

BIOFUELS OF FIRST AND SECOND GENERATION

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Abstract

Sustainable economic and industrial growth requires safe, sustainable resources of energy. For the future re-arrangement of a sustainable economy to biological raw materials, completely new approaches in research and development, production, and economy are necessary. The biofuels produced from the renewable resources could help to minimize the fossil fuel burning and CO₂ production. Biofuels produced from biomass such as plants or organic waste could help to reduce both the world's dependence on oil and CO₂ production. These biofuels have the potential to cut CO₂ emission because the plants they are made from use CO₂ as they grow. Biofuels and bio products produced from plant biomass would mitigate global warming. The 'first-generation' biofuels appear unsustainable because of the potential stress that their production places on food commodities. For organic chemicals and materials these needs to follow a biorefinery model under environmentally sustainable conditions. Where these operate at present, their product range is largely limited to simple materials (i.e. cellulose, ethanol, and biofuels). Second generation biorefineries need to build on the need for sustainable chemical products through modern and proven green chemical technologies such as bioprocessing including pyrolysis, Fisher Tropsch, and other catalytic processes in order to make more complex molecules and materials on which a future sustainable society will be based. The article presents the basic processes of converting liquid and gaseous biofuels and second-generation.

Keywords: *First generation biofuel, Second generation biofuel, biomass*

1. Introduction

In the twentieth century major research emphasis was given for the development of petroleum, coal, and natural gas based refinery to exploit the cheaply available fossil feed stock. These feedstocks are used in industry to produce multiple products such as fuel, fine chemicals, pharmaceuticals, detergents, synthetic fibre, plastics, pesticides, fertilizers, lubricants, solvent, waxes, coke, asphalt, etc. to meet the growing demand of the population [4]. Currently, the fossil resources are not regarded as sustainable and questionable from the economic, ecology and environmental point of views [6]. The burning of fossil fuels is a big contributor to increasing the level of CO₂ in the atmosphere which is directly associated with global warming observed in recent decades. The adverse effects of greenhouse gas emissions on the environment, together with declining petroleum reserves, have been realized. Therefore, the quest for sustainable and environmentally benign sources of energy for our industrial economies and consumer societies has become urgent in recent years [9]. Consequently, there is renewed interest in the production and use of fuels from plants or organic waste.

Biofuels produced from biomass such as plants or organic waste could help to reduce both the world's dependence on oil and CO₂ production. This may due to the CO₂ released in burning equals the CO₂ tied up by the plant during photosynthesis and thus does not increase the net CO₂ in the atmosphere. Additionally, biofuel production along with bio products can provide new income and employment opportunities in rural areas. 21st Century is looking for a shift to alternate industrial feedstock and green processes to produce these chemicals from renewable biomass resources [18].

First generation biofuels can offer some CO₂ benefits and can help to improve domestic energy

security. But concerns exist about the sourcing of feedstocks, including the impact it may have on biodiversity and land use and competition with food crops. A first generation biofuel is characterized either by its ability to be blended with petroleum-based fuels, combusted in existing internal combustion engines, and distributed through existing infrastructure, or by the use in existing alternative vehicle technology. The main disadvantage of first generation biofuels is the food-versus-fuel debate, one of the reasons for rising food prices is due to the increase in the production of these fuels. Additionally it is claimed that biodiesel is not a cost efficient emission abatement technology.

Therefore, lignocellulosic feedstock can offer the potential to provide novel biofuels, the biofuels of the second generation [16]. Second-generation biofuels produced from plant biomass refers largely to lignocellulosic materials, as this makes up the majority of the cheap and abundant non-food materials available from plants. Plant biomass represents one of the most abundant and underutilized biological resources on the planet, and is seen as a promising source of material for fuels and raw materials. At its most basic, plant biomass can simply be burned in order to produce heat and electricity. However, there is great potential in the use of plant biomass to produce liquid biofuels. The examples of 2nd generation biofuels are cellulosic ethanol and FT fuels.

2. First generation biofuels

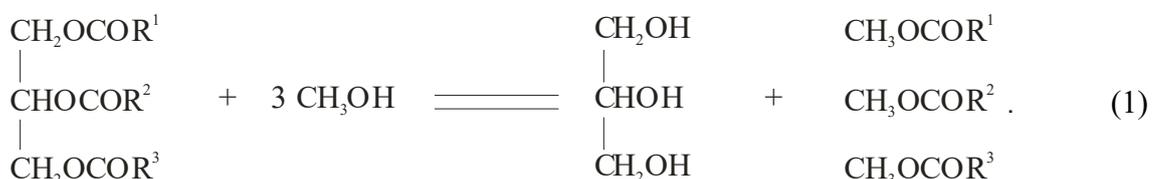
The three main types of first generation biofuels used commercially are biodiesel (bio-esters), ethanol, and biogas of which worldwide large quantities have been produced so far and for which the production process is considered “established technology”. Biodiesel is a substitute of diesel and is produced through transesterification of vegetable oils, and residual oils and fats, with minor engine modifications; it can serve as a full substitute as well. Bioethanol is a substitute of gasoline and it is a full substitute for gasoline in so-called flexi-fuel vehicles. It is derived from sugar or starch through fermentation. Bioethanol can also serve as feedstock for ethyl tertiary butyl ether (ETBE) which blends more easily with gasoline.

Biogas, or biomethane, is a fuel that can be used in gasoline vehicles with slight adaptations. It can be produced through anaerobic digestion of liquid manure and other digestible feedstock. At present, biodiesel, bioethanol and biogas are produced from commodities that are also used for food. There are some potential crops for biodiesel production, which can be taken up as Industrial crop on unproductive lands. Such multipurpose uses oilseeds crops can be introduced, so that the biomass produced by them can be utilized for production of various bio products.

2.1. Conversion processes for first generation biofuels

The vegetable oil based fatty acid methyl esters (FAME), popularly known as biodiesel, is gaining importance as an environment-friendly diesel fuel substitute or extender. Biodiesel is an alternative diesel, made from renewable biological sources such as vegetable oils and animal fats by chemically reacting oil or fat with an alcohol, in the presence of a homogeneous and heterogeneous catalyst. The product of the reaction is a mixture of methyl esters, which are known as biodiesel, and glycerol, which is a high value co-product [7, 10].

Transesterification is a reversible reaction and proceeds essentially by mixing the reactants in which the catalysts is a liquid acid or a liquid base. The process known as transesterification, as shown in Eq. (1).



It is not possible to perform a basic transesterification process for high free fatty acid (FFA) content oil and decreases the conversion of oil to methyl ester due to saponification reaction. The use of solid catalyst is recommended for high free fatty acid containing oil. This is because the solid acid catalysts can simultaneously catalyse the transesterification of triglycerides and esterification of free fatty acid (FFA) present in oil to methyl esters. Solid acid catalysts have the strong potential to replace homogeneous catalysts, eliminating separation, corrosion and environmental problems. The solid acid catalysed biodiesel production by simultaneous esterification and transesterification of low quality oil containing high FFA was performed by Kulkarni et al. [7].

Ethanol conversion processes. A wide variety of carbohydrates containing raw materials has been used for production of ethanol by fermentation process. These raw materials are classified under three major categories:

- a) Sugar containing crops: Sugar cane, wheat, beet root, fruits, palm juice, etc.
- b) Starch containing crops: Grain such as wheat, barely, rice, sweet sorghum, corn, etc. and root plants like potato, cassava.
- c) Cellulosic biomass: Wood and wood waste, cedar, pine, wood, etc. agricultural residues, fibres.

The alcohol produced from food crops like corn, wheat, barley, sweet sorghum is called grain alcohol, whereas ethanol produced from lingo-cellulosic biomass such as agro residue (i.e. rice straw, wheat straw) grasses (switch grass) is known as biomass ethanol or bioethanol. Both these alcohols are produced through biochemical process [8]. Chemical structure of starch consists of long chain polymer of glucose. The macromolecular starch cannot be directly fermented to ethanol by conventional fermentation technology. The macromolecular structure first broke down in to simpler and smaller glucose. In this process, starch feedstocks are grounded and mixed with water to produce a mash typically contained 15–20% starch. The mash is then cooked at or above its boiling point and treated subsequently with two-enzyme preparation. The first enzyme hydrolyses starch molecules to short chains to glucose. The first enzyme is amylase; amylase liberates "maltodextrin" oligosaccharides by liquefaction process. The dextrin and oligosaccharides are further hydrolysed by enzyme such as pullulanase and glucoamylase in a process known as saccharification. Saccharification converts all dextrans to glucose, maltose and isomaltose. The mash is then cooled to 30°C and yeast is added for fermentation [8].

The term fermentation can generally be defined as the metabolic process in which an organic substrate goes under chemical changes due to activities of enzymes secreted by microorganisms. There are two basic types of fermentation (a) aerobic and (b) anaerobic depending upon oxygen needed in the process or not. There are thousands of microorganisms in nature capable of providing fermentative changes. Some of these are capable of producing ethanol from sugar and starch. The microorganisms employed for ethanol production are classified into three categories viz. yeast, bacteria and mold (mycelium). These microorganisms found in nature and are very selective in their fermentation characteristics, some of this ferment specific to hexoses or pentose, or mixtures of both. Efforts are being made by various researchers to produce ideal microorganism, which will be able to produce ethanol from any carbohydrate.

Anaerobic digestion of solid waste is a process very similar to that used in biogas production. Anaerobic bacteria in the absence of oxygen are used to break down the organic matter of biomass, and during the conversion a mixture of methane and carbon dioxide gases are produced. The typical ratio of gas mixture is 60-70% methane and 30% carbon dioxide. Due to increase cost of energy, the anaerobic digestion of biomass is an attractive alternative for production of fuel and bio fertilizer for organic cultivation. Anaerobic digestions in landfills are potential source of methane production from solid waste. Anaerobic digestion of biodegradable portion of the municipal solid waste (mostly biomass and biological waste) produces methane and carbon dioxide in roughly equal amount. These two principal components together with atmospheric nitrogen, oxygen and traces of organic compounds are known as landfill gas.

Oleochemicals refer to chemicals derived from natural oils and fats of both plant and animal origins. Basically, oleochemicals refer to the fatty acids and glycerol derived from the splitting of the triglyceride structures of oils and fats. However, they also include those derivatives derived from the subsequent modification of the carboxylic acid group of the fatty acids by chemical or biological means, and other compounds obtained from further reactions of these derivatives. Oleochemicals are often categorised into basic oleochemicals such as fatty acids, fatty methyl esters, fatty alcohols, fatty amines and glycerol, and their further downstream derivatives obtained from further chemical modifications of these basic oleochemicals.

In fact, until the 1980s, almost 95% of natural oils and oils were used in foods and only a small percentage was used in non-food applications such as soap manufacturing and drying oils. It was only after the 1980s that oleochemicals found wide uses in both food and non-food, or technical applications, which previously are the domains of “synthetic chemicals” derived from petroleum or better known as petrochemicals. At this moment, oleochemicals are used in the manufacture of such products as foods and specialty fats, soaps and detergents, cosmetics and personal care products, lubricants and greases, drying oil, surface coatings and polymers and biofuels. In theory, oleochemicals can replace petrochemicals in all their applications [2].

Why oleochemicals? The reasons are simple First, oleochemicals are derived from renewable resources, as compared to petrochemicals which are obtained from exhaustible or non-renewable petroleum, Secondly, products derived from oleochemicals are more readily biodegradable and hence do not pose a threat to the environment, Thirdly, products derived from petroleum sources use more energy and cause higher emissions of such pollutants as NO_x, SO₂, CO and hydrocarbons.

Biomass used for production of biodiesel would generate million tons of residual protein (De-oilcake). The use of protein for non-food applications is currently more limited compared to the utilization fatty acids derivatives. The edible protein can be utilized for production of essential amino acids for animal feeds and human consumption. Some of the nonedible oil seeds cake like jatropha, neem, karanja, etc. would use to produced bio pesticides and amino acids for non-food applications. Sanders et al. [30] have reported the application of protein based raw materials for production of 1.2-ethane diamine and 1.4-butane diamine from amino acids. The production of amino acids from de-oil cake would add value to biofuel crops produce in large scale. 1.2-Ethane diamine is produced starting with ethylene by various routes. 1.2-Ethane diamine and 1.4-butane diamine can be synthesized from amino acids such as serine and arginine respectively. Decarboxylation of serine will form ethanolamine, which is converted into diamine by addition of ammonia. Arginine can be hydrolysed to ornithine and urea. Ornithine will form 1.4-butane diamine after carboxylation. Protein based surfactants are the most valuable mild surfactants. Since the structure and properties of the amino acids in the surfactants are similar to the tissue of the skin amino acids, this cause strong affinity and soft feeling on skin. Acyl derivatives from glutamic acid and serine are very effective in comparison with conventional surfactants. The production of protein based surfactant involves hydrolysis of protein with sulphuric acid followed by acylation with RCOCl to form acyl amino acid sodium salts which are converted into acyl esters of amino acids by esterification with fatty alcohol [15]. 3q.

3. Second generation biofuels

Second generation biofuels are produced from biomass in a more sustainable fashion, which is truly carbon neutral or even carbon negative in terms of its impact on CO₂ concentrations. In the context of biofuel production, the term ‘plant biomass’ refers largely to lignocellulosic material as this makes up the majority of the cheap and abundant non-food materials available from plants [19]. At present, the production of such fuels is not costeffective because there are a number of technical barriers that need to be overcome before their potential can be realized. Plant biomass represents one of the most abundant and underutilized biological resources on the planet, and is

seen as a promising source of material for fuels and raw materials. As it is most basic, plant biomass can simply be burnt in order to produce heat and electricity. However, there is great potential in the use of plant biomass to produce liquid biofuels. Plant biomass is comprised mostly of plant cell walls, of which typically 75% is composed of polysaccharides [12]. These polysaccharides represent a valuable pool of potential sugars, and even in traditional food crops such as wheat there is as much sugar tied up in the stems as there is in the starch of the grains. To date, the potential of many crop residues, such as straw and wood shavings, to provide sugar feedstocks for biofuel production has not been realized.

Lignocellulosic materials are a collection of feedstocks for advanced biofuels and can be obtained either through hydrolysis and fermentation (i.e. bioethanol) or through gasification (i.e. FT-biodiesel, bio-DME and bio-SNG). Typical resources for these fuels are short rotation forestry crops (poplar, willow and eucalyptus), perennial grasses (miscanthus, switch grass and reed canary grass) and residues from the wood industry, forestry and from agriculture. Advanced biofuels, also referred to as 2nd generation biofuels, are carbon-based fuels that are produced by innovative processes mainly using lignocellulosic materials.

Bioethanol (advanced) is a substitute of gasoline. It is a full substitute for gasoline in so-called flexi-fuel vehicles. With hydrolysis, sugars are extracted from lignocellulosic feedstock, after which the sugars are fermented into ethanol. Fischer-Tropsch diesel (FT-diesel) or BTL (Biomass-to-Liquids) is a full substitute of diesel. Lignocellulosic biomass is gasified to produce syngas which is in turn transformed into liquid hydrocarbons, mostly diesel and kerosene. Bio-SNG (Synthetic Natural Gas) is a fuel that can be used in gasoline vehicles with slight adaptations. Lignocellulosic biomass is gasified to produce syngas which is in turn transformed into methane. Bio-DME (Dimethyl Ether) is a fuel that can be used in diesel vehicles with slight adaptations. Lignocellulosic biomass is gasified to produce syngas which is in turn transformed into DME [1].

3.1. Conversion processes for second generation biofuels

There are two main routes available for producing liquid biofuels from biomass; one involves thermochemical processing and the other biochemical processing. Thermochemical processing defines the conversion of biomass into a range of products, by thermal decay and chemical reformation, and essentially involves heating biomass in the presence of different concentrations of oxygen. The clear advantage of thermochemical processing is that it can essentially convert all the organic components of the biomass compared with biochemical processing which focuses mostly on the polysaccharides.

Mechanical extraction. Crude vegetable oils are recovered from the oil seeds by applying a mechanical pressure using screw press (expeller). Screw press can be applied in two ways: prepressing and full pressing. In pre-pressing, only part of the oil is recovered and the partially de-oiled meal is further treated by solvent extraction. Combined pre-pressing and solvent extraction is commonly applied for oilseeds with high oil content [18].

Distillation is the most important method for extracting essential oil and relies on the evaporation of the more volatile constituents of a blend to separate them from the nonvolatile parts. Plants are crushed to encourage them to release their oils. The plants are steam distilled, and the essential oils vaporize and rise up with the steam. The vapours are captured, and are allowed to condense back into liquids. A more high tech chemical process is molecular distillation. It is used to produce fragrances that cannot be distilled by conventional methods [18].

Biomass can be converted to energy by mainly two processes. They are either thermo-chemical or biological. The thermochemical conversion process includes direct combustion, gasification, liquefaction, and pyrolysis. When biomass is heated under oxygen deficient conditions, it generates synthesis gas, or syngas, which consists primarily of hydrogen and carbon monoxide. This syngas can be directly burned or further processed for other gaseous or liquid products. In this sense, thermal or chemical conversion of biomass is very similar to that of coal [8].

Combustion is the chemical reaction between a fuel and oxygen which usually takes place in air and is more commonly known as burning. The products are carbon dioxide and water with the release of heat. When the direct combustion of biomass is conducted in a well vented area, biomass burning used for domestic stoves and boilers can be a sound substitute for combustion of conventional fissile fuel. Sulphur emissions are much lower and the formation of particulate can be controlled at the source [8].

Generally gasification is not a new technology however its use for the conversion of biomass into a viable fuel has only been investigated for past thirty years. Syngas can be produced from biomass by two routes namely catalytic and noncatalytic. Noncatalytic process requires a very high temperature of operation, as high as 1300°C, whereas catalytic process can be operated at substantially lower temperature. With more advances in the catalysis, the temperature requirement is expected to go downward further from the current value of about 900°C [8].

The gasification step involves reacting biomass with air, oxygen, or steam to produce a gaseous mixture of CO, CO₂, H₂, CH₄, and N₂ either known as producer gas or synthesis or syngas, depending on the relative proportions of the component gases [13]. Producer gas is primarily useful as a fuel for stationary power generation, whereas syngas may be, and is presently, used to make a range of fuels and chemical intermediates. For transportation fuels, the main syngas derived routes to fuels are hydrogen by water-gas-shift reaction (WGS) [17], hydrocarbons by Fischer-Tropsch (F-T) synthesis or methanol synthesis followed by further reaction to produce hydrocarbon or oxygenated liquid fuels [1]. The WGS reaction uses CO, H₂O to give H₂ and CO₂. It can be used to upgrade producer gas to syngas by enriching the H₂ content or to produce H₂ as an end product in its own right.

In the field of thermochemical conversion of biomass, lignocellulosic materials can be converted directly to a liquid similar to heavy fuel oils by reacting them with synthesis gas in the presence of suitable catalyst. Aqueous liquefaction of lignocellulosic involves desegregation of the wood ultrastructure, followed by partial depolymerisation of the constitutive compounds.

The pyrolysis is thermal degradation of biomass by heat in the absence of oxygen, which results in the production of charcoal (solid), bio-oil (liquid), and fuel gaseous products. The pyrolysis of biomass has been studied with the final objectives of recovering a biofuel with medium-low calorific power [3]. Depending on the operating conditions, the pyrolysis process can be divided into three subclasses: (a) Conventional pyrolysis, (b) Fast pyrolysis, and (c) Flash pyrolysis.

Bio-oil/pyrolysis oil is produced by fast pyrolysis process. In this process, organic class of compounds, such as cellulose, hemicellulose, and lignin, etc. are thermally decomposed at moderate temperature (400-600°C) in absence of oxygen to produce liquid product viz. bio-oil, char and gas such as CO, H₂, light hydrocarbons. The yield and chemical composition of bio-oil depends upon feed stocks and process condition: particle size of biomass, residence time and reactor type. In general, reactor types which are presently used are; fluidized bed reactor, circulating fluid bed, fast fluidized bed, etc. The bio-oil is a dark brown viscous, corrosive and acidic with distinctive smoky odor used as fuel for boiler, gas turbine, diesel engines, furnaces and stationary engines. Bio-oil has a complex chemical composition contained chemical products of lignocelluloses biomass like aliphatic alcohols/aldehydes, furanoids, pyranoids, benzenoids, fatty acids and high molecular mass hydrocarbons, etc. these constituents are mixed with water (25-45%), which is formed in pyrolysis process to form an emulsion with organic constituents.

Franz Fisher and Hans Tropsch first studied conversion of syngas (CO + H₂) in to large number of useful organic compounds in 1923. The syngas produced by gasification of biomass can be converted into large number of organic compounds. The process of converting CO and H₂ mixture into liquid fuels or hydrocarbons over transition metal catalyst is known as Fisher-Tropsch oil (FT-oil) or Green motor fuel. The FT synthesis processes have flexibility in feed stocks (coal, biomass, natural gas) and the fuel produced by FTS process contains low sulphur. The major

drawback of FTS process is the polymerization in the process which yields very high molecular mass waxes which need to be hydrocracked to produce green diesel. Some of the recent publication indicates that the use of FT process technology for biomass conversion to synthetic hydrocarbon may be promising and carbon neutral alternative to conventional fuels. Biomass gasification can provide the opportunity to convert biosyngas into green fuels such as H₂ and FT oil. The biomass gasification produces biosyngas, which contains degraded products of biomass such as carbohydrate (cellulose, hemicellulose) and lignin. The gas mixtures consists of carbon monoxide, carbon dioxide, hydrogen, methane, benzene/toluene/xylene, ethane and tar [1].

The products from FTS are mainly aliphatic straight chain hydrocarbons. Besides the straight chain hydrocarbons, branched hydrocarbons and primary alcohol are also formed in minor quantities. The product distribution obtained from FTS include light hydrocarbon methane (CH₄), ethylene (C₂H₄) and ethane (C₂H₆), LPG, propane, butane, gasoline, diesel fuel and wax. Some raw biomass contained traces of contaminants such as NH₃, H₂S, HCl, dust and alkali in ash. The distribution of products depends upon the catalyst and process parameters such as temperature, pressure, and residence time [11].

Bioethanol from lignocellulosic biomass Biological conversion technologies are based on microbial and enzymatic process for producing sugars from biomass such as lignocellulosic, starch, cellulosic. The sugars later can be converted into alcohol and other solvents of interest to fuel and chemicals. Solid waste has been used to produce methane through anaerobic digestion in fabricated digesters or landfill. The production of ethanol from corn, sugarcane by biochemical means has already been commercially established. It is essential to hydrolyze lignocellulose for biological conversion. Enzymatic hydrolysis of lignocellulosic biomass required some research and developmental work to increase the yield of alcohol. The conversion of biomass feed stocks to liquid fuels such as ethanol requires a number of basic unit operations including pretreatment, enzyme production, hydrolysis, fermentation and ethanol recovery [8].

The important specific factors in chemical hydrolysis are surface to volume ratio, acid concentration, temperature, and time. The surface to volume ratio is especially important, in that it also determines the magnitude of the yield of glucose. Hence smaller the particle size the better the hydrolysis in terms of the extent and rate of reaction. With respect to the liquid to solid ratio, the higher the ratio the faster the reaction [5].

Solvent extraction involves different unit operations: extraction of the oil from the oil seeds using hexane as a solvent; evaporation of the solvent; distillation of the oil–hexane mixture (called miscella); and toasting of the de-oiled meal. In special cases, other solvents can be used: halogenated solvents (mostly dichloromethane), acetone, ethanol or isopropanol. Supercritical extraction can also be performed using CO₂ [18]. Extraction refers to a process in which the desired substance is selectively removed from the raw materials by allowing the desired substance to dissolve into the solvent, and subsequently recovering the substance from the solvent. To remove the particular substance from biomass, extraction and separation are both essential. In the biorefinery process these chemicals are initially extracted from biomass by using solvent extraction or supercritical fluid extraction.

4. Conclusions

National governments strongly support the development of refineries producing biofuels on a commercial scale. The European Union aims to meet the objectives set out in Decree 20/20/20, which is to increase energy efficiency by 20 percent, reduce greenhouse gas emissions by 20 percent and ensure that 20 percent of the total produced energy will come from renewable sources by 2020. This opens up great opportunities for the biofuel market. From the point of view of limiting carbon dioxide emissions it is important to limit the pool of raw material for biofuel production to areas where it is feasible, effective control, i.e. To the Community, otherwise the use of biofuels may increase its emissions.

According to several analyses of second-generation biofuels may soon completely replace the first generation biofuels derived from edible materials. Until then you must deal with the problem of very high costs of biomass production. The solution may be optimization of processing technology of various raw materials for biofuels and more efficient use of by-products.

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