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Biofuels sources, biofuel policy, biofuel economy and global biofuel projections

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ABSTRACT

The term biofuel is referred to liquid, gas and solid fuels predominantly produced from biomass. Biofuels include energy security reasons, environmental concerns, foreign exchange savings, and socioeconomic issues related to the rural sector. Biofuels include bioethanol, biomethanol, vegetable oils, biodiesel, biogas, bio-synthetic gas (bio-syngas), bio-oil, bio-char, Fischer-Tropsch liquids, and biohydrogen. Most traditional biofuels, such as ethanol from corn, wheat, or sugar beets, and biodiesel from oil seeds, are produced from classic agricultural food crops that require high-quality agricultural land for growth. Bioethanol is a petrol additive/substitute. Biomethanol can be produced from biomass using bio-syngas obtained from steam reforming process of biomass. Biomethanol is considerably easier to recover than the bioethanol from biomass. Ethanol forms an azeotrope with water so it is expensive to purify the ethanol during recovery. Methanol recycles easier because it does not form an azeotrope. Biodiesel is an environmentally friendly alternative liquid fuel that can be used in any diesel engine without modification. There has been renewed interest in the use of vegetable oils for making biodiesel due to its less polluting and renewable nature as against the conventional petroleum diesel fuel. Due to its environmental merits, the share of biofuel in the automotive fuel market will grow fast in the next decade. There are several reasons for biofuels to be considered as relevant technologies by both developing and industrialized countries. Biofuels include energy security reasons, environmental concerns, foreign exchange savings, and socioeconomic issues related to the rural sector. The biofuel economy will grow rapidly during the 21st century. Its economy development is based on agricultural production and most people live in the rural areas. In the most biomass-intensive scenario, modernized biomass energy contributes by 2050 about one half of total energy demand in developing countries.

1. Introduction

Known petroleum reserves are limit resources. Various studies put the date of the global peak in oil production between 1996 and 2035. Biomass energy technologies use waste or plant matter to produce energy with a lower level of greenhouse gas emissions than fossil fuel sources [1]. In developed countries there is a growing trend towards employing modern technologies and efficient bio-energy conversion using a range of biofuels, which are becoming cost-wise competitive with fossil fuels [2].

The term biofuel is referred to as liquid or gaseous fuels for the transport sector that are predominantly produced from biomass. A variety of fuels can be produced from biomass resources including liquid fuels, such as ethanol, methanol, biodiesel, Fischer-Tropsch diesel, and gaseous fuels, such as hydrogen and methane. Liquid biofuels are primarily used to fuel vehicles, but can also fuel engines or fuel cells for electricity generation. There are several reasons for biofuels to be considered as relevant technologies by both developing and industrialized countries [3]. They include energy security reasons, environmental concerns, foreign exchange savings, and socioeconomic issues related to the rural sector. Due to its environmental merits, the share of biofuel in the automotive fuel market will grow fast in the next decade. Advantages of biofuels are the following: (a) biofuels are easily available from common biomass sources, (b) they are represent a carbon dioxide-cycle in combustion, (c) biofuels have a considerable environmentally friendly potential, (d) there are many benefits the environment, economy and consumers in using biofuels, and (e) they are biodegradable and contribute to sustainability [4].

The biggest difference between biofuels and petroleum feedstocks is oxygen content. Biofuels have oxygen levels from 10% to 45% while petroleum has essentially none making the chemical properties of biofuels very different from petroleum. All have very low sulfur levels and many have low nitrogen levels.

Biomass can be converted into liquid and gaseous fuels through thermochemical and biological routes. Biofuel is a non-polluting, locally available, accessible, sustainable and reliable fuel obtained from renewable sources [5]. Liquid biofuels being considered world over fall into the following categories: (a) bioalcohols; (b)

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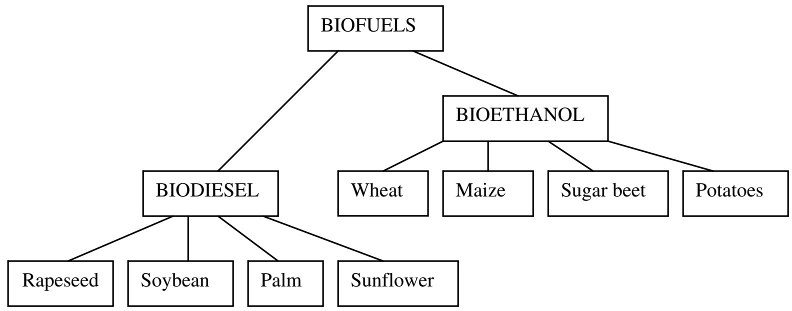

Fig. 1. Resources of bioethanol and biodiesel.

vegetable oils and biodiesels; and (c) biocrude and bio-synthetic oils. Fig. 1 shows the resources of bioethanol and biodiesel.

Biomass appears to be an attractive feedstock for three main reasons. First, it is a renewable resource that could be sustainably developed in the future. Second, it appears to have formidably positive environmental properties resulting in no net releases of carbon dioxide and very low sulfur content. Third, it appears to have significant economic potential provided that fossil fuel prices increase in the future [6]. Lignocellulosic biomethanol have such low emissions because the carbon content of the alcohol is primarily derived from carbon that was sequestered in the growing of the bio-feedstock and is only being re-released into the atmosphere [7].

Biomass energy potential is addressed to be the most promising among the renewable energy sources (RES), due to its spread and its availability worldwide. Apart from that, biomass has the unique advantage among the rest of the RES, to be able to provide solid, liquid and gaseous fuels that can be stored, transported and utilized, far away from the point of origin. Due to the negligible amounts of sulfur and nitrogen biomass contains, the energy that is being utilized does not contribute to environmental pollution. Biofuels are generally considered as offering many priorities, including sustainability, reduction of greenhouse gas emissions, regional development, social structure and agriculture, security of supply [8].

The increased utilization of biofuels for heat and power production has provided to increase political support in European countries. This has resulted in a large number of biofuels being processed for energy conversion necessities and suitability for choosing the most appropriate method of valorizing the conversion products with depending on the variability of using raw materials as well as their composition. In addition, new standard analytical methods are necessary to develop in order to apply new technologies for biofuel production from biomass materials.

2. Biofuels

2.1. Bioalcohols

Biofuels stand for liquid or gaseous fuel for transport produced from biomass. They may be pure (100%) biofuels for dedicated vehicles or blend fuels in such a proportion that they can substitute conventional motor fuels without affecting car performance. For example, ethanol can be blended with gasoline without problems with as much as 15–20% alcohol by volume (E15-20) [9].

The alcohols can be used for motor fuels are methanol (CH_3OH), ethanol (C_2H_5OH), propanol (C_3H_7OH), butanol (C_4H_9OH). However only first two of the alcohols are technically and economically suitable as fuels for internal combustion engines (ICEs).

The alcohol fuels are usually of biological rather than petroleum sources. When obtained from biological sources, they are sometimes known as bioalcohols. The biologically produced ethanol contains about 5% water. This mixture may also not be purified by simple distillation, as it forms an azeotropic mixture. Bioalcohols are still in developmental and research stages.

Gasoline and ethanol mixtures are called as gasohol. E10, sometimes called gasohol, is a fuel mixture of 10% ethanol and 90% gasoline that can be used in the ICEs of most modern automobiles. Gasohol a gasoline extender made from a mixture of gasoline (90%) and ethanol (10%; often obtained by fermenting agricultural crops or crop wastes) or gasoline (97%) and methanol (3%). Gasohol has higher octane, or antiknock, properties than gasoline and burns more slowly, coolly, and completely, resulting in reduced emissions of some pollutants, but it also vaporizes more readily, potentially aggravating ozone pollution in warm weather.

Anhydrous ethanol will readily blend with petrol. Hydrated ethanol containing more than 2% by volume of water is not completely miscible with petrol. Hydrated ethanol is not miscible with diesel but can form an emulsion using a suitable emulsifier. Diesohol is a mixture of diesel fuel and hydrated ethanol blended using a chemical emulsifier. Diesohol is a fuel containing alcohol that comprises a blend of diesel fuel (84.5%), hydrated ethanol (15%) and an emulsifier (0.5%). The emulsifier that allows the ethanol and the diesel to blend consists of a styrene-butadiene copolymer which is dissolved in the diesel fuel and a polyethyleneoxide-polystyrene copolymer which is dissolved in the hydrated alcohol.

Hydrated (or azeotropic) ethanol is ethyl alcohol that contains approximately 5% water. Hydrated ethanol derived from sugar, or ethanol derived from wheat starch, may be used for production of diesohol. Hydrated ethanol production is a one-stage refining. Ethanol is produced by the fermentation of sugar solutions from sugar cane or grain crops. The action of yeast on the sugar produces a solution containing about 12% ethanol. The alcohol can be concentrated by distillation to produce up to 96% ethanol. Removal of the remaining 4% water requires special treatment.

The major effect of diesohol on engine performance is a significant reduction in visible smoke and particulate emissions. Engine thermal efficiency increases by up to eight percent when operating on diesohol. There is also a significant overall reduction in emission of carbon dioxide.

Ethanol or ethyl alcohol produced by hydrolysis and then fermentation processes from biomass is called as bioethanol. Carbohydrates (hemicelluloses and cellulose) in plant materials can be converted to sugars by hydrolysis process. Fermentation is an anaerobic biological process in which sugars are converted to alcohol by the action of microorganisms, usually yeast. The resulting alcohol from the processes is ethanol. The value of any particular type of biomass as feedstock for fermentation depends on the ease with which it can be converted to sugars.

Bioethanol is a fuel derived from renewable sources of feedstock; typically plants such as wheat, sugar beet, corn, straw, and wood. Bioethanol is a petrol additive/substitute. It is possible that wood, straw and even household wastes may be economically converted to bioethanol. Fig. 2 shows ethanol production in different continents.

Bioethanol can be used as a 5% blend with petrol under the EU quality standard EN 228. This blend requires no engine modification and is covered by vehicle warranties. With engine modification, bioethanol can be used at higher levels, for example, E85 (85% bioethanol).

Bioethanol can be produced from a large variety of carbohydrates with a general formula of $(CH_2O)_n$. Fermentation of sucrose is performed using commercial yeast such as *Saccharomyces ceveresiae*. Chemical reaction is composed of enzymatic hydrolysis of sucrose followed by fermentation of simple sugars [10–14]. First, invertase enzyme in the yeast catalyzes the hydrolysis of sucrose to convert it into glucose and fructose. Second, *zymase*, another enzyme also present in the yeast, converts the glucose and the fructose into ethanol. A major processing step in an ethanol plant is enzymatic saccharification of cellulose to sugars through treatment by enzymes; this step requires lengthy processing and normally follows a short term pretreatment step [15]. Fig. 3 shows the flow chart for the production of bioethanol from cereal grain or straw.

Methanol, also known as "wood alcohol," generally, methanol is easier to find than ethanol. Methanol, one of the most industrially important chemicals, may be directly used as a clean fuel or as an additive to the gasoline. It may be converted to gasoline by using a shape-selective (ZSM-5) catalyst. Sustainable methods of methanol production are currently not economically viable. The production of methanol from biomass is a cost intensive chemical process. Therefore, in current conditions, only waste biomass such as old wood or bio-waste is used to produce methanol [5]. Most processes require supplemental oxygen for the intermediate conversion of the biomass into a synthesis gas (H_2 + CO). A readily available supply of hydrogen and oxygen, therefore, should improve the overall productivity of biomass derived methanol [16].

Methanol is currently made from natural gas but can also be made using biomass via partial oxidation reactions [17]. Fig. 4 shows the production of biomethanol from carbohydrates by gasification and partial oxidation with O_2 and H_2O. Biomass can be considered as a potential fuel for gasification and further syngas production and methanol synthesis [18]. Adding sufficient hydrogen to the synthesis gas to convert all of the biomass into methanol carbon than double the methanol produced from the same biomass base [19]. As a renewable resource, biomass represents a potentially inexhaustible supply of feedstock for methanol production. The composition of bio-syngas from biomass for producing methanol is presented in Table 1.

Methanol is considerably easier to recover than the ethanol. Ethanol forms an azeotrope with water so it is expensive to purify the ethanol during recovery. If the water is not removed it will interfere with the reactions. Methanol recycles easier because it does not form an azeotrope. These two factors are the reason that even though methanol is more toxic, it is the preferred alcohol for producing biodiesel. Methanol has a flash point of 283 K, while the flash point of ethanol is 281 K, so both are considered highly flammable.

Ethanol is produced a more environmentally benign fuel. The systematic effect of ethyl alcohol differs from that of methyl

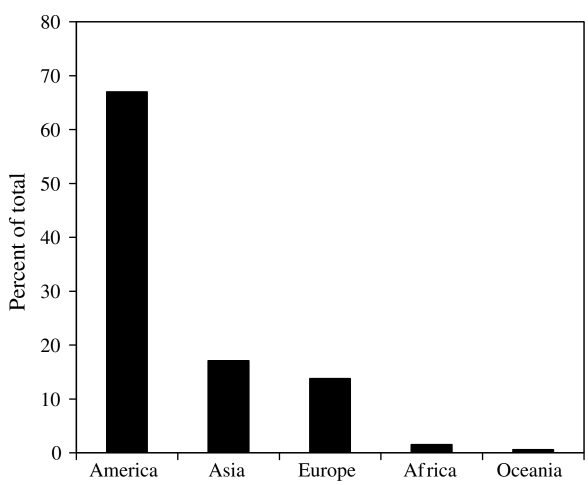

Fig. 2. Ethanol production in different continents.

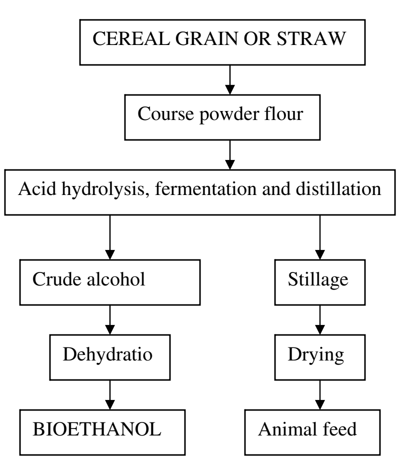

Fig. 3. Flow chart for the production bioethanol from cereal grain or straw.

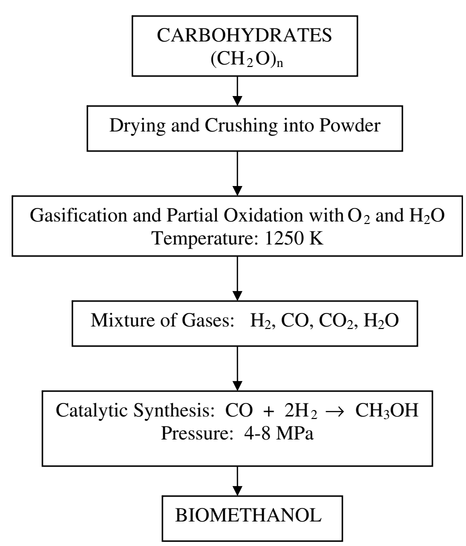

Fig. 4. Biomethanol from carbohydrates by gasification and partial oxidation with O_2 and H_2O.

Table 1
Composition of bio-syngas from biomass gasification

Constituents	% by volume (dry and nitrogen free)
Carbon monoxide (CO)	28–36
Hydrogen (H_2)	22–32
Carbon dioxide (CO_2)	21–30
Methane (CH_4)	8–11
Ethene (C_2H_4)	2–4

alcohol. Ethyl alcohol is rapidly oxidized in the body to carbon dioxide and water, and in contrast to methyl alcohol no cumulative effect occurs. Ethanol is also a preferred alcohol in the transesterification process compared to methanol because it is derived from agricultural products and is renewable and biologically less objectionable in the environment.

Since alcohols, especially methanol, can be readily ignited by hot surfaces, pre-ignition can occur. It must be emphasized here that pre-ignition and knocking in alcohol engine is a much more dangerous condition than gasoline engines. Other properties, however, are favorable to the increase of power and reduction of fuel consumption. Such properties are as follows: (1) number of molecules or products is more than that of reactants; (2) extended limits of flammability; (3) high octane number; % (4) high latent heat of vaporization; (5) constant boiling temperature; and (6) high density.

2.2. Vegetable oils and biodiesel

Vegetable oils are chemically triglycerides molecules in which three fatty acids groups are esters attached to one glycerol molecule. Vegetable oils from renewable oil seeds can be use when mixed with diesel fuels. World annual petroleum consumption and vegetable oil production is about 4.018 and 0.107 billion tons, respectively.

Vegetable oils can be used as fuels for diesel engines, but their viscosities are much higher than usual diesel fuel and require modifications of the engines. Different ways have been considered to reduce the viscosity of vegetable oils such as dilution, microemulsification, pyrolysis, catalytic cracking and transesterification. Compared with transesterification, pyrolysis process has more advantages. The liquid fuel produced from pyrolysis has similar chemical components to conventional petroleum diesel fuel. Vegetable oils can be converted to a maximum of liquid and gaseous hydrocarbons by pyrolysis, decarboxylation, deoxygenation, and catalytic cracking processes [20,21].

The pyrolysis liquids products of vegetable oils can be used as alternative engine fuel. The vegetable oils could be converted to liquid product containing gasoline boiling range hydrocarbons. The results show that the product compositions are affected by catalyst content and temperature. In pyrolysis, the high molecular materials are heated to high temperatures, so their macromolecular structures are broken down into smaller molecules and a wide range of hydrocarbons are formed [22–25].

Vegetable oil (m)ethyl esters, commonly referred to as "biodiesel," are prominent candidates as alternative diesel fuels. The name biodiesel has been given to transesterified vegetable oil to describe its use as a diesel fuel [26]. There has been renewed interest in the use of vegetable oils for making biodiesel due to its less polluting and renewable nature as against the conventional diesel, which is a fossil fuel leading to a potential exhaustion [27]. Biodiesel is technically competitive with or offer technical advantages compared to conventional petroleum diesel fuel. The vegetable oils can be converted to their (m)ethyl esters via transesterification process in the presence of catalyst. Methyl, ethyl, 2-propyl and butyl esters were prepared from vegetable oils through transesterification using potassium and/or sodium alkoxides as catalysts. The purpose of the transesterification process is to lower the viscosity of the oil. Ideally, transesterification is potentially a less expensive way of transforming the large, branched molecular structure of the bio-oils into smaller, straight-chain molecules of the type required in regular diesel combustion engines. The biodiesel esters were characterized for their physical and fuel properties including density, viscosity, iodine value, acid value, cloud point, pure point, gross heat of combustion and volatility. The biodiesel fuels produced slightly lower power and torque, and higher fuel consumption than No. 2 diesel fuel. Biodiesel is better than diesel fuel in terms of sulfur content, flash point, aromatic content and biodegradability [28].

The cost of biodiesels varies depending on the base stock, geographic area, variability in crop production from season to season, the price of the crude petroleum and other factors. Biodiesel has over double the price of petroleum diesel. The high price of biodiesel is in large part due to the high price of the feedstock. However, biodiesel can be made from other feedstocks, including beef tallow, pork lard, and yellow grease [29].

Most of the biodiesel that is currently made uses soybean oil, methanol, and an alkaline catalyst. The high value of soybean oil as a food product makes production of a cost-effective fuel very challenging. However there are large amounts of low-cost oils and fats such as restaurant waste and animal fats that could be converted to biodiesel. The problem with processing these low-cost oils and fats is that they often contain large amounts of free fatty acids (FFA) that cannot be converted to biodiesel using an alkaline catalyst [30,31].

Biodiesel is an environmentally friendly alternative liquid fuel that can be used in any diesel engine without modification. There has been renewed interest in the use of vegetable oils for making biodiesel due to its less polluting and renewable nature as against the conventional petroleum diesel fuel. If the biodiesel valorized efficiently at energy purpose, so would be benefit for the environment and the local population, job creation, provision of modern energy carriers to rural communities, avoid urban migration and reduction of CO_2 and sulfur levels in the atmosphere.

2.3. Bio-oil

The term bio-oil is used mainly to refer to liquid fuels. There are several reasons for bio-oils to be considered as relevant technologies by both developing and industrialized countries. They include energy security reasons, environmental concerns, foreign exchange savings, and socioeconomic issues related to the rural sector.

Bio-oils are liquid or condensable gaseous fuels made from biomass materials, such as agricultural crops, municipal wastes and agricultural and forestry by-products via biochemical or thermochemical processes [32]. They can substitute conventional fuels in vehicle engines – either totally or partially in a blend [33].

Pyrolysis can be used for the production of bio-oil if flash pyrolysis processes are used and are currently at pilot stage [34]. Some problems in the conversion process and use of the oil need to be overcome; these include poor thermal stability and corrosivity of the oil. Upgrading by lowering the oxygen content and removing alkalis by means of hydrogenation and catalytic cracking of the oil may be required for certain applications [17].

Pyrolysis produces energy fuels with high fuel-to-feed ratios, making it the most efficient process for biomass conversion, and the method most capable of competing and eventually replacing non-renewable fossil fuel resources [35]. The conversion of biomass to bio-oil can be having an efficiency of up to ~70% for flash pyrolysis processes. Table 2 shows the properties of bio-oil from rapeseed cake. The HHV of rapeseed cake was found as 36.4 MJ/kg. This bio-oil can be used in engines and turbines in practice. Its use as feedstock for refineries is also being considered. Some interesting trends have been obtained, especially with respect to the effect of net heating rate and temperature on the pyrolysis time.

Pyrolysis/cracking, defined as the cleavage to smaller molecules by thermal energy. Hydrogen can be produced economically from woody biomass [36]. Biomass can be thermally processed through gasification or pyrolysis to produce hydrogen. The main gaseous products from biomass are the following [37]:

Table 2
Composition of bio-syngas from biomass gasification

Property	Bio-oil
Density, at 15 vC (kg/m^3)	993
Elemental composition (wt%)	
Carbon	73.74
Hydrogen	10.69
Oxygen	10.51
Sulphur	0.11
Nitrogen	4.65
Ash, wt%	0.30
Empirical formula (ash free basis)	$C_{18.67}$ $H_{32.48}$ NO_2
Heating value (MJ/kg)	36.4

Source: Ref. [35].

$$\text{Pyrolysis of biomass} \rightarrow H_2 + CO_2 + CO + \text{Gaseous and liquid hydrocarbons} \quad (4)$$

$$\text{Catalytic steam reforming of biomass} \rightarrow H_2 + CO_2 + CO \quad (5)$$

$$\text{Fisher—Tropsch synthesis of } (H_2 + CO) \rightarrow \text{Gaseous and liquid hydrocarbons} \quad (6)$$

The conventional pyrolysis of biomass is associated with the product of interest that is the high charcoal continent, but the fast pyrolysis is associated with the products of interest are tar, at low temperature (675–775 K) [38], and/or gas, at high temperature [36]. Fischer–Tropsch liquids from natural gas and ethanol from biomass may become widespread. The Fischer–Tropsch liquids will penetrate if there are large amounts of stranded natural gas selling for very low prices at the same time that petroleum is expensive or extremely low sulfur is required in diesel fuel. [39]. Fig. 5 shows the production facilities of green diesel and green gasoline and other fuels from bio-syngas by FTS.

The FTS can be carried out in supercritical fluid medium (SFM). When hexane uses as fluid, with increasing pressure in the supercritical medium, the density and heat capacity of the hexane-dominated phase increase. The decrease in mass transfer rates at the higher pressure is offset somewhat by the increase in the intrinsic reaction rates. At a space velocity of 135 g hexane/g catalyst/h, end of run (8 h) isomerization are roughly two fold higher and deactivation rates are three-fold lower in near-critical when compared to subcritical reaction mixture [40].

2.4. Biogas

The organic fraction of almost any form of biomass, including sewage sludge, animal wastes and industrial effluents, can be broken down through anaerobic digestion into methane and carbon dioxide mixture called as "biogas". Biogas is an environment friendly, clean, cheap and versatile fuel [41]. Biogas is a valuable fuel which is produced in digesters filled with the feedstock like dung or sewage. The digestion is allowed to continue for a period of from ten days to a few weeks [42].

The first methane digester plant was built at a leper colony in Bombay, India in 1859 [43]. A methane digester system, commonly referred to as an anaerobic digester (AD) is a device that promotes the decomposition of manure or digestion of the organics in manure to simple organics and gaseous biogas products. There are three types of continuous digesters: vertical tank systems, horizontal tank or plug-flow systems, and multiple tank systems. Proper design, operation, and maintenance of continuous digesters produce a steady and predictable supply of usable biogas.

Several types of bio-digesters have been developed including the floating drum, the fixed dome, the bag, the plastic tube [44], the plug flow and the up-flow anaerobic sludge blanket digesters. Fig. 6 shows an on-farm biogas system.

Anaerobic decomposition is a complex process. Methane is produced in environments where organic matter accumulates, and oxygen is absent [45]. The process by which anaerobic bacteria decompose organic matter into methane, carbon dioxide, and a nutrient-rich sludge involves a step-wise series of reactions requiring the cooperative action of several organisms. It occurs in three basic stages as the result of the activity of a variety of microorganisms. Initially, a group of microorganisms converts organic material to a form that a second group of organisms utilizes to form

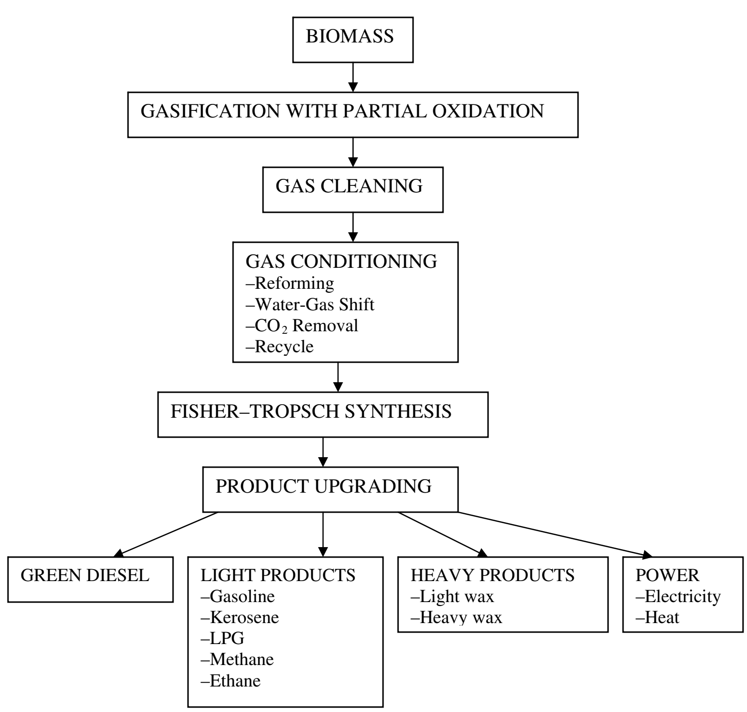

Fig. 5. Green diesel and green gasoline facilities from biomass via Fisher–Tropsch synthesis.

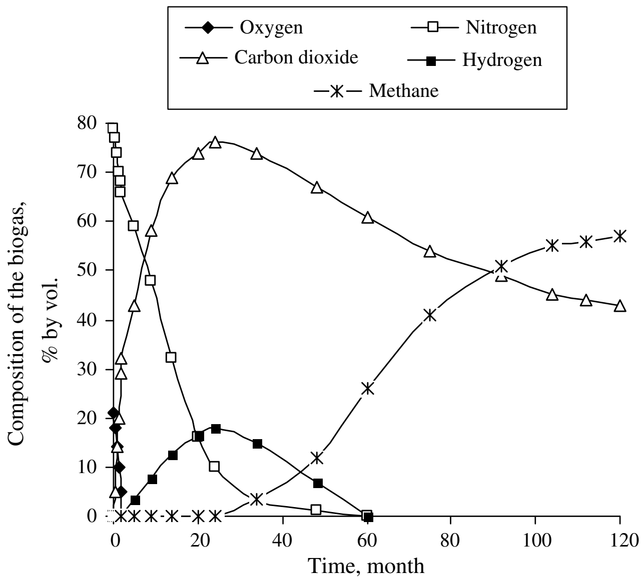

Fig. 6. Production of biogas components with time in landfill. *Source*: Ref. [62].

organic acids. Methane-generating (methanogenic) anaerobic bacteria utilize these acids and complete the decomposition process. In the first stage, a variety of primary producers (acidogens) break down the raw wastes into simpler fatty acids. In the second stage, a different group of organisms (methanogens) consume the organic acids produced by the acidogens, generating biogas as a metabolic byproduct. On average, acidogens grow much more quickly than methanogens. Finally, the organic acids are converted to biogas.

A variety of factors affect the rate of digestion and biogas production. The most important is temperature. Anaerobic bacteria communities can endure temperatures ranging from below freezing to above 330.4 K, but they thrive best at temperatures of about 309.9 K (mesophilic) and 327.6 K (thermophilic). Bacteria activity, and thus biogas production, falls off significantly between about 312.6 K and 324.9 K and gradually from 308.2 K to 273.2 K. Average 68% of the cultivated land produces grains with wheat ranking first, barley second, and corn third in developing countries. Agricultural solid residues are potential renewable energy resources [46]. Wheat straw wastes represent a potential energy resource if they can be properly and biologically converted to methane. They are renewable and their net CO_2 contribution to the atmosphere is zero. Manures and manure/straw mixtures have been extensively investigated as sources of biogas [47–53].

In a process of manure and straw mixture digestion, for first 3 days, methane yield was almost 0% and carbon dioxide generation was almost 100%. In this period, digestion occurred as aerobic fermentation to carbon dioxide. The yields of methane and carbon dioxide gases were fifty–fifty at 11th day. At the end of the 20th day, the digestion reached the stationary phase. The methane content of the biogas was in the range of 73–79% for the runs, the remainder being principally carbon dioxide. During a 30-day digestion period, ~80–85% of the biogas was produced in the first 15–18 days. This implies that the digester retention time can be designed to 15–18 days instead of 30 days [54].

Decomposition in landfills occurs in a series of stages, each of which is characterized by the increase or decrease of specific bacterial populations and the formation and utilization of certain metabolic products. The first stage of decomposition, which usually lasts less than a week, is characterized by the removal of oxygen from the waste by aerobic bacteria [55]. In the second stage, which has been termed the anaerobic acid stage, a diverse population of hydrolytic and fermentative bacteria hydrolyzes polymers, such as cellulose, hemicellulose, proteins, and lipids, into soluble sugars, amino acids, long-chain carboxylic acids, and glycerol [56]. Fig. 6 shows the behavior of biogas production with time, in terms of the biogas components. Fig. 6 indicates that the economic exploitation of CH_4 is worthwhile after one year from the start of the landfill operation. The main components of landfill gas are by-products of the decomposition of organic material, usually in the form of domestic waste, by the action of naturally occurring bacteria under anaerobic conditions [42].

Agricultural residues are difficult to degrade bio-chemically. Pretreatment of straw by mechanical size reduction, heat treatment and/or chemical treatment with strong acids or bases usually improves the digestibility. Chemical pretreatment methods are bicarbonate treatment, alkaline peroxide treatment and ammonia treatment. Ammonia treatment has several advantages over the other treatments, such as being a source of nitrogen for biodegradation and the fact that no separate wastewater streams are generated from the pretreatment process.

Agricultural residues contain low nitrogen and have carbon-to-nitrogen ratios (C/N) of around 60–90. The proper C/N ratio for anaerobic digestion is 25–35 [57]; therefore, nitrogen needs to be supplemented to enhance the anaerobic digestion of agricultural solid residues. Nitrogen can be added in inorganic form such as ammonia or in organic form such as livestock manure, urea, or food wastes. Once nitrogen is released from the organic matter, it becomes ammonium which is water soluble. Recycling nitrogen in the digested liquid reduces the amount of nitrogen needed.

Anaerobic biological treatment of the agricultural solid waste is a process which has received increased attention during the last few years. Conversion of these wastes to methane provides some energy and can have a beneficial effect on the environment, and during the digestion process bacteria in the manure are killed, which is a great benefit to environmental health. The production of methane during the anaerobic digestion of biologically degradable organic matter depends on the amount and kind of material added to the system.

2.5. Bio-char

Many reports have appeared on the development of activated carbon from cheaper and readily available materials. Activated bio-chars are obtained through one of two general methods: (a) either by partial gasification of the primary char with steam or carbon dioxide or a mixture of both to increase their porosity or (b) by chemical activation of the precursor with a chemical like zinc chloride or phosphoric acid [58].

Agricultural residues, such as fruit stones, nutshells and corcobs, are very good precursors for the production of activated carbons [59,60]. In the sense of environmental protection, the utilization of these wastes has awakened the interest for development of processes for production of carbon adsorbents based on agricultural wastes. Both the nature of the precursors and the production process has a strong influence on the porous structure and adsorption properties of the resulting activated carbons.

The starting materials used in commercial production of activated carbons are those with high carbon contents such as wood, lignite, peat, and coal of different ranks or low-cost and abundantly available agricultural by-products. Active carbons can be manufactured from virtually any carbonaceous precursor, but the most commonly used materials wood, coal and coconut shell [61].

Fig. 7 shows the effect of temperature on carbon and oxygen contents in bio-char from biomass. Fig. 8 shows the effect of temperature on hydrogen content in the bio-char. The results of the elemental analysis (Figs. 7 and 8) indicate that contents of carbon increase with pyrolysis temperature while these corresponding to

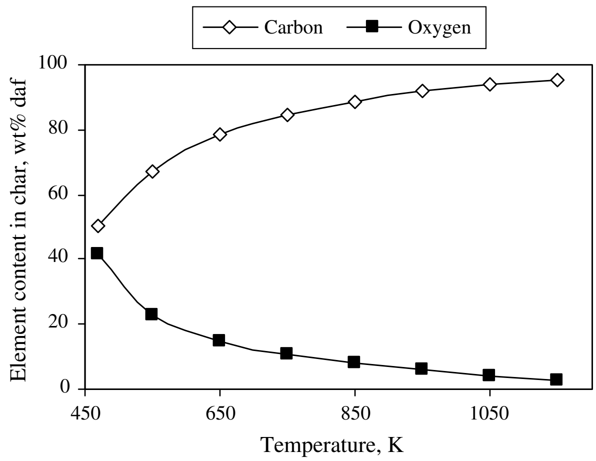

Fig. 7. Effect of temperature on carbon and oxygen contents in bio-char from biomass.

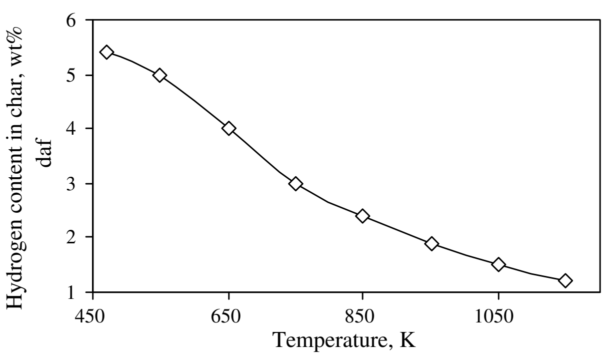

Fig. 8. Effect of temperature on hydrogen content in bio-char from biomass.

hydrogen and oxygen decrease [62]. Losses in hydrogen and oxygen correspond to the scission of weaker bonds within the bio-char structure favored by the higher temperature [63].

Active carbons are carbonaceous materials with highly developed internal surface area and porosity. Activated carbon is widely used as an effective adsorbent in many applications such as air separation and purification, vehicle exhaust emission control, solvent recovery and catalyst support because of its high specific pore surface area, adequate pore size distribution and relatively high mechanical strength. The large surface area results in high capacity for adsorbing chemicals from gases and liquids [64].

Lignin gives higher yields of charcoal and tar from wood although lignin has three-fold of methoxyl content than that of wood [65–67]. The formation of char from lignin under mild reaction conditions is a result of the breaking of the relatively weak bonds, like the alkyl–aryl ether bond(s), and the consequent formation of more resistant condensed structures, as has already been noted by Domburg et al. [68]. One additional parameter which may also have an effect on the char formation is the moisture content of the kraft lignin used. It has been found that the presence of moisture increased the yield of char from the pyrolysis of wood waste at temperatures between 660 and 730 K, while Stray et al. [69] found only a slight effect for water added on the hydrogenolysis of both hardwood and softwood lignins at temperatures between 470 and 675 K. The thermolysis reactions of the kraft lignin is comprised mainly of breaking the most reactive bonds like the methyl C–O bond of the methoxyl group and the condensation reactions to high molecular weight products (char) that follows.

The stronger effect of the heating rate on the formation of bio-char from biomass than from coal may be attributed to the cellulose content of the biomass [70]. It is well known that heating rate has a significant effect on the pyrolysis of cellulose. Heating rate has a much greater effect on the pyrolysis of biomass than on that of coal. The quick devolatilization of the biomass in rapid pyrolysis favors the formation of char with high porosity and high reactivity [71]. The decreased formation of char at the higher heating rate was accompanied by an increased formation of tar. The net effect is a decrease in the volatile fuel production and an increased yield of bio-char cellulose converted to levoglucosan at above 535 K temperatures [72].

2.6. Biohydrogen

Hydrogen is not a primary fuel. It can be burned to produce heat or passed through a fuel cell to produce electricity. Widespread use of hydrogen as an energy source could improve global climate change, energy efficiency, and air quality. Hydrogen gas has potential if used in an electricity generating fuel cell. Fuel cells have no moving parts, produce only clean water as emissions, and are around 70% efficient (compared with the highest IC engine efficiencies of only around 45%). The problem with fuel cells is that realistic, cost-efficient mass production of hydrogen gas is years away.

Hydrogen can be produced by pyrolysis from biomass [73–75]. Hydrogen production from biomass requires multiple reaction steps: for the production of high purity hydrogen, the reforming of fuels is followed by two water gas-shift reaction steps, a final carbon monoxide purification and carbon dioxide removal.

The thermochemical conversion processes, such as pyrolysis, gasification and steam gasification is available for converting the biomass to a more useful energy. The yield from steam gasification increases with increasing water-to-sample ratio. The yields of hydrogen from the pyrolysis and the steam gasification increase with increasing of temperature. The list of some biomass material used for hydrogen production is given in Table 3. Hydrogen powered fuel cells are an important enabling technology for the hydrogen future and more-efficient alternatives to the combustion of gasoline and other fossil fuels. Hydrogen has the potential to solve two major energy problems: reducing dependence on petroleum and reducing pollution and greenhouse gas emissions.

Biological generation of hydrogen (biohydrogen) technologies provide a wide range of approaches to generate hydrogen, including direct biophotolysis, indirect biophotolysis, photo-fermentations, and dark-fermentation [76]. Biological hydrogen production processes are found to be more environment friendly and less energy intensive as compared to thermochemical and electrochemical processes [77]. Researchers have started to investigate hydrogen production with anaerobic bacteria since 1980s [78,79].

There are three types of microorganisms of hydrogen generation: cyano-bacteria, anaerobic bacteria, and fermentative bacteria. The cyano-bacteria directly decompose water to hydrogen and

Table 3
List of some biomass material used for hydrogen production

Biomass species	Main conversion process
Bio-nut shell	Steam gasification
Olive husk	Pyrolysis
Tea waste	Pyrolysis
Crop straw	Pyrolysis
Black liquor	Steam gasification
Municipal solid waste	Supercritical water extraction
Crop grain residue	Supercritical fluid extraction
Pulp and paper waste	Microbiol fermentation
Petroleum basis plastic waste	Supercritical fluid extraction
Manure slurry	Microbiol fermentation

oxygen in the presence of light energy by photosynthesis. Photosynthetic bacteria use organic substrates like organic acids. Anaerobic bacteria use organic substances as the sole source of electrons and energy, converting them into hydrogen. Biohydrogen can be generated using bacteria such as *Clostridia* by temperature, pH control, reactor hydraulic retention time (HRT) and other factors of the treatment system.

Biological hydrogen can be generated from plants by biophotolysis of water using microalgae (green algae and cyanobacteria), fermentation of organic compounds, and photodecomposition of organic compounds by photo-synthetic bacteria. To produce hydrogen by fermentation of biomass, a continuous process using a nonsterile substrate with a readily available mixed micro6ora is desirable [80]. A successful biological conversion of biomass to hydrogen depends strongly on the processing of raw materials to produce feedstock which can be fermented by the microorganisms [81].

Hydrogen production from the bacterial fermentation of sugars has been examined in a variety of reactor systems. Hexose concentration has a greater effect on H_2 yields than the HRT. Flocculation also was an important factor in the performance of the reactor [82].

Hydrogen gas is a product of the mixed acid fermentation of *Escherichia coli*, the butylene glycol fermentation of *Aerobacter*, and the butyric acid fermentations of *Clostridium* spp. [83]. It was conducted to improve hydrogen fermentation of food waste in a leaching-bed reactor by heat-shocked anaerobic sludge, and also to investigate the e1ect of dilution rate on the production of hydrogen and metabolites in hydrogen fermentation [84].

In the steam-reforming reaction of biomass, steam reacts with hydrocarbons in the feed to predominantly produce carbon monoxide and hydrogen, commonly called synthesis gas. Steam reforming can be applied various solid waste materials including, municipal organic waste, waste oil, sewage sludge, paper mill sludge, black liquor, refuse-derived fuel, and agricultural waste.

3. Biofuel economy

Even with today's high oil prices, biofuels cost more than conventional fuels. The biofuel economy will grow rapidly during the 21st century. The biofuel economy, and its associated biorefineries, will be shaped by many of the same forces that shaped the development of the hydrocarbon economy and its refineries over the past century. President Bush spoke in his January 31, 2006, State of the Union address of producing biofuels by 2012 using "woodchips, stalks and switchgrass" as the source of cellulosic biomass. These represent both existing and potential biomass resources. Due to its environmental merits, the share of biofuel in the automotive fuel market will grow fast in the next decade. There are several reasons for biofuels to be considered as relevant technologies by both developing and industrialized countries.

National indicative targets can only be achieved if biofuels benefit from some kind of public support system. Some support is available to encourage the supply of biofuels and their feedstocks. This includes aids for the cultivation of raw materials and for the capital cost of biofuel processing. Support systems designed to encourage demand for biofuels play a larger role. The main approaches are: (a) tax reductions/exemptions for biofuels and (b) Biofuel obligations.

In the most biomass-intensive scenario, modernized biomass energy contributes by 2050 about one half of total energy demand in developing countries [85]. The biomass intensive future energy supply scenario includes 385 million hectares of biomass energy plantations globally in 2050 with three quarters of this area established in developing countries [86]. Various scenarios have put forward on estimates of biofuel from biomass sources in the future energy system. The availability of the resources is an important factor cogenerative use of biofuel in the electricity, heat or liquid fuel market. There are two global biomass based liquid transportation fuels that might replace gasoline and diesel fuel. These are bioethanol and biodiesel. Transport is one of the main energy consuming sectors. It is assumed that biodiesel is used as a fossil diesel replacement and that bioethanol is used as a gasoline replacement. Biomass-based energy sources for heat, electricity and transportation fuels are potentially carbon dioxide neutral and recycle the same carbon atoms. Due to widespread availability opportunities of biomass resources biomass-based fuel technology potentially employ more people than fossil-fuel based technology [86]. Demand for energy is increasing every day due to the rapid outgrowth of population and urbanization. As the major conventional energy resources like coal, petroleum and natural gas are at the verge of getting extinct, biomass can be considered as one of the promising environment friendly renewable energy options.

Agricultural energy "green energy" production is the principal contributor in economic development of a developing country. Its economy development is based on agricultural production and most people live in the rural areas. Implementation of integrated community development programs is therefore very necessary. It is believed that integrated community development contributes to push up socio-economic development of the country.

Agriculture-(m)ethanol is at present more expensive of synthesis-ethanol from ethylene and of methanol from natural gas. The simultaneous production of biomethanol (from sugar juice) in parallel to the production of bioethanol, appears economically attractive in locations where hydro-electricity is available at very low-cost (~0.01$ kWh) and where lignocellulosic residues are available as surpluses [87].

Current natural gas feedstocks are so inexpensive that even with tax incentives renewable methanol has not been able to compete economically. Technologies are being developed that may eventually result in commercial viability of renewable methanol.

Methanol can be produced from biomass essentially any primary energy source. Thus, the choice of fuel in the transportation sector is to some extent determined by the availability of biomass. As regards the difference between hydrogen and methanol production costs, conversion of natural gas, biomass and coal into hydrogen is generally more energy efficient and less expensive than conversion into methanol [88].

The FTS based gas to liquids (GTL) technology includes the three processing steps namely syngas generation, syngas conversion and hydroprocessing. In order to make the GTL technology more cost-effective, the focus must be on reducing both the capital and the operating costs of such a plant [89]. For some time now the price has been up to $60 per barrel. It has been estimated that the FT process should be viable at crude oil prices of about $20 per barrel [90]. The current commercial applications of the FT process are geared at the production of the valuable linear alpha olefins and of fuels such as LPG, gasoline, kerosene and diesel. Since the FT process produces predominantly linear hydrocarbons the production of high-quality diesel fuel is currently of considerable interest [91]. The most expensive section of an FT complex is the production of purified syngas and so its composition should match the overall usage ratio of the FT reactions, which in turn depends on the product selectivity [92]. The industrial application of the FT process started in Germany and by 1938 there were nine plants in operation having a combined capacity of about 660×10^3 t per year [93].

4. Biofuel policy

Energy is an essential input driving economic development. Therefore, in developed economies energy policies constitute an important component of overall regulatory frameworks shaping the improving overall competitiveness and market integration of the private business sector. Overall competitiveness includes liberalisation of the electricity and gas markets as well as by separation of energy production, transportation, and distribution activities.

Renewable energy sources are indigenous, and can therefore contribute to reducing dependency on oil imports and increasing security of supply. The biofuel policy aims to promote the use in transport of fuels made from biomass, as well as other renewable fuels. Biofuels provide the prospect of new economic opportunities for people in rural areas in oil importer and developing countries. The central policy of biofuel concerns job creation, greater efficiency in the general business environment, and protection of the environment.

Current European Union (EU) policies on alternative motor fuels focus on the promotion of biofuels. In a proposed biofuels directive the introduction of a mandatory share scheme for biofuels, including as from 2009 minimum blending shares. Table 4 shows the shares of alternative fuels compared to the total automotive fuel consumption in the EU under the optimistic development scenario of the European Commission. The EU has set the goal of obtaining 5.75% of transportation fuel needs from biofuels by 2010 in all member states in February 2006. In the Commission's view mandating the use of biofuels will (a) improve energy supply security and (b) reduce greenhouse gas (GHG) emissions and (c) boost rural incomes and employment [94,95].

The general EU policy objectives considered most relevant to the design of energy policy are: (1) competitiveness of the EU economy, (2) security of energy supply, and (3) environmental protection [94].

Producing and using biofuels for transportation offers alternatives to fossil fuels that can help provide solutions to many environmental problems. Using biofuels in motor vehicles helps reduce green house gases (GHG) emissions. Biodiesel and ethanol provide significant reductions in GHG emissions compared to gasoline and diesel fuel. Due to the low or zero content of pollutants such as sulfur in biofuels, the pollutant emission of biofuels is much lower than the emission of conventional fuels. Numerous low emission scenarios have demonstrated that the Kyoto Protocol cannot be achieved without establishing a large role for biofuel in the global energy economy by 2050. Low emission scenarios imply 50–70 EJ of biofuel raw material in 2050. Well-designed biofuels projects would have very significant sustainable development benefits for rural areas, including creation of rural employment, rural electricity supply, soil conservation and environmental benefits [96].

The main biofuel opportunities where suitable land is available are in developing countries. The issue of energy security has been accorded top-most priority. Every effort needs to be made to enhance the indigenous content of energy in a time-bound and planned manner. The additional benefit of biofuel development is creation of new employment opportunities in manufacturing, construction, plant operation and servicing, and fuel supply. Rural jobs are created in fuel harvesting, transport and maintenance of processing areas [96].

Table 4
Shares of alternative fuels in total automotive fuel consumption in the EU under the optimistic development scenario of the European Commission

Year	Biofuel	Natural gas	Hydrogen	Total
2010	6	2		8
2015	7	5	2	14
2020	8	10	5	23

Source: Ref. [94].

5. Global biofuel projections

Various scenarios have resulted in high estimates of biofuel in the future energy system. The availability of the resources is an important factor if high shares of biofuel penetrate the electricity, heat or liquid fuel market. The rationale is to facilitate the transition from the hydrocarbon economy to the carbohydrate economy by using biomass to produce bioethanol and biomethanol as replacements for traditional oil-based fuels and feedstocks. The biofuel scenario produced equivalent rates of growth in GDP and per capita affluence, reduced fossil energy intensities of GDP, reduced oil imports and gave an energy ratio. Each scenario has advantages whether it is rates of growth in GDP, reductions in carbon dioxide emissions, the energy ratio of the production process, the direct generation of jobs, or the area of plantation biomass required to make the production system feasible [96].

Renewable resources are more evenly distributed than fossil and nuclear resources, and energy flows from renewable resources are more than three orders of magnitude higher than current global energy use. Today's energy system is unsustainable because of equity issues as well as environmental, economic, and geopolitical concerns that have implications far into the future [97].

According to International Energy Agency (IEA), scenarios developed for the USA and the EU indicate that near-term targets of up to 6% displacement of petroleum fuels with biofuels appear feasible using conventional biofuels, given available cropland. A 5% displacement of gasoline in the EU requires about 5% of available cropland to produce ethanol while in the USA 8% is required. A 5% displacement of diesel requires 13% of USA cropland, 15% in the EU. The recent commitment by the USA government to increase bio-energy three-fold in 10 years has added impetus to the search for viable biofuels [98].

The dwindling fossil fuel sources and the increasing dependency of the USA on imported crude oil have led to a major interest in expanding the use of bio-energy. The recent commitment by the USA government to increase bio-energy three-fold in 10 years has added impetus to the search for viable biofuels. The EU have also adopted a proposal for a directive on the promotion of the use of biofuels with measures ensuring that biofuels account for at least 2% of the market for gasoline and diesel sold as transport fuel by the end of 2005, increasing in stages to a minimum of 5.75% by the end of 2010 [95].

Fig. 9 shows the shares of alternative fuels compared to the total automotive fuel consumption in the world as a futuristic view.

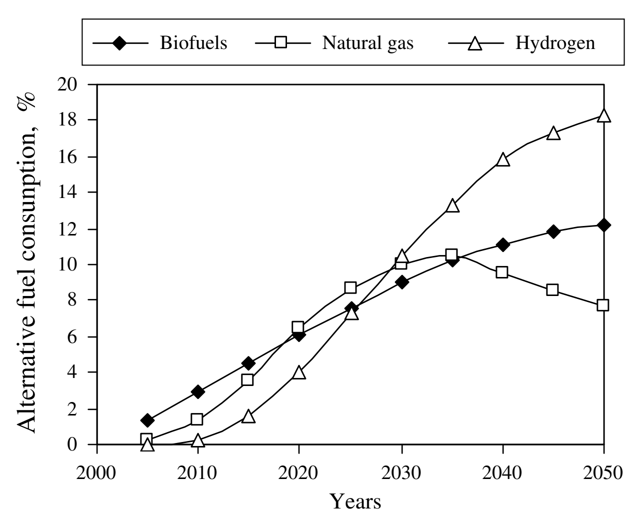

Fig. 9. Shares of alternative fuels compared to the total automotive fuel consumption in the world. *Source*: Ref. [96].

Hydrogen is currently more expensive than conventional energy sources. There are different technologies presently being practiced to produce hydrogen economically from biomass. Biohydrogen technology will play a major role in future because it can utilize the renewable sources of energy [74].

Hydrogen for fleet vehicles would probably dominate in the transportation sector. To produce hydrogen via electrolysis and the transportation of liquefied hydrogen to rural areas with pipelines would be expensive. The production technology would be site specific and include steam reforming of methane and electrolysis in hydropower rich countries. In the long run, when hydrogen is a very common energy carrier, distribution with pipeline is probably the preferred option. The cost of hydrogen distribution and refueling is very site specific.

6. Conclusion

The term biofuel is referred to as liquid or gaseous fuels for the transport sector that are predominantly produced from biomass. There are several reasons for biofuels to be considered as relevant technologies by both developing and industrialized countries. They include energy security reasons, environmental concerns, foreign exchange savings, and socioeconomic issues related to the rural sector.

Biomass can be converted to biofuels via chemical, such as biomethanol and biodiesel production, thermochemical, such as bio-oil, bio-syngas, biohydrogen production, and biochemical, such as bioethanol, biogas, biodiesel and biohydrogen production, methods. Bioethanol is a fuel derived from renewable sources of feedstock; typically plants such as wheat, sugar beet, corn, straw, and wood. Bioethanol is a petrol additive/substitute. Biodiesel is better than diesel fuel in terms of sulfur content, flash point, aromatic content and biodegradability [28].

Bioethanol can be produced from plentiful, domestic, cellulosic biomass resources such as herbaceous and woody plants, agricultural and forestry residues, and a large portion of municipal solid waste and industrial waste streams. Production of bioethanol from biomass is one way to reduce both the consumption of crude oil and environmental pollution.

As a renewable resource, biomass represents a potentially inexhaustible supply of feedstock for methanol production. Biomethanol can be produced from biomass using bio-sythetic gas (bio-syngas) obtained from steam reforming process of biomass.

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