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

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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.

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 (CO2) emissions. CO2 emissions from a gallon of gasoline are about 8 kg. For example:

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

(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
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 cellulosic bio-ethanol. 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 cellulosic bio-ethanol. 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].

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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].

### Table 1

<table>
<thead>
<tr>
<th>Country</th>
<th>2005</th>
<th>2006</th>
<th>Share of total in 2006 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>USA</td>
<td>15.0</td>
<td>18.3</td>
<td>46.9</td>
</tr>
<tr>
<td>Brazil</td>
<td>15.0</td>
<td>17.5</td>
<td>44.9</td>
</tr>
<tr>
<td>China</td>
<td>1.0</td>
<td>1.0</td>
<td>2.6</td>
</tr>
<tr>
<td>India</td>
<td>0.3</td>
<td>0.3</td>
<td>0.8</td>
</tr>
<tr>
<td>France</td>
<td>0.15</td>
<td>0.25</td>
<td>0.6</td>
</tr>
<tr>
<td>Others</td>
<td>1.55</td>
<td>1.65</td>
<td>4.2</td>
</tr>
<tr>
<td>Total</td>
<td>33.0</td>
<td>39.0</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. Global ethanol production from 2000 to 2007.
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 C2H5OH 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 an 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].

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 IAMNET (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>
<thead>
<tr>
<th>Table 2</th>
<th>Some properties of alcohol fuels.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel property</td>
<td>Isooctane</td>
</tr>
<tr>
<td>Octane number</td>
<td>108</td>
</tr>
<tr>
<td>Auto-ignition temperature (K)</td>
<td>530</td>
</tr>
<tr>
<td>Latent heat of vaporization (MJ/Kg)</td>
<td>0.26</td>
</tr>
<tr>
<td>Lower heating value (MJ/Kg)</td>
<td>44.4</td>
</tr>
</tbody>
</table>
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, \(\alpha\)-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 \(\text{CO}_2\) 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.

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

<table>
<thead>
<tr>
<th>Country</th>
<th>Ethanol feedstocks</th>
<th>Ethanol yield (l/hectare)</th>
<th>Ethanol share (%)</th>
<th>Implied feedstock area (Mha(^a))</th>
<th>Country total (Mha(^a))</th>
<th>Arable land Area (Mha(^a))</th>
<th>Ethanol share (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brazil</td>
<td>Sugar cane (100%)</td>
<td>6641</td>
<td>2.99</td>
<td>5.1</td>
<td>59</td>
<td>174</td>
<td>0.7</td>
</tr>
<tr>
<td>USA</td>
<td>Corn (98%)</td>
<td>3770</td>
<td>6.35</td>
<td>–</td>
<td>143</td>
<td>0.6</td>
<td>–</td>
</tr>
<tr>
<td>China</td>
<td>Corn (70%)</td>
<td>1365</td>
<td>0.28</td>
<td>–</td>
<td>114</td>
<td>0.6</td>
<td>–</td>
</tr>
<tr>
<td>EU-27</td>
<td>Wheat (30%)</td>
<td>1730</td>
<td>0.65</td>
<td>–</td>
<td>107</td>
<td>0.6</td>
<td>–</td>
</tr>
<tr>
<td>Canada</td>
<td>Corn (70%)</td>
<td>3460</td>
<td>0.12</td>
<td>–</td>
<td>46</td>
<td>0.6</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Wheat (30%)</td>
<td>1075</td>
<td>0.16</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

\(^a\) Million hectares.

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. 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 thermochemical 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 fibrils 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→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 CH2OH 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. 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.

Bioconversion of lignocellulosics 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 lignocellulosic 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 5
Bio-ethanol pathways from different raw materials.

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Processing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood</td>
<td>Acid hydrolysis + fermentation</td>
</tr>
<tr>
<td>Wood</td>
<td>Enzymatic hydrolysis + fermentation</td>
</tr>
<tr>
<td>Straw</td>
<td>Acid hydrolysis + fermentation</td>
</tr>
<tr>
<td>Straw</td>
<td>Enzymatic hydrolysis + fermentation</td>
</tr>
<tr>
<td>Wheat</td>
<td>Malting + fermentation</td>
</tr>
<tr>
<td>Sugar cane</td>
<td>Fermentation</td>
</tr>
<tr>
<td>Sugar beet</td>
<td>Fermentation</td>
</tr>
<tr>
<td>Corn grain</td>
<td>Fermentation</td>
</tr>
<tr>
<td>Corn stalk</td>
<td>Acid hydrolysis + fermentation</td>
</tr>
<tr>
<td>Sweet sorghum</td>
<td>Fermentation</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Hardwood</th>
<th>Hybrid poplar</th>
<th>Eucalyptus</th>
<th>Softwood</th>
<th>Grass</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Black locust</td>
<td>Hybrid poplar</td>
<td>Eucalyptus</td>
<td>Pine</td>
<td>Switchgrass</td>
</tr>
<tr>
<td>Cellulose</td>
<td>41.61</td>
<td>44.70</td>
<td>49.50</td>
<td>44.55</td>
<td>31.98</td>
</tr>
<tr>
<td>Glucan 6C</td>
<td>41.61</td>
<td>44.70</td>
<td>49.50</td>
<td>44.55</td>
<td>31.98</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>17.66</td>
<td>18.55</td>
<td>13.07</td>
<td>21.90</td>
<td>25.19</td>
</tr>
<tr>
<td>Xylan 5C</td>
<td>13.86</td>
<td>16.45</td>
<td>10.73</td>
<td>6.30</td>
<td>21.09</td>
</tr>
<tr>
<td>Arabinan 5C</td>
<td>0.94</td>
<td>0.82</td>
<td>0.31</td>
<td>1.60</td>
<td>2.84</td>
</tr>
<tr>
<td>Galactan 6C</td>
<td>0.93</td>
<td>0.97</td>
<td>0.76</td>
<td>2.56</td>
<td>0.95</td>
</tr>
<tr>
<td>Mannan 6C</td>
<td>1.92</td>
<td>2.20</td>
<td>1.27</td>
<td>11.43</td>
<td>0.30</td>
</tr>
<tr>
<td>Lignin</td>
<td>26.70</td>
<td>26.44</td>
<td>27.71</td>
<td>27.67</td>
<td>18.13</td>
</tr>
<tr>
<td>Ash</td>
<td>2.15</td>
<td>1.71</td>
<td>1.26</td>
<td>0.32</td>
<td>5.95</td>
</tr>
<tr>
<td>Acids</td>
<td>4.57</td>
<td>1.48</td>
<td>4.19</td>
<td>2.67</td>
<td>1.21</td>
</tr>
<tr>
<td>Extractives</td>
<td>7.31</td>
<td>7.12</td>
<td>4.27</td>
<td>2.88</td>
<td>17.54</td>
</tr>
<tr>
<td>Heating value (G_{Heateq}/tonne_{dry})</td>
<td>19.5</td>
<td>19.6</td>
<td>19.5</td>
<td>19.6</td>
<td>18.6</td>
</tr>
</tbody>
</table>
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.

Lignocellulosic is often hydrolyzed by acid treatment; the hydrolysate obtained is then used for bio-ethanol fermentation by microorganisms such as yeast. Because such lignocellulosic 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:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$  \hspace{1cm} (2)

Sugar $\rightarrow$ Alcohol + Carbon dioxide gas

Glucose (Ethyl alcohol)

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:

$$C + H_2O \rightarrow CO + H_2$$  \hspace{1cm} (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; biofuels 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.

\[\begin{array}{|c|c|}
\hline
\text{Amount of cornstalk (kg)} & 1000 \\
\text{Cellulose content (kg)} & 430 \\
\text{Cellulose conversion and recovery efficiency} & 0.76 \\
\text{Bio-ethanol stoichiometric yield} & 0.51 \\
\text{Glucose fermentation efficiency} & 0.75 \\
\text{Bio-ethanol yield from glucose (kg)} & 130 \\
\hline
\end{array}\]
in the implementation of bio-fuels supporting policies and regulations: (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 allow 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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