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Recent trends in global production and utilization of bio-ethanol fuel

Mustafa Balat *, Havva Balat

Sila Science and Energy Unlimited Company, Mekan Sok, No 24, Trabzon, Turkey

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ABSTRACT

Bio-fuels are important because they replace petroleum fuels. A number of environmental and economic benefits are claimed for bio-fuels. Bio-ethanol is by far the most widely used bio-fuel for transportation worldwide. Production of bio-ethanol from biomass is one way to reduce both consumption of crude oil and environmental pollution. Using bio-ethanol blended gasoline fuel for automobiles can significantly reduce petroleum use and exhaust greenhouse gas emission. Bio-ethanol can be produced from different kinds of raw materials. These raw materials are classified into three categories of agricultural raw materials: simple sugars, starch and lignocellulose. Bio-ethanol from sugar cane, produced under the proper conditions, is essentially a clean fuel and has several clear advantages over petroleum-derived gasoline in reducing greenhouse gas emissions and improving air quality in metropolitan areas. Conversion technologies for producing bio-ethanol from cellulosic biomass resources such as forest materials, agricultural residues and urban wastes are under development and have not yet been demonstrated commercially.

Contents

1. Introduction

With increasing gap between the energy requirement of the industrialized world and inability to replenish such needs from the limited sources of energy like fossil fuels, an ever increasing levels of greenhouse pollution from the combustion of fossil fuels in turn aggravate the perils of global warming and energy crisis [1]. Motor vehicles account for a significant portion of urban air pollution in much of the developing world. According to Goldemberg [2], motor vehicles account for more than 70% of global carbon monoxide (CO) emissions and 19% of global carbon dioxide (CO_2) emissions. CO_2 emissions from a gallon of gasoline are about 8 kg. For example:

$$CO_2 \text{ emissions from a gallon of octane} = 3.78\ \mathrm{L} \times 0.699\ \mathrm{kg\ L^{-1}} \times (96/114) \times (44/12) = 8.16\ \mathrm{kg} \quad (1)$$

There are 700 million light duty vehicles, automobiles, light trucks, SUVs and minivans, on roadways around the world. These numbers are projected to increase to 1.3 billion by 2030, and to over 2 billion vehicles by 2050, with most of the increase coming in developing

* Corresponding author. Tel.: +90 462 871 3025; fax: +90 462 871 3110.
E-mail address: mustafabalat@yahoo.com (M. Balat).

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countries [3]. This growth will affect the stability of ecosystems and global climate as well as global oil reserves.

The world's total proven oil, natural gas and coal reserves are respectively, 168.6 billion tons, 177.4 trillion cubic meters, and 847.5 billion tons by the end of 2007, according to the recently released 2008 BP Statistical Review of World Energy [4]. With current consumption trends, the reserves-to-production (R/P) ratio of world proven reserves of oil is lower than that of world proven reserves of natural gas and coal — 41.6 years versus 60.3 and 133 years [4], respectively. In 2007, world oil production was 3.90 billion tons, a decrease of 0.2% from the previous year [4]. According to International Energy Agency statistics [5], the transportation sector accounts for about 60% of the world's total oil consumption. Interest in the use of bio-fuels worldwide has grown strongly in recent years due to the limited oil reserves, concerns about climate change from greenhouse gas emissions and the desire to promote domestic rural economies.

The term bio-fuels can refer to fuels for direct combustion for electricity production, but is generally used for liquid fuels in transportation sector [6]. The use of bio-fuels can contribute to the mitigation of greenhouse gas emissions, provide a clean and therefore sustainable energy source, and increase the agricultural income for rural poor in developing countries. Today, bio-fuels are predominantly produced from biomass resources. Biomass appears to be an attractive feedstock for three main reasons [7–9]: (1) it is a renewable resource that could be sustainably developed in the future, (2) it appears to have formidably positive environmental properties resulting in no net releases of carbon dioxide and very low sulfur content, and (3) it appears to have significant economic potential provided that fossil fuel prices increase in the future.

Bio-fuels are liquid or gaseous fuels made from plant matter and residues, such as agricultural crops, municipal wastes and agricultural and forestry by-products. Liquid bio-fuels can be used as an alternative fuel for transport, as can other alternatives such as liquid natural gas (LNG), compressed natural gas (CNG), liquefied petroleum gas (LPG) and hydrogen. Bio-fuels could significantly reduce the emissions from the road-transport sector if they were widely adopted. They have been shown to reduce carbon emissions, and may help to increase energy security. There are many different types of bio-fuels, which are produced from various crops and via different processes. Bio-fuels can be classified broadly as bio-diesel and bio-ethanol, and then subdivided into conventional or advanced fuels [10]. This paper summarizes policy and regulatory drivers for bio-ethanol fuel in the major producing countries, describes usage trends and projections, development of biomass feedstocks, and improved conversion technologies.

2. Policy drivers for bio-ethanol

Bio-fuels are attracting growing interest around the world, with some governments announcing commitments to bio-fuel programs as a way to both reduce greenhouse gas emissions and dependence on petroleum-based fuels. The United States, Brazil, and several EU member states have the largest programs promoting bio-fuels in the world. The recent commitment by the United States government to increase bio-energy threefold in ten years has added impetus to the search for viable bio-fuels [11–16]. In South America, Brazil continued policies that mandate at least 22% bio-ethanol on motor fuels and encourage the use of vehicles that use hydrous bio-ethanol [(96 bio-ethanol + 4 water)/100] to replace gasoline [17]. Future conditions for an international bio-fuel market in Europe will largely be decided by the EU policies on renewable energy and their interplay with national energy policies. So far, the European Commission has indicated that biomass will play an important role in the future [18].

In the United States, the desire to promote the production and use of bio-fuels, particularly bio-ethanol produced from maize, started in the early 1980s, largely to revitalize the farming sector at a time of oversupply of agricultural produce [19]. Bio-ethanol can be used in fuel mixtures such as E85 (a blended fuel of 85% bio-ethanol and 15% gasoline) in vehicles specially designed for its use, although E85 represents only approximately 1% of US bio-ethanol consumption [20]. To promote the development of E85 blend fuel and other alternative transportation fuels, the US Congress has enacted various legislative requirements and incentives. At the national level, the Energy Policy Act of 2005 (EPAct 2005) is one of the most significant steps [21]. The legislation set a target of 28.4 billion liters consumption of bio-ethanol by 2012 (Renewable Fuels Standard [RFS]), it represents around 5% (in volume) of gasoline consumption projected for the year 2012 [22]. The act also gave additional incentives for cellulosic bio-ethanol, extended the bio-diesel fuel excise tax credit through 2008, and authorized a US$0.03 per liter income tax credit to small bio-diesel producers [23]. Gasoline prices surged over US$0.79 per liter in the spring of 2007, stayed near that level during the summer driving season, and after a brief retreat returned there at the beginning of 2008. However, consumption of gasoline continued above nine million barrels per day, setting a record high summer peak of over 9.7 million barrels per day during 2007 [24]. To help improve vehicle fuel economy and reduce dependence on foreign oil sources, the US Congress passed, and the President signed the Energy Independence and Security Act of 2007 (EISA) on December 18, 2007. Congress has agreed by approving new fuel and vehicle fuel economy standards (Corporate Average Fuel Economy [CAFE] standards) as part of the EISA. These standards require a fleet–wide average of 35 miles per gallon for cars and light trucks by 2020. The legislation also requires 34 billion liters of bio-fuels (mainly bio-ethanol) in 2008, increasing steadily to 57.5 billion liters in 2012 and to 136 billion liters in 2022. Also for the first time, the 2007 Energy Act includes the concept of a low carbon fuel standard (similar to California) requiring renewable fuels to have at least a 20% reduction in carbon intensity over the fuels' life-cycle [21].

Brazil has a long history of bio-fuel production dating to 1975 when the National Alcohol Fuel Program (ProAlcool) was initiated. The program aimed to increase production of bio-ethanol as a substitute for expensive and extremely scarce gasoline. With substantial governmental interventions to increase alcohol demand and supply, Brazil created assets and developed institutional and technological capabilities for using renewable energy on a large-scale. By 1984, a majority of new cars sold in Brazil required hydrous bio-ethanol [(96 bio-ethanol + 4 water)/100] as fuel [25]. In 1993, the government passed a law in which all gasoline marketed in Brazil would be blended with 20–25% of bio-ethanol [26]. As the sugar–ethanol industry matured, policies evolved and the ProAlcool program was phased out in 1999, permitting more incentives for private investment and reducing government intervention in allocations and pricing. Widespread availability of flex-fuel vehicles (promoted through tax incentives) combined with rising oil prices have led to rapid growth in bio-ethanol and sugar cane production since 2000 [25]. Today, more than 80% of Brazil's current automobile production has flexible-fuel capability, up from 30% in 2004. With bio-ethanol widely available at almost all of Brazil's 32,000 gas stations, Brazilian consumers currently choose primarily between anhydrous bio-ethanol/gasoline and a 25% bio-ethanol/gasoline blend on the basis of relative prices [27].

In the European Commission's view mandating the use of bio-fuels will: (1) improve energy supply security, (2) reduce greenhouse gas emissions, and (3) boost rural incomes and employment

[6,28–31]. The European Commission White Paper [32] calls for dependence on oil in the transport sector to be reduced by using alternative fuels such as bio-fuels. In addition, due to the increasing mobility of people and goods, the transport sector accounts for more than 30% of final energy consumption in the EU and is expanding. Therefore, an increasing use of bio-fuels for transport is emerging as an important policy strategy to substitute petroleum-based fuels [33]. The EU bio-fuels directive (2003/30/EC) [34] set a target of an indicative 5.75% total bio-fuel share of all consumed gasoline and diesel fuel for transport placed on the market by 2010. This indicative target has been adopted by most Member States in their national bio-fuel objectives [35]. France established an ambitious bio-fuels plan, with goals of 7% by 2010, and 10% by 2015. Belgium set a 5.75% target for 2010. The European Commission's Green Paper on "A European Strategy for Sustainable, Competitive and Secure Energy" (March 2006) [36] and its 2007 strategic energy review, "An Energy Policy for Europe" (January 2007) [37] have both emphasized the need to take effective actions to address climate change (including actions to mitigate greenhouse gas emissions), promote jobs and growth and enhance security of energy supply in the internal market. On 23 January 2008, the European Commission [38] proposed a binding minimum target of 10% for the share of bio-fuels in transport in the context of the "EU directive on the promotion of the use of energy from renewable sources" that envisages a 20% share of all renewable energy sources in total energy consumption by 2020. In 2007, the EU agreed amendment of the Fuel Quality Directive to allow adequate levels of blending. In these proposed rules the commission set a minimum value of 35% of greenhouse gas savings [39,40], which bio-fuels must achieve in order to count towards the bio-fuels target. Without the present set of subsidies, tax reductions and exemptions as well as mandatory incorporation rates, the EU production would certainly be much more limited [41]. Fuel tax reductions are the most widely used of all the support measures for bio-fuels. This fiscal instrument depends on the magnitude of excise taxes levied on petroleum fuels would find it difficult to launch commercially viable bio-fuel markets because bio-fuels have historically required large tax reductions to compete with petroleum-based fuels [23]. In 2003, the EU's framework for the taxation of energy products and electricity was amended to allow Member States to grant tax reductions and/or exemptions in favor of renewable fuels under certain conditions. However, to minimize the tax revenue loss for EU member states, the final tax on bio-fuels intended for transport use may not be less than 50% of the normal excise duty [42]. Tax reductions for bio-ethanol in EU countries have been as high as US$0.84 per liter [23].

Chinese policy instruments for the promotion of bio-fuels include research, subsidies, tax, price limits, quotations, limits and changes established by law [43]. Starting from 2001 two major fuel bio-ethanol programs have been implemented in China with the objective to promote renewable energy sources, enhance national energy security and improve domestic environment [44]. More recently, China promulgated new laws (e.g. for the creation of risk reserves, changes in financial incentives, and availability of venture capital) that are reportedly intended to help the bio-ethanol industry become more economically self-sufficient [45]. Bio-fuels program grew out of China's aggressive Renewable Energy Act passed in February 2005. The government has pledged that 10% of the nation's energy will come from renewable energy sources by 2020 [46]. The Chinese government set the selling price of bio-ethanol at about US$0.44 per liter as 91.1% of the selling price of gasoline. However, production of bio-ethanol from corn at US$147 per dry ton costs about US$0.49 per liter, resulting in large subsidy payments by the government [47]. During the 10th Five-Year-Plan, the Ministry of Science and Technology continued with the promotion of bio-ethanol.

3. Bio-ethanol trends and projections

Global production of bio-ethanol increased from 17.25 billion liters in 2000 [16] to over 46 billion liters in 2007 [48]. Fig. 1 shows global bio-ethanol production between 2000 and 2007. Bio-ethanol production in 2007 represented about 4% of the 1300 billion liters of gasoline consumed globally [48]. The United States, Brazil, and several EU member states have the largest programs promoting bio-fuels in the world. National bio-fuel policies tend to vary according to available feedstock for fuel production and national agriculture policies. With all of the new government programs in America, Asia, and Europe in place, total global fuel bio-ethanol demand could grow to exceed 125 billion liters by 2020 [49].

The United States is the world's largest producer of bio-ethanol fuel, accounting for nearly 47% of global bio-ethanol production (Table 1). The United States produced 18.3 billion liters of bio-ethanol in 2006 [48], up from 15 billion liters in 2005 [50]. EISA set a target of 57 billion liters consumption of bio-fuels (mainly bio-ethanol) by 2012.

Brazil is the world's largest exporter of bio-ethanol and second-largest producer after the United States (Table 1). All of Brazil's bio-ethanol is produced from sugar cane, most is used domestically substituting 40% of Brazilian petrol consumption and approximately 20% is exported to the United States, EU and other markets [51]. On March 9, 2007, the United States and Brazil signed a Memorandum of Understanding (MOU) to advance cooperation on bio-fuels. The two countries agreed to: (1) advance research and development bilaterally, (2) help build domestic bio-fuels industries in third countries, and (3) work multilaterally to advance the global development of bio-fuels [52].

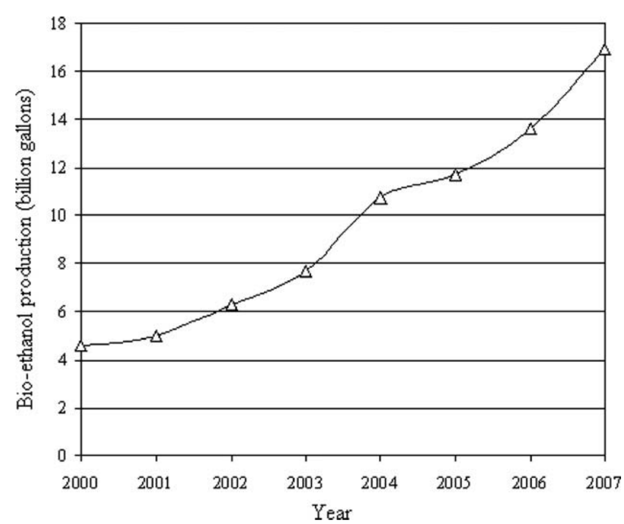

Fig. 1. Global ethanol production from 2000 to 2007.

Table 1
World bio-ethanol production during 2005 and 2007 (billion liters) [48,50].

Country	2005	2006	Share of total in 2006 (%)
USA	15.0	18.3	46.9
Brazil	15.0	17.5	44.9
China	1.0	1.0	2.6
India	0.3	0.3	0.8
France	0.15	0.25	0.6
Others	1.55	1.65	4.2
Total	33.0	39.0	

The bio-ethanol sectors in many EU member states have responded to policy initiatives and have started growing rapidly. EU-27 bio-ethanol production increased by 71% in 2007, reaching 2.9 billion liters. Bio-ethanol consumption reached 2.44 billion liters in 2007, an increase of 58%. Net imports of bio-ethanol increased to 0.16 billion gallons in 2007 [53]. The potential demand for bio-ethanol as a transportation fuel in the EU countries, calculated on the basis of Directive 2003/30/EC, is estimated at about 12.6 billion liters in 2010 [54].

4. Bio-ethanol as a transportation fuel

Bio-ethanol is ethyl alcohol, grain alcohol, or chemically C_2H_5OH or EtOH. Bio-ethanol and bio-ethanol/gasoline blends have a long history as alternative transportation fuels. It has been used in Germany and France as early as 1894 by the then incipient industry of internal combustion (IC) engines [55]. Brazil has utilized bio-ethanol as a transportation fuel since 1925. The use of bio-ethanol for fuel was widespread in Europe and the United States until the early 1900s. Because it became more expensive to produce than petroleum-based fuel, especially after World War II, bio-ethanol's potential was largely ignored until the oil crisis of the 1970s [56]. Since the 1980s, there has been an increased interest in the use of bio-ethanol as an alternative transportation fuel. Countries including Brazil and the United States have long promoted domestic bio-ethanol production. In addition to the energy rationale, bio-ethanol/gasoline blends in the United States were promoted as an environmentally driven practice, initially as an octane enhancer to replace lead. Bio-ethanol also has value as oxygenate in clean-burning gasoline to reduce vehicle exhaust emissions [57].

Bio-ethanol has a higher octane number (108), broader flammability limits, higher flame speeds and higher heats of vaporization. These properties allow for a higher compression ratio and shorter burn time, which lead to theoretical efficiency advantages over gasoline in an IC engine [16]. Octane number is a measure of the gasoline quality for prevention of early ignition, which leads to cylinder knocking. The fuels with higher octane numbers are preferred in spark-ignition internal combustion engines. An oxygenate fuel such as bio-ethanol is provides a reasonable antiknock value.

Disadvantages of bio-ethanol include its lower energy density than gasoline (bio-ethanol has 66% of the energy that gasoline has), its corrosiveness, low flame luminosity, lower vapor pressure (making cold starts difficult), miscibility with water, toxicity to ecosystems [58], increase in exhaust emissions of acetaldehyde, and increase in vapor pressure (and evaporative emissions) when blending with gasoline. Some properties of alcohol fuels are shown in Table 2.

Bio-ethanol can be used in various methods as a transportation fuel. It can be directly used as a transportation fuel or it can be blended with gasoline. Bio-ethanol can be mixed with gasoline it is substituting for and can be burned in traditional combustion engines with virtually no modifications needed. Bio-ethanol is most commonly blended with gasoline in concentrations of 10% bio-ethanol to 90% gasoline, known as E10 and nicknamed "gasohol". In Brazil, bio-ethanol fuel is used pure or blended with gasoline in a mixture called gasohol (24% bio-ethanol and 76% gasoline) [59]. Bio-ethanol 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, bio-ethanol can be used at higher levels, for example, E85 (85% bio-ethanol) [8].

Table 2
Some properties of alcohol fuels.

Fuel property	Isooctane	Methanol	Ethanol
Octane number	100	112	108
Auto-ignition temperature (K)	530	737	606
Latent heat of vaporization (MJ/Kg)	0.26	1.18	0.91
Lower heating value (MJ/Kg)	44.4	19.9	26.7

Bio-ethanol is an oxygenated fuel that contains 35% oxygen, which reduces particulate and nitrogen oxides (NOx) emissions from combustion. Using bio-ethanol blended fuel for automobiles can significantly reduce petroleum use and exhaust greenhouse gas emission [60]. Adding bio-ethanol to gasoline increases the oxygen content of the fuel, improving the combustion of gasoline and reducing the exhaust emissions normally attributed to imperfect combustion in motor vehicles, such as CO and unburned hydrocarbons [33].

5. Biomass sources for bio-ethanol

There is a growing interest worldwide to find out new and cheap carbohydrate sources for production of bio-ethanol [61]. Currently, a heavy focus is on bio-fuels made from crops, such as corn, sugar cane, and soybeans, for use as renewable energy sources. Though it may seem beneficial to use renewable plant materials for bio-fuel, the use of crop residues and other biomass for bio-fuels raises many concerns about major environmental problems, including food shortages and serious destruction of vital soil resources [62]. For a given production line, the comparison of the feedstocks includes several issues [63]: (1) chemical composition of the biomass, (2) cultivation practices, (3) availability of land and land use practices, (4) use of resources, (5) energy balance, (6) emission of greenhouse gases, acidifying gases and ozone depletion gases, (7) absorption of minerals to water and soil, (8) injection of pesticides, (9) soil erosion, (10) contribution to biodiversity and landscape value losses, (11) farm-gate price of the biomass, (12) logistic cost (transport and storage of the biomass), (13) direct economic value of the feedstocks taking into account the co-products, (14) creation or maintain of employment, and (15) water requirements and water availability.

Bio-ethanol feedstocks can be divided into three major groups: (1) sucrose-containing feedstocks (e.g. sugar cane, sugar beet, sweet sorghum and fruits), (2) starchy materials (e.g. corn, milo, wheat, rice, potatoes, cassava, sweet potatoes and barley), and (3) lignocellulosic biomass (e.g. wood, straw, and grasses). In the short-term, the production of bio-ethanol as a vehicular fuel is almost entirely dependent on starch and sugars from existing food crops [64]. The drawback in producing bio-ethanol from sugar or starch is that the feedstock tends to be expensive and demanded by other applications as well [65]. Any bio-ethanol project attacks seven major national issues: (1) sustainability, (2) global climate change, (3) biodegradability, (4) urban air pollution, (5) carbon sequestration, (6) national security, and (7) the farm economy. Lignocellulosic biomass is envisaged to provide a significant portion of the raw materials for bio-ethanol production in the medium and long-term due to its low cost and high availability [63].

A recent EU funded (LAMNET program) research program investigated the possibilities to combine from several crops all waste products for use in the processing of bio-ethanol. One of the studies concluded that sweet sorghum is a very useful plant, whereby the complete plant can be used without leaving any waste. It is concluded that bio-ethanol produced from sugar cane is an attractive proposition [66]. The cost levels and comparison of bio-ethanol yield produced from different energy crops is presented in Table 3 [66,67].

About 60% of global bio-ethanol production comes from sugar cane and 40% from other crops [68,69] before 2003. Brazil utilizes

Table 3
Comparison of production cost and bio-ethanol yield from different energy crops[a] [66,67].

Type	Annual yield (ton/ha)	Conversion rate to sugar or starch (%)	Conversion rate to ethanol (l/ton)	Annual ethanol yield (kg/ha)	Cost[a] (US$/m^3)
Sugar cane	70	12.5	70	4900	~160
Cassava	40	25	150	6000	700
Sweet sorghum	35	14	80	2800	200–300
Corn	5	69	410	2050	250–420
Wheat	4	66	390	1560	380–480

[a] Adapted from Ref. [66].

Table 4
Bio-ethanol production and land use by major producing countries, 2006/07.

Country	Ethanol feedstocks	Ethanol yield (l/hectare)	Implied feedstock area (Mha)[a]	Country total (Mha)[a]	Arable land	
					Area (Mha)[a]	Ethanol share (%)
Brazil	Sugar cane (100%)	6641	2.99	2.99	59	5.1
USA	Corn (98%)	3770	6.35	6.64	174	3.8
	Sorghum (2%)	1365	0.28	–	–	–
China	Corn (70%)	2011	0.65	0.97	143	0.7
	Wheat (30%)	1730	0.32	–	–	–
EU-27	Wheat (48%)	1702	0.53	0.65	114	0.6
	Sugar beet (29%)	5145	0.12	–	–	–
Canada	Corn (70%)	3460	0.12	0.28	46	0.6
	Wheat (30%)	1075	0.16	–	–	–

[a] Million hectares.

sugar cane for bio-ethanol production while the United States and Europe mainly use starch from corn, and from wheat and barley, respectively [70]. Brazil is the largest single producer of sugar cane with about 27% of global production and a yield of 18 dry Mg ha^{-1} [71]. During the period 2006–2007, 6.45 million hectares of sugar cane crops were cultivated and around three million hectares were dedicated to bio-ethanol production, which represents more than 5% of Brazil's arable land (Table 4) [72]. In 2007, approximately 11.4 million hectares were used to provide bio-ethanol feedstocks in the five major producing countries. This would account for about 2.2% of arable land in these countries. Brazilian bio-ethanol is less expensive than that produced in the United States from corn or in Europe from sugar beet, because of shorter processing times, lower labor costs, lower transport costs and input costs [73]. In Asia (India, Thailand, and Philippines) sugar cane is produced on small fields owned by small farmers. For example India has around seven million small farmers with an average of around 0.25 ha sugar cane fields [66].

In European countries, beet molasses is the most utilized sucrose-containing feedstock [74]. Sugar beet crops are grown in most of the EU-25 countries, and yield substantially more bio-ethanol per hectare than wheat [75]. The advantages with sugar beet are a lower cycle of crop production, higher yield, and high tolerance of a wide range of climatic variations, low water and fertilizer requirement. Compared to sugar cane, sugar beet requires 35–40% less water and fertilizer [76].

Starch is a high yield feedstock for bio-ethanol production, but its hydrolysis is required to produce bio-ethanol by fermentation [77]. Starch is a biopolymer, defined as a homopolymer consisting only one monomer, D-glucose [78]. To produce bio-ethanol from starch it is necessary to break down the chains of this carbohydrate for obtaining glucose syrup, which can be converted into bio-ethanol by yeasts. This type of feedstock is the most utilized for bio-ethanol production in North America and Europe. Corn and wheat are mainly employed with these purposes [74]. The United States is predominantly a producer of bio-ethanol derived from corn, and production is concentrated in Midwestern states with abundant corn supplies [79]. Corn-based bio-ethanol production in most of the countries assessed is limited, especially compared to the United States. Only Canada reported explicit plans for significant future development of corn-based bio-ethanol, although China has used corn as a feedstock in the past and Argentina is looking at the possibility of corn as bio-fuel feedstock in the future [80].

Biomass, such as agricultural residues (corn stover and wheat straw), wood and energy crops, is attractive materials for bio-ethanol fuel production since it is the most abundant reproducible resources on earth. Biomass could produce up to 442 billion liters per year of bio-ethanol [81]. Thus, the total potential bio-ethanol production from crop residues and wasted crops is 491 billion liters per year, about 16 times higher than the current world bio-ethanol production [71]. Advantages of bio-fuels are the following [6,28,82]: (1) bio-fuels are easily available from common biomass sources, (2) they are represent a CO_2 cycle in combustion, (3) bio-fuels have a considerable environmentally friendly potential, (4) there are many benefits the environment, economy and consumers in using bio-fuels, and (5) they are biodegradable and contribute to sustainability.

6. Bio-ethanol production routes from biomass

To ensure that "good" ethanol is produced, with reference to greenhouse gas (GHG) benefits, the following demands must be met [83]: (1) ethanol plants should use biomass and not fossil fuels, (2) cultivation of annual feedstock crops should be avoided on land rich in carbon (above and below ground), such as peat soils used as permanent grassland, etc., (3) by-products should be utilized efficiently in order to maximize their energy and GHG benefits, and (4) nitrous oxide emissions should be kept to a minimum by means of efficient fertilization strategies, and the commercial nitrogen fertilizer utilized should be produced in plants which have nitrous oxide gas cleaning. Bio-ethanol is a fuel derived from renewable sources of feedstock; typically plants such as wheat, sugar beet, corn, straw, and wood. Bio-ethanol is an alternative fuel that is produced almost entirely from food crops. It represents an important, renewable liquid fuel for motor vehicles. Producing bio-ethanol as a transportation fuel can help reduce CO_2 buildup in two important ways: by displacing the use of fossil fuels, and by recycling the CO_2 that is released when it is combusted as fuel. An important advantage of crop-based ethanol is its GHG benefits [49,84].

6.1. Bio-chemical production of ethanol

Bio-ethanol can be produced from different kinds of raw materials. Table 5 shows the bio-ethanol pathways from different raw materials [8,49]. Lignocellulosic biomass can be converted to bio-ethanol by hydrolysis and subsequent fermentation. Also thermo-chemical processes can be used to produce bio-ethanol: gasification followed either by fermentation, or by a catalyzed reaction [85].

The components of biomass include cellulose, hemicelluloses, lignin, extractives, ash, and other compounds. Cellulose, hemicelluloses and lignin are three major components of a plant biomass material. Cellulose, which is an abundant component in plants and wood, comes in various forms and a large fraction comes from domestic and industrial wastes [86]. Cellulose fibers provide wood's strength and comprise ~40–50 wt% of dry wood [87]. Cellulose is a remarkable pure organic polymer, consisting solely of units of anhydroglucose held together in a giant straight chain molecule [88]. Cellulose is a homopolysaccharide polymer composed of β-D-glucopyranose units linked together by $(1 \rightarrow 4)$-glycosidic bonds. The cellulose molecules are linear; the β-D-glucopyranose chain units are in a chair conformation and the substituents HO-2, HO-3, and CH_2OH are oriented equatorially [89]. The basic repeating unit of the cellulose polymer consists of two glucose anhydride units, called a cellobiose unit [87]. Cellulose is insoluble in most solvents and has a low accessibility to acid and enzymatic hydrolysis [90]. A second major wood chemical constituent is hemicellulose, which is also known as polyose. Hemicellulose is a mixture of various polymerized monosaccharides such as glucose, mannose, galactose, xylose, arabinose, 4-*O*-methyl glucuronic acid and galacturonic acid residues [87]. Xylose is the predominant pentose sugar derived from the hemicellulose of most hardwood feedstocks, but arabinose can constitute a significant amount of the pentose sugars derived from various agricultural residues and other herbaceous crops, such as switchgrass, that are being considered for use as dedicated energy crops. Whereas arabinose makes only 2–4% of the total pentoses in hardwoods, arabinose represents 10–20% of the total pentoses in many herbaceous crops. Arabinose contents can be as high as 30–40% of the total pentoses in corn fiber, a byproduct of corn processing [91]. Lignin is an aromatic polymer synthesised from phenylpropanoid precursors [92]. Lignin is covalently linked with xylans in the case of hardwoods and with galactoglucomannans in softwoods. Even though mechanically cleavable to a relatively low molecular weight, lignin is not soluble in water [93]. It is generally accepted that free phenoxyl radicals are formed by thermal decomposition of lignin above 525 K and that the radicals have a random tendency to form a solid residue through condensation or repolymerization [94–96]. Cellulose is insoluble in most solvents and has a low accessibility to acid and enzymatic hydrolysis. Hemicelluloses are largely soluble in alkali and, as such, are more easily hydrolyzed [8,14,49,90,91,97]. Table 6 shows typical lignocellulosic biomass compositions.

Table 5
Bio-ethanol pathways from different raw materials.

Raw material	Processing
Wood	Acid hydrolysis + fermentation
Wood	Enzymatic hydrolysis + fermentation
Straw	Acid hydrolysis + fermentation
Straw	Enzymatic hydrolysis + fermentation
Wheat	Malting + fermentation
Sugar cane	Fermentation
Sugar beet	Fermentation
Corn grain	Fermentation
Corn stalk	Acid hydrolysis + fermentation
Sweet sorghum	Fermentation

Bioconversion of lignocellosics to bio-ethanol is difficult due to: (1) the resistant nature of biomass to breakdown, (2) the variety of sugars which are released when the hemicellulose and cellulose polymers are broken and the need to find or genetically engineer organisms to efficiently ferment these sugars, and (3) costs for collection and storage of low density lignocellosic feedstocks. Fig. 2 shows the flow chart for the production of bio-ethanol from lignocellulosic biomass materials. Processing of lignocellulosics to bio-ethanol consists of four major unit operations: (1) pretreatment, (2) hydrolysis, (3) fermentation, and (4) product separation/distillation.

Hydrolysis of lignocelluloses followed by fermentation is much more complicated than just fermentation of sugar. In hydrolysis the cellulosic part of the biomass is converted to sugars, and fermentation converts these sugars to bio-ethanol. To increase the yield of hydrolysis, a pretreatment step is needed that softens the biomass and breaks down cell structures to a large extent [85]. A successful pretreatment must meet the following requirements [98]: (1) improve formation of sugars or the ability to subsequently form sugars by hydrolysis, (2) avoid the degradation or loss of carbohydrate; (3) avoid the formation of by-products inhibitory to the subsequent hydrolysis and fermentation processes, and (4) be cost-effective. Hydrolysis without preceding pretreatment

Table 6
Typical lignocellulosic biomass compositions (% dry basis) [85].

Feedstock	Hardwood			Softwood	Grass
	Black locust	Hybrid poplar	Eucalyptus	Pine	Switchgrass
Cellulose	41.61	44.70	49.50	44.55	31.98
Glucan 6C	41.61	44.70	49.50	44.55	31.98
Hemicellulose	17.66	18.55	13.07	21.90	25.19
Xylan 5C	13.86	14.56	10.73	6.30	21.09
Arabinan 5C	0.94	0.82	0.31	1.60	2.84
Galactan 6C	0.93	0.97	0.76	2.56	0.95
Mannan 6C	1.92	2.20	1.27	11.43	0.30
Lignin	26.70	26.44	27.71	27.67	18.13
Ash	2.15	1.71	1.26	0.32	5.95
Acids	4.57	1.48	4.19	2.67	1.21
Extractives	7.31	7.12	4.27	2.88	17.54
Heating value ($GJ_{HHV}/tonne_{dry}$)	19.5	19.6	19.5	19.6	18.6

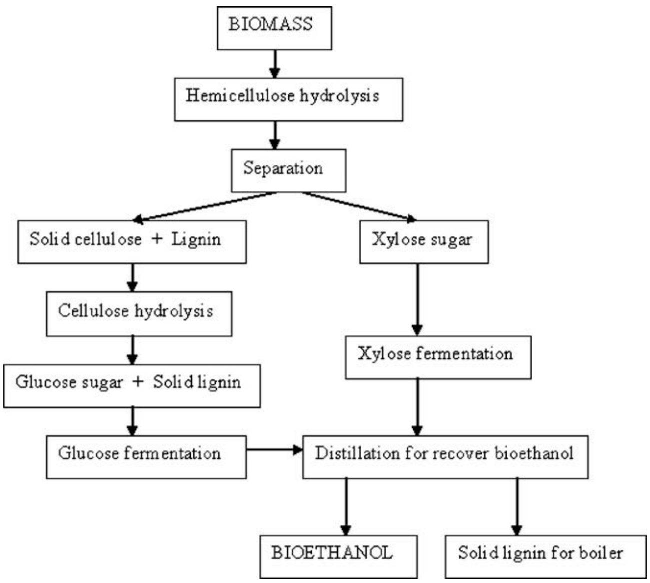

Fig. 2. Flow chart for the production of bio-ethanol from lignocellulosic biomass materials.

yields typically <20%, whereas yields after pretreatment often exceed 90% [85].

There are two types of processes to hydrolyze the cellulosic biomass. The most commonly applied methods can be classified in two groups: acid and enzymatic hydrolysis. Acid hydrolysis is one of the oldest and most applied technologies for converting lignocellulose into fermentable sugars [99]. There are two basic types of acid hydrolysis processes commonly used: dilute and concentrated acid hydrolysis.

In the process evaluated, prehydrolysis with dilute sulfuric acid is employed to hydrolyze hemicellulose and make the cellulose more accessible to hydrolysis by enzymes [100,101]. Since 5-carbon sugars degrade more rapidly than 6-carbon sugars, one way to decrease sugar degradation is to have a two-stage process. The first stage is conducted under mild process conditions to recover the 5-carbon sugars while the second stage is conducted under harsher conditions to recover the 6-carbon sugars [8].

Concentrated acid process provides a complete and rapid conversion of cellulose to glucose and hemicelluloses to 5-carbon sugars with little degradation. The critical factors needed to make this process economically viable are to optimize sugar recovery and cost-effectively recover the acid for recycling [57,90]. The concentrated hydrolysis process offers more potential for cost reductions than the dilute sulfuric acid process [102]. The concentrated and dilute sulfuric acid processes are performed at high temperatures (373 and 495 K) which can degrade the sugars, reducing the carbon source and ultimately lowering the bio-ethanol yield [103]. Table 7 shows the yields of bio-ethanol by concentrated sulfuric acid hydrolysis from cornstalks.

Lignocellulose is often hydrolyzed by acid treatment; the hydrolysate obtained is then used for bio-ethanol fermentation by microorganisms such as yeast. Because such lignocellulose hydrolysate contains not only glucose, but also various monosaccharides, such as xylose, mannose, galactose, and arabinose, and oligosaccharides, microorganisms should be required to efficiently ferment these sugars for the successful industrial production of bio-ethanol [104] The overall chemistry process of fermentation is to convert glucose sugar ($C_6H_{12}O_6$) to alcohol (C_2H_5OH) and carbon dioxide gas (CO_2). The reactions within the yeast to make this happen are very complex but the overall process is as follows:

Table 7
Yields of bio-ethanol by concentrated sulfuric acid hydrolysis from cornstalks (% dry weight) [57].

Amount of cornstalk (kg)	1000
Cellulose content (kg)	430
Cellulose conversion and recovery efficiency	0.76
Bio-ethanol stoichiometric yield	0.51
Glucose fermentation efficiency	0.75
Bio-ethanol yield from glucose (kg)	130
Amount of cornstalk (kg)	1000
Hemicelluloses content (kg)	290
Hemicelluloses conversion and recovery efficiency	0.90
Bio-ethanol stoichiometric yield	0.51
Xylose fermentation efficiency	0.50
Bio-ethanol yield from xylose (kg)	66
Total bio-ethanol yield from 1000 kg of cornstalks	196 kg (225.7 L = 59 gallons)

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 \quad (2)$$
$$\underset{\text{(Glucose)}}{\text{Sugar}} \rightarrow \underset{\text{(Ethyl alcohol)}}{\text{Alcohol}} + \text{Carbon dioxide gas}$$

Theoretically, 1 kg of glucose will produce 0.51 kg of bio-ethanol and 0.49 kg of carbon dioxide. However, in practice, the microorganisms use some of the glucose for growth and the actual yield is less than 100% [57].

6.2. Thermochemical bio-ethanol production processes

There are two ethanol production processes that currently employ thermochemical reactions in their processes. The first system is actually a hybrid thermochemical and biological system [105]. Lignocellulosic biomass materials are first thermochemically gasified and the synthesis gas (a mixture of hydrogen and carbon monoxide) bubbled through specially designed fermenters. Biomass gasification reaction is:

$$C + H_2O \rightarrow CO + H_2 \quad (3)$$

A microorganism that is capable of converting the synthesis gas is introduced into the fermenters under specific process conditions to cause fermentation to bio-ethanol [57].

The second thermochemical ethanol production process does not use any microorganisms. In this process, biomass materials are first thermochemically gasified and the synthesis gas passed through a reactor containing catalysts, which cause the gas to be converted into ethanol. Numerous efforts have been made since then to develop commercially viable thermochemical-to-ethanol processes. Ethanol yields up to 50% have been obtained using synthesis gas-to-ethanol processes. Some processes that first produce methanol and then use catalytic shifts to produce ethanol have obtained ethanol yields in the range of 80%. Unfortunately, like the other processes, finding a cost-effective all-thermochemical process has been difficult [105].

7. Bio-ethanol economy

The cost of bio-fuels is also an important consideration; bio-fuels must be competitive with each other and with mineral fuels such as petrol and diesel. This competitiveness ensures a market for the bio-fuel is available, as people will have an incentive to convert to a renewable source of energy. Thus when analyzing crop rotations cost optimization must also be considered [106].

Considering that up to now the cost of bio-ethanol was considerably higher than the cost of fossil gasoline supply, national governments had to enact special policies in order to encourage production and use of bio-ethanol in the transportation sector. In general, the following three main approaches can be distinguished

Table 8
Estimates of the costs of bio-ethanol production from different feedstock (exclusive of taxes), (US cents per liter) [112].

	2006	Long-term about 2030
Price of oil, US$/barrel	50–80	
Corresponding pre-tax price of petroleum products, US cents/l	35–60[a]	
Corresponding price of petroleum products with taxes included,	150–200 in EU[b]	
US cents/l (retail price)	About 80 in USA	
Bio-ethanol from sugar cane	25–50	25–35
Bio-ethanol from corn	60–80	35–55
Bio-ethanol from beet	60–80	40–60
Bio-ethanol from wheat	70–95	45–65
Bio-ethanol from lignocellulose	80–110	25–65

[a] Note range differs from row 1, for several factors such as refinery costs.
[b] Excluding a few outliers above and below this range.

in the implementation of bio-fuels supporting policies and regulation: (1) taxation-based policies, (2) agriculture-based policies/subsidies, and (3) fuel mandates [64]. At present, the development and promotion of bio-fuels are mainly driven by the agricultural sector and green lobbies rather than the energy sector. In fact, most bio-fuel programs depend on subsidies and government programs, which can lead to market distortion and is costly for governments. Nevertheless, at sustained high oil prices and with a steady progression of more efficient and cheaper technology, bio-fuels could be a cost-effective alternative in the near future in many countries [107].

The price of the raw materials is highly volatile, which can highly affect the production costs of the bio-ethanol [108]. Feedstock represents 60–75% of the total bio-ethanol production cost. Production technology from sugar/starch containing crops is relatively mature and most likely will not be improved to decrease production costs. Bio-ethanol from sugar cane in Brazil costs US$0.23–0.29 per liter [109], while in the EU and the United States sugar and corn-derived bio-ethanol cost US$0.29 per liter [110] and US$0.53 per liter [111], respectively. Estimates of the costs of bio-ethanol production from different feedstock are shown in Table 8 [112]. On energy content comparison basis, bio-diesel production costs are generally lower than bio-ethanol production costs.

8. Limitations on bio-ethanol production

Bio-ethanol production generally utilizes derivatives from food crops such as corn grain and sugar cane, but the limited supply of these crops can lead to competition between their use in bio-ethanol production and food provision [113]. Corn-based bio-ethanol production in most of the countries assessed is limited, especially compared to the United States. Only Canada reported explicit plans for significant future development of corn-based bio-ethanol, although China has used corn as a feedstock in the past and Argentina is looking at the possibility of corn as bio-fuel feedstock in the future [25].

Currently, a large amount of studies regarding the utilization of lignocellulosic biomass as a feedstock for producing fuel ethanol is being carried out worldwide. For countries where the cultivation of energy crops is difficult, lignocellulosic materials are an attractive option for the production of bio-fuels [74]. Lignocellulosic materials serve as a cheap and abundant feedstock, which is required to produce fuel ethanol from renewable resources at reasonable costs [114]. Producing bio-ethanol from lignocellulosic materials may allay many of the environmental and food-versus-fuel concerns that are drawbacks of producing bio-ethanol from food crops like sugar or corn [52].

9. Conclusion

Bio-fuels are being promoted in the transportation sector. Many research programs recently focus on the development of concepts such as renewable resources, sustainable development, green energy, eco-friendly process, etc., in the transportation sector. Increasing the use of bio-fuels for energy generation purposes is of particular interest nowadays because they allow mitigation of greenhouse gases, provide means of energy independence and may even offer new employment possibilities. Bio-ethanol is by far the most widely used bio-fuel for transportation worldwide. It will continue to be developed as a transport fuel produced in tropical latitudes and traded internationally, for use primarily as a gasoline additive.

Global production of bio-ethanol increased from 17.25 billion liters in 2000 to over 46 billion liters in 2007. With all of the new government programs in America, Asia, and Europe in place, total global fuel bio-ethanol demand could grow to exceed 125 billion liters by 2020. In 2007, bio-ethanol production represented about 4% of the 1300 billion liters of gasoline consumed globally.

Bio-ethanol is a fuel derived from biomass sources of feedstock; typically plants such as wheat, sugar beet, corn, straw, and wood. Bio-ethanol is currently made by large-scale yeast fermentation of sugars that are extracted or prepared from crops followed by separation of the bio-ethanol by distillation. One major problem with bio-ethanol production is the availability of raw materials for the production. The availability of feedstocks for bio-ethanol can vary considerably from season to season and depend on geographic locations. The price of the raw materials is also highly volatile, which can highly affect the production costs of the bio-ethanol.

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