine	NO emission is found to decrease with increasing fraction of coconut in the biodiesel binary blends

penalty. Blending alcohols namely methanol, ethanol and butanol with biodiesel helps biodiesel-NO_x control due to their cooling effects because of high latent heat of vaporization. Several investigations on multi-cylinder engines using biodiesel-methanol blends reported reduction in NO_x with penalties in fuel consumption, CO, UHC, aldehyde emissions (Cheng et al. 2008). Research works concerning alcohol blending with biodiesel are summarized in Table 3.3.

As discussed, the favorable physicochemical properties result in lowering the engine exhaust emissions. For a compression ignition engine, the oxygenated diesel fuel blends have a potential to decrease the PM generation during the combustion process. The presence of fuel bound oxygen (refer Fig. 3.9) in biofuels enhances the oxidation process and thus relatively lowers the hydrocarbon, carbon monoxide and soot emissions than the fossil fuels.

Meanwhile, for a spark ignition engine, the blend of alcohol assist in reducing knock tendency, carbon monoxide and unburned hydrocarbon emissions (Yusri et al. 2017). A considerable amount of literature highlighted that the emissions of methanol or ethanol blends in internal combustion engines have yielded a considerable reduction in NO_x, Smoke, HC and CO emissions with an increase in BSFC. Thus it can be concluded that aliphatic alcohol family (methanol, ethanol, propanol and butanol) are capable of reducing harmful engine exhaust emissions, however, at the expense of lower engine performance characteristics.

Table 3.3 Investigations on biodiesel-NO_x control using alcohol blends

Authors	Engine and fuels	Merits	Demerits
Cheng et al. (2008)	Four-cylinder, naturally aspirated diesel engine. Waste cooking biodiesel blended with methanol (10% by vol.)	The brake specific CO_2 drops by 2.5% and 5% reduction in NO_x with methanol addition	Higher fuel consumptions with methanol blends
Cheung et al. (2009)	Four-cylinder, naturally aspirated diesel engine. 5, 10 and 15% by vol. of methanol in waste cooking oil biodiesel	With increase in the proportion of methanol, NO_x and PM emissions decreased and are less than those of the diesel	Higher fuel consumptions, CO, HC, formaldehyde and acetaldehyde emissions with methanol blends
Qi et al. (2010)	Single-cylinder, naturally aspirated diesel engine. Soybean biodiesel 50%+ diesel 50% (BD50) as baseline fuel. 5 and 10% vol. of methanol in BD50 (BDM5 and BDM10)	At higher loads, the combustion parameters of BDM5 and BDM10 are higher than BD50.BDM5 and BDM10 reduced the smoke	The performance characteristics of BDM5 and BDM10 are slightly lower than BD50. NO_x and HC emissions are almost similar for BDM5 and BDM10 compared to those of BD50
Yilmaz (2012)	Two-cylinder, naturally aspirated DI Diesel operated with blends of waste cooking biodiesel 85 and 15% alcohols (methanol and ethanol)	The biofuel blends reduced the NO emission compared to fossil diesel, however increased the CO and HC emissions	Ethanol blended biofuel is prominent than methanol blends for enhanced engine performance and lowering the emissions
Yilmaz and Sanchez (2012)	Two-cylinder, naturally aspirated DI Diesel, waste cooking biodiesel, ethanol, methanol and diesel blends	Methanol blends are effective in lowering the CO and HC emissions, whereas NO is controlled via ethanol blends	Biodiesel-methanol diesel blends show a higher brake specific fuel consumption than biodiesel ethanol diesel blends

It is also important to recognize the greenhouse gas emissions (GHG) of biofuels during its life cycle period. European council has proposed a 35% reduction in GHG emissions as the sustainability criterion for biofuels relative to fossil fuels. Carbon dioxide being one of the primary greenhouse gases is produced not only during consumption/combustion of a biofuel, but also during cultivation, processing and transportation. This indirect CO_2 production is associated with energy inputs in these processes and inherent nature of the processes involved. During its life cycle biodiesel

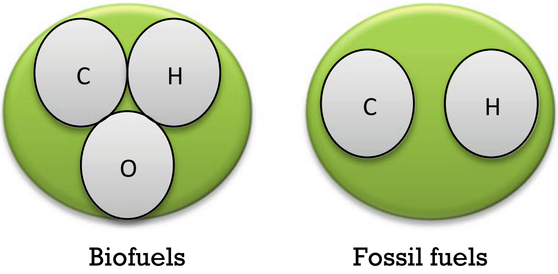

Fig. 3.9 The chemical composition of biofuel and fossil fuels

possess a significant GHG reduction potential relative to fossil diesel. The values of GHG reduction potential arrived by various authors are provided in Fig. 3.10. The result variation could be attributed to the choice of feedstock, selected region for cultivation and the co-product allocation or displacement methods adopted. However all the samples abide by the sustainability mandate of European Union as seen in Fig. 3.10.

GHG emissions are not always produced directly from the process but released during the upstream of energy transfer processes. For example, electricity used by mechanical stirrer in the transesterification process is acquired from thermal or hydro-electric power plant, thus the electricity consumed can be related to the amount of CO_2 released in the particular plant. Also the oil extraction method, esterification process and the fertilizer production are the major source of GHG emissions. Ethanol production from sugarcane is energy efficient than from sugar beets, sweet sorghum, palm or vegetable oils, especially when bagasse is used in the process of generating

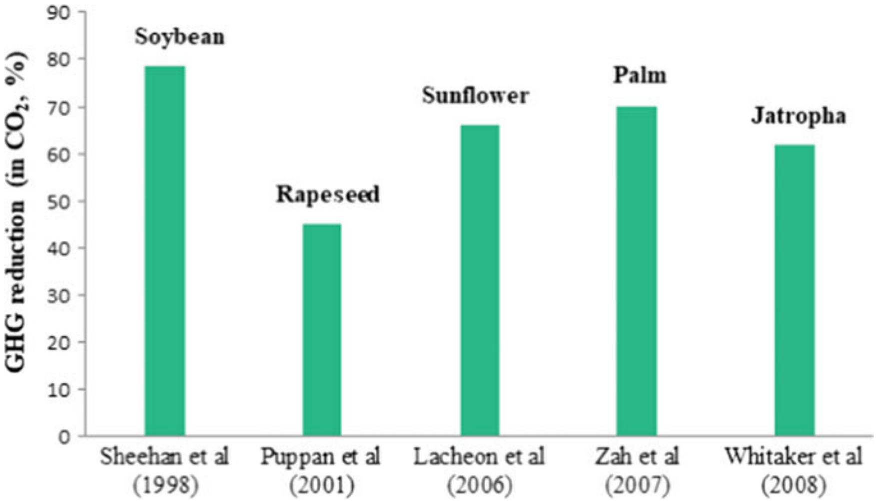

Fig. 3.10 Maximum reduction in greenhouse gas with various biodiesel fuels

heat and power. A study conducted by Khatiwada et al. (2016) has analyzed the sustainability of ethanol production from sugarcane molasses in Indonesia and reported a reduction of greenhouse gas emission (~67%) compared to the fossil fuels, whereas Brazilian sugarcane bioethanol exhibits some of the highest greenhouse gas (GHG) savings. To summarize the direct emissions, namely, the emissions associated with the biofuel production and its consumption is less carbon intensive than their counterpart viz. fossil fuel. It is crucial to consider the indirect emissions, which refer to emissions from changes induced during cultivation of energy crops and to emissions from changes induced in the oil market. One such potential effect is the indirect land use change (ILUC) and will be discussed briefly to rate the overall emission perspective of biofuels.

3.3.2 Indirect Emissions

Indirect land use change (ILUC) emissions occur when forest and grass lands are converted to cropland to meet the demand for goods displaced by the production of biofuel feedstock (Plevin et al. 2010). Thus alternate field of arable land has to be looked for to meet the rising demand for food and animal feed. The associated change of land use causes an increase in the monetary value of agricultural land and CO_2 emissions, a process known as indirect land use change. Further, this process will cause the conversion of non-cultivable land that tends to be carbon-rich into relatively carbon-poor agrarian land (Rajagopal et al. 2011). Table 3.4 provides the ILUC estimates by California Air Resources Board (CARB 2009).

Hence, ILUC is one of the primary potential greenhouse gas (GHG) sources in life cycle analysis of biofuels and also has become a central issue in the ongoing food-versus-fuel arguments. In countries like Brazil and Malaysia where palm oil is a major biodiesel feedstock, plantations are being grown through deforestation. This has raised major concerns around the world about these practices. Such plantations destroy local ecosystems and endanger many species of flora and fauna. Tough the direct emissions from biofuel are claimed to be advantageous; the overall scenario considering the indirect emissions is alarming. Although biofuels present an opportunity for renewable energy production, significant land-use change resulting from biofuels may contribute to negative environmental, economic, and social impacts (Transport & Environment 2016).

Table 3.4 Indirect land use change for biofuel production (CARB 2009)

Biofuel feedstock	ILUC (gCO_2/MJ)
Corn ethanol	30
Sugarcane ethanol	46
Soybean biodiesel	62

3.3.3 *Economic Impacts*

It is also important to study the economic potential of biofuels, which demands techno-economic analysis on their production method and refinery process. Further, economics plays a major role in promoting a biofuel for its application and sustenance. The production costs of biofuels tend to vary widely based on the chosen feedstock, adopted conversion process, scale of production and also the area of cultivation. Among these parameters, the cost of feedstock (up to 90% of the total costs) plays a major factor in determining the overall costs of the biofuel.

3.3.3.1 Ethanol Fuel

Ethanol is the low cost, high octane fuel additive available to gasoline operated systems. Environmental protection agency has approved the usage of E15 and concomitantly the auto makers are extending their warranty coverage for the new vehicles. Minimum ethanol selling price (MESP) is the cost of ethanol required for a zero net present value for the project when the cash flows are discounted at 10% real-after tax (Eggeman and Elander 2005). The National Renewable Energy Laboratory (NREL) projected a representative MESP value of 0.57 US$/L in 2011. A study conducted by Gubicza et al. (2016) has claimed the MESP value ranging between 0.50 and 0.62 US$/L. Some of the significant contributors to the MESP of ethanol include the cost of the feedstock (23–28%), capital cost (40–49%), the ethanol yield, and the cost of enzymes (Chovau et al. 2013). Also the production costs of ethanol from sugarcane in Brazil have declined continuously over the last three decades. Inclusion of co-products like the excess power generated could be sold to the main power grid for further cost benefits.

3.3.3.2 Biodiesel Fuels

Several research works have been carried out to analyze the economic requirements of producing biodiesel fuels (Zhang et al. 2003; Marchetti et al. 2008; Apostolakou et al. 2009). In general the production cost of biodiesel is higher than diesel and most of the studies has emphasized that the higher cost of source material/feedstock is creditworthy for the biodiesel production, with waste cooking biodiesel being an exception. Graboski and McCormick (1998) recommended accounting for the credit benefits from glycerol to reduce the production cost of biodiesel. The distribution of production cost of palm biodiesel for a plant capacity of 143 million liters is provided in Fig. 3.11.

Explicitly, the feedstock cost is predominant and with an economic return on glycerol, the choice of larger plant has lowered the price to 0.82 $/liter.

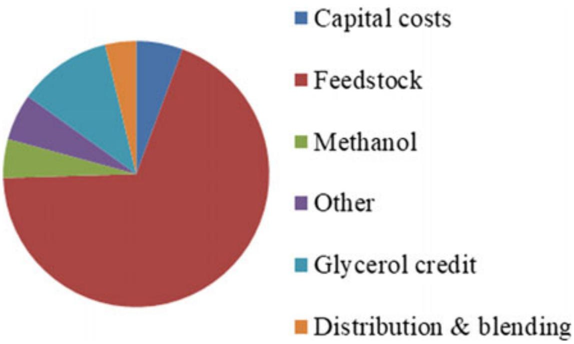

Fig. 3.11 Production cost of palm biodiesel Demirbas (2009a, b)

3.4 Conclusions and Future Scope

This chapter presented the various production process of biofuel from renewable biomass resources and touched upon the economics of biofuel and their environmental impacts. In conclusion, biofuel production is set to rise in a drastic manner, considering the rise in human population and demand for energy security. While these favor the government revenues as an indigenous resource and create jobs, consequently there are a number of environmental concerns. Like the indirect or non-regulated emissions need to be monitored carefully and assessed precisely for biofuel sustainability. Sustainability plays a major role in ensuring advanced biofuels are available for end-users. Biofuels are measured against the broad claims of sustainability “to meet the requirements of the existing populations without negotiating the ability of future generations to satisfy their own requirements”. These claims constitute to the following;

(i) Climate safety and proper land usage,
(ii) Societal subjects such as jobs and community well-being,
(iii) Economical profitability in the existing and future viable environment,
(iv) Advancement in technology along with sustainable standards and
(v) Reassuring government plan for offering a smooth legislative agenda.

Apprehensions over the effect of GHG emissions on the climate change have encouraged looking for long-term approaches for producing biofuels from sustainable sources. In many countries biofuels are being produced from their major agricultural products. For example, Malaysia’s biofuel policies are biased towards palm biodiesel production. In a long run, this scenario has adverse effects on the environment and sharp rises in food prices especially edible oils. Thus the chances and options relating to biofuel production vary considerably between different countries. Thus the future scope is to regulate the biofuel production process, explore for alternative feedstock, flex crops and adopt multi-functionality of lands. The capability to reduce greenhouse gas emissions by limiting the carbon capacity of biofuels can also be pursued. Further only through the mutual effect of various government agencies and biofuel industries, the market price of biofuel could be affordable in par with the fossil fuels.

References

Ali Y, Hanna MA, Leviticus LI (1995) Emissions and power characteristics of diesel engines on methyl soyate and diesel fuel blends. Biores Technol 52:185–195

Alonso DM, Bond JQ, Dumesic JA (2012) Catalytic conversion of biomass to biofuels. Green Chem 1493–1513

Anand K, Sharma RP, Mehta PS (2009) Experimental investigations on combustion, performance, and emissions characteristics of a neat biodiesel-fuelled, turbocharged, direct injection diesel engine. Proc IMechE: Part D – J Automobile Eng 224:661–679

Apostolakou AA, Kookos IK, Marazioti C, Angelopoulos K (2009) Techno-economic analysis of a biodiesel production process from vegetable oils. Fuel Process Technol 90:1023–1031

Appell HR, Fu YC, Friedman S, Yavorsky PM, Wender I (1971) Converting organic wastes to oil. US Burea of Mines Report of Investigation. No. 7560

Balat M (2008) Mechanisms of thermochemical biomass conversion processes. Part 1: Reactions of pyrolysis. Energy Sources Part A 30:620–625

Bisio A, Boots S, Siegel P (eds) (1997) The Wiley encyclopedia of energy and the environment, vol I, II. Wiley, New York

Canakci M (2005) Performance and emissions characteristics of biodiesel from soybean oil. Proc Int J Mech Eng, Part D: J Automobile Eng 219:1–8

CARB (California Air Resources Board) (2009) California's low carbon fuel standard final statement of reasons. Sacramento: State of California Environmental Protection Agency, Air Resources Board. http://www.arb.ca.gov/fuels/lcfs/010611lcfs_lutables.pdf

Chen G, Spliethoff H, Andries J, Glazer MP, Yang LB (2004) Biomass gasification in a circulating fluidised bed-Part I: preliminary experiments and modeling development. Energy Sources 26:485–498

Cheng CH, Cheung CS, Chan TL, Lee SC, Yao CD, Tsang KS (2008) Comparison of emissions of a direct injection diesel engine operating on biodiesel with emulsified and fumigated methanol. Fuel 87:1870–1879

Cheung CS, Zhu L, Huang Z (2009) Regulated and unregulated emissions from a diesel engine fueled with biodiesel and biodiesel blended with methanol. Atmos Environ 43:4865–4872

Chornet E, Overend RP (1985) Fundamentals of thermochemical biomass conversion. Elsevier, New York, pp 967–1002

Demirbas A (2000) Mechanisms of liquefaction and pyrolysis reactions of biomass. Energy Convers Manege 41:633–646

Demirbas A (2007) The influence of temperature on the yields of compounds existing in bio-oils obtaining from biomass samples via pyrolysis. Fuel Proc Technol 88:591–597

Demirbas A (2009) Biofuels (Chap. 6). In: Thermochemical conversion processes, Springer, Berlin, pp 261–304

Demirbas A (2009b) Political, economic and environmental impacts of biofuels: a review. Appl Energy 86:S108–S117

Di Serio M, Ledda M, Cozzolino M, Minutillo G, Tesser R, Santacesaria E (2006) Ind Eng Chem Res 45:3009–3014

Dorado MP, Ballesteros E, Arnal AM, Gomez J, Gimenez FJL (2003) Testing waste olive oil methyl ester as a fuel in a diesel engine. Energy Fuels 17:1560–1565

Dudaa K, Wierzbickia S, Śmiejaa M, Mikulski M (2018) Comparison of performance and emissions of a CRDI diesel engine fuelled with biodiesel of different origin. Fuel 212:202–222

Eggeman T, Elander RT (2005) Process and economic analysis of pretreatment technologies. In: Bioresoure technology, vol 96(18 SPEC. ISS.), pp 2019–2025. https://doi.org/10.1016/j.biortech.2005.01.017

Feng W, van der Kooi HJ, Arons JDS (2004) Biomass conversions in subcritical and supercritical water: driving force, phase equilibria, and thermodynamic analysis. Chem Eng Proc 43:1459–1467

Goudriaan F, Peferoen D (1990) Liquid fuels from biomass via a hydrothermal process. Chem Eng Sci 45:2729–2734

Graboski MS, McCormick RL (1998) Combustion of fat and vegetable oil derived fuels in diesel engines. Prog Energy Combust Sci 24:125–164

Granados ML, Poves MDZ, Alonso DM, Mariscal R, Galisteo FC, Moreno-Tost R, Santamaria J, Fierro JLG (2007) Appl Catal B 73:317–326

Gubicza K et al (2016) Techno-economic analysis of ethanol production from sugarcane bagasse using a liquefaction plus simultaneous saccharification and co-fermentation process. Bioresour Technol 208:42–48. https://doi.org/10.1016/j.biortech.2016.01.093 (Elsevier Ltd)

Haas MJ (2005) Improving the economics of biodiesel production through the use of low value lipids as feedstocks: vegetable oil soapstock. Fuel Process Technol 86:1087–1096

Hao H, Guo L, Zhang X, Guan Y (2005) Hydrogen production from catalytic gasification of cellulose in supercritical water. Chem Eng J 110:57–65

How HG, Masjuki HH, Kalam MA, Teoh YH (2018) Influence of injection timing and split injection strategies on performance, emissions, and combustion characteristics of diesel engine fueled with biodiesel blended fuels. Fuel 213:106–114

https://www.transportenvironment.org/publications/globiom-basis-biofuel-policy-post-2020. Accessed 29 May 19

Jomaa S (2001) Combined sludge treatment and production of useful organic by-products using hydrothermal oxidation, PhD thesis. Brisbane, Australia: Department of Civil Engineering, Queensland University of Technology

Jomaa S, Shanableh A, Khalil W, Trebilco B (2003) Hydrothermal decomposition and oxidation of the organic component of municipal and industrial waste products. Adv Environ Res 7:647–653

Khatiwada D, Venkata BK, Silveira S, Johnson FX (2016) Energy and GHG balances of ethanol production from cane molasses in Indonesia. Appl Energy 164:756–768. https://doi.org/10.1016/j.apenergy.2015.11.032

Kim HJ, Kang BS, Kim MJ, Park YM, Kim DK, Lee JS, Lee KY (2004) Catal Today 93–95:315–320

Lin CY, Lin HA (2006) Diesel engine performance and emission characteristics of biodiesel produced by the peroxidation process. Fuel 85:298–305

Liu B, Zhang Z (2016) Catalytic conversion of biomass into chemicals and fuels over magnetic catalysts. ACS Catalysis 61:326–338

Lotero E, Liu YJ, Lopez DE, Suwannakarn K, Bruce DA, Goodwin JG (2005) Ind Eng Chem Res 44:5353–5363

Marchetti JM, Miguel VU, Errazu AF (2008) Techno-economic study of different alternatives for biodiesel production. Fuel Process Technol 89:740–748

Mccormick RL, Graboski MS, Alleman TL, Herring AM, Tyson KS (2001) Impact of biodiesel source material and chemical structure on emissions of criteria pollutants from a heavy-duty engine. Environ Sci Technol 35:1742–1747

Melero JA, Iglesias J, Morales G (2009) Green Chem 11:1285–1308

Monyem A, Van Gerpen JH (2001) The effect of biodiesel oxidation on engine performance and emissions. Biomass Bioenerg 20:317–325

Owusu PA, Asumadu-Sarkodie S (2016) A review of renewable energy sources, sustainability issues and climate change mitigation. J Cogent Eng 3:1–14

Plevin RJ et al (2010) The greenhouse gas emissions from indirect land use change are uncertain, but potentially much greater than previously estimated. Environ Sci Technol 44(21):1–19

Qi DH, Chen H, Matthews RD, Bian YZH (2010) Combustion and emission characteristics of ethanol–biodiesel–water micro-emulsions used in a direct injection compression ignition engine. Fuel 89:958–964

Rajagopal D, Hochman G, Zilberman D (2011) Indirect fuel use change (IFUC) and the lifecycle environmental impact of biofuel policies. Energy Policy 39(1):228–233. https://doi.org/10.1016/j.enpol.2010.09.035 (Elsevier)

Rajkumar S, Thangaraja J (2019) Effect of biodiesel, biodiesel binary blends, hydrogenated biodiesel and injection parameters on NO_x and soot emissions in a turbocharged diesel engine. Fuel 240:101–118 (Elsevier). https://doi.org/10.1016/j.fuel.2018.11.141

Silva FND, Prata AS, Teixeira JR (2003) Technical feasibility assessment of oleic sunflower methyl ester utilization in diesel bus engines. Energy Convers Manage 44:2857–2878

Stevens DJ (2001) Hot gas conditioning: recent progress with larger-scale biomass gasification systems. National Renewable Energy Laboratory, NREL/SR-510-29952, 1617

Szybist JP, Song J, Alam M, Boehman AL (2007) Biodiesel combustion, emissions and emission control. Fuel Process Technol 88:679–691

Usta N (2005) Use of tobacco seed oil methyl ester in a turbocharged indirect injection diesel engine. Biomass Bioenergy 28:77–86

Warnecke R (2000) Gasification of biomass: comparison of fixed bed and fluidized bed gasifier. Biomass Bioenergy 18:489–497

Yilmaz N (2012) Comparative analysis of biodiesel-ethanol-diesel and biodiesel-methanol-diesel blends in a diesel engine. Energy, 1–4

Yilmaz N, Sanchez TM (2012) Analysis of operating a diesel engine on biodiesel-ethanol and biodiesel-methanol blends. Energy, 1–4

Yung MM (2016) Catalytic conversion of biomass to fuels and chemicals. Top Catal 59:1

Yusri IM et al (2017) Alcohol based automotive fuels from first four alcohol family in compression and spark ignition engine: a review on engine performance and exhaust emissions. Renew Sustain Energy Rev 77:169–181. https://doi.org/10.1016/j.rser.2017.03.080

Zhang Y, Dube M, McLean D, Kates M (2003) Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis. Bioresour Technol 90:229–240