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Alcohol Fuels

Current Technologies and Future Prospect

Edited by Yongseung Yun

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Published in London, United Kingdom

IntechOpen

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Alcohol Fuels - Current Technologies and Future Prospect
http://dx.doi.org/10.5772/intechopen.77645
Edited by Yongseung Yun

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First published in London, United Kingdom, 2020 by IntechOpen
IntechOpen is the global imprint of INTECHOPEN LIMITED, registered in England and Wales,
registration number: 11086078, 7th floor, 10 Lower Thames Street, London,
EC3R 6AF, United Kingdom
Printed in Croatia

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library

Additional hard and PDF copies can be obtained from orders@intechopen.com

Alcohol Fuels - Current Technologies and Future Prospect
Edited by Yongseung Yun
p. cm.
Print ISBN 978-1-78985-043-7
Online ISBN 978-1-78985-044-4
eBook (PDF) ISBN 978-1-78985-654-5

Meet the editor

Dr. Yongseung Yun majored in chemical engineering, received his PhD at the University of Utah in 1990, Masters degree from KAIST, Korea in 1981, and BSc degree at Yonsei University, Korea in 1979. He currently works as Vice President at the Institute for Advanced Engineering in Korea. At KAIST from 1981-1984, he researched the oil agglomeration and fluidized bed combustion. For his PhD, he worked on the low temperature air oxidation of coal. At Brown University in 1991-1992, he researched the pretreatment methods to enhance coal liquefaction yield. From 1993 until now, he has concentrated on process developments to produce clean synthetic liquid/gas from coal and wastes including biomass. During 2013-2018, he was the President of the Korea Association of Waste to Energy (KAWET), and is currently the Vice President of the Korea Society of Waste Management, Korea DME Association, and Korea Society of Industrial and Engineering Chemistry (KSIEC). He also served for eight years as Chief Editor for the Korean Industrial Chemistry News of KSIEC.

Contents

Preface

Alcohol fuels have been utilized from the 1970s to replace crude oil. Alcohol fuels have been actively used in Brazil and US. Their role and quantity were expected to increase dramatically during the high oil price period of the early 2000s when the crude oil price jumped from US$20 to US$140 per barrel. Unfortunately, the expected widespread usage was not accomplished due to several reasons, such as drops in oil price, feedstock limitation of edible resources, and resistance from existing energy infrastructures, etc. Brazil has been the key role model until now through many ups and downs in price and availability. US has also been actively involved in alcohol fuels by using locally abundant corn. Besides these two countries, the progress in market expansion in other areas of world is not active. In this sense, when considering whether the supplying capacity of alcohol fuels has been fully utilized worldwide, most people will agree that it's not the case and more efforts should be exercised to meet the demand for replacing fossil-fuel based liquid fuels with environmentally benign and non-food resources. Since alcohol fuels started to replace crude oil, the oil price dictates the market scale. With crude oil costing less than US$80/barrel, alcohol fuels remain a niche market fuel source instead of one of the primary energy sources.

Alcohol fuels rely heavily on governmental allocated rations to add to the current petroleum-based liquid fuels. The current market has been dominated by corn-based and sugarcane-based alcohols in US and Brazil. The feedstock change from these 1st generation resources to lignocellulosic-based (2nd generation) and algae-based (3rd generation) resources, which are non-food feedstock, has not reached a mature level for wide acceptance in the market. The requirement for feedstock of non-food origin becomes a key part for the future alcohol fuels. Unfortunately, however, the non-food feedstock inherently exhibits heterogeneous characteristics in the converting process. Simply put, it's expensive than the product obtained from mass-produced rather-simple feedstock like corn or sugarcane.

World energy and the liquid fuel market has changed dramatically since the availability of cheap shale gas and shale oil. Although it seems irrational, there might come a time when it is no longer normal to guarantee the free procurement of liquid fuels through long ship lanes in some countries. Utilizing the available feedstock that has not been properly regarded as a legitimate resource due to economic and social reasons should be a focal point as a possible resource for alcohol fuels, with the additional benefits of reducing cost in energy imports and helping local economy. Lignocellulosic biomass and algal species are the feedstocks that suit the purpose. As described in this book, these 2nd and 3rd generation feedstocks are far away in proper economic competition with the 1st generation alcohol fuels, which have advantages in price and mature technologies. In most countries, simply importing the alcohol fuels made in US or in Brazil can be much cheaper than trying to manufacture it using local feedstock like molasses or cassava.

Whether alcohol fuels can compete with clean gaseous fuels such as shale gas and even with hydrogen or synthetic natural gas produced through excess electricity of wind/solar renewable sources may be an interesting topic of the future. For the time being, alcohol fuels should compete with fossil liquid fuels as well as with the 1st generation alcohol fuels that are easily available in the world market.

The current worldwide energy trend focuses on key conditions such as CO_2 reduction in coping with climate change and increasing the use of renewable/ sustainable energy resources in an environmentally benign way. In addition to these conditions, alcohol fuel requires another condition that asks to use non-food feedstock rather than food resources. The current trend succinctly depicts more use of renewable resources like biomass and abundant ocean algae, which are typically in low energy density and difficult to convert.

The future of alcohol fuels could be classified as negative as was expected decades ago. Liquid fuel is being switched to clean gas or electricity in many transportation applications through CNG cars or electric cars. In addition, electricity generation from renewable energy like wind and solar is being pushed as a strategic energy policy by many OECD countries. The hydrogen society is now more realistic than the methanol society. In reality, however, it will take at least several decades to transform liquid fuels to other energy forms for transportation applications.

But even after reflecting all these adverse situations, when considering the poor availability of environmentally benign liquid fuel resources in most developing countries, it is clear that alcohol fuels should be pursued from 2nd and 3rd generation feedstocks, which are typically not utilized properly and are locally available in large quantities. The current technology level for the future types of alcohol fuels is not cheaper than petroleum-based or 1st generation feedstock. Technological breakthroughs are in great need in this aspect. In the development of the 2nd generation alcohol fuel technologies, in particular, pretreatment and enzyme technologies are key areas that need a major improvement for cheaper and reliable production. It can be said that finding the cheap feedstock was the most important factor in the 1st generation alcohol fuels, while finding a cheap enzyme is the key factor in the 2nd generation alcohol fuels.

In a broad sense, hydrogen and electricity will eventually replace liquid fuels. But it looks like this will take several decades for full societal adaptation even in the developed OECD countries. With the recent new crude oil production in Canada, Norway, Brazil, and Guyana, in addition to already stabilized world oil supply, an era of cheaper oil might come instead of peak oil. According to IEA, Southeast Asia has already become a net oil importer of 4 million bpd in 2018. Thus, attaining energy security should be a factor in considering alcohol fuels. Overall bioenergy including biomass-based alcohol fuels and syngas, biogas should be promoted in parallel. More specifically, the future direction of alcohol fuel, especially in developing countries, should be to maximize the utilization of biomass and wastes that are locally abundant but are not effectively used as resources for alcohol fuels. The reason is clear. There have not been adequate and economic converting technologies that can compete with cheap oil and with imported alcohol fuels. It should be noted that soils and climates in much of Africa have similar characteristics for biomass production to those in Brazil where the bio-alcohols infrastructure is well established. Africa and South America have great potential in increasing bio-energy products including alcohol fuels.

For the 3rd generation algae feedstock, recent concerted national efforts in Netherlands to transform the North Sea into an energy- and raw-material-generating region provide an important benchmark to the future of bio-fuels including alcohol fuels. Increasing the macroalgae (seaweed) growth productivity and utilizing it for liquid fuels as well as for useful high-value compounds are the primary technical targets. Bio-butanol is one of the key target products that can replace diesel. It has been reported that sea-grown algae can yield the oil yield of more than 20 times the land-grown plants, which require vast land, water, and longer cultivation time. Algae is an essential future source of liquid fuel that can meet the renewable, sustainable, and CO_2-minimizing standards.

The last few decades have seen maintenance of a stable energy supply chain worldwide. There might be an argument whether the future decades can lead to a time of energy supply chain disruption. When it comes to dealing with the worst-case scenario in securing liquid fuels, it's not a bad choice to make alcohol fuels that are made by locally available cheap resources. It has to be emphasized again that an important factor for alcohol fuels must be the technical/social capability in developing countries where no expensive energy infrastructure is available during the upcoming years.

The book was prepared with many depths on broad views on alcohol fuels that are not activated as predicted before. Nowadays active roles of renewable energy and hydrogen energy are more emphasized than the conventional alcohol fuels that are replacing transportation fuels. Due to more concerns on CO_2 and environmental issues such as fine dust, society seems to go towards options that are more fundamental in changing the current liquid fuels infrastructure. Even though they are the final goals to achieve, there exists firm barriers before the actual implementation. Technical maturity and economic sustainability in renewable energies and in hydrogen economy are in the process of producing some successful cases, but are not yet fully realized in a widespread way.

Biological conversion methods are well documented in human history through brewing ethanol liquor, but the technological level cannot be said that it has reached the maximum efficiency with full accommodation in environmental aspects. A large-scale, environmentally benign, and economical way still needs to be found.

When the book concept was initiated, the title was chosen ambitiously as 'Alcohol Fuels – Current Technologies and Future Prospects'. The book intended to cover the various recent development areas with more than ten chapters. After reviewing the manuscripts for chapters, several authors withdrew to finally yield just seven chapters. Then there needed to be a decision whether to maintain the original title with only the seven chapters that cannot cover the recent advancement in many parts on alcohol fuels. In the end, it was decided to keep the original title since the key aspects are at least noted although they are not included in as detailed a description as hoped.

The book contains seven chapters with three sections. The first section deals with the technology status on alcohol fuels and its future direction. The second section talks about the ethanol production from lignocellulosic biomass, which should replace the 1st generation corn-based feedstock. The third section involves three chapters on the process and application of alcohol fuels. The book provides a brief introduction regarding the recent advances in alcohol fuel field that is in constant challenge from recent issues on CO_2, shale oil, power-to-gas, and hydrogen. etc.

I'd like to thank all authors who shared their ideas and results for this book, and Ms. Marina Dusevic who helped with the entire reviewing/editing process during the last nine months. The product might not be a marvelous work, but it can be a small signpost in the journey to reach the sustainable liquid fuel production in the form of alcohols.

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Section 1

Technology Status and Future Direction

Chapter 1

Alcohol Fuels: Current Status and Future Direction

Yongseung Yun

Abstract

Worldwide demand for liquid fuels will increase steadily, but not in the form of CO_2-emitting scheme, rather in a renewable and sustainable way. Keywords for the future energy direction must be clean, renewable, and sustainable. Alcohol fuels are again becoming a frequent keyword for clean fuel utilization in connection with mitigation of climate change and clean fuel technology suitable for less-used local energy sources. There are a lot of interests in widening the raw feedstock to lignocellulosic biomass and algae from grain-based raw materials. Using the locally available, underutilized feedstock becomes important for local energy security as well as an option for distributed energy infrastructure.

Keywords: alcohol fuel, biomass, bio-ethanol, low-grade feedstock, alternative fuel

1. Introduction

High strategic risk of dependence on imported energy sources is attracting profoundly alarming concerns as indicated by recent international trend and past experience. Self-sufficient energy supply system is at least needed to maintain a certain minimum living standard in a nation in general and the society in particular so that easy access to domestic and neighboring energy sources is a key factor to maintain. Alcohol fuels are very promising alternative energy sources from this point of view.

Worldwide demand for liquid fuels will increase steadily at least through the mid-twenty-first century, but not in the form of CO_2-emitting scheme, rather in a renewable and sustainable way. Actually, there had been many options that can use locally plentiful energy resources, typically in a biomass type.

The major energy source nowadays is most certainly (hydrocarbon) gas, electricity, and liquid fuel, which is almost unanimously agreed upon. Current energy infrastructure has already been solidly established with (hydrocarbon-based) gas, electricity, and liquid fuel as convenient energy sources and such energy infrastructure appear to get more and more solidly implemented. Inconvenience related to the utilization of solid fuels is no longer tolerable, and rapid commercialization of electric vehicle is also foreseen in the near future. Liquid fuel gets replaced to the ultra-clean fuel that meets the ever-stringent environmental regulations. Electricity is produced from atomic energy, coal, natural gas, and petroleum oil products, but safety, environmental friendliness, and global warming issues must also be comprehensibly considered. Many Asian countries almost exclusively depend on imported liquid natural gas for energy source. This raises dual issues on the feasibilities of steady supply in energy sources and of reasonably affordable cost. In fact, natural gas that emits 40–55% level of reduced CO_2 evolution compared to coal is surely a promising source of energy. Ethanol produced from sugarcane is one of the most carbon-efficient biofuels available globally, with life cycle greenhouse gas emissions around 70% lower than conventional hydrocarbon transport fuels [1]. Current worldwide trend of shifting to alternative clean, sometimes ultra-clean, gas/liquid fuel from more conventional liquid fuel of gasoline/light oil necessitated a new definition of role and position of alcohol fuels in the emerging picture.

Alcohol fuels were originally regarded as an alternative energy sources for petroleum oil to realize energy independence during oil crisis of the 1970s. A brief look into the history of bio-ethanol shows Ford Motor Company's development of ethanol-fueled car in 1899, which was terminated by low-priced gasoline then. Oil crisis of the 1970s revived similar interest in the form of gasohol by mixing ethanol, which was developed and commercialized mainly in Brazil.

The first starting point on alcohol fuels in the 1970s tells the basic background at that time. It is prompted by concerns about reliance on foreign sources of oil and a desire to support domestic agriculture. In the United States, in particular, E10 gasohol was implemented during the oil crisis of 1970s to reduce petroleum oil dependence and simultaneously to utilize surplus farm crops. At present, E15 product with 15% ethanol content is distributed for consumer market.

In the twenty-first century, alcohol fuels are again becoming a frequent keyword for clean fuel utilization in connection with mitigation of climate change and clean fuel technology suitable for less-used local energy sources. As a matter of fact, demand for alcohol fuels is mainly derived from socioeconomic and political motivations rather than from consumer conscious reasons and economic viability.

The centralized energy system that emphasizes cost-effectiveness had diminished the key driving force for technological advances in alcohol fuels. Petroleum-based liquid fuel has dominated the transportation area till now. Also, low petroleum oil cost lessened the motivation for further technology development for alcohol fuels. Global oil shock of the 1970s are not expected to break out again within the foreseeable future, and the prospect for alcohol fuel as a remedy to soaring petroleum price is not a plausible picture either. On the other hand, clean energy generation policy by utilization of locally acquired biomass or sea algae will be emphasized to replace local consumption of liquid fuel and to produce electricity or pure alcohols for fuel cells or other means, as a rather cleaner way.

For the future energy sources, renewable-based energy society must be the final goal to reach, but unfortunately it takes a long time to reach the economics and technological easiness to be a common practice, which appears to take at least one or two decades. In order to bring the technology in earlier time, there exist many hurdles and require efforts in scientific and societal side.

All in all, future energy generation direction had been solidly established as "to be clean, renewable, and sustainable," but low petroleum cost lessened the necessity of alternative clean energy source development, e.g., alcohol fuels.

Recently, global warming is becoming a central social issue attracting worldwide attention and provides a kind of consensus that society should be changed to deal with alleviating the prime causes of CO_2 evolution in addition to pollution-related issues such as fine dust. The utilization of alcohol fuels reduces carbon dioxide contents in the atmosphere, thus significantly alleviating global warming potential.

Alcohol fuels have been known as a good replacement of fossil-based liquid fuels [2]. Brazil and the United States consume alcohol fuels in the most significant proportions, and such trend will not easily change. In particular, bio-ethanol are well known for its use in Brazil as a gasoline supplement (**Figure 1**).

When we say alcohol fuels, they comprise of methanol, ethanol, ethers (MTBE, ETBE, TAME, TAEE, and DME and DEE), and esters (biodiesels: methyl and

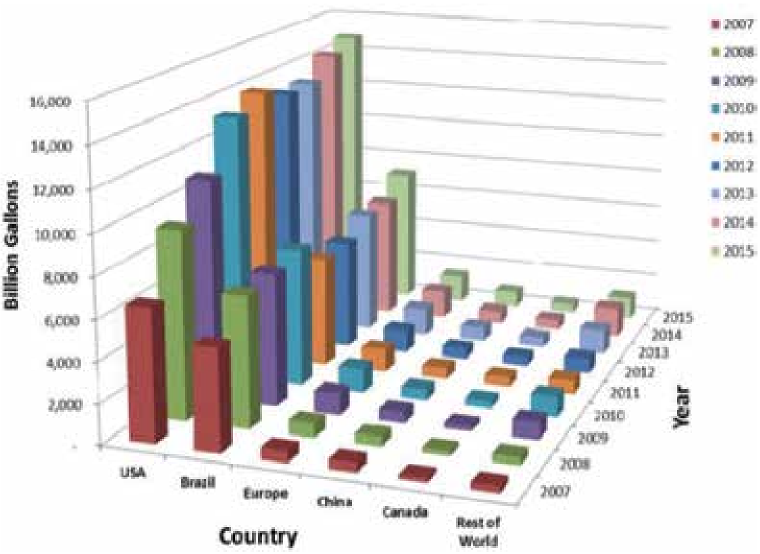


Figure 1.
Worldwide ethanol production by country and year 2007–2015 [3].

ethyl esters of fatty acids derived from vegetable oils and animal fat), in a broad sense. Most widely used alcohol fuels typically include methanol, ethanol, and bio-butanol. Ethanol that is produced through yeast-based fermentation using corn or sugarcane is the most well-known. Bio-butanol is capable of overcoming technological limitations surrounding bio-ethanol, and it is currently becoming another promising focal issue of clean energy.

The chapter deals with the current status of alcohol fuels and tries to elaborate the future direction for more wider utilization and the possible roles of alcohol fuels in attaining the far-reaching goal of low-carbon economy using sustainable energy resources.

2. Properties of alcohol fuels

Alcohols and ethers can replace gasoline and oil. **Table 1** exhibits properties of n-butanol, ethanol, and gasoline for comparison. In **Table 1**, RON, MON, and RVP values for butanol and ethanol are meant for gasoline blend fuels.

Table 2 contains a more wide range of properties of alcohols and ethers compared to gasoline and fusel oil. Fusel oil or fusel alcohol is defined as a mixture of several alcohols produced as a by-product of alcoholic fermentation.

In general, alcohols contain higher values than gasoline in oxygen content, octane number, and autoignition/flash point temperatures, while freezing point temperature is lower.

Tetraethyllead has been banned for use as an additive to improve octane number of gasoline fuel. Methyl tertiary-butyl ether (MTBE) and alcohols are thus used as alternative additives to gasoline, but MTBE has also been banned after the 2000s, and alcohols have become useful additives to increase octane number of gasoline.

Water solubility of alcohols is an important property when alcohols are being used as fuel. Gasoline has a water solubility value of less than 0.01, whereas ethanol exhibits a full miscibility as 100. When alcohols contain a high solubility in water, spill or leakage of the mixed alcohol fuels can cause polluting the underground water.

Item	n-Butanol	Ethanol	Gasoline
Specific gravity @ 60°F	0.814	0.794	0.720–0.775
Heating value, MJ/L	26.9–27.0	21.1–21.7	32.2–32.9
Research octane number (RON)	94	106–130	95
Motor octane number (MON)	80–81	89–103	85
Reid vapor pressure (RVP) of 5 and 10% Alcohol/gasoline blends, psi	6.4/6.4	31/20	<7.8/15 (summer/winter)
Oxygen, wt%	21.6	34.7	<2.7
Water solubility at 25°C, %	9.1	100.0	<0.01

Table 1.
Properties of n-butanol and ethanol with gasoline [4].

Item\fuel	Gasoline	Butanol	Methanol	Ethanol	MTBE	DME	Fusel oil
Chemical formula	$C_{5-10}H_{12-22}$	$C_4H_{10}O$	CH_3OH	C_2H_5OH	$C_5H_{12}O$	$CH_3\text{-}O\text{-}CH_3$	$C_5H_{12}O$
Molecular weight	106.22	74.12	32.04	46.7	88.15	46.07	76.42
Carbon, mass%	87.5	64.91	37.5	52.2	66.1	52.2	54.8
Hydrogen, mass%	12.5	13.49	—	34.7	13.7	13	15
Oxygen, mass%	0	21.6	49.93	34.7	18.2	34.8	30.32
Density, g/ml	0.737	0.810	0.792	0.785	0.74	0.661	0.847
Boiling temperature, °C	27–225	117.25	78	78.25	52.2	−25.1	53.4–54.4
Reid vapor pressure, Kpa	53–60	18.6	32.4	17	54.47	—	—
Research octane no.	90–100	98	108.7	108.6–110	118	—	106.85
Motor octane no.	82–90	78	86.6	92	102	—	103.72
Low heating value, MJ/kg	44.0	33.2	20.1	26.9	34.9	28.8	29.536
Freezing point, °C	−40	—	−97.5	−114	−108	—	−52
Viscosity, mm^2/s	0.5–0.6	—	0.596	1.2–1.5	0.35	—	0.61
Flash point, °C	−45 to −13	—	11	12–20	−25.5	—	—
Autoignition temperature, °C	257	385	423	425	435	253	41.6

Table 2.
Detailed properties of alcohols, ethers, and related fuels [3].

Methanol, ethanol, and propanol are completely miscible in water, which means that they dissolve in water in any amount. Both methanol and ethanol dissolve readily in water, are fortunately biodegradable, and do not bioaccumulate. They are not rated as toxic to aquatic organisms [5].

Starting with the four-carbon alcohol (butanol), solubility is starting to decrease, and from the seven-carbon length heptanol, alcohols are practically immiscible in water (**Table 3**) [6]. This is one of the backgrounds for the development of butanol as another alcohol fuel.

Other important properties of alcohol fuels reside in its inherent swelling of plastics and corroding power for metals. These properties ask modification in the existing infrastructure of automobiles and other appliances.

Alcohol name	Chemical formula	Water solubility
Methanol	CH_3OH	Miscible
Ethanol	C_2H_5OH	Miscible
Propanol	C_3H_7OH	Miscible
Butanol	C_4H_9OH	0.11
Pentanol	$C_5H_{11}OH$	0.03
Hexanol	$C_6H_{13}OH$	0.0058
Heptanol	$C_7H_{15}OH$	0.0008

Table 3.
Alcohol solubility in water in mol/100 g of H_2O *(1 bar, 25°C) [6].*

2.1 Ethanol

Ethanol is a clear, colorless, toxic liquid and has a characteristic odor. Ethanol is not classified as toxic to humans. Ethanol has a higher octane number than gasoline, providing premium blending properties as a liquid fuel. Ethanol contains less energy per volume than gasoline, and denatured ethanol (98% ethanol) contains about 30% less energy than gasoline per volume [7]. Since ethanol contains oxygen, using it as a gasoline additive results in up to 25% fewer carbon monoxide emissions than conventional gasoline [8].

Ethanol is soluble in polar and nonpolar solvents and has a clearly higher vapor pressure than gasoline and an oxygen content of approximately 35%. Ethanol itself is a good solvent and can be mixed with water in unlimited quantities. Because ethanol is a short-lived compound in surface water and subsurface aquifer, substantially limiting the risk to aquatic organisms, environmental problem is minimal even when it is spilled. Ethanol degrades quickly in the natural environment, and the biodegradation is rapid in soil, groundwater, and surface water, with predicted half-lives ranging from several hours to 10 days [9].

2.2 Methanol

Methanol, or wood alcohol, is a colorless, odorless, toxic liquid and is the simplest form (CH_3OH) among alcohols [8]. Methanol is corrosive to some materials. Methanol can be produced from several sources: synthetic gas (syngas), formic acid, formaldehyde, and methane. Methanol is classed as toxic so it requires additional considerations during usage to limit inhalation exposure and skin contact.

Methanol is hygroscopic, meaning that it will absorb water vapor directly from the atmosphere. Because absorbed water dilutes the fuel value of the methanol and may cause phase separation of methanol-gasoline blends, containers of methanol fuels must be kept tightly sealed [10].

2.3 Butanol

Butanol has higher energy densities and could be distributed in the existing infrastructure [8]. The use of ethanol as an additive to gasoline to increase octane number has downside effects such as corrosion of metal component and vapor lock. Such troubleshooting can be remedied by modification of engine and fuel system, but addition of alcohols with high carbon number such as bio-butanol enables utilization in existing system without rendering any change.

Alcohols with high carbon contents such as butanol can be synthesized from syngas through catalytic reaction that employs modified catalysts used in Fischer-Tropsch or methanol synthesis.

3. Feedstock for alcohol fuels

Alcohols fuels can be made from all available organic materials. Natural gas, coal, biomass, and organic wastes are good sources. Alcohol fuels have been synthesized from corn and sugar cane as major raw materials, but focal issues nowadays are synthesis and production of alcohol fuels from non-food crops and agricultural residues. Non-food lignocellulosic biomass includes energy crops, cellulosic residues, and wastes.

Grain-based ethanol as a first generation has been tried to change to the second-generation cellulosic ethanol and other advanced cellulosic biofuels. Cellulosic ethanol has identified as a key biochemical route of converting biomass to fuels after the 2000s [8]. Algae-based third-generation feedstock for alcohol fuels emerged as a candidate that can provide a vast raw material for future alcohol fuel industry. **Figure 2** illustrates the generations of raw feedstock for the alcohol fuel production and also shows the most apparent material that is being utilized in different countries.

Definitely there exists a clear difference between developing countries and developed countries in the priority choice, but basic understanding should be identical: use the locally available, underutilized feedstock, and choose the feedstock that tipping fee is available to treat the feedstock like municipal/industrial wastes. However, when wastes are involved as feedstock, it should be noted that not-in-my-backyard (NIMBY) problem occurs as a norm in almost every countries nowadays.

The European Commission has recently resolved by voting against utilization of biofuels synthesized from biomass of food crop sources by the year 2030. Intensive interdisciplinary efforts are anticipated for timely commercialization of cellulosic bio-ethanol, which is the second-generation bio-alcohol.

Agricultural waste typically contains a relatively high content of alkali metals (potassium and sodium) and other inorganic elements including calcium, magnesium, and sometimes chlorine and sulfur. When applying thermal methods in

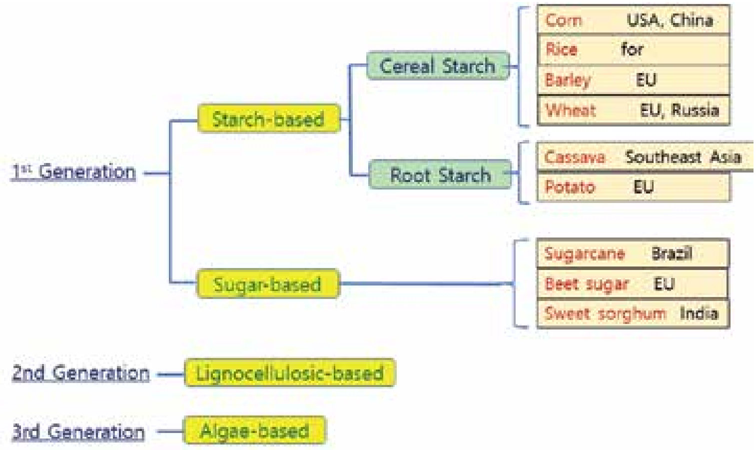


Figure 2.
Key raw materials for bio-ethanol production in different countries (modified figure from Ref. [11]).

converting these wastes to alcohol fuels, alkali metal components act to produce low-melting salts that will cause plugging and other ash-related problems during the process. In contrast, fermenting method can reduce the tendency of ash problems, which is a beneficial aspect in actual manufacturing process.

In particular, rice husk contains ash content of over 90%, and rice straw consists of more than 30% as silica, although there is a variation with rice stock, climate, and geographical environment. Such inorganic contents work as a barrier to thermal conversion process, and fermenting can be a more appropriate way in converting this biomass feedstock.

3.1 First generation: grain feedstock

Starch and carbohydrates have been used as a first-generation raw material to produce ethanol. During the year 2013, more than 90% of bio-ethanol had been produced from the starch and carbohydrates. Corn, grain, and cassava are major such crops. Downside issues are the destruction of environment during the crop cultivation and ethanol production as well as the use of valuable food resources as fuel production. Therefore, at current situation, large agricultural countries like the United States, Brazil, and China are major production places of biofuels including alcohol fuels. In the United States, 95% of ethanol has been produced from the starch in corn grain [7].

3.2 Second generation: lignocellulosic biomass

Recently, the production of bio-ethanol from grain-based raw materials is gradually becoming limited, and the second-generation bio-ethanol production from non-grain-based biomass is now receiving a gradually increasing priority.

Bio-ethanol is currently becoming a solid option as automobile fuel, and it has been usually produced from starch of corn and cassava or sugary contents of sugar cane and sugar turnip. Bio-ethanol is also produced from lignin cellulose-based material of crop wastes. Sugar and starch are readily convertible to bio-ethanol but their availability is limited and they are costly. Therefore, work is underway to investigate into various processes to produce bio-ethanol from lignocellulose-based raw materials to utilize their abundant amount in nature and to meet the economic viability in the market [11]. Wood chips or crop residues are common lignocellulosic feedstock (**Figure 3**).

Non-edible xylem parts that constitute most of the botanical stocks or cellulose are used to produce ethanol. Rice straws, weeds, and other shrubbery are good examples as raw material for alcohol production, and valuable food resources are not wasted in this case. However, a large-scale forest or farmland is still used and the low-production efficiency is a problem. Also, economically, viability is not satisfactory yet and is not applied at measurable proportion [13].

The main obstacle of using lignocellulosic biomass resides in the difficulty in extracting the essential parts from the hard-binding components of lignin, hemicellulose, and cellulose in plants as shown in **Figure 3**.

High-growth productivity of lignocellulosic crops compared to corn and sugarcane is one of the key factors that bio-alcohols can be produced economically in the future. **Figure 4** clearly shows the high growth rates in lignocellulosic crops like sorghum, energy cane, and water hyacinth.

3.3 Third generation: algae species

Sea algae grow relatively faster than most of the land-based plants as shown in **Table 4**, and they are good source of raw material to produce alcohol fuels.

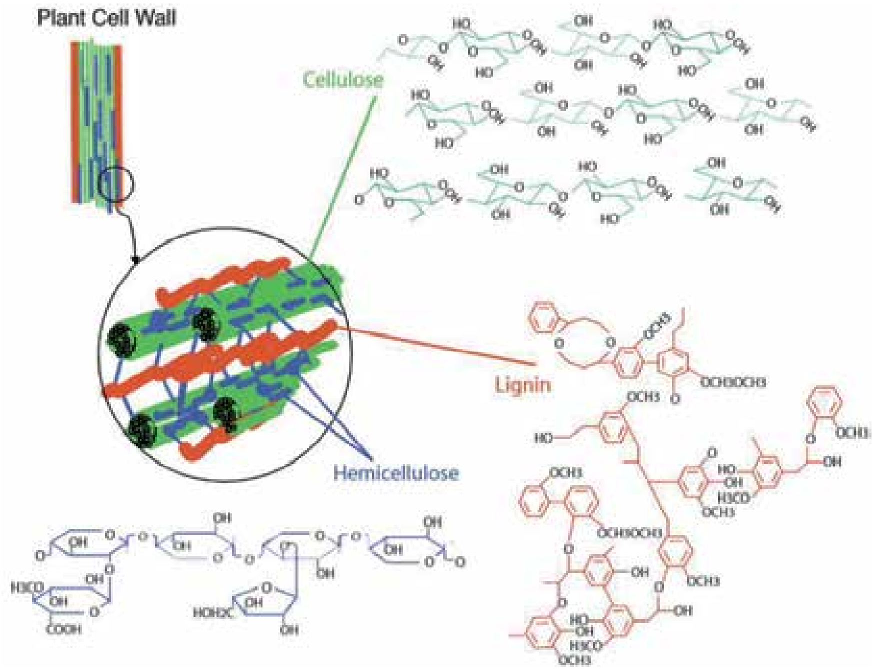


Figure 3.
Three key components of lignocellulose [12].

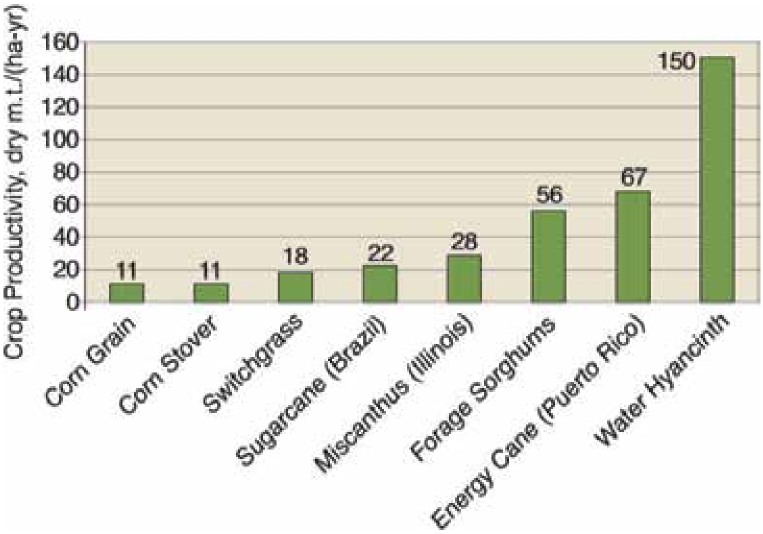
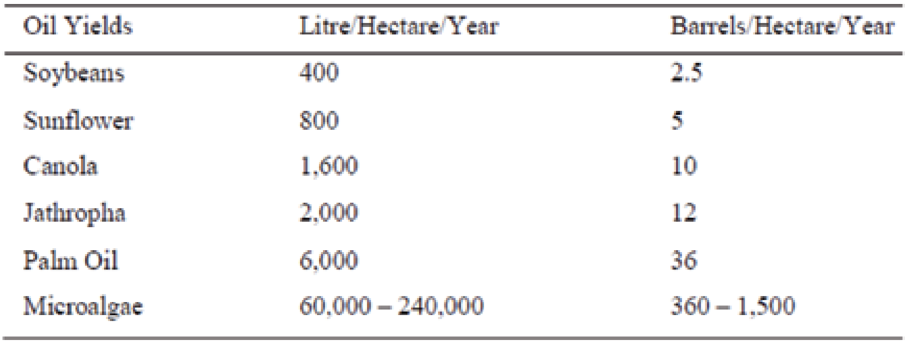


Figure 4.
High-growth productivity of lignocellulosic crops to corn and sugarcane [12].

They do not require large-scale farmland to cultivate, and non-edible algae are also a good source of bio-ethanol. Due to their fast growth rate, large-scale farming for 4–6 times cropping per year is possible and their carbon dioxide sequestration is 3–7 times more effective than that of grains. However, large-scale acquisition of the raw sea algae and its economic viability remains to be overcome before commercialization. Most of algae-related efforts are still under R&D probing stage.

Fundamental background to try algae species for biofuel production relies on their higher efficiency in converting solar energy than higher plant biomass.



Oil Yields	Litre/Hectare/Year	Barrels/Hectare/Year
Soybeans	400	2.5
Sunflower	800	5
Canola	1,600	10
Jathropha	2,000	12
Palm Oil	6,000	36
Microalgae	60,000 – 240,000	360 – 1,500

Table 4.
Current biofuel yields from various biomass [14].

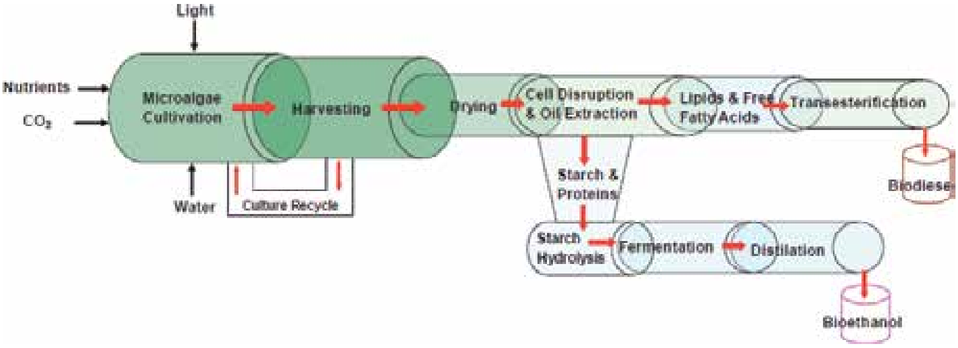


Figure 5.
Biofuel production sequence from microalgae [14].

However, actual cultivation of microalgal biomass is not easy, rather quite challenging and still expensive than growing crops. It is a similar situation as comparing the product that has been updated for several decades and the one that is starting to experience initial trial and errors.

Figure 5 illustrates the typical biofuel production procedures in which the basic process is identical with the hydrolysis/fermentation/separation parts of bio-ethanol production, except the feedstock cultivation and harvesting parts.

4. Manufacturing processes

Ethanol can be produced in various ways: syngas from coal and biomass, synthesized from petroleum-based ethylene, or by fermentation of sugary contents. Bio-ethanol is produced through the procedures of fermentation of regenerative biomass, distillation, and purification.

Sugar canes and corns are mainly used to produce bio-ethanol in Brazil and the United States, respectively. Overall manufacturing process for bio-ethanol composes the following key parts: pretreatment, saccharification (hydrolysis), fermentation, and purification as shown in **Figures 6** and **7**.

Ethanol is mainly made by fermenting the sugars found in grains, such as corn and wheat, as well as potato wastes, cheese whey, corn fiber, rice straw, urban wastes, and yard clippings. There are several processes that can produce alcohol (ethanol) from biomass. The most commonly used processes today use yeast to

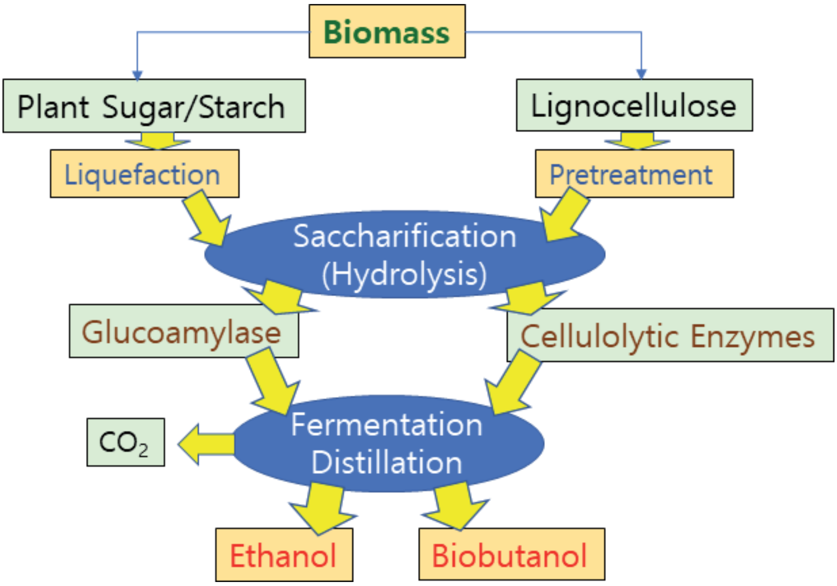


Figure 6.
Steps involved in biochemical conversion of biomass to alcohol fuels (modified from Ref. [8]).

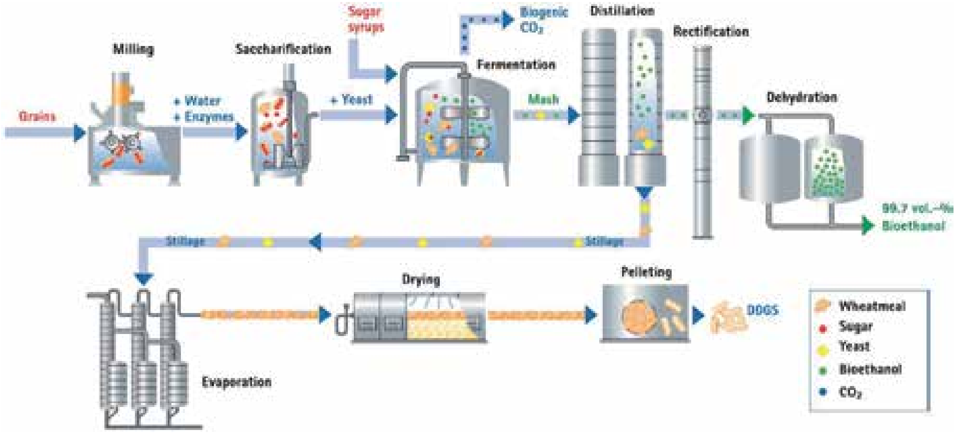


Figure 7.
Schematic flow diagram of bio-ethanol production process [15].

ferment the sugars and starch in the feedstock to produce ethanol. Another process uses enzymes to break down the cellulose in woody fibers, making it possible to produce ethanol from trees, grasses, and crop residues [8].

Synthesis of ethanol as a sustainable source of energy, especially related to more high-end product form of alcohol with high carbon contents, requires the accumulation of technical know-how in preparation for future depletion of petroleum oil resources. The bio-alcohol production process is shown in schematic flow diagram for bio-butanol manufacturing in **Figure 8**.

4.1 Pretreatment

Recently, the conversion of valuable food resources into alcohol fuel is facing very negative criticism worldwide, and work is underway to switch the raw material for bio-ethanol to non-edible biomass. However, the production of bio-alcohol

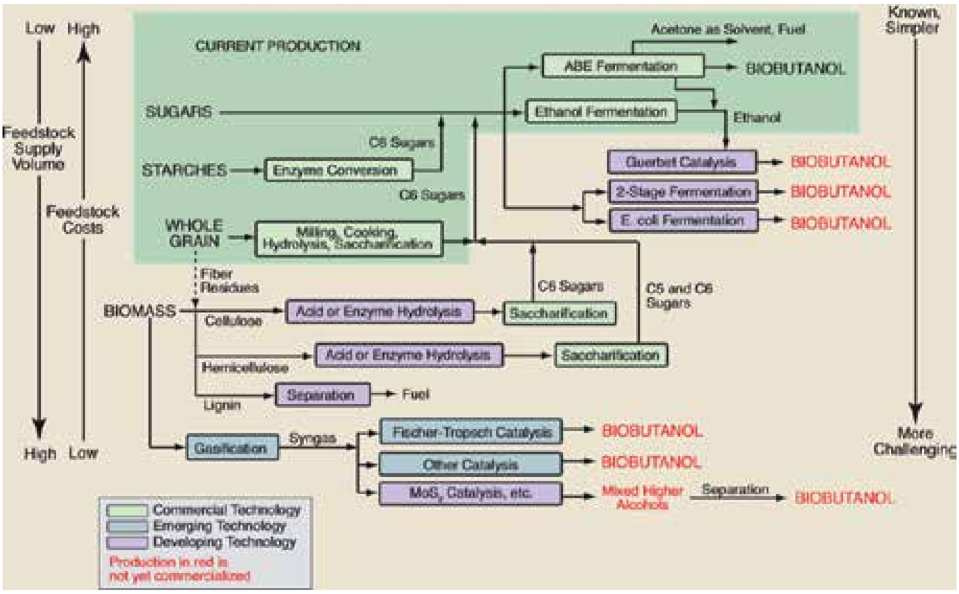


Figure 8.
Schematics of bio-butanol production process [4].

from non-edible cellulosic biomass requires solving the problem of breaking the hard biomass structure before converting into alcohol fuels. Pretreatment step is important. The pretreatment process is costly since it involves several process steps and costs for enzymes. It is very important to develop the low-energy/energy-saving process scheme and the suitable enzyme to overcome such technical/cost barriers.

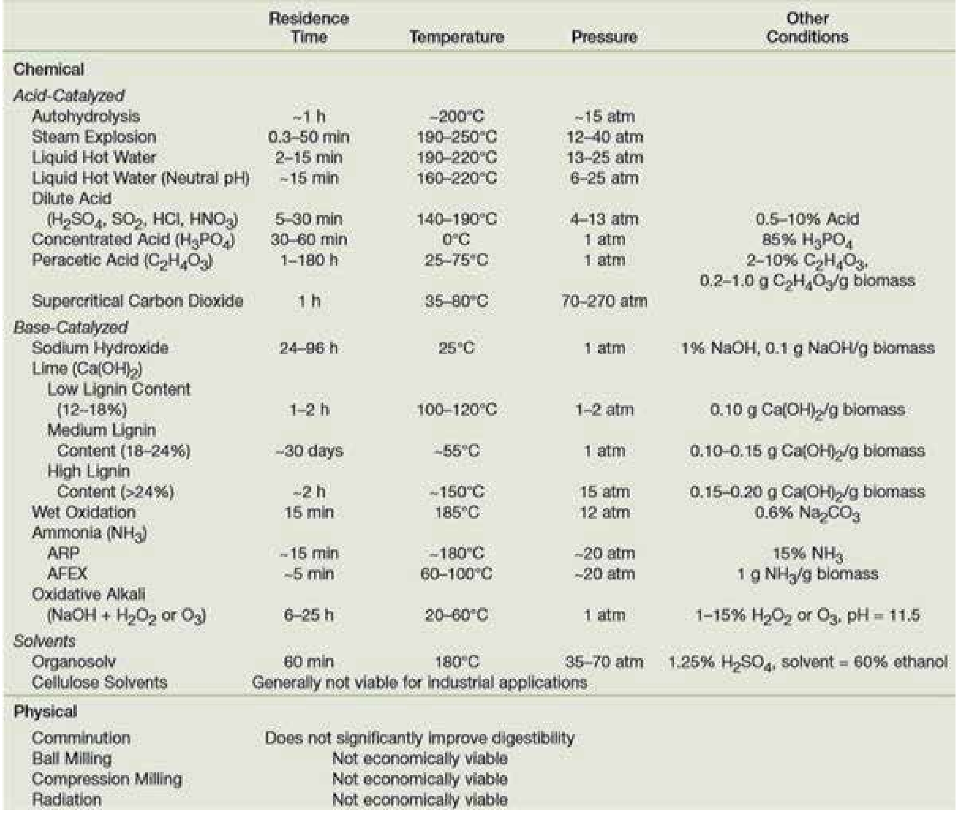
The first challenge in the conversion of biomass to alcohol fuels starts with the difficulty in breaking down the recalcitrant structure of biomass cell walls and further breaking down the cellulose to 5–6 carbon sugars that can be fermented by microorganisms [8]. Size reduction and uniformization in density/size are the first preparation step. Pretreatment by steam, hot water, or slight carbonization is a common procedure.

Various ways of pretreatment are used in biomass conversion to alcohols as illustrated in **Table 5**. Recent types include steam explosion auto-hydrolysis, wet oxidation, organosolv, and rapid steam hydrolysis (RASH) [16]. Organosolv is a pulping technique that uses an organic solvent to solubilize lignin and hemicellulose. The principal purpose of most pretreatment is to increase the susceptibility of cellulose and lignocellulose parts of biomass at the next process in which acid and enzymatic hydrolysis occur. Cellulose enzyme systems react very slowly with un-pretreated biomass, whereas the rates of enzymatic hydrolysis enhance dramatically when the lignin barrier around the plant cell is partially disrupted [16].

4.2 Saccharification (hydrolysis)

Saccharification is basically a step of breaking down the cellulose/hemicellulose through hydrolysis to make sugars such as glucose and xylose. The overall hydrolysis is based on the synergistic action of three distinct cellulase enzymes depending on the concentration ratio and the adsorption ratio of the component enzymes (endo-beta-gluconases, exo-beta-gluconases, and beta-glucosidases) [16].

Two main procedures exist in hydrolysis: acid hydrolysis and enzymatic hydrolysis. Most commonly employed procedure is the enzymatic one because it has a



	Residence Time	Temperature	Pressure	Other Conditions
Chemical				
Acid-Catalyzed				
Autohydrolysis	~1 h	~200°C	~15 atm	
Steam Explosion	0.3–50 min	190–250°C	12–40 atm	
Liquid Hot Water	2–15 min	190–220°C	13–25 atm	
Liquid Hot Water (Neutral pH)	~15 min	160–220°C	6–25 atm	
Dilute Acid (H_2SO_4, SO_2, HCl, HNO_3)	5–30 min	140–190°C	4–13 atm	0.5–10% Acid
Concentrated Acid (H_3PO_4)	30–60 min	0°C	1 atm	85% H_3PO_4
Peracetic Acid ($C_2H_4O_3$)	1–180 h	25–75°C	1 atm	2–10% $C_2H_4O_3$, 0.2–1.0 g $C_2H_4O_3$/g biomass
Supercritical Carbon Dioxide	1 h	35–80°C	70–270 atm	
Base-Catalyzed				
Sodium Hydroxide	24–96 h	25°C	1 atm	1% NaOH, 0.1 g NaOH/g biomass
Lime ($Ca(OH)_2$)				
Low Lignin Content (12–18%)	1–2 h	100–120°C	1–2 atm	0.10 g $Ca(OH)_2$/g biomass
Medium Lignin Content (18–24%)	~30 days	~55°C	1 atm	0.10–0.15 g $Ca(OH)_2$/g biomass
High Lignin Content (>24%)	~2 h	~150°C	15 atm	0.15–0.20 g $Ca(OH)_2$/g biomass
Wet Oxidation	15 min	185°C	12 atm	0.6% Na_2CO_3
Ammonia (NH_3)				
ARP	~15 min	~180°C	~20 atm	15% NH_3
AFEX	~5 min	60–100°C	~20 atm	1 g NH_3/g biomass
Oxidative Alkali (NaOH + H_2O_2 or O_3)	6–25 h	20–60°C	1 atm	1–15% H_2O_2 or O_3, pH = 11.5
Solvents				
Organosolv	60 min	180°C	35–70 atm	1.25% H_2SO_4, solvent = 60% ethanol
Cellulose Solvents	Generally not viable for industrial applications			
Physical				
Comminution	Does not significantly improve digestibility			
Ball Milling	Not economically viable			
Compression Milling	Not economically viable			
Radiation	Not economically viable			

Table 5.
Pretreatment technologies currently available for alcohol fuels [12].

better environmental and economic performance. Acid hydrolysis operates under severe conditions of high temperature and low pH, which results in corrosive conditions and requires a special construction material [17].

4.3 Fermentation

Fermentation is the biological process using microorganisms to convert sugar and starch into ethanol. The production of bio-ethanol from starch-containing cereals typically includes the following five steps [15]:

1. Milling, which is the mechanical crushing of the cereal grains to release the starch components

2. Heating and addition of water and enzymes for conversion into fermentable sugar

3. Fermentation of the mash using yeast, whereby the sugar is converted into bio-ethanol and CO2

4. Distillation and rectification, which is a step of concentrating and cleaning the ethanol produced by distillation

5. Drying (dehydration) of bio-ethanol

In Brazil, bio-ethanol is produced from sugar cane. Sugar cane is a sugar-bearing crop, and it is readily converted into ethanol by fermentation with yeast. Harvested sugar cane is thoroughly washed and crushed into pieces, the juice is extracted, and finally it is converted into sugary juice, which is further fermented by yeast. During the process, hydrous alcohol is produced by non-dehydration process and anhydrous one by dehydration process. Anhydrous ethanol is mixed with gasoline for the prevention of phase separation, and hydrous alcohol is used as fuel for all kinds of vehicles. The process wastes during the washing and crushing are again utilized as a boiler fuel to generate steam and electricity for subsequent ethanol production. In addition, for each ton of bio-ethanol, 1 ton of GMO-free, high-protein animal feed can be produced.

4.4 Comparison between SSF and SHF processes

Cellulose hydrolysis and fermentation can be achieved through two different process schemes, depending on where the fermentation occurs: separate hydrolysis and fermentation (SHF) and simultaneous saccharification and fermentation (SSF) [16].

In SHF, hydrolysis is performed in one reactor and the hydrolysates are fermented in the next second reactor. In SHF, feedstock and utility costs are high due to the cellulosic conversion that shows only about 73% to ethanol in 48 hours, while the remainders are burned. In SSF, hydrolysis and fermentation are carried out in a single reactor, and the operating cost is in general lower than the SHF case. In SSF, yeast ferments the glucose into ethanol as soon as the glucose is produced, which results in preventing the sugars from accumulating/inhibiting the final product.

The SSF system offers a large advantage over SHF processes, because of their reduction of final product inhibition of the cellulase enzyme complex [16]. The SSF process shows a higher yield (88 vs. 73%) and greatly increases product concentrations (equivalent glucose concentration, 10 vs. 4.4%). The most significant advantage is that enzyme loading can be reduced from 33 to 7 IU/g-cellulose, which results in lowering the ethanol cost significantly.

A hybrid hydrolysis and fermentation (HHF) process is also proposed in converting lignocellulosic biomass into ethanol. This process configuration begins with a separate hydrolysis step which involves a higher temperature enzymatic cellular saccharification and ends with SSF step which involves a simultaneous step of mesophilic enzymatic hydrolysis and sugar fermentation.

5. Utilization of alcohol fuels

About 66% of worldwide ethanol products are used for transportation purpose and 21% goes to industrial use. Most widely used area is gasohol in that alcohols are mixed to replace a portion of gasoline. In the near future, alcohol-using fuel cells and alcohol-mixed jet fuels are promising area of application.

Figure 9 shows the ethanol consumption trend for mixing to gasoline in the United States during the period of 1980–2020. During the years 2005–2010, ethanol use has drastically increased and remains as ca. 10% of the total gasoline consumed amount.

5.1 Fuel for automobiles

The most abundant application of alcohol fuels is related to internal combustion engine of automobiles. Mixing alcohol fuels into gasoline has also a purpose of reducing pollutants by oxygenating the fuel. Since methanol is less expensive

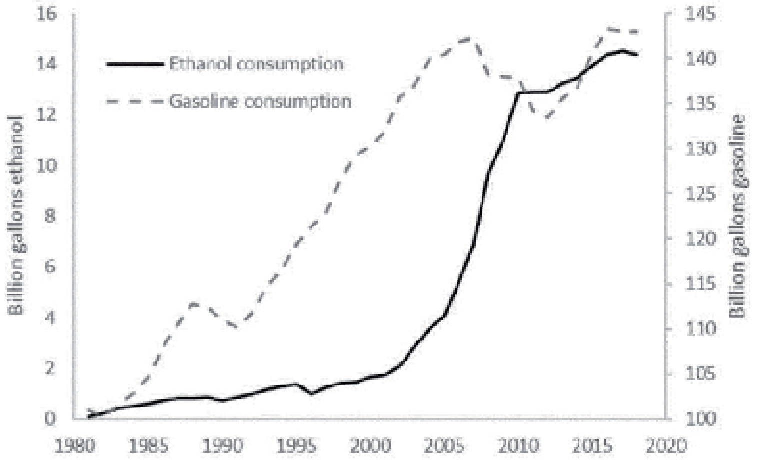


Figure 9.
Trend of alcohol additive consumption for gasoline in the United States [18].

Country	Ethanol program
Brazil	Mandatory of bio-ethanol proportion as mixture of 24 ± 2%
United States	10% target for bio-ethanol proportion among primary energy sources (2010)
EU	Biofuel proportion increase to 2% in 2005, to 5.75% in 2010
Canada	Mandatory of bio-ethanol proportion in fuel set at 10%
China	Mandatory mixing of bio-ethanol at regional government level
India	Current mandatory 5% mixing of bio-ethanol and to be increased to 20%
Columbia	10% bio-ethanol to be mandatory at metropolitan area
Thailand	10% mandatory mixing of bio-ethanol to be enforced within Bangkok area
Argentina	5% bio-ethanol to be mandatory

Table 6.
Ethanol mixing program to gasoline in different countries [11].

to produce than ethanol, although methanol is generally more toxic and has lower energy density than ethanol, it has been used with ethanol as automobile fuels. Compared to gasoline, methanol and ethanol have characteristics of burning at lower temperatures and lower volatility, which results in difficulty in starting the automobile engine in cold weather.

Current alcohol mixing status of ethanol-based fuel utilization in different countries is tabulated in **Table 6**.

Currently, flexible fuel vehicle (FFV) with dual fuel supply system for ethanol and gasoline is commercialized and widely distributed. In the case of methanol blending to gasoline, it is limitedly used in China from the 2000s. In China, M15 (15% methanol/85% gasoline) is the most familiar type [19].

Low-molecular weight alcohols such as ethanol have replaced conventional octane boosting additives like MTBE in automobile fuels. Alcohols that are added to gasoline make the mixed fuel to combust more completely by acting of higher oxygen content by alcohols and provide the ensuing effects of higher combustion efficiency and lower air pollution emissions [20].

In the United States, bio-ethanol is mandatorily mixed with transportation fuels. It has been reported that the bio-ethanol policy reduced crude oil reliance to 25%

from 60%, and simultaneously creating 400,000 jobs, reducing 43% in greenhouse gas generation and cost-saving effect of $1.5/gallon-gasoline to the consumer [13].

Small amounts of methanol and higher alcohols are also allowed to be blended into gasoline within EN228 limits. E85 is used in FFVs in certain areas within the EU (such as Sweden, France, and Germany) [21]. There was a trial to use a near-neat fuel as M85 which contains 85% methanol/15% gasoline.

Racing cars used methanol for a long time, mainly by not producing black smoke which otherwise will block the view of ensuing other racing cars. Other than this application to racing cars, methanol fuel has not applied widespread other than some experience in China, methanol programs in California during the 1980–1990s, and a trial in Sweden as a marine fuel.

More than 98% of US gasoline contains typically 10% ethanol as E10 (10% ethanol/90% gasoline) [7]. Flexible fuel automobiles that can use E85 (85% ethanol/15% gasoline) exist in the United States and Brazil.

In Brazil, 95% of automobiles are using fuel-flex engine system. Around 70% of automobiles in Brazil are able to run on ethanol, and the Brazil's demand for ethanol is estimated to increase by around 70% by 2030 (**Figure 10**) [1, 22].

As for bio-butanol, the commercial scale production facility has not been constructed in sufficient numbers. In the United States, bio-butanol can be mixed up to 12.5%, and the 16% mixture is reported to be equivalently effective to existing E10 [13].

Ethers such as dimethyl ether (DME) contain oxygen in chemical structure which acts as an oxidant in minimizing soot formation. Other exhaust emissions such as unburned hydrocarbons, NOx, and particulate matter are also reduced [8]. DME is an ultra-clean fuel that has similar properties to LPG.

5.2 Fuel cells

Alcohol fuel cell is an energy conversion device to generate electricity via electrochemical reactions on the catalytically active electrodes without direct combustion of alcohol fuel. Direct alcohol fuel cell (DAFC) is named for its direct supply of alcohol to fuel electrode and is called with specific terminologies as direct methanol fuel cell or direct ethanol fuel cell depending on the alcohol fuel source.

The mechanism of electricity generation is based on the oxidation of methanol fuel at the anode (fuel electrode) and conduction of electron(s) to the cathode (air or oxygen electrode) via external conducting circuit and simultaneous electrolytic conduction of proton (H^+) via polymer electrolyte to the cathode.

DAFC can provide portable energy source to electronic devices such as cellular phones and notebook computers [23]. DAFC that uses alcohol can have several

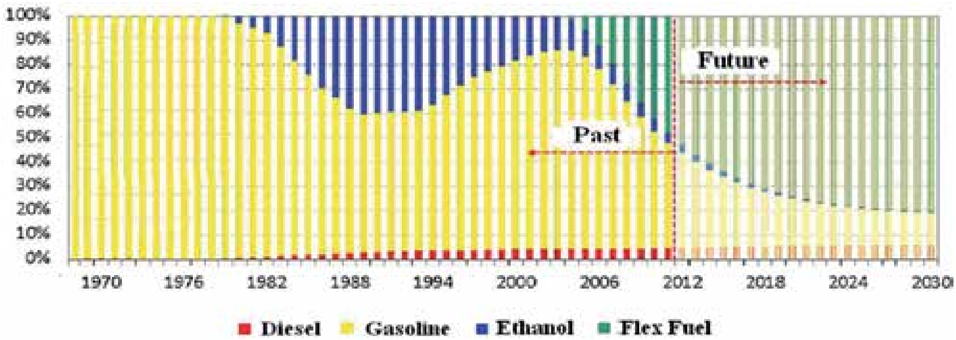


Figure 10.
Changing trend of automobile fuel in Brazil [22].

advantages in terms of storage, transportation, safety, etc. over fuel cell systems like proton exchange membrane fuel cell (PEMFC) that use hydrogen.

5.3 Jet fuel

Alternative jet fuel typically contains a complex mixture of primarily n/iso-paraffins, cycloparaffins, and alkylbenzenes with a carbon number range of 9–15 [24]. Carbon tax accelerates the development of jet fuel from renewable resources. Lowering emissions of particles and greenhouse gases during the flight are the fundamental reason of trying alcohol fuels as a jet fuel option.

Using a 50/50 (v/v) blend of petroleum-based and lipid-based jet fuels for flight was already approved by the American Society for Testing and Materials (ASTM) committee. However, the lack of raw materials and relatively low jet fuel yield of this process limit its application [24].

6. Environmental aspects

Global recognition regarding the significant long-term impact due to climate change provides a key foundation for utilizing alcohol fuels, which means that alcohol fuels should be able to accommodate chances in reducing climate change gases(CO_2, methane, N_2O, etc.). Bio-ethanol is highly effective in reducing greenhouse gas evolution. Corn-based bio-ethanol is reported to generate 43% less greenhouse gases compared to pure gasoline.

From purely theoretical point of view, ethanol can be finally produced from the biomass that is made based on the CO_2 absorbed by plants during photosynthesis, and thus it can be called carbon neutral. Unlike hydrocarbons which evolve voluminous amount of CO_2 from their internal carbon atoms during combustion, ethanol can be regarded as carbon neutral without generating as much CO_2 from internal carbon atoms. In practice, however, significant amount of greenhouse gas evolution is directly and indirectly caused by cultivation of biomass crops and synthesis of alcohol fuels.

The range of CO_2 reduction potential is large when alcohol fuels are used. Values range between 0.5 kg CO_2-equivalent/liter of ethanol for ethanol produced from wheat and up to 2.24 kg CO_2-equivalent/liter of ethanol for ethanol manufactured from sugar cane (**Figure 11**) [25].

According to the result shown in **Figure 11**, among alternative liquid fuels, only cellulosic ethanol, biomass to liquid (BTL), and CCS-involved processes (BTL-CCS, CBFT-CCS, CBMTG-CCS) exhibit the CO_2-negative performance in life cycle analysis (LCA) perspective. Carbon capture and storage (CCS) process is not fully economically feasible and technically proven till now; moreover, considering public objection on CCS, connecting the process to CCS is not practical for the time being. In CO_2 reduction aspect, cellulosic ethanol is the most reasonable choice as a renewable alternative fuel.

Adding ethanol to gasoline fuel of automobile, oxygen contents of fuel mixture increases and yielding the effect of reducing pollutants evolution. As alcohol fuels are inherently sulfur-free, it suits for cleaner environment. Besides, since ethanol is produced by fermentation with crops that contains starch, its purity is high, and no hazardous combustion by-products such as SO_2 or metal oxides are generated during the combustion when compared to the petroleum-based fuel. But, high solubility into water by short carbon chain alcohols such as ethanol and methanol can cause an underground water pollution, although short carbon chain alcohols are well degradable in few days under normal circumstances. This problem can be minimized with the use of higher carbon chain alcohols like bio-butanol.

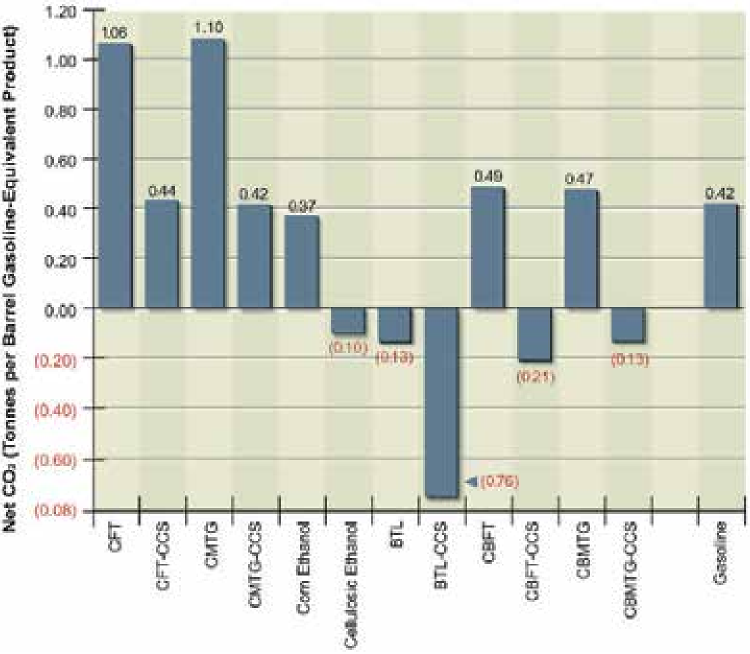


Figure 11.
Estimated carbon dioxide (CO_2) emissions over the life cycle of alternative fuels [8, 26]. Note: BTL, biomass to liquid; CBFT, coal and biomass to liquid, Fisher-Tropsch; CBMTG, coal and biomass to liquid, methanol to gasoline; CCS, carbon capture and storage; CFT, coal to liquid, Fisher-Tropsh; CMTG, coal to liquid, methanol to gasoline.

Forest clearing and chemical fertilizer are involved to grow corn and other grains for the first-generation bio-ethanol, which eventually ends up with CO_2 production and countervailing the CO_2 reduction amount by bio-ethanol use, sometimes more than the reduced amount. In this regard, the second-generation lignin-based or third-generation algae-based raw material is a better candidate for bio-alcohols.

It is especially noteworthy that the definition of (environment friendly) bio-energy is rather more stringently defined in the EU and United States: more than 35% reduction of greenhouse gas is required to qualify compared to fossil fuels of the same calorific value [27].

The issue of required water amount asks the approach of water-energy nexus in that technology development will follow for the process of better environment-friendliness and sustainability [13]. As an example, recent water shortage encountered in Chennai, India, might be attributable to global warming, and the water quantity consumed for the production of alcohol fuels is emerging as an important issue. Chennai region went without rain for 200 days in 2018.

The process consuming the largest amount of water is the cultivation of biomass crops. Among the production processes for alcohol fuels, refinery step consumes the largest amount of water. The water quantity consumed for US corn-based ethanol production is approximately equivalent to the water requirement that can sustain 5000 people for 1 year.

Moreover, the refinery process that is going to be extended for the second-generation cellulosic ethanol is expected to consume 2.9 times more water needed for corn-based ethanol refinery process. At present, cellulosic ethanol production process consumes about 9.8 L/L-ethanol [13], which is unduly high.

7. Incentive system: renewable fuel standard (RFS)

To a great extent, expanding the distribution of bio-alcohol depends on the RFS system currently implemented in many countries. Basically, biomass ethanol cannot compete in normal market situation with petroleum-based fuels. As shown in **Figure 12**, liquid fuel cost of corn ethanol and cellulosic ethanol is similar to the level of crude oil price around $90–110/barrel. Considering the crude oil price during the 2000s, this high level of biomass-based ethanol price cannot compete in normal market situation. To make a room to enter the fuel market, incentive system of renewable fuel standard (RFS) was introduced.

Important aspect in **Figure 12** is that bio-ethanol route (corn ethanol, cellulosic ethanol) is cheaper than the biomass to diesel/gasoline (BTL) route and comparable to the coal/biomass to diesel/gasoline (CBFT) route.

Mandatory addition of renewable energy sources in regulated proportions for transportation fuel is underway in 64 countries worldwide in connection with greenhouse reduction effects. Most such countries employ ethanol-based mixing program, while a few countries including Korea implement mandatory mixing of biodiesel only [13].

In the EU, 27 countries operate the mandatory mixing policy for bio-alcohol. Many countries in different continents implement similar policy: 13 nations in North and South America, 12 nations in Asia-Pacific, 11 nations in Africa and contiguous nations along Indian Ocean, and 2 nations in non-EU sphere [13]. All in all, current trend regarding bio-ethanol mixing in major countries is summarized as follows: mandatory mixing ratios are 27% in Brazil since 2015, while nine provincial governments of China mandate 10% mixing and, it will be expanded to the entire China by 2020. RFS program was newly initiated in Vietnam since 2018 for 5% ethanol mixing. Canadian E5 mandates 5% mixing and E8.5 program is implemented in five Canadian states. Columbia implemented E8 since 2008, but E5 was targeted in Chile but not mandatorily regulated. Costa Rica mandatorily implement E7 while E10 and E2 are regulated in Jamaica and Mexico, respectively. The EU currently mandates 5.75% mixing with 10% objective for 2020 and recommends EU member nations to accomplish target 10% ratios of 2020 [13].

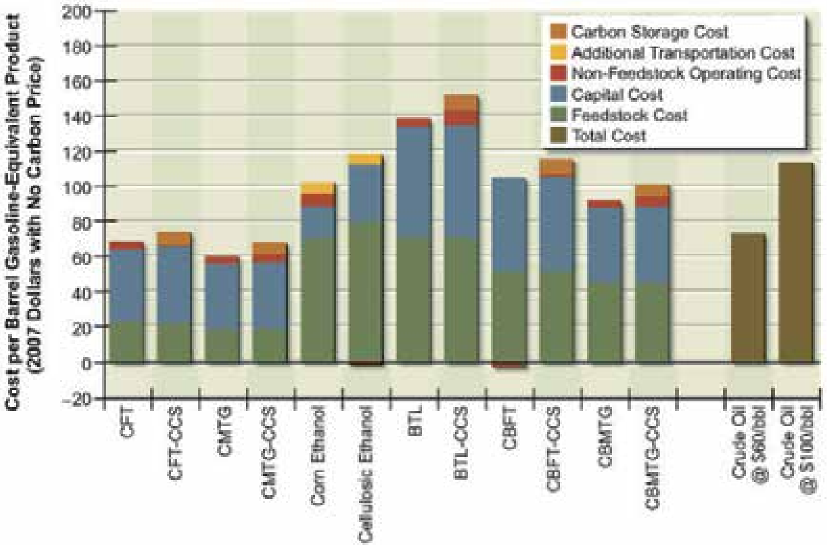


Figure 12.
Costs of alternative liquid fuels of different origins with zero carbon price [8, 26].

In the United States, MTBE additive to transportation fuel was gradually becoming prohibited since 2002 to prevent the groundwater pollution, and 25 US states had banned the use of MTBE by 2007. Bio-ethanol has thus become a replacement for MTBE. Mandatory mixing of bio-ethanol in transportation fuel has been implemented for dual purposes of using US surplus corn products as raw material for bio-ethanol and simultaneously safeguarding US farm economy, which prompted legislation and implementation of mandatory mixing of bio-ethanol in transportation fuel.

More specifically, Energy Policy Act of 2005 paved a way for RFS program which led to more concrete implementation plan in 2007 via Energy Independence and Security Act. The US Environmental Protection Agency (EPA) announced Regulatory Impact Assessment (RIA) in 2010, and RFS2 program was thus made available to the public, where LCA was required for the greenhouse gas evolution during the bio-ethanol production.

In many countries, government-level subsidies are being curtailed for bio-alcohols with no significant contribution to the greenhouse gas reduction. For example, cellulosic bio-ethanol is given higher Renewable Identification Number (RIN) credit in the United States for its efficient greenhouse gas reduction and non-edible nature of raw material. RIN credit ratio is 0.85:2.85 for corn-based ethanol/cellulosic bio-ethanol, which sets a higher ratio for the cellulosic ethanol.

8. Methanol economy

Methanol economy had been touted as a possible replacement for fossil fuel society. Now, hydrogen economy is starting to replace the momentum of methanol economy. Methanol has quite versatile usages in many sectors of modern industries for energy source and chemical raw material, which is a very good point when selling the product. Compared to the recent unmatched supply-demand issue in bio-ethanol, the point that there are many selling market can be a major advantage.

Related technologies to methanol are mostly mature such that there are only economic uncertainties, not major technical difficulties. Its related utility can expand as an energy media for society if cost is appropriate with eventual goal of replacing fossil fuels with methanol.

Methanol is produced from various raw materials including biomass or wastes which has not been fully utilized till now. Methanol-based energy can be quite useful especially for developing countries to cope with global climate change issue and related environmental issues while simultaneously securing some portion of national energy security. But, the issue of slipping into underground water stream when it is not properly regulated might be an issue that is to be solved. Underground water contamination shall be much smaller than the case by petroleum-based liquid fuels, but it needs to be comparable eventually to hydrogen and clean gas energy sources.

9. Relationship with hydrogen society

Hydrogen economy that is being a focal point in several developed countries can be a chance as well as danger to alcohol fuels. It is a chance because hydrogen can be manufactured with easily distributable alcohols but can be a danger when all liquid fuel-based infrastructure might be changed to the fully gas-based or hydrogen system in the long run.

Due to the concerns on climate change that requires CO_2 reduction and the concerns on environmental pollutants like fine particulate and NOx, hydrogen has been hoped eventually to replace all other energy mainstream options. During the last few years, hydrogen economy has reborn as a cure for CO_2 and environmental issues like an ultra-fine particles and PM2.5. But due to its high cost in hydrogen production as well as in application tools such as fuel cell and still-unstable infrastructure, hydrogen era might come after few decades of development and trial and errors. In contrast, alcohol fuels have been viewed as a cheap and reliable option in replacing fossil fuels. Especially, the possibility of utilizing abundant biomass prompts to try many ways in technology development and commercialization.

Hydrogen is the most abundantly available element in the universe with immense possibility as essential energy source sometime in the future. At present, however, technologically and economically viable means of its utilization as an affordable energy source are not ready and many countries opt to pursue the hydrogen economy path as a mean for dealing with climate change and pollution problems in their major cities.

Hydrogen economy involves the generation of renewable electricity from photovoltaic cell or wind turbine, and the so-called water-to-gas (PtG or P2G) which involves water electrolysis using the excess electricity to produce hydrogen. Green hydrogen energy generation and utilization is the ultimate goal in hydrogen economy in which society of no CO_2 evolution and no fossil fuels will eventually be accomplished. On the other hand, methanol society focuses on the production of CO_2-free energy source from renewable biomass or sea algae which grow by photosynthesis in nature. Green hydrogen energy will be further refined to maturity, at least by the 2030s, in such countries that can afford to bear the related high costs.

More specifically, introduction of fuel cell vehicle using hydrogen will initiate and further expand in those countries which suffer from persistent air pollution (China, Korea, Japan, large metropolis areas of the EU and United States). In contrast, alcohol-based energy source such as ethanol and methanol is most suitably applicable in tropical or semitropical countries where biomass resources are abundantly available, while domestic energy sources are not plentiful.

For realization of such alcohol-based energy generation from raw material of (very low) calorific value per unit volume, the current high-cost situation related to the pretreatment and production processes should be solved.

10. Ways for wider utilization

Changing the basic liquid fuel infrastructure that can accommodate alcohol fuels in a global scale will be slow like maneuvering a massive ship and very competitive even with right environmental slogans such as renewable, clean, and sustainable for the society. It is a well-known hidden fact that major local oil companies as well as auto manufacturers do not want to change their market unless certain compulsory regulation applies or proper incentives are given.

A report in July 2019 [28] on the US ethanol industry nearing breaking point succinctly shows the problem related to enlarged supply and dwindling demand. Report says that US ethanol production in early June 2019 reached almost 1.1 million barrel/day, the highest seasonally on record, but the economic margins to produce ethanol are at the lowest seasonally since 2015. Infrastructure for E85 gasoline as well as government policy like US Small Refinery Exemptions (SREs) plays key roles in demand side of alcohol fuels. This situation illustrates the weak point of alcohol fuel industry. Technical endeavor only cannot make a way for wider utilization. Policy and infrastructure should follow in parallel.

Food vs. fuel controversy is the main topic in utilization of alcohol fuels, which pushed the feedstock from corn to non-food lignocellulosic biomass. Technical breakthroughs in solving the difficulties in non-uniform/hard-to-break lignocellulosic biomass and in lowering the process cost are key factors, although it would not be an easy task, considering the already established relatively cheaper bio-ethanol industry from corn.

There are clear directions, especially in developing countries in Africa and Southeast Asian countries, where environmentally benign liquid fuel supply is in great need and the centralized energy supply infrastructure might be too costly. When alcohol fuels can be supplied in enough quantity with reasonable cost, securing energy security and installing the distributed energy infrastructure can be a socially acceptable justification.

10.1 Securing energy security

When a large volatility exists in oil and gas prices, a niche market of alternative fuels like alcohols can act a role. In the time of large availability of shale gas and shale oil in addition to a remarkably fast-advancing market share by renewable electricity, the probability in global energy price jump might be low. When the energy market situation goes down to local scale, however, there are many volatility in liquid fuel supply chain.

Countries with scant energy resources are expected to be more actively searching for a way to utilize pre-existing affordable energy source and raw materials for chemical industries instead of solely relying on imported natural gas and petroleum oil. It is necessary to diversify energy sources to satisfy domestic demand even for a small proportion at the start. Alcohol fuel could take some of such small proportion.

Since most countries prefer to use gas as a basic energy source, resulting in more demand for clean and easy-to-use gas resources, even Southeast countries which are currently gas-exporting countries are going to be net importer from the 2030s, as shown in **Figure 13** [29]. Energy diversification through alcohol fuels must be a practical option to ease the burden in transportation and energy utilities in these countries.

Because the demand for natural gas is large and the accommodating space is limited in urban areas, the centralized gas supply by pipeline appears to be essential. On the other hand, local villages and smaller township can satisfy their energy needs in a distributive way by alcohol fuels produced from locally available biomass

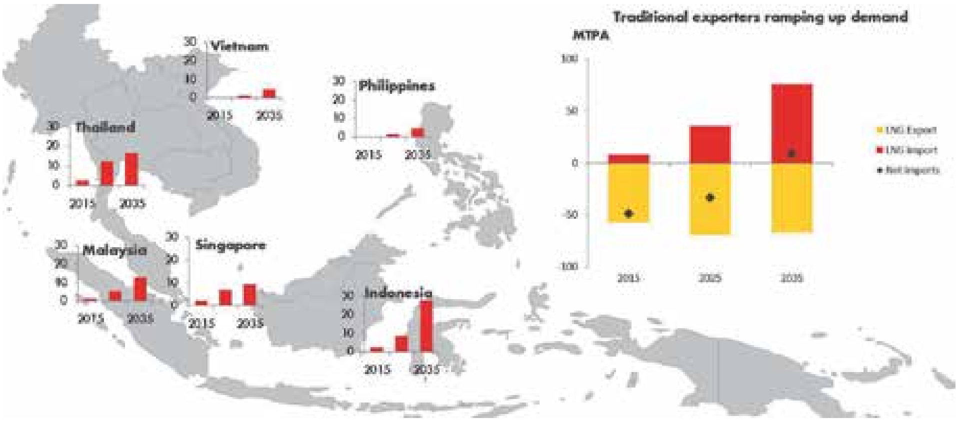


Figure 13.
LNG trend change into net importer by 2035 of Southeast Asian countries [29].

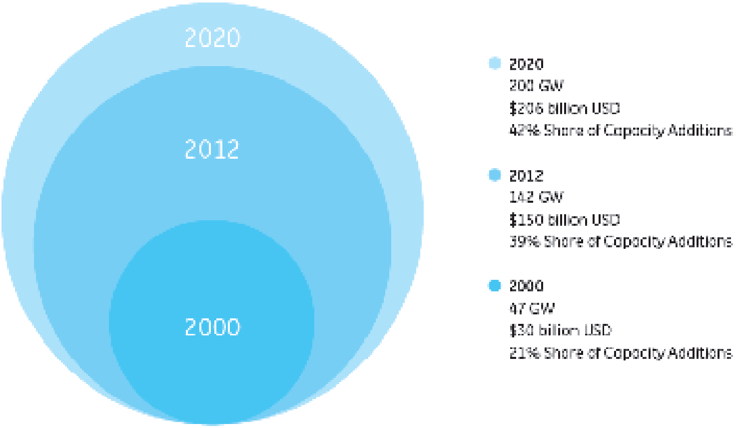


Figure 14.
Worldwide distributed energy market prospect of less than 50 MW scale [30].

and wastes. At present level, relevant technologies are not fully ripe, which necessitates international cooperation for comprehensive and interdisciplinary R&D.

10.2 Distributed energy applications

Future trend of energy utilization is in the type of distributed application. There are many limitations for making the system that will be competitive to the centralized big-scale system that has a huge advantage in the economics of scale.

Nevertheless, the preference for the distributed energy system that is more suitable in effectively responding to the local energy demand is on the increase worldwide recently over centralized energy distribution systems. Distributed energy system market is expected to steadily expand, and this trend is most significant in the field of less than 50 MW output, where the gas turbine is taking large proportion of market share. Alcohol fuel is also expected to play a significantly important role in the distributed energy system market (**Figure 14**).

Locally produced biomass, wastes, and agricultural by-products are converted to alcohol fuels for energy sources, and they are locally distributable and consumed. Such system is cost-competitive by minimizing the transportation distance and is important as the basic infrastructure in securing the clean energy source as well as in proceeding to the sustainable society. However, the distributed energy application system costs more than the centralized energy distribution system, in general. It can be accomplished only by meeting the pre-conditions that cost should be down significantly and proper commercialization with reliable technologies should be available for greenhouse gas reduction and for alleviation of environmental pollution.

11. Future direction

There emerged several candidates that compete with alcohol fuels in the twenty-first century liquid fuel field. Green hydrogen and green electricity are the most prominent players. Whether alcohol fuels can compete with these two players will depend on the future progress in dealing with key required target: CO_2 reduction, environmental cleanness, convenience in existing infrastructure, and price competitiveness. Moreover, energy-related focal points nowadays are sustainability, suitability for carbon-free (green energy) status, and alleviation of polluting materials such as fine dust, which are primarily emerging and ecologically important topics.

Replacement of fossil fuels with alternative clean fuel will eventually lead to green energy-based sustainable society. However, currently available technology is not up to the level of commercially viable standard for social acceptance in terms of CO_2 evolution and fine dust, etc., which must be comprehensively overcome.

Currently available elementary and applied technology can be utilized to synthesize liquid fuel in various forms. Although synthesis of liquid fuel is more costly than direct mining of petroleum, the application of currently available technology to alcohol fuel synthesis should be tried to make ways that can be economically feasible and lucrative when commercialized. In a sense, it is rather a problem-solving for cost-effective technology rather than the technology itself. Mass production of lignocellulosic ethanol necessitates economically competitive technology rather than the barely profitable or only technically feasible technologies.

Actually, bio-alcohol such as bio-ethanol is an industry of low unit cost. Without installing a proper scale of plant size, cost competitiveness with other liquid fuels must be quite low [13]. Actual plant construction cost remains high because of the inherent limitation of using low-energy density raw feedstock and of complex nature involved in converting into alcohol fuels. Among these, pretreatment/detoxification and hydrolysate conditioning processes are especially costly. Such auxiliary processes have to be developed in such a way that overall process cost can be dramatically reduced through the introduction of more energy-efficient and process simplification [13].

Another important aspect is that soils and climates in much of Africa have similar characteristics to those in Brazil [31]. Africa and South America have a great potential in increasing bio-energy products including alcohol fuels.

In short, alcohol fuels should work as an energy source that can minimize the environmental impact as lower than natural gas at all applications while opening more applicable places as well as manufacturing a cheaper liquid fuel that can be used in big scales also in developing countries where plentiful but low-grade raw materials exist in plenty.

12. Conclusions

Alcohol fuel is one of the most important source of energy in view of its renewable nature and the abundance of feedstock on earth. Even when many bright prospects of alcohol fuels shed light on possible options for the environmental conscious society, still cost dictates and it will be that way. Carbon taxation might help, but the market might lead to a totally different direction such as hydrogen or green electricity from renewable energy, instead of choosing alcohol fuels. Abundant shale natural gas might play a replacing act of cheap oil that had prevented most of other energy source developments from the 1950s till the 1970s. All these situation point that the future of alcohol fuels depends upon the technological advances in cost and convenience in use.

As discussed in this chapter, the direction of future energy is simple and clear. It is the low-carbon economy using sustainable energy resources but with affordable cost. Alcohol fuels can act as connecting threads between current conventional oil/gas society and the future hydrogen society in attaining this far-reaching goal.

Current status regarding alcohol fuels can be summarized as stagnant in scale and also in utilizing market. Since bio-ethanol dominates the alcohol fuel market, the system has an inherently sensitive structure to changes in supply-demand and government's policies. More wide application ranges of alcohol fuels should be sought in areas such as fuel cells, marine ships, and jet fuels. Alcohol fuels must remain as an essential component for the realization of sustainable low-carbon society, and continuous research on key bottlenecks should be pursued systematically.

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Chapter 2

Alcohol Fuels as an Alternative Fuels - Bringing New Heights in Sustainability

Sivakumar Kasibhatta

Abstract

Since the middle of 1970s, the enthusiasm for using alcohols as alternate convenient fuels in internal combustion engine (IC) has been increased and it has reached peak stage by the middle of 1980s. The usage of alcohol as an alternate fuel, due to its minimal undesired effects on atmosphere, has gained importance. Harmful effects on environment are caused by various fossil fuels and their exhaust emissions such as carbon monoxide, carbon dioxide, hydrocarbons, nitrogen oxides and particulate matter. Alcohol type of fuels is alternative to petroleum-based fuels due to reduced greenhouse gas emission, toxic exhaust emission and enhancement of overall energy efficiency. Moreover, they are convenient for internal combustion engines due to their high octane rating, burning velocities and wider flammability limits. In order to achieve better environmental sustainability, it is the right time to use lower molecular weight alcohols (alcohols possessing lower molecular weight, such as methanol, ethanol) replacing other additives as octane boosters in automotive fuels in the present situation.

Keywords: methanol, ethanol, alcohol fuel, sustainable development, environment

1. Introduction

Around the world, energy is one of the major sources for the improvement and development of human beings life standards and its sustainable development. With rapid growth in the world population during the past few decades, the energy requirements that have also increased at an even large rate in industrialization and transportation sectors lead to an increase in crude oil prices, which is directly affected by global economic activity [1]. Now a days, worldwide 80% of fossil fuels consumed as primary energy, of which 58% of fossil fuels are consumed by the transportation sector only [2]. Since 1973, worldwide the primary energy demand has been increased at the rate of 2.0% on average per every year. As well as, still around one third of world's population are dependent on non-commercial fuels (United Nations 2007, 1). One of the significant environmental related issues is the widespread usage or burning of fossil fuels in many industries and transportation which are major contributors to air pollution, ozone depletion, global warming, climatic changes and human health-related problems. However, CO_2 is an important pollutant, which is produced by improper combustion of fuel and other major pollutant is NO_x, which is produced from both natural and man-made processes.

Moreover, SO_2 is one of the major air pollutants; it is released by the burning of fossil fuels like coal, petroleum and other factory combustibles.

In the 1960s, environmental awareness was brought to public attention, when smog became a major issue in developed cities such as Mexico, Los Angeles and Tokyo City. According to National Energy Strategy in February, 1992, The United States of America used more than 185 million busses, cars and trucks for transportation, which consume two-thirds of the oil used by the United States. Likewise, in India 50% of oil was consumed for transportation in 1991; it has been increased to up to 61% by the year 2010. Day to day the oil usage was rapidly increased, it causes the severe damage of environment. In the year of 1992 June, Earth Summit conducted by the United Nations on Environment and Development (UNCED). In this summit mainly the delegates all over the world aimed to decrease the global warming.

Thus, the search for possible alternatives to fossil fuels becomes essential. In this regard, an ideal replacement would be characterized by renewable, sustainable, efficient, and cost effective energy sources with fewer emissions [3, 4]. Among many energy alternatives, alternative fuels are the most environment friendly energy source. A worrying statistical analysis is that, the global oil and gas production is approaching its maximum production level and the world is now finding one new barrel of oil for every four it consumes. Therefore, alcohol fuels are the best alternative to fossil fuels; alcohol fuels have been represented as a future leading supplier of energy sources that have the ability to increase the security of supply, reduce the amount of vehicle emissions, and offered a stable income for farmers. Right now, alcohol fuel used as alternative fuel instead of fossil fuels in different motor vehicles (busses, cars, trucks, etc.) in most of the countries and **Figure 1** shows the bus running with alcohol fuel [5].

1.1 Why alcohol used as alternative fuel

At present, the future of the world ecosystem is obviously the most important issue. Recently, our young researchers improved the awareness on environmental protection and usage of alcohol fuels or non-fossil fuels for internal combustion engines. Generally, lower molecular weight alcohols, particularly ethanol or methanol, comprise one group of alternative fuels which is considered attractive for this

Figure 1.
Alcohol fuel bus [5].

purpose. The alcohol fuel has more advantages compared with fossil fuels, and they are given below:

- Both lower molecular weight alcohols can be made out of indigenous energy resources such as biomass, coal and natural gas, which are available with low cost.
- Combustion of alcohol in internal combustion engines (ICE) produces more combustion pressures compared to gasoline because of higher molal products to reactants ratio. Also, this improves power output and thermal efficiency compared to gasoline
- Greenhouse gases emissions can be reduced.
- Compared with gasoline, alcohols having higher average octane rating can increase power and fuel efficiency
- Decreases the releasing of toxic gases into the environment.
- The leaks and spillages of alcohol fuel from the oil tankers; alcohols are miscible in water and could be washed out with water for quick and easy removal. They are easily metabolized if absorbed by the ground.
- Alcohol fuels have a lower evaporative emission.
- The negligible amount of ash was released into the atmosphere by the combustion of alcohol fuel in ICE due to presence of less carbon content in alcohol fuel.
- The overall energy efficiency of fuel can be improved.

2. Current situations in key countries

In the year 1896 Henry Ford used pure ethanol as a fuel to run his first car. After that in 1908, he designed another famous car, i.e., Ford Model T, it is capable of moving with both combination of gasoline and ethanol [6]. Brazil was one of the largest country to implement the bio-fuel programs in the production of ethanol fuel from sugarcane in the world [7]. In the year 2006, Brazilians are utilized 18% of ethanol fuel for their country's road transport sector and by April 2008, more than 50% of fuel consumption for the gasoline market. Up to 2005, Brazil was topper in the world to produce alcohol fuel, when it was surpassed by the United States. Both the countries together (Brazil and the United States) are responsible in the year of 2011 for 87.1% world's alcohol fuel produced [8].

However, China was directly campaigning alcohol fuel in five central and northeastern major cities in order to reduce consumption of fossil fuels. These cities are Zhaodong in Heilongjiang province, Luoyang, Nanyang in central China's Henan province, Zhengzhou, Harbin and northeast China. In the present situations, compared to any country in the world the United States produces and consumes more alcohol fuel. These days, majority of the cars on road in the United States can run with alcohol fuel and motor vehicle manufacturers already produce vehicles designed to run on much higher ethanol blends. The major countries were given in **Table 1** based on the annual production of alcohol fuel [9].

Annual production alcohol fuel from different countries in the year of 2014 to 2016 [9] (Million US gallons per year)				
According to 2017 worldwide ranking	**Country/Provence**	**2014 (Million US gallons)**	**2015 (Million US gallons)**	**2016 (Million US gallons)**
1	U.S	14,300	14,806	15,330
2	Brazil	6,190	7,093	7,295
3	European Union	1,445	1,387	1,377
4	China	635	813	845
5	Canada	510	436	436
6	Thailand	310	334	322
7	Argentina	160	211	264
8	India	155	211	225
******	Remaining the world	865	391	490
******	Throughout the world	24,570	25,682	26,094

Table 1.
Annual production alcohol fuel by various countries.

3. Sources and products in alcohol fuel synthesis

3.1 Production of methanol

The simplest form of alcohol is methanol, it is also known as methyl alcohol, wood alcohol, or wood spirits, is frequently abbreviated as MeOH. It is a colorless, volatile, flammable liquid with a distinctive odor and polar liquid at room temperature. Methanol was miscible with gasoline or petrol, water and most of the organic compounds. It can be synthesized by different methods.

3.1.1 Synthesized from biomass

MeOH can be synthesized industrially from biomass like plants, fruits and animal wastes through anaerobic metabolism by many bacteria. Also, methanol was formed as a by-product during the ethanol fermentation process. Moreover, mainly in China and South Africa methanol can be produced from coal because of majority coal deposits was found in both countries and throughout the world. Most of the industrialists preferred for synthesis of MeOH from biomass due to process simplification, reduction of cost and energy consumption. The production scheme of methanol [10] was given in **Figure 2**.

3.1.2 Methanol from catalytic synthesis

The reactions relevant for the production of methanol have been known for a longtime. A mixture of CO_2, CO and H_2 can react with each other to form methanol and water as a byproduct. Equations (1) and (2) show the stoichiometry of these reactions and their reaction enthalpy [11].

$$CO + 2H_2 \leftrightarrows CH_3OH \quad \Delta H_{298.15\,K,5MPa} = -90.7\,kJmol^{-1} \qquad (1)$$

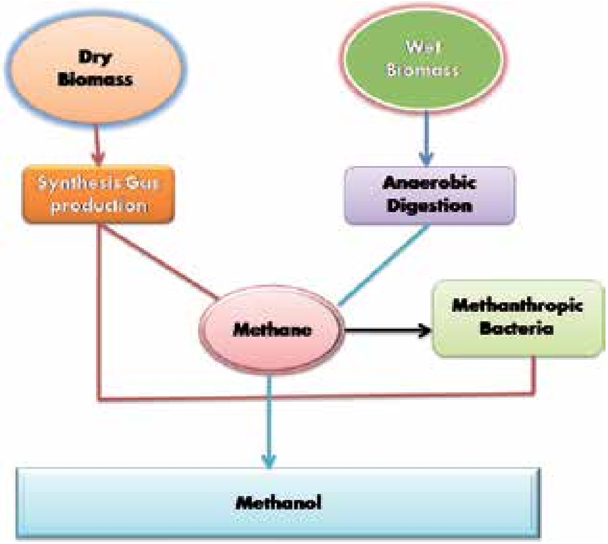

Figure 2.
The schematic representation of methanol production [10].

$$CO_2 + 3H_2 \leftrightarrows CH_3OH + H_2O \quad \Delta H_{298.15\,K,5MPa} = -90.7\ kJmol^{-1} \tag{2}$$

3.2 Production of ethanol

Ethanol also called as grain alcohol or ethyl alcohol. The purest form of ethanol is colorless liquid, flammable and boiling point 78.5°C. Compared to many other fuels, ethanol burns more cleanly and produces carbon dioxide and water. Hence, ethanol was considered as eco-friendly fuel for transportation process. Moreover, ethanol has high octane rating than gasoline, requiring changes to the spark timing in engines.

3.2.1 Ethanol from cane and other sugar plants

Fermentation is the fundamental method to synthesize the ethanol used in industries. Sugarcane molasses was the important raw material for ethanol production, which is byproduct of sugar industry [3]. Also, in fermentation process grain starches (wheat and corn), potato mashes, fruit juices, non-sugar lignocelluloses fractions of crops such as grasses and plants used as raw materials. Generally, molasses contain up to 50% simple sugar that can be easily fermented into ethanol and it is an ideal raw material for ethanol production with high availability and low cost. However, once the raw materials are delivered to the ethanol production plant, it is stored in the warehouse and conditioned to prevent from early fermentation and contamination [12]. Moreover, an enzyme such as microscopic yeasts plays a vital role in the fermentation process to convert carbohydrates to ethanol in the absence of oxygen. The possible equations in the process of fermentation by yeast in the absence of Oxygen are shown here under [13]. The synthesis route of ethanol [14] is represented in **Figure 3**.

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 2C_6H_{12}O_6 \tag{3}$$

$$2C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2 \tag{4}$$

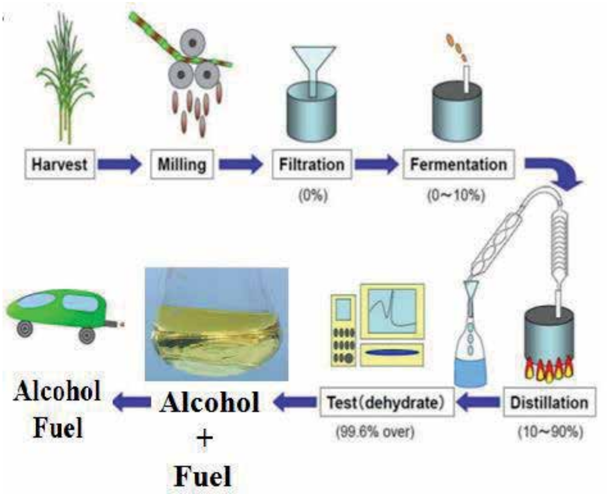

Figure 3.
The schematic representation of ethanol production [14].

3.3 Usage of alcohol fuels as gasohol

Traditionally, after the production of industrial methanol or ethanol, it has been used for alcohol fuel blending to manufacture gasohol. However, after fermentation and distillation process, it can be blended with petrol/gasoline in distinct proportion. The 10% ethanol was blended with 90% gasoline is considered as Low-level ethanol blends like E10, it can be used in conventional vehicles. Moreover, 85% ethanol was blended with 15% gasoline is considered as high-level blends, such as E85, it can be used in specially designed motorized vehicles like flexible fuel vehicles [15].

Alcohol fuel effectively used as an alternative liquid transportation fuels by varying their properties by the addition of certain additives, which must be physically and chemically compatible with the base alcohol fuel and have the same or higher specific energy content. Especially, both MeOH and ethanol are poorly miscible in gasoline containing traces of water, but completely miscible with water. The alcohols are blended with gasoline in presence of water, which may leads to a phase separation problem. In this situation to avoid the phase separation problem, few additives was added to alcohol fuel like higher alkanols such as 1-butanol, n-decanol, iso-propanol, different anionic fatty acid surfactants and various commercial non-ionic surfactants. Here, the avoidance of phase separation would have exact benefits for overall drivability, as well as in corrosion of water-sensitive components such as aluminum. In spark ignition engines, alcohol fuel can run at a much higher exhaust gas recirculation rates and with higher compression ratios [16].

The combustion MeOH:

$$2CH_3\,OH + 3O_2 \rightarrow 2CO_2 + 4H_2\,O + \text{Heat} \tag{5}$$

The combustion ethanol:

$$C_2\,H_5\,OH + 3O_2 \rightarrow 2CO_2 + 3H_2\,O + \text{Heat.} \tag{6}$$

The properties of gasoline, MeOH and ethanol such as air–fuel ratio, density, combustion energy, Percentage of oxygen, Reid Vapor Pressure (RVP), Research Octane Number (RON) and Motor Octane Number (MON) [17, 18] were listed in **Table 2**.

Properties	Gasoline	Methanol	Ethanol
Air–fuel ratio	14.6	6.5	9.0
Density (kg/l)	0.74	0.796	0.794
Combustion energy (Btu/lb)	—	10, 260	13,160
%of O_2 (wt%)	—	49.9	34.7
RVP (kPa)	—	250	130
Research octane number (RON)	91–99	136	129
Motor octane number (MON)	81–89	104	102

Table 2.
Properties of liquid fuels [17, 18].

Table 2 illustrates that, alcohols having lower air–fuel ratio compared with gasoline, which helps to alcohol fuel to produce more power inside of an engine when these fuels are burned. However, the efficiency and quality of fuel are expressed in terms of difference between Research Octane Number (RON) Motor octane number (MON). Generally, RON is greater than MON in most of the fuel components. The RON and MON of alcohol fuel were measured in test engines at a relatively low speed (600 rpm) to simulate city driving speed with frequent acceleration and at a higher speed (900 rpm), which simulates highway driving respectively. The maximum octane sensitivity value defined as the difference between RON and MON of gasoline. While, methanol has the highest percentage of oxygen, its sensitivity is 30 when compared with ethanol, having a sensitivity of 15. Moreover, the percentage of oxygen and Reid vapor pressure (RVP) of ethanol was less than that of methanol. In this regard, ethanol has more advantages when comparing with sensitivity, % of O_2 content and RVP with those other fuels.

4. Economic, environmental issues and sustainable development

4.1 Economic aspects

Oil plays an important role in everyday life in terms of supplying goods or food, transportation sector and labor etc. Throughout the world, the oil deposits are located in limited number of countries, many of which struggled from political and economic instabilities. In addition, the trade between oil exporters and importers are increasingly tense and vulnerable. Therefore, alcohol fuel is one of the best alternatives replacing fossil fuels. The production of alternative fuel considerably cost less because of alcohol produced from the cost effective biomass, coal and natural gas. Consequently, the production of alcohol fuel spreads into a wider geographical area, contributing to an alcohol fuel supply that is less vulnerable to disruption. Alcohol fuel also offers an opportunity for a more dispersed and equitably distributed revenue stream [14]. Therefore, for those countries with more dependencies on fossil fuels, alcohol fuel can be a more vital substitute.

4.2 Environmental issues

Alcohol fuel shows a significant impact in diminishing the threat of global climate change. Mainly, the fossil fuels are used for the transportation sector, which may lead the exhaustion of air pollutants like nitrogen oxides (NO_x), hydrocarbons, particulate matter, carbon monoxide and carbon dioxide, etc. Those air pollutants are seriously responsible for climate change, greenhouse gas (GHG) emissions, global warming, ozone layer depletion and human health-related issues [19]. Thus, it is necessary to search alternatives for reducing the demand for fossil fuels and the associated transportation sector-related warming emissions for future generations. Alcohol fuel is one of the best alternative fuels in the transportation sector to reduce the dangerous exhaustion resources into the environment. Scientists have been investigated the effects of GHG emissions on the large amount of natural land that is being changed to cropland globally to support alcohol fuels development. The first time of these studies, conducted at the University of Minnesota, examined the carbon debt released by direct land use changes when pristine lands are clear for new crops aimed for alcohol fuel production.

4.3 Sustainable development

It is essential to ensure that there is no conflicts between the actions of each country planning's and sustainable development in both the short and long run. There are three pillars for sustainable development, i.e., social, economic, and environmental, and each policy must consider all three [20]. The term "Development" indicates that, the notion of a clean or healthy environment and priority in terms of social development, along with the satisfaction of economic needs and that the present generation must not, through the damage of ecological processes essential to life, endangers the capability of future generations to be at least as well as the current generation. Sustainable development meets the needs of the present without compromising the ability of future generations to meet their own needs. The concept of sustainable development emerged on the international level though since from three decades. Moreover, recently international debates have much more priority about sustainable development and energy [20].

Energy plays a crucial role in sustainable development and reduction of poverty. It has an impact on all development's dimensions—economic, social and environmental—along with livelihoods, productivity of agricultural and access to water, education and health. These days, the lasting increase of the world's population brings up serious concerns. The sufficient and reasonable energy provision plays an important role in improvement of economy, changing from agricultural economies to advanced industrial and service based societies. Also, energy is an essential for social and economic good developments and indispensable to most forms of industrial and commercial wealth generation.

Though, present energy supply and consumption depends on finite resources of fossil fuels, and are considered to be environmentally unsustainable. On the other hand, there is no any kind of energy production or conversion technology which is completely without risk or waste. Generally, the energy chain was started with resource extraction and ended with the rule of energy services, pollution, health related issues and harmful environmental impacts. However, at the point of usage of resources, a certain technology might not produce dangerous materials, but emissions and wastes are always associated with its manufacture and other stages of the life cycle. Therefore, the situation highlights the need for sustainable alcohol fuels, using feedstocks that reduce competition for major croplands.

These are forest, farm and municipal waste streams; energy crops grown on marginal lands, and algae. Moreover, the second generation alcohol fuels feedstock is expected significantly reduce GHG compared with first generation alcohol fuels like corn ethanol. The relation between alcohol fuel and sustainable development is shown in **Figure 4**. In all types of energies, burning of fossil fuels is chiefly responsible for air pollution, climate changes, local acidification, human health related problems [21]. Still, while accepting that the basic responsibility for sustainable energy policy rests with governments, a participating approach including all

Figure 4.
The cyclic representation of between alcohol fuel and sustainable development.

stakeholders is desirable to facilitate progress [20]. The fundamental principles guiding the approach to energy for sustainable development were summarized by the UN Economic and Social Council (UN ESC) society. The group of international communities can simplify the movement from the current energy system to a more sustainable development by supporting exchange of technology, capability building, and investments in developing countries [22]. The UN ESC summarized seven challenges that are given bellow:

1. Progress in the utilization of renewable energy sources.
2. Enhancement of the availability of energy.
3. Increment of energy efficiency.
4. Establish the more advance and sophisticated fossil-fuel technologies.
5. Expansion of nuclear energy technologies.
6. Development of the rural energy situation.
7. Decreasing the emissions in transportation and development of energy efficiency.

5. Conclusion

The production of alcohol fuel has gradually increased and become an important industry in various countries such as the United States, Brazil, and China. Methanol was produced from biomass or coal and natural gas while ethanol is mainly produced from food crops or sugarcane molasses by fermentation process. So that, rural area's sugarcane industry is one of the major industrial corridors, meanwhile the agriculture economy was increased and generates employment for more people by the collaborating with sugar industry either directly or indirectly.

After production of methanol or ethanol, it was blended with petrol/gasoline in different proportion like E10 considered as low-level ethanol blends and E85 considered as high-level ethanol blends. Day to day, the usage of alcohol fuels has been rapidly increased due to their positive impacts such as reducing GHG emissions, reduction in the emission of toxic gases, and helping to mitigate climate change. Likewise, it has an impact on sustainable development in economic, social and environmental aspects. Therefore, alcohol fuel can be used as best transportation fuel instead of gasoline, but it is still years far away from extensive adoption. More researches and improvements are necessary if we are to use alcohol as a fuel of the future.

Acknowledgements

The author gratefully acknowledges valuable suggestions given by Dr. Sreenivasulu Karlapudi, Post Doctoral Fellow, Xian Jiaotong University, Xian, Shanxi, P.R. China, in successful completion of this chapter.

Abbreviations

UNCED	United Nations on Environment and Development
IC	internal combustion engine
MeOH	methanol
RON	research octane number
MON	motor octane number
RVP	Reid vapor pressure
GHG	greenhouse gas
UN ESC	UN Economic and Social Council

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Section 2

Alcohol Fuels from Lignocellulosic Biomass

Chapter 3

Lignocellulosic Ethanol: Technology and Economics

Cheng Zhang

Abstract

The accelerated global warming calls for fast development of solutions to curb excessive Greenhouse gas emission. Like most of other forms of renewable energy, lignocellulosic ethanol can help the human beings mitigate the climate deterioration and gain independence from fossil fuels. This chapter gives a survey of bioethanol production in the U.S. and world, describes classifications of three generations of bioethanol, provides an overview of all the stages of currently adopted process for the second-generation bioethanol production, briefs on new development on enzymes for hydrolysis and fermentation and new processes for ethanol generation, summarizes on recent life-cycle assessments of greenhouse gas emission and techno-economic evaluation of ethanol production. To sustain the infant cellulosic ethanol industry, substantial improvement in the following areas need to happen in a timely manner: (1) Effective and low-cost biomass pretreatment method, (2) efficient fermentation of all sugars released during the pretreatment and hydrolysis steps, (3) development of enzymes that tolerate various inhibitors including monosaccharides (mainly glucose) and ethanol, and (4) heat-tolerant fermentation microbes and enzymes for efficient simultaneous saccharification and fermentation. Genetic engineering is expected to play a key role in addressing most of the issues in these areas.

Keywords: global warming, lignocellulosic biomass, second-generation bioethanol, saccharification, fermentation, life cycle analysis, techno-economic evaluation

1. Introduction

The need to slow down and eventually stop global warming has driven commercial production of the bioethanol in the past two decades because the use of renewable fuel is one of the few ways to mitigate climate change as it helps reduce GHG emissions. Multiple independently produced datasets confirm that between 1880 and 2012, the global average land and ocean surface temperature increased by 0.85 [0.65–1.06]°C [1]. Since 1979 the rate of warming has approximately doubled (0.13°C/decade, against 0.07°C/decade) [2, 3]. The scientific consensus as of 2013 stated in the intergovernmental panel on climate change (IPCC) Fifth Assessment Report is that it "is extremely likely that human influence has been the dominant cause of the observed warming since the mid-20th century." In 2018 the IPCC published a Special Report on Global Warming of 1.5°C which warned that, if the current rate of greenhouse gas (GHG) emissions is not mitigated, global warming is likely to reach 1.5°C between 2030 and 2052 causing major crises. The report said that preventing such crises will require a swift transformation of the global economy that has "no documented historic precedent" [4].

A mandate required developed countries to take the lead in reducing their emissions and was sustained in the Kyoto Protocol to the United Nations Framework Convention on Climate Change (UNFCCC), which entered into legal effect in 2005. In ratifying the Kyoto Protocol, most developed countries accepted legally binding commitments to limit their emissions. Biofuel mandates are set in more than 60 nations and incentives are provided by the governments to boost bioethanol production [5].

In the U.S., production, transportation and fermentation of the corn was adapted quickly by industry for fuel ethanol production, primarily because corn was the only crop that had the existing infrastructure to easily modify for this purpose, especially when initially incentivized with tax credits, subsidies and import tariffs. **Figure 1** shows total U.S. corn use from 1986 to 2018. The amount of corn used for ethanol production increased substantially between 2001 and 2010, as nearly all gasoline was transitioned to 10% ethanol. From 2013, the trend remains consistent with production and usage remaining relatively constant.

There is still some debate on whether biofuel production from food feedstock can truly reduce GHG emissions. The United Nations Intergovernmental Panel on Climate Change released two of its Working Group reports state that "Biofuels have direct, fuel-cycle GHG emissions that are typically 30–90% lower than those for gasoline or diesel fuels. However, since for some biofuels indirect emissions—including from land use change—can lead to greater total emissions than when using petroleum products, policy support needs to be considered on a case by case basis" (IPCC 2014 Chapter 8). The report lists many potential negative risks of ethanol production from food feedstock, such as direct conflicts between land for fuels and land for food, other land-use changes, water scarcity, loss of biodiversity and nitrogen pollution through the excessive use of fertilizers.

Also, the potential of using bioethanol from food feedstock to replace petroleum fuels is limited. The United States will use over 130 billion gallons of gasoline in 2014, and over 50 billion gallons of diesel. On average, one bushel of corn can be used to produce just 2.8 gallons of ethanol. If all of the production of corn in the U.S. were converted into ethanol, it would only displace 25% of that 130 billion.

On the other hand, there is less controversy over GHG reduction from production of lignocellulosic ethanol production as cellulosic materials are mostly the wastes of the agriculture and forest industry. The shift from food crop feedstocks to waste residues and native grasses offers significant opportunities for a range of players, from farmers to biotechnology firms, and from project developers to

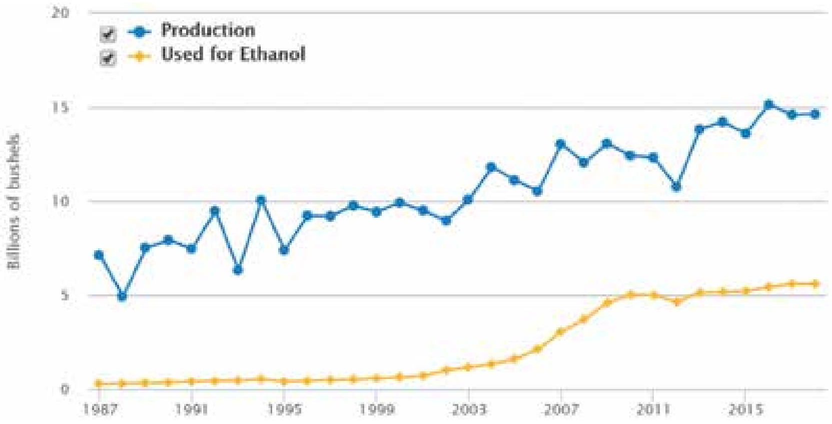

Figure 1.
The U.S. corn for fuel ethanol, feed, and other use. Source: the United States Department of Agriculture Economic Research Service Feed Grain Yearbook.

Company	Location	Feedstock	Capacity (mg year^{-1})	Status
Abengoa Bioenergy	Hugoton, KS	Wheat straw	25–30	2013–2016 Bankrupt [8]
BlueFire Ethanol	Fulton, MS	Multiple sources 19	20	Construction halted 2011 [9]
DuPont	Nevada, Iowa		30	Sold to Verbio in Nov. 2018 [10]
Mascoma	Kinross, MI	Wood waste	20	Construction halted in 2013 [11]
POET LLC	Emmetsburg, IA	Corn stover	20–25	Operational in Sep. 2014 [12]

Table 1.
The status of the U.S. commercial lignocellulosic ethanol facilities.

investors [6]. However, the process to convert lignocellulosic materials to ethanol is much more complex than that used to covert starch and sugars into ethanol.

Cellulosic ethanol industry is still in its infancy. In the U.S., as of 2013, the first commercial-scale plants to produce cellulosic biofuels have begun operating. In the following 5 years, cellulosic ethanol production grown from 0 to 10 million gallons [7], and most likely topping 15 million in 2018. However, that is far from the Renewable Fuel Standard's original target of 7 billion gallons of cellulosic biofuel by 2018 and 16 billion by 2022. Of all five commercial cellulosic ethanol plants that were built/to be built in the U.S. from 2010 to 2016, only POET's Emmetsburg, Iowa facility is still in operation in 2019 (**Table 1**). In 2017, the total cellulosic ethanol produced was less than half the nameplate capacity (25 million gallons year^{-1}) of this single plant [13].

The future of bioethanol generation from lignocellulosic materials is not clear at this point of time. The sustainability of this renewable fuel business will depend on the success of development of cost-cutting technologies for every stage of lignocellulosic ethanol production.

2. Ethanol generation from biomass

2.1 First-generation bioethanol

First-generation biofuel includes biodiesel produced from vegetable oils through transesterification and bioethanol generated from food feedstock, mainly starchy materials (e.g., corn, wheat, barley, cassava, potato) and sucrose-containing feedstock (e.g., sugarcane, sugar beet, sweet sorghum) [14]. First-generation bioethanol is produced from fermentation of these starchy and sucrose-containing materials in four basic steps: enzymatic saccharification or hydrolysis of starch into sugars, microbial (yeast) fermentation of sugars, distillation, and dehydration.

Figure 2 shows global ethanol production by country or region, from 2007 to 2017. Together, the U.S. and Brazil produce 85% of the world's ethanol. The vast majority of Brazil ethanol is produced from sugarcane.

The United States is the world's leading producer of ethanol, with nearly 16 billion gallons in 2017 alone, mainly produced from corn. The annual U.S. production of ethanol from 1981 to 2018 is shown in **Figure 3**.

2.2 Second generation bioethanol

Second and subsequent generations of biofuels including bioethanol are produced from non-food raw materials [16]. Second-generation bioethanol is typically produced

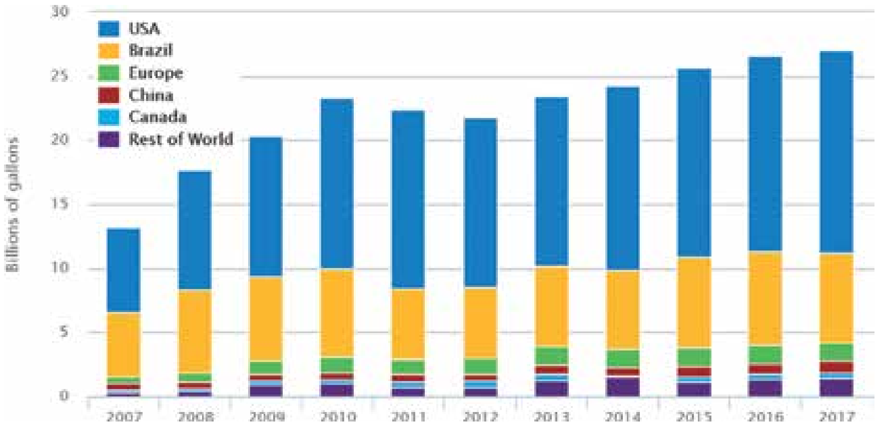

Figure 2.
Global ethanol production by country or region, from 2007 to 2017. Source: Renewable Fuels Association. Last updated October 2018.

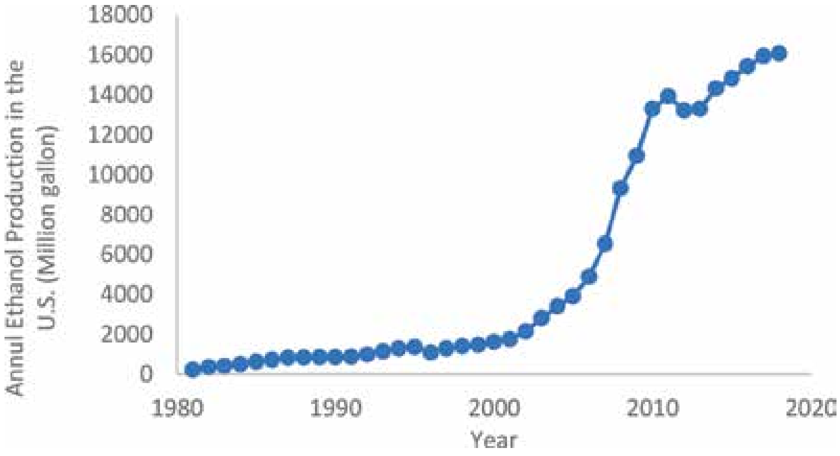

Figure 3.
The U.S. annual production of ethanol from 1981 to 2018 [15].

from sugars derived from lignocellulosic biomass. Various types of biomass have been studied for production of biofuels including agricultural wastes (e.g., corn stover, wheat straw, corn cob, rice husk, and sugar cane bagasse), energy crops which grow on low-quality soil (perennial grasses such as *Miscanthus sinensis* and *M. giganteus* and switchgrass), forest-based woody wastes (bark, sawdust, softwood trimmings and hardwood chips), waste from parks and gardens (leaves, grasses, and branches), municipal solid wastes such as food waste, kraft paper and paper sludge, the whey-a byproduct of the cheese industry, and crude glycerol from the biodiesel industry.

The amount of available lignocellulosic biomass far exceeds the amount of food feedstock that can be used for biofuel production. However, the production of lignocellulosic bioethanol requires feedstock preparation prior to fermentation and finding/developing microbes that are able to hydrolyze polysaccharides and ferment sugars from cellulose and hemicellulose breakdown.

2.3 Third generation bioethanol

The term third generation biofuel refers to biofuel derived from algae and has only recently enter the mainstream. Previously, algae were grouped with other non-food biomass types as feedstock for second generation biofuels. However, the uniqueness in algae's production methods and potential of much higher yields of biofuel production warrants its separation from other types of non-food biomass to form their own category.

When it comes to the potential to produce fuel, algae is unique in several ways. First, algae produce an oil that can easily be refined into diesel or even certain components of gasoline [17]. Second, it can be genetically manipulated to produce a wide list of fuels including biodiesel, butanol, gasoline, methane, ethanol, vegetable oil, and jet fuel [18]. Third, it is also capable of producing outstanding yields. In fact, algae have been used to produce up to 9000 gallons of biofuel per acre, which is 10-fold what the best traditional feedstock have been able to generate. Yields as high as 20,000 gallons per acre are believed to be attainable. According to the US Department of Energy, yields of 10-fold high mean that only 0.42% of the U.S. land area would be needed to generate enough biofuel to meet all the U.S. needs.

Algae do have a down side: they require large amounts of water, nitrogen and phosphorus to grow. So much that the production of fertilizer to meet the needs of algae used to produce biofuel would produce more greenhouse gas emissions than were saved by using algae-based biofuel. It also means the cost of algae-base biofuel is much higher than fuel from other sources. This single disadvantage means that the large-scale implementation of algae to produce biofuel will not occur for a long time, if at all. In fact, after investing more than $600 million USD into research and development of algae, Exxon Mobil came to the conclusion in 2013 that algae-based biofuels will not be viable for at least 25 years which was calculated on strictly economical term without considering the environmental impacts that have yet to be solved [19].

3. Overview of bioethanol generation from lignocellulosic biomass

3.1 Composition of lignocellulosic feedstock for bioethanol

Dry plant materials are mainly comprised of three types of biopolymers: cellulose, hemicellulose, and lignin. Cellulose and hemicellulose account for more than half of the entire dry biomass (see **Table 2**) [28]. Ethanol yield and conversion efficiency depend on the type of biomass, and benefit from a high content of cellulose and hemicellulose and low lignin content [29]. The domains of the three polymers in plant cell walls are connected strongly through covalent and hydrogen bonds. These bonds make lignocellulosic material resistant to degradation [30] and different methods of pretreatment [31].

Cellulose is a β-glucan linear polymer of 500–14,000 D-glucose units D-glucose linked by β-1,4-glycosidic bonds. Around 36 hydrogen-bonded glucan chains form insoluble microfibrils in secondary cell wall [32]. The cellulose structure is highly crystalline and thus is difficult to break in enzymatic hydrolysis [33]. High temperature (320°C) and pressure (25 MPa) are needed to melt and dissolve this rigid crystalline structure in water, in sharp contrast with the liquefaction temperature 95–105°C of starch at pH = 6.0–6.5, and the saccharification temperatures of 60–65°C at pH = 4.0–4.5 [34, 35].

Hemicellulose is a branched heteropolymer of different monosaccharides including pentoses (D-xylose and L-arabinose) and hexoses (D-mannose, D-galactose, D-glucose) and a small amount of sugar acids called uronic acids [36]. The D-pentose sugars are dominant with occasionally small amounts of L-sugars as well. Among pentoses, xylose is present in the largest amount, although in softwoods mannose can be the most abundant sugar. Typical sugar acids in the hemicellulose structure include D-glucuronic, 4-O-ethylglucuronic and D-galacturonic

Biomass	Cellulose %	Hemicellulose %	Lignin %
Corn stover	37.5	30	10.3 [20]
Corn cobs	33.6	37.2	19.3 [21]
Sugarcane bagasse	45	20	30 [22]
Grasses	25–40	35–50	10–30 [23]
Switchgrass	31.98	25.19	18.13 [24]
Wheat straw	35.9	23.9	19.3 [25]
Oat straw	39.4	27.1	20.7 [23]
Rice straw	44.3	35.5	20.4 [26]
Rice husk	34.4	29.3	19.2 [27]
Hardwood			
Black locust	41.61	17.66	26.70 [24]
Hybrid poplar	44.70	18.55	26.44 [24]
Eucalyptus	49.50	13.07	27.71 [24]
Hardwood stems	40–55	24–40	18–25 [23]
Softwood-pine	44.55	21.90	27.67 [24]
Nut shells	25–30	25–30	30–40 [23]
Newspaper	40–55	24–40	18–25 [23]

Table 2.
Biomass composition.

acids. Meaningful quantities of L-arabinose are contained in corn fiber and specific herbaceous crops [37].

C5 sugars such as xylose and arabinose are mostly found in xyloglucan, xylan, arabinan and arabinogalactan (substructures of pectin), which are components of polysaccharides in the plant cell wall [38]. Xylan is the largest hemicellulose component, consisted of β-1,4-linked xylose residues with side branches of α-arabinofuranose and α-glucuronic acids and contribute to cross-linking of cellulose microfibrils and lignin through ferulic acid residues [39].

Lignin is a natural three-dimensional polymer (600–15,000 kda) bio-synthesized from phenylpropanoid units via radical reactions [40]. Lignin accounts for 20–35 wt% in woody biomass (40–50 wt% in bark) and 10–20 wt% in agricultural stems [41]. In lignin, phenolic units are connected by more than eight different linkages, among them arylglycerol β-aryl ether (β-O-4) is the dominant linkage in both softwood and hardwood in most plants, consisting of ~50% of spruce linkages and 60% of birch and eucalyptus linkage [42]. It has long been recognized as the major renewable source of aromatic chemicals such as phenols and aromatic hydrocarbons.

Due to the complex polymer structure and heterogeneity in the ways monomeric units are linked, lignin is particularly difficult to biodegrade, making it an undesirable component in plant cell walls for bioethanol production. In plant cell wall, lignin functions like a glue to hold all components together [43]. As such, its recalcitrant character makes this three-dimensional polymer molecule a physical barrier to the enzymes that act on cellulose and hemicellulose.

In biorefinery, around 62 million tonnes of lignin is obtained in the commercial production of lignocellulosic ethanol. A large amount of lignin is also being generated in the pulp industry as lignin has also to be separated from cellulose for a different reason: the aromatic components in lignin can turn yellow as it is oxidized slowly in air. Despite that lignin has mainly been burned to supply heat and to generate electricity, it has long been recognized as the major renewable source of aromatic polymer and chemicals [44].

Due to the lower oxygen content in lignin as compared to that in cellulose, the energy value of lignin could be as high as cellulose despite of its lower weight percentage in lignocellulosic biomass. This has generated a lot of interest in converting lignin into liquid fuels using thermochemical and biological methods including pyrolysis, hydrothermal liquefaction, and enzymatic decomposition [45]. Among these methods, hydrothermal liquefaction has been more investigated recently and appears to be a promising way to decompose lignin into bio oil which could be further processed into liquid transportation fuels.

3.2 Biochemical conversion of biomass into ethanol

Second-generation bioethanol is produced using a process involving the four primary steps of (i) pre-treatment, (ii) hydrolysis to sugars, (iii) fermentation, and (iv) product/coproduct recovery [46]. During pre-treatment, the feedstock is subjected to physical (heat, steam) or chemical (acid or base) conditions that disrupt the fibrous matrix of the material, resulting in the separation of the hemicelluloses from the cellulose chains and the lignin that binds them together. Hydrolysis follows pre-treatment, releasing individual glucose from cellulose and hexose and pentose from hemicellulose. These monomers can then be fermented to ethanol by yeasts that have been modified to ferment both hexose and pentose sugars and adapted to deal with the inhibitors that are produced during pre-treatment and unavoidably associated with the hexose and pentose sugars [34]. Distillation and dehydration of the aqueous ethanol solution produces ethanol of 99.9% purity. Coproduct recovery will depend upon the feedstock and pre-treatment process used and can include a range of products such as extractives, lignin, and unhydrolyzed cellulose [47].

In the following three sections (Sections 4–7), each of the four primary steps will be reviewed. Current topics of research, which are concentrated on recombinant fermentative microbes development and a consolidated process of hydrolysis and co-fermentation of hexoses and pentoses, will be covered in Section 8. A review on cost analysis is given in Section 9 to present opportunities for cost reduction for second-generation bioethanol production.

4. Pretreatment of lignocellulosic biomass

4.1 Objectives of pretreatment and basic methods

Without pretreatment before the enzymatic saccharification stage, the non-biodegradable lignin in lignocellulosic material presents as a major obstacle to the enzymatic hydrolysis of crystalline cellulose and hemicellulose which themselves already have low digestibility [48]. Pretreatment removes or decomposes the lignin (delignification) [49] and thus makes cellulose and hemicellulose more readily available to cellulases and hemicellulose's.

In principle, there are three methods for pretreatment: biological, chemical and physical processes. Some processes, where chemical and physical actions are inherently inseparable, are termed physiochemical. Two or all of these basic methods can be used in combination to gain benefits from each method. Various pretreatment methods have been described and compared critically in a recent review [50].

Biological treatment uses microorganisms such as white, brown or soft rot fungi which break up the structure of lignin via the action of extracellular lignolytic enzymes released by the fungi [51]. Further research is needed to overcome the issues of selectivity, cost, retention time and effectiveness to make it a practical choice [50].

Chemical treatments include treatment with bases, diluted acids, and oxygen as an oxidizer. These reagents react with lignin and cause the polymer to breakdown into smaller and more soluble fragments. Physical pretreatment is usually performed before chemical or biological treatment to reduces cell wall crystallinity and particle size by physical milling or grinding [50]. In some treatment methods, both physical action and chemical reaction play important roles in lignin removal. Such physico-chemical pretreatment can involve steam explosion, liquid hot water, ammonia fiber explosion, ammonia recycle percolation or a supercritical carbon dioxide.

Pretreatment contributes a vital role in the cost evaluation process of whole technology, because they contribute about 30–35% of overall production cost [52]. There are many issues that arise from this process [50] including loss of sugars (mainly pentose sugars derived from hemicellulose degradation), and generation of toxic substances that inhibits the downstream fermentation process. Both need to be minimized to make ethanol production more efficient.

4.2 Steam explosion

Steam explosion has become one of the most adopted pretreatment processes, where hydrolysis of hemicellulose also happens which improves cellulose digestibility. It is a physiochemical method that uses both physical changes caused by sudden pressure reduction and heat- and catalyst-induced chemical changes. An impregnation agent is sometimes used before the pretreatment step. Upon steam explosion after 1–5 min soaking in 160–270°C and 20–50 bar steam, fibers loose up and sugar polymers (mainly hemicellulose) partially degrade into sugars via hydrolysis of glycoside bonds in polysaccharides and lignin into soluble fragments including some inhibitors and phenolic products [50]. The process allows for subsequent solubilization of hemicellulose in water and lignin in organic or alkaline solvent. Cellulose undergoes some degree of polymerization but is still insoluble in water or organic solvents and remains in the solid phase. Acid (sulfuric acid and sulfur dioxide) impregnation before steam explosion reduce the time and temperature necessary for proper depolymerization of the feedstock, increases the efficiency of enzymatic hydrolysis of polysaccharides to glucose and xylose and reduce enzyme consumption [53]. Compared to other methods of biomass fractionation, steam explosion uses less dangerous chemicals, less demanding on investment and energy consumption [54]. Steam explosion is not recommended for agricultural and hardwood wastes with high contents of pentoses and low levels of lignin, due to the susceptibility of pentoses to thermal degradation. Steam explosion is recommended for processing straw and bagasse.

4.3 Inhibitors generated in pretreatment

One of the lasting issues in the second-generation bioethanol production is the formation of inhibitors during the pretreatment. The inhibitors create unfriendly environments for fermentative microbes, increases the length of lag phase, causes loss of cell density and lower growth rates of fermenting microbes, and consequently decreases ethanol yields [55]. The commonly observed inhibitors are aldehydes such as 5-hydroxymethyl-2-furaldehyde and 2-furaldehyde (furfural), weak organic acids (formic, acetic and levulinic acids) and phenolic compounds [56]. Acetic acid is the major organic acid found in hydrolysates coming from the hydrolysis of acetyl side-chain groups in hemicellulose [57]. Cell growth of fermentative microbes is inhibited by the intracellular process of anions of weak acids. Furan aldehydes are poisonous for microbes and phenolic compounds interfere with the function and integrity of cell membranes [58].

There are several methods used for the removal of inhibitors [59]. The detoxification of lignocellulosic hydrolysates can be performed using inhibitor sorbents such as excess of lime, active carbon or lignite (brown coal).

5. Enzymatic hydrolysis of polysaccharides

After pretreatment to partially remove lignin and loose up polysaccharide structures, polysaccharides need to be hydrolyzed into sugar molecules which will be converted into ethanol by fermentation [38]. The hydrolysis can be accomplished chemically via acid-catalyzed cleavage of glycosidic bonds or by enzymes produced by microbes. Enzymatic method is more popular due to less impact on the environment and higher selectivity in the hydrolysis. Glucose and xylose are the main products in hydrolysates from the enzymatic breakdown of polysaccharides.

Enzymes produced by the filamentous fungi such as *Aspergillus nidulans*, *Aspergillus niger*, *Penicillium* spp. and *Trichoderma reesei* are dominant in commercial biorefinery [38]. Among different types of cellulases, endoglucanases attack the internal glycosidic bonds in the amorphous cellulose regions, causing fragmentation of the cellulose structure, and exoglucanase works of the termini of β-glucan molecules to release glucose molecules one at a time, while β-glucosidase attacks catalyzes the hydrolysis of the glycosidic bonds to terminal non-reducing residues in beta-D-glucosides and oligosaccharides to release one or two glucose units at a time [60]. The costs of cellulases are high, spurring the development of methods to recycle hydrolysis enzymes [61]. Inclusion of hemicellulose's, such as endoxylanases, xylosidases, exoxylanases and other accessory enzymes, such as esterase's and arabinosidase's, in the hydrolysis step improves the efficiency of enzymatic hydrolysis of lignocellulosic biomass and helps reduce enzyme loading and costs [62].

Various strains of yeasts and bacteria are being investigated with the goal of developing a consolidated process of hydrolysis and co-fermentation of glucose and xylose, without the need for adding exogenous cellulases [63].

6. Fermentation of lignocellulosic hydrolysates

Sugars in the hydrolysate are converted into ethanol by fermentation using microorganisms such as yeasts. Ethanol-producing ability of yeasts depends on lignocellulosic hydrolysate, their strain and fermentation conditions (temperature, pH, aeration and nutrient supplementation). For use in industrial bioethanol production, microorganisms (mainly yeasts) must show thermotolerance and high fermentative activity for simple carbohydrates such as glucose and xylose. They should also be resistant to environmental stressors, including inhibitors mentioned in Section 4.3, acidic pH, high sugar level at the beginning of fermentation (causing hyperosmotic stress), and higher temperatures which prevents microbiological contamination, and are able to grow on various lignocellulosic substrates at a fast growth rate [58, 64].

Saccharomyces cerevisiae JRC6 and *Candida tropicalis* JRC1 are recommended for hydrolysates after alkali pretreatment and acid pretreatment, respectively [41]. *Saccharomyces* sp. yeasts are used in biorefineries to ferment glucose released during starch hydrolysis. Apart from glucose, they are capable of fermenting galactose and mannose.

Zymomonas mobilis is a Gram negative, facultative anaerobic, non-sporulating, polarly-flagellated, rod-shaped bacterium. It has notable bioethanol-producing capabilities, which surpass yeast in some respects. However, it only ferments glucose, fructose and sucrose [65]. This prevents them from being used in industrial production of bioethanol. The *Z. mobilis* strains are tolerant to ethanol concentration up to 120 g/L, and have low nutritional requirements for growth [58]. However, its tolerance to acetic acid is low: as little as 2.5 g/L of HOAc. Its recombinant strain AX101 also has low tolerance to acetic acid.

7. Distillation and dehydration (drying) of bioethanol

After fermentation, the mash is heated so that the ethanol evaporates. This process, known as distillation, separates the ethanol, but its purity is limited to 95–96% due to the formation of a water-ethanol azeotrope with maximum 96.5% v/v) ethanol. This hydrous ethanol can be used as a fuel alone, but is not miscible in all ratios with gasoline, so the water fraction is typically removed before ethanol is added to gasoline.

Water can be removed by passing hydrous ethanol vapor through a bed of molecular sieve beads. The bead's pores are sized to allow adsorption of water while excluding ethanol. Two beds are often used so that one is available to adsorb water while the other is being regenerated. This dehydration technology can save 3000 BTUs/gallon over the azeotropic distillation and has been adopted by most modern ethanol plants.

Recent research has demonstrated that complete dehydration prior to blending with gasoline is unnecessary. When the azeotropic mixture is blended directly with gasoline, water separates from the gasoline/ethanol phase and can be removed in a two-stage counter-current setup of mixer-settler tanks with minimal energy consumption [66].

8. LCA on GHG emissions and techno-economic evaluation of lignocellulosic ethanol production

Numerous life cycle analyses (LCAs) of lignocellulosic ethanol have been published over the last 15 years and several reviews of these LCA studies have been completed and are cited in a more recent review [67]. These studies show a clear reduction in GHG emissions for lignocellulosic ethanol compared to gasoline. However, accurate quantification of GHG emission reduction is hard to obtain as gaps remain in understanding life cycle performance due to insufficient data, and model and methodological issues. Critical unresolved issues that are expected to impact its energy/GHG emissions performance include feedstock-related emissions, consequential versus attributional life cycle aspects, choice of system boundaries, and allocation methods.

Decisions regarding feedstock, process technology and co-products can significantly impact GHG emissions calculations. Predicted life cycle GHG emissions vary widely depending on how the following key parameters are considered: nitrogen-related emissions due to supplemental fertilizer requirements and the N content of feedstock, cellulase requirements, farming energy, ethanol yield, and how the value of co-products such as lignin are realized, among others.

Government support (i.e., Ethanol mandate, tax credit, etc.) is not expected to last forever. To be sustainable, lignocellulosic biofuels production must meet or exceed the economic performance of their first-generation counterparts.

The growth in the capacity of commercial lignocellulosic ethanol production has been slow in the past decade, despite significantly better predicted performance on various environmental and energy security criteria than corn-based ethanol in the various techno-economic evaluations published before 2010 [68]. The slow growth has been due to both large technological risk, large capital cost, and the poor predicted economic performance of biorefineries in the short term.

An LCA of US softwood cellulosic ethanol was reported in 2012 by Stephen et al. [68]. In the paper, the base case (capacity: 50 mL ethanol year^{-1}) softwood ethanol production cost was compared with costs of ethanol produced from corn and sugarcane found in the literature. Softwood lignocellulosic ethanol was predicted to have a production cost of \$0.90 L^{-1}, 250–300% higher than US corn and Brazilian sugarcane ethanol production costs, which were in the range of \$0.30–\$0.40 L^{-1}. The lignocellulosic base case scale of 50 mL year^{-1}, compared to 150 mL year^{-1} of US corn and 365 mL year^{-1} of and Brazilian sugarcane, is much smaller as it was chosen based both on the projects funded under the US Department of Energy's commercial biorefinery program and those operating in other places such as Denmark. Production costs of sugar- or starch-based ethanol are expected to continue to decline to \$0.22–\$0.25 L^{-1} by 2020. Thus, second-generation ethanol is not going to catch up with first-generation ethanol on production cost soon.

Another very recent techno-economic evaluation was performed on production cost of ethanol produced from corn stover using either biochemical or thermochemical methods. For heat integrated biochemical route, the predicted bioethanol product costs at \$2.00 for a production capacity of 43,300,000 gallon year^{-1} [69]. This result was clearly an underestimation of lignocellulosic ethanol as a major cost item, capital investment cost, was not included. Furthermore, the corn stover price of 46.8 \$/ton was an underestimation, and feedstock transportation cost was not included in LCA. Feedstock cost can impact total cost by 40 percent according to a Lux Research report of 2016 [70]. The Brazilian birefinery company Raizen has the lowest projected minimum ethanol selling price of \$2.17 per gallon while Abengoa's capital-intensive \$500 million Hugoton facility has the highest price of \$4.55 with feedstock cost emerging as the most critical variable. The low cost of Raizen's cellulosic ethanol is largely attributed to its access to low cost sugarcane straw and sugarcane bagasse (\$40 and \$38 per dry metric ton), respectively, compared with corn stover (\$90) used by Abengoa and POET-DSM and wheat straw (\$75) used by Beta Renewables [71].

9. Opportunities for cost reduction

It is apparent that second-generation ethanol is currently much more costly to produce than first-generation ethanol. It is hard to predict when the cost of lignocellulosic ethanol will be reduced to the level of corn/sugar cane ethanol. Dramatic reductions in the capital and operational costs must occur before the potential superior environmental benefits from cellulosic ethanol relative to corn ethanol can be realized. Pretreatment, enzymatic hydrolysis and distillation are responsible for much of the cost of producing bioethanol. Currently, intensive research is being conducted to improve each of the processes to make them more economical.

9.1 Pretreatment

An effective pretreatment increases specific surface area of biomass, making cellulose better available for the action of hydrolytic enzymes obtained from fungi and bacteria, minimizing reductions in enzyme activity, and thus improving the rate of biomass hydrolysis and providing the highest possible concentration of fermentable sugars. Effective pretreatment also reduces the degradation of monosugars [72]. In selecting pretreatment methods, factors such as their environmental impact and recycling of chemical compounds (for example ammonia in the ammonia fiber explosion process [73, 74]) must be considered. Different pretreatment methods and their combinations are being explored for different types of biomass [50].

Better results, e.g., improved ethanol yield, have been obtained from combination of two or more pretreatment methods, but have resulted often at the cost of more energy consumption compared to single method of pretreatment. Among single treatment methods, dilute acid pretreatment is more suitable for various types of biomass as it solubilizes most of hemicellulose and partially remove lignin [50].

It is vital to analyze the pros and cons of each pretreatment technology before scaling up for industrial application. However, technoeconomic assessment will only give a rough estimate on capital cost and the final fuel cost in commercial scale production when many research findings are still in pilot scale level and demonstration plant level [52].

9.2 Pentose fermentation

Efficient fermentation of pentoses helps reduce ethanol production cost since pentoses can be 25.8 wt% as in sugarcane bagasse [75, 76] 22.3–74.9 wt% in corn stover (**Table 3**). Wild microorganisms are incapable of producing ethanol in high yields, as they are unable to utilize both pentoses and hexoses. Pentose-specific transporter proteins and enzymatic reactions determining the metabolism of pentoses such as L-arabinose and D-xylose have not been found in naturally occurring baker's yeast.

Owing to large microbial biodiversity, fermentation of pentoses can be achieved either by finding a potent naturally occurring pentose utilizing microorganism or by a genetically engineered C5 utilizing strain [78, 79]. One effective strategy is to create recombinant strain with genes for xylose metabolism [80]. Genetic engineering has been conducted mainly on *Saccharomyces cerevisiae* yeast, [81] the Gram-positive bacteria *Clostridium cellulolyticum* and *Lactobacillus casei* and the Gram-negative bacteria *Zymomonas mobilis*, *Escherichia coli* and *Klebsiella oxytoca* [43]. Recombinant yeasts consume xylose much slower than glucose, thus requiring prolonged fermentation time due to a lack of reaction intermediates and efficient pentose transporters [82].

A common problem of xylose-fermenting strains is the production of xylitol or the reabsorption of ethanol, which lead to low ethanol yield. One grand challenge is glucose repression, which results in di-auxic fermentation of a mixture of glucose and pentoses since glucose prevents the catabolism and/or utilization of other non-glucose sugars, leading reduced volumetric ethanol yield [83]. Approaches and conditions sought to improve glucose and xylose fermentation to ethanol are reviewed in a recent paper with emphasis on microbial systems used to maximize biomass resource efficiency, ethanol yield, and productivity [64].

9.3 Simultaneous saccharification and fermentation (SSF)

Separate processes have been established for enzymatic hydrolysis of cellulose and hemicellulose and fermentation (SHF) of sugars in hydrolysate. In the SHF processes, saccharification and fermentation take place in separate vessels, so the two processes can be optimized separately. One drawback of SHF is that accumulation of simple carbohydrates (such as cellobiose) causes end-product inhibition of hydrolytic enzymes, for example cellulases or cellobioses. To prevent end-product inhibition, extra doses of β-glucosidase are needed together with the commercial cellulase preparations [84].

Biomass	Lignin	Hexoses			Pentoses		Carbohydrate
		Glucan	**Mannan**	**Galactan**	**Xylan**	**Arabinan**	
Corn stover	18.2	30.6	0.5	0.7	16.0	1.9	49.7 [76]
	20.2	38.1	0.4	0.7	20.3	2.0	61.5 [76]
	17.2	36.1	N/A	2.5	21.4	3.5	65.3 [77]
Corn leaf	N/A	34.2	1.8	2.5	22.1	3.5	64.1 [68]
Corn stalk	N/A	36.5	1.7	2.4	21.6	3.2	65.4 [68]
Corn fiber	6.9	36.5	N/A	2.9	18.4	13.3	71.1 [77]
DDG	3.1	22.0	N/A	0.3	9.5	5.5	37.3 [77]
Wheat straw	14.5	36.6	0.8	2.4	19.2	2.4	61.4 [77]
	16.9	32.6	0.3	0.8	19.2	2.4	55.3 [76]
Switchgrass	23.2	32.2	0.4	0.0	20.3	3.7	56.6 [77]
	23.1	35.9	0.4	0.5	19.6	1.5	57.9 [76]
	27.6	31.9	0.3	0.3	10.6	1.1	44.2 [76]
	24.1	42.6	0.3	0.5	23.1	1.5	68.0 [76]
S. bagasse	18.4	38.1	0.4	0.0	23.3	2.5	65.0 [77]
Softwood							
Spruce	28.3	43.2	11.5	2.7	5.7	1.4	64.5 [76]
Red pine	29.0	42.0	7.4	1.8	9.3	2.4	62.9 [76]
Lodgepole pine	27.9	42.5	11.6	2.1	5.5	1.6	63.3 [76]
Ponderosa pine	26.9	41.7	10.8	3.9	6.3	1.8	64.5 [76]
Loblolly pine	28.0	45.0	11.0	2.3	6.8	1.7	66.8 [76]
Douglas-fir	32.0	44.0	11.0	4.7	2.8	2.7	65.2 [76]
Hardwood							
Red maple	24.0	46.0	2.4	0.6	19.0	0.5	68.5 [76]
Aspen	23.0	45.9	1.2	0.0	16.7	0.0	63.8 [76]
Yellow poplar	23.3	42.1	2.4	1.0	15.1	0.5	61.1 [76]
Poplar	N/A	39.8	2.4	0.0	14.8	1.2	58.2 [77]
Poplar stem	N/A	40.3	3.1	0.7	17.6	0.6	62.3 [68]
Poplar DN34	23.9	43.7	2.9	0.6	17.4	0.6	65.2 [76]
Euclyptus saligna	26.9	48.1	1.3	0.7	10.4	0.3	60.8 [76]
Salix	26.4	41.4	3.2	2.3	15.0	1.2	63.1 [76]

S. bagasse = sugarcane bagasse.

Table 3.
Hexose, pentose and lignin contents in different types of biomass.

There is a strong incentive to develop a process to perform simultaneous saccharification and fermentation (SSF) as it reduces investment costs by reducing the number of vessels and has the potential to become the preferred approach. In SSF, the problem of end-product feedback inhibition is largely eliminated because glucose molecules are fermented immediately by the fermentative microbes as it is produced from hydrolysis of cellulose [85]. However, the benefits come with a major downside which is an inherent mismatch between the optimal temperatures for the enzymes (fungal cellulases and hemicellulose's) on the one hand, and yeast biocatalysts on the other. The temperature optima for saccharifying enzymes (50–55°C for cellulase) are higher than those for fermenting mesophilic culture.

The optimal temperature for yeasts is below 35°C. Mesophilic yeasts (that thrive best in a moderate temperature) exhibit slower growth rates at higher temperatures. Currently, SSF must run at temperatures between the optimum temperature for cellulase and the optimum temperature for fermentative organisms. The compromise results in higher cellulase loading and an increase in enzyme costs. Efficient bioethanol production by SSF requires the use of thermotolerant ethanologenic yeast. It is a hot topic for research to genetically modify microorganisms with the ability to ferment at higher temperatures [43]. Some isolated yeasts, including *Pichia*, *Candida*, *Saccharomyces* and *Wickerhamomyces*, are found to grow at temperatures of 40°C and ferment sugars at higher temperatures [41]. To make SSF process highly efficient in ethanol production, the pentose metabolic pathway is been engineered into microorganisms to enables the use of C5 sugars by microbes that do not ferment them earlier [86].

Reduction in enzyme cost is been sought by searching for new organisms with cellulolytic and hemicellulytic activities [87], lowering the enzyme dosage through protein engineering [86, 88], and improving cellulase thermostability for performing hydrolysis at elevated temperatures to increase the efficiency of cellulose hydrolysis [89]. Cellulase enzyme cost reductions are challenging as cellulase costs need to be significantly lower than those of amylase enzymes on a unit-of-protein basis. The high price of the enzymes encouraged research into solutions to the problem of glucose inhibition and to the deactivation caused by lignin by-products [90].

Further integration of enzyme production with SSF leads to a new technology of consolidated bioprocessing (CBP). One area of research is aimed at engineering all three capabilities (saccharification, hexose fermentation and pentose fermentation) into a single strain for the CBP process [91, 92]. Cellulase-encoding genes may be introduced into specific species during recombination [63] to eliminate the need for exogenous cellulases in the process of SSF and decrease the capital costs of processing. CBP technology promises to eliminate costs associated with enzyme production and additional infrastructure/vessels [93].

9.4 Other opportunities for cost reduction

Working with a high dry matter (DM) concentration is also potentially an effective way to reduce the hydrolytic enzyme costs. However, high DM content causes an increase in viscosity, inadequate mass and heat transfer within the bioreactor, and, consequently, a strong reduction in the conversion of cellulose/hemicellulose to fermentable sugars. This problem could be overcome by adopting various fed-batch strategies or coprocessing substrates with different degrees of porosity [94].

A variation of SSF, simultaneous saccharification and co-fermentation (SSCF), in which a starch material is co-fermented, has been adopted to address low ethanol concentration issue in lignocellulosic ethanol production. SSCF can reduce ethanol production cost by increasing ethanol concentration and thus reducing distillation cost [95].

Recycling yeasts and enzymes is also an effective way to reduce the cost of ethanol production. The remaining unhydrolyzed solids with some enzymes adsorbed are collected by filtration or centrifuge and are recycled to the next cycle for further hydrolysis. In one study, the enzyme loading was reduced from 36 to 22.3 and 25.8 mg protein per gram glucan, respectively, for separate hydrolysis and fermentation (SHF) and for SSCF on AFEX™ pretreated corn stover [96]. Enzyme adsorption to the residual solids is probably inhibited at high sugar concentrations in the fast SHF process [97] and hence affected enzyme recycling. The fast SSCF process removed most of the sugars by fermentation but produced ethanol whose effect on enzyme adsorption is unclear.

10. Conclusion

Cost effect renewable fuel generation from lignocellulosic materials is one of the few options the human beings have to slow down/eliminate global warming and achieve energy independence from fossil fuels. Second generation bioethanol is a promising path in the roadmap to the future world of renewable energy. The cellulosic ethanol industry is still in its infancy and its survival is relying on heavy policy support. Major technological advances at every stage of the cellulosic ethanol production are critically needed to lower the ethanol production cost to a level comparable to the corn ethanol. The key problems that remain to be solved include: (1) Effective and low-cost biomass pretreatment method that exposes polysaccharides to enzymes for efficient saccharification, (2) efficient fermentation of all sugars (pentoses and hexoses) released during the pretreatment and hydrolysis steps into ethanol, (3) development of enzymes that tolerate various inhibitors including monosaccharides (mainly glucose), and ethanol accumulation, and (4) heat-tolerant fermentation microbes and enzymes for efficient simultaneous saccharification and fermentation.

Acknowledgements

The support of the South Dakota NSF EPSCoR Program (Grant No. IIA-1330842) is greatly appreciated.

Conflict of interest

There is no conflict of interest involved in this work.

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Chapter 4

Bioethanol Production from Lignocellulosic Biomass

Thi Tuong An Tran, Thi Kim Phung Le, Thanh Phong Mai and Dinh Quan Nguyen

Abstract

An overview of the basic technology to produce bioethanol from lignocellulosic biomass is presented in this context. The conventional process includes two main steps. First, lignocellulose must be pretreated in order to remove lignin and enhance the penetration of hydrolysis agents without chemically destruction of cellulose and hemicellulose. Second, the pretreated material is converted to bioethanol by hydrolysis and fermentation. Some typical published studies and popular processing methods in attempts to improve the biomass conversion to bioethanol and increase the cost-effectiveness are also introduced briefly. Herein, the refinery of the resulted raw bioethanol mixture to obtain higher concentrated solution is not regarded.

Keywords: bioethanol, lignocellulose, pretreatment, hydrolysis, fermentation

1. Background

For thousands of years in the human being history, production of alcohol from natural and agricultural products with high starch or sugar contents, such as fruits, grains, sugarcane, or corn, has been well known. Microorganisms are cultivated in these carbohydrate materials to convert sugars and starches to ethanol through metabolism. Since these polysaccharides are polymers of monosaccharides, also known as single sugars, such as glucose, fructose, xylose, etc., they can be first enzymatically hydrolyzed and then fermented to ethanol by the microorganisms. Through such bioprocesses, alcoholic mixtures are obtained [1].

Nowadays, biofuels attract intensive interests from over the world due to its environmental friendliness. Biofuels are renewable as a neutral carbon source, which does not break the balance in atmosphere's air contents leading to global warming. Biofuels are among the most feasible ways to free the human being from dependence on traditional fossil resources [2].

In the last 20 years, the crude oil crisis causes an increasingly high demand of renewable energy, especially biofuels. America and Brazil are the two leading countries in producing bioethanol from sugarcane and corn. A report in 2009 claimed that Brazil produced annually 12.5 billion liters of bioethanol from sugarcane as fuels for the industry, while America also produced 5 billion liters of bioethanol from corn with establishing 111 gas stations selling E85 gasoline (a gasoline mixture composed of 85 vol.% as bioethanol) [3]. However, the production of biofuels from starches and sugars vigorously violates against the world's food security for humanity.

	Starch	Cellulose	Glycogen
Existence in the nature	Popularly found in plants as carbohydrate storage	The main component of cell wall of plants	Found in fungi and animals as their energy sources
Monomer unit	Alpha glucose	Beta glucose	Alpha glucose
Chemical structure of the polymer	1,4-Glycosidic bonds in amylose; 1,4- and 1,6-glycosidic bond in amylopectin	1,4-Glycosidic bonds	1,4- and 1,6-Glycosidic bond
Molecular morphology	Amylose as unbranched, coiled chain; amylopectin as long branched chain, partially coiled	Straight, long, unbranched chain with H bonds among adjacent chains	Short, many branched chains, partially coiled
Average molecular weight	Variable	162.14 g/mol	666.6 g/mol

Table 1.
A comparison of starch vs. cellulose and glycogen.

In an attempt to find an alternative approaches to bioethanol production, lignocellulosic biomass raises an intensive attention as cellulose is similar to starch and sugar because it is also a polymer of glucose. A comparison between three popular polysaccharides, starch, cellulose, and glycogen, is presented in **Table 1**; the most difference between cellulose and starch is their glycosidic linkages and the complex form of cellulose in plants, where it strongly incorporates with lignin and hemicellulose. In contrast, lignocellulose is the most abundant biomass in the world, which can be found as leaves, peels, bodies, branches, etc. of almost all the existing plants. Therefore, lignocellulosic bioethanol production is definitely a strategy of energy supply, especially suitable for countries with agricultural and forestry wastes to be utilized as the input materials.

2. Lignocellulose

Cellulose and hemicellulose, like starch, are made up of sugars. However, most of the cellulose in the nature is in the form of lignocellulose. Lignocellulose is a complex structure of natural materials found in plants. It represents the most abundant source of renewable organic matter on the earth. Cheap lignocellulosic biomass resources can be forestry, agricultural, and agro-industrial wastes. A variety of such materials can be mentioned here including sawdust, poplar trees, sugarcane bagasse, brewer's residue, grasses and straws, stems, leaves, husks, shells, and peels from grains, corn, sorghum, and barley. In contrast to a desire of utilizing these materials to produce valuable products, lignocellulose wastes are still accumulated every year in large quantities, causing environmental problems [3].

Lignocellulose consists of cellulose, hemicellulose, and lignin and always exists beside other extracts and mineral traces. The general composition of lignocellulose is presented in **Table 2**. In lignocellulose, cellulose fiber strands are formed by cellulose linking to each other via hydrogen bonding. The cellulose structure within the polymer is not homogenous. Crystalline regions are where cellulose nano-fibrils are organized in order and compact, while amorphous regions are disordered and easier to be hydrolyzed [1]. Cellulose fibers are like skeletons surrounded by hemicellulose and lignin (**Figure 1**). This structure naturally protects the polysaccharides from hydrolysis by enzymes and chemicals, thus raising a difficulty in both chemical and bioconversion of lignocellulose to other products, i.e., ethanol.

In lignocellulose, besides cellulose, hemicellulose is also a noticeable polysaccharide. Hemicellulose is a linear and branched heterogeneous polymer typically made up of five different sugars—L-arabinose, D-galactose, D-glucose, D-mannose, and D-xylose. The backbone of the chains of hemicelluloses can be either a homopolymer or a heteropolymer (mixture of different sugars). Hemicelluloses differ from cellulose not only by the different sugar units but also by their molecular morphology of being amorphous, where shorter chains are branching from the main chain molecules. As a result of this chemical characteristic, hemicellulose is easier to be hydrolyzed than cellulose [3].

Coating the fibrils and playing the role as an adhesive bunching the fibers in lignocellulose, lignins are high-molecular-weight, hydrophobic heteropolymer with complex and variable structures. Lignins are composed of phenylpropanoid alcohols, mainly coniferyl, sinapyl, and coumaryl alcohols with hydroxyl, methoxyl, and carbonyl functional groups (**Figure 2**). The ratio of these three monomers in lignins varies between angiosperms and gymnosperms and

Raw material	Lignin (wt.%)	Cellulose (wt.%)	Hemicellulose (wt.%)
Hardwoods	18–25	45–55	24–40
Softwoods	25–35	45–50	25–35
Grasses	10–30	25–40	25–50

Table 2.
Typical chemical compositions of lignocellulosic biomass [4, 5].

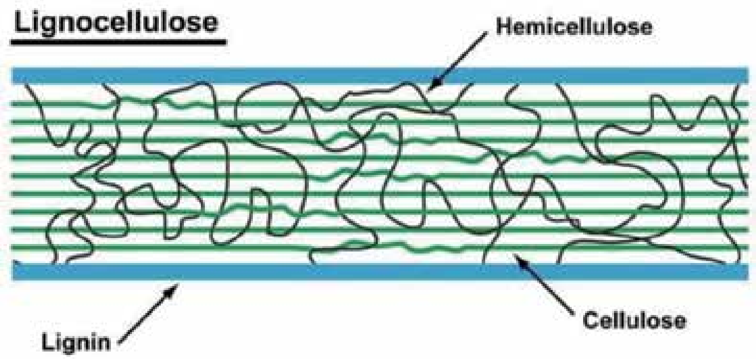

Figure 1.
Lignocellulose and its components (Image: USDA Agricultural Research Service).

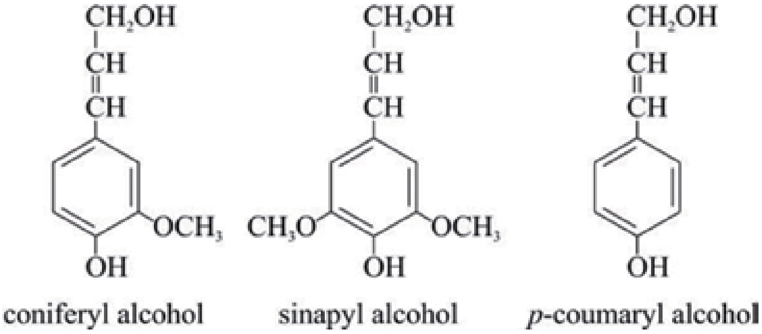

Figure 2.
The typical aromatic alcohols as monomers of lignins.

between different plants. Lignins play a role as cross-linking cellulose and hemicellulose in the matrix. Lignins can be dissolved in acidic and alkaline solutions with the solubility depending on their precursors. These properties of lignins make the lignocellulose structure more robust and hard in nature, resisting hydrolysis agents. Therefore, pretreatment to remove lignins from lignocellulose and enhance the penetration of hydrolysis agents is a vital step in the process of converting biomass to bioethanol [2].

3. Conventional process of converting lignocellulose to bioethanol

For a general chemical expression of converting natural glucose-based carbohydrates to bioethanol, it can be expressed as the following:

$$(C_6H_{10}O_5)_n + n\,H_2O \rightarrow n\,C_6H_{12}O_6 \rightarrow 2n\,C2H_5OH + 2n\,CO_2$$

The input materials can be fruit juices, brewery residues, soya residue, peanut residue, rice, wheat, and especially lignocellulose types like straw, woods, grasses, etc. **Figure 3** presents a conventional flowchart of the process.

As mentioned above, pretreatment is a vital step followed by hydrolysis and fermentation of the pretreated lignocellulose. To hydrolyze lignocellulose, in principles, enzymes and chemicals can be employed. However, in this chapter, only enzymatic hydrolysis is the mean due to its feasibility, while the other leads to solutions with high concentration of chemicals (acid, alkaline, or salt), which is not friendly to the growth of fermentation microorganisms.

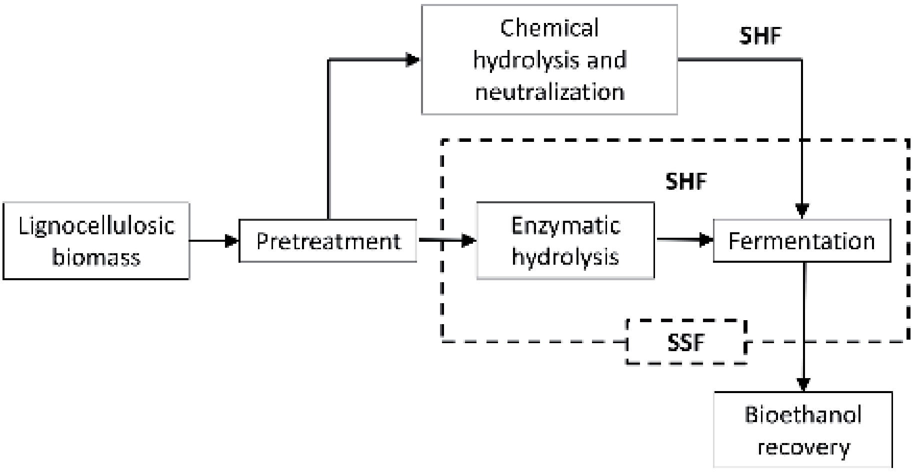

Figure 3.
Scheme of lignocellulosic ethanol production in general principle.

4. Pretreatment of lignocellulosic biomass

Pretreatment processes are applied to lignocellulose prior to hydrolysis and fermentation in order to:

- Increase the amorphous regions, which is easier to be hydrolyzed than crystalline cellulose.

- Increase the porosity of the fiber matrixes to promote the penetration of chemicals and enzymes into the structure.

- Liberate cellulose from the surroundings of lignins and hemicelluloses.

Physical, chemical, and biological pretreatment methods are used in pretreating lignocellulose. For a classification of pretreatment methods, the following are a brief summary:

4.1 Physicochemical pretreatment methods

- Mechanical processes reduce the size of the biomass and thus enhance the contact surface. Mechanical processes do not change the chemical properties of the materials. Therefore, they just can be a step to process raw materials before other steps of the pretreatment. Cutting, crushing, milling, and grinding can be carried out with specific equipment.

- Thermophysical methods: milling, steam exploding, high-pressure steaming, etc. improve the contact surface, decrease the polymerization degree of cellulose, decrease the crystallinity of cellulose, and somewhat crack the lignin cross-linking. In 1925, WH Mason invented steam explosion method to pretreat woody materials. The method was quickly applied in other industries, such as animal feedings, producing wood powder from hardwoods, veneer production, etc. [6–8]. In the 1980s, Iotech Corporation researched about steam explosion's effects on the hydrolysis of the puffed lignocellulose biomass. According to Iotech, the optimal conditions for steam explosion of natural lignocellulose were 500–550 psi with retention time of 40 seconds [9]. Shultz et al. also investigated the efficiency of steam explosion pretreatment on a variety of lignocellulosic biomass, such as hardwood chips, rice husk, corn straw, and sugar cane [10]. Effects of time, temperature, and pH during the steam explosion of poplar wood were studied with the aim of optimizing both pentose recovery and enzymatic hydrolysis efficiency [11, 12]. As a common conclusion, steam explosion pretreatment can puff the lignocellulose to enhance significantly the contact surface of the substrate, which yields much higher hydrolysis degree in the following step.

- Critical CO_2 extraction method: at the first glance, this method was expected to make a winding turn in lignocellulose pretreatment [13]. However, the system cost was too high with high-pressure equipment, which makes it not feasible for industrial production. Moreover, other similar studies showed that this method was not effective to enhance the conversion yield of the biomass to bioethanol [14, 15].

- Ionic liquid methods: ionic liquids are also known as melting organic salts with several special properties, such as nonvolatile, highly thermally durable, and, especially, cellulose dissolvable. Therefore, ionic liquid was studied to pretreat lignocellulose as a green solvent. Marzieh Shafiei et al. used 1-ethyl-3-methylimidazolium to pretreat hardwood for bioethanol conversion. The final conversion yield was 81.5%, very positive in terms of academy [16]. Unfortunately, this method is also not feasible for industrial scales due to the very high cost of ionic liquids.

Pretreatment by using organic solvents and surfactants to remove lignin is also in some interests, but the results have been not rather than just academic investigation or only for lignin extraction [17, 18].

4.2 Chemical methods

Aqueous acidic and alkaline solutions are known for their dissolvability of lignin. Acidic and alkaline pretreatments of lignocellulose have been so far the most effective and feasible for lignocellulosic bioethanol production technology [19, 20]:

- Acidic pretreatments: H_2SO_4 and HCl are popularly employed in pretreating lignocellulose. High-concentrated acidic solutions are not preferred because of toxicity and hydrolysis of cellulose and hemicellulose during pretreatment. Moreover, the corrosion of equipment and safety for human operators when using high-concentrated acids are the issues. Diluted acids are also not very recommended because of the generation of furfural compounds during the pretreatment process, which inhibits the growth of microorganism in fermentation process. Despite that fact, some studies still showed that acidic pretreatments with the acidic solution's concentration lower than 4.0 wt.% were still efficient and economic [21]. Lu et al. used diluted aqueous H_2SO_4 with concentrations of 2.0, 4.0, and 6.0 wt.% at 80, 60, and 120°C to pretreat corn stalks prior to fermenting the material to bioethanol. They found that an optimal concentration of acid was 2.0 wt.% to pretreat the corn stalk in 43 minutes at 120°C [22]. Cara et al. also suggested using 1.0 wt.% aqueous H_2SO_4 to pretreat dried olive tree at 170–210°C [23].

- Alkaline pretreatments: comparing to acids, pretreatment of lignocellulose with alkaline solutions minimizes the loss of carbohydrates due to hydrolysis. Alkali also helps to remove acetyl groups, promoting the later hydrolysis, and inhibit furfural formation [24]. Sodium hydroxide is the most popular alkali to pretreat lignocellulose due to its low cost and high efficiency. Calcium hydroxide is also considered because it is cheap despite low efficiency and precipitation [25].

Figure 4a–c shows the scanning electron microscopic (SEM) photos of pretreated rubber wood (*Hevea brasiliensis*) by acidic and alkaline solutions (Dr. Nguyen et al.). As seen from **Figure 4a**, before the pretreatment, the structure of rubber wood was well intact and recognized in order. After alkaline pretreatment (**Figure 4b**), the fibril structure was flaked due to loss of adhesive lignin and disorder. In addition, an alkaline pretreatment followed by acidic solution soaking like that at **Figure 4c** yielded an over-destruction of the material, where delignified cellulose was strongly hydrolyzed by the acid.

4.3 Biological methods

Employing microorganism to pretreat lignocellulose is an attractive way, promising low cost in both equipment and operation expenses. *Pleurotus*, *Pycnoporus*, *Ischnoderma*, *Phlebia*, etc. have been cultivated on lignocellulose with expectation of utilizing the metabolism of the microorganism to destruct the crystallinity of cellulose and remove lignin. However, most studies were based on laboratory scales and showed limited results [26–29].

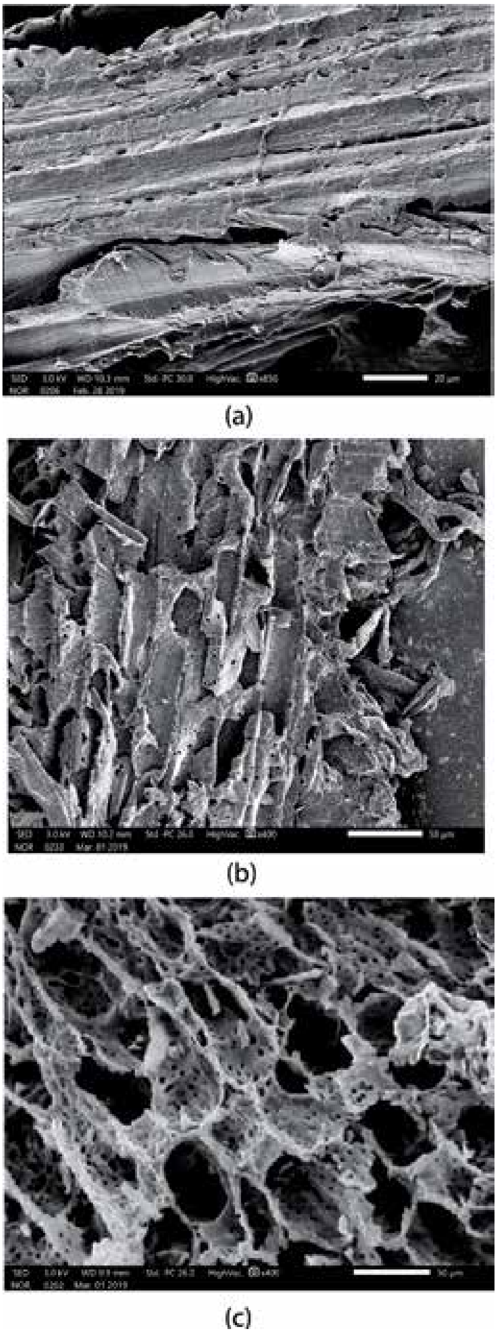

Figure 4.
(a) SEM photo of rubber wood as starting material. (b) SEM photo of rubber wood pretreated by aqueous alkaline solution (2.0 wt.% NaOH for 24 h, the ratio of dry-biomass/solution was of 1/10 wt./wt.). (c) SEM photo of alkaline-pretreated rubber wood soaked in acidic solution for 24 h (2.0 wt.% H_2SO_4*, the ratio of dry-biomass/solution was of 1/10 wt./wt.).*

4.4 Combination of pretreatment methods

It seems that a single pretreatment method cannot yield an expected result. The combination of pretreatment methods has been a conventional procedure in producing bioethanol from lignocellulose. First, the biomass needs to be size-reduced by a mechanical process, such as milling, cutting, and crushing, optionally followed by steam explosion before being soaked in alkaline or acidic solution (alkaline pretreatment is more preferred). Second, the pretreated material is washed and neutralized. The final product of this step is always a puffing material, which is ready for further fermentation [30, 31]. In addition, the reusability of internal waste was also discussed to enhance the sustainability of the lignocellulosic bioethanol production and reduce chemical cost [32].

5. Conversion of pretreated lignocellulose to bioethanol

Pretreated biomass can be converted to bioethanol by both direct microbial conversion (DMC) and hydrolysis along with fermentation [33]. In fact, DMC method requires much time, while the conversion yields were rather low with high risk of contamination [34, 35]. In contrast, enzymatic hydrolysis combining microorganism fermentation is a more preferable method with proven much better performance [33].

5.1 Saccharification of lignocellulose

After lignocellulose being pretreated, the polysaccharide-enriched material is hydrolyzed to single sugars (hexoses and pentoses) with enzymes. The commercialized enzyme to hydrolyze cellulose and hemicellulose is in fact a mixture of some different kinds of enzymes, commonly called cellulase, extracted from microorganism. These enzymes cleave glycosidic linkages in carbohydrates, typically via inverting or retaining mechanisms, the latter of which proceeds via a two-step mechanism that includes formation of a glycosyl-enzyme intermediate [36].

In contrast with hemicellulose, which can be hydrolyzed more easily, cellulose is somewhat stable with crystalline structure, resisting depolymerization. To enzymatically hydrolyze cellulose effectively, the following three cellulose enzymes are popularly together employed [37]:

- Endo-1,4-β-glucanases (EG) or 1,4-β-D-glucan 4-glucanohydrolases (EC3.2.1.4). This enzyme randomly breaks the 1,4-β-glucan bonds.

- Exo-1,4-β-D-glucanases including 1,4-β-D-glucan glucohydrolase (EC 3.2.1.74), to free D-glucose from 1,4-β-D-glucan and slowly hydrolyze D-cellobiose, and enzyme 1,4-β-D-glucan cellobiohydrolase (EC 3.2.1.91) (CBH) to free cellobiose from 1,4-β-glucan.

- β-D-Glucosidase or β-D-glucoside glucohydrolase (EC 3.2.1.21) to form D-glucose from cellobiose, as well as other oligomers of glucose.

The cellulase enzyme activity can be measured by a standard method described in Technical Report NREL/TP-510-42628 (National Laboratory of the US Department of Energy Office of Energy Efficiency and Renewable Energy). Enzymatic hydrolysis gives an advantage to the growth of microorganism in fermentation although there is a little difference in optimal temperature for the two processes.

5.2 Fermentation

Microorganisms are employed to metabolize the liberated single sugars from enzymatic hydrolysis to convert them to bioethanol. There are two approaches:

- Separate hydrolysis and fermentation (SHF): the hydrolysis is carried out until finish, and then microorganisms are added to the mixture to ferment the sugars. This method has some inherent weak points, including contamination, formation of inhibitors, and requirement of more time and extra equipment.

- Simultaneous saccharification and fermentation (SSF): the enzymatic hydrolysis and microorganism fermentation are carried out in the same equipment at the same time. Both enzymes and microorganisms are loaded to the mixture. This method is proven much better than the SHF above with shorter time, less equipment, and minimized risk of contamination.

SSF is currently considered the optimal method to convert lignocellulose to bioethanol. The process is reported with high conversion yield [21]. However, there are still some small backwards of this method. The optimal temperature for enzymatic hydrolysis is 45–50°C, while fermentation is at its highest efficiency at 28–35°C. Moreover, some intermediate products also resist the growth of microorganisms [25, 38].

Different microorganisms can be employed to enhance the fermentation. **Table 3** presents popular microorganisms, which can metabolize sugars and excrete ethanol.

From **Table 3**, it is easy to understand why *Saccharomyces cerevisiae* is a favorable choice of yeast to ferment sugar solution to bioethanol. Thanks to its tolerance to high ethanol concentration and material's inhibitors, *Saccharomyces cerevisiae* is known not only a traditional but also the most popular yeast in bioethanol production.

In fermentation process, an additional nutrient is necessarily added to provide organic nitrogen source for the growth of microorganisms. Peptone, corn steep liquor (CSL), urea, and even the distillation residue of bioethanol production process have been employed and investigated [32].

Production of lignocellulosic ethanol is still cost-inefficient. In attempts to improve bioethanol fermentation yield, more than one microorganism strain can

Characteristic	**Microorganism**			
	E. coli	***Z. mobilis***	***Saccharomyces cerevisiae***	***Pichia stipitis***
D-Glucose fermentation	+	+	+	+
Other hexose utilization (D-galactose and D-mannose)	+	—	+	+
Pentose utilization (D-xylose and L-arabinose)	+	—	—	+
Direct hemicellulose utilization	—	—	—	w
Anaerobic fermentation	—	+	+	w
Mixed-product formation	+	w	w	w
High ethanol productivity (from glucose)	—	+	+	w
Ethanol tolerance	w	w	+	w
Tolerance to lignocellulose-derived inhibitors	w	w	+	w
Acidic pH range	—	—	+	w

+, positive; –, negative; w, weak.

Table 3.
Some popular microorganisms for bioethanol production [39].

be loaded to the fermentation mixture as simultaneous saccharification and cofermentation (SSCF) method [39]. Hereby, both hexose and pentose can be utilized to produce bioethanol.

6. Conclusion

Renewable fuels and energy are a vital demand of the human being when fossil resources are exhausted and the global warming is at the red alarming level. The production of lignocellulosic bioethanol can meet the requirement of food security and the sustainable vision of a green world. The process includes pretreatment, enzymatic hydrolysis, and fermentation stages. Intensive studies are being carried out in over the world, in order to increase the cost-effectiveness of ethanol production and to make the transition from the laboratory to the industrial/commercial scale. This brief background was written in hope to spot out some noticing information for the readers about lignocellulose-based bioethanol's technology, which currently attracts a lot of studies to shorten the gap between research and commercialization.

Acknowledgements

This study was funded by the Vietnam National University Ho Chi Minh City (VNU-HCM) under grant number B2018-20-02.

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Section 3

Process and Applications

Chapter 5

Simultaneous Saccharification and Fermentation and Factors Influencing Ethanol Production in SSF Process

Manikandan Kanagasabai, Karuppaiya Maruthai and Viruthagiri Thangavelu

Abstract

Ethanol production from agricultural products mainly corn, wheat, sweat potato and residue are gaining importance and requires an industrially viable novel technology namely simultaneous saccharification and fermentation process. This process has an advantage of carrying out saccharification using enzyme and fermentation using yeast in a single fermenter. The investment cost for industrial ethanol production using cheap agricultural residues can be well achieved using SSF process. The success of SSF process greatly depends upon the pretreatment methods using different enzymes to break the complex carbohydrates to simple sugars. Optimization of key process variables is essential to maximize the ethanol yield from suitable substrates. The key process variables affecting the SSF process are pH, temperature, fermentation time, enzyme concentration and substrate concentration. The medium components are to be screened for effective nitrogen, potassium and phosphorous sources to increase the ethanol yield.

Keywords: simultaneous saccharification and fermentation, pretreatment, enzymes, ethanol, yeast pH and temperature

1. Introduction

The raw materials for ethanol production can be classified based on the type of carbohydrates they contain, i.e., sugar, starch, or cellulose by fermentation. Sucrose, glucose, or fructose for ethanol production for simultaneous saccharification and fermentation process are derived from any of the two classes of raw materials namely, starchy and cellulosic materials [1].

Ethanol production from simple sugars derived from sugarcane molasses, beet sugar is commercially well established. The yeast or bacterial cells can metabolize the simple sugars directly without the necessity of pretreatment step. The starch and cellulose polymers must be hydrolyzed to simple sugars before they can be fermented by yeast or bacteria [2–4]. Although cellulosic materials are available in plenty than starchy and sugar-containing raw materials, the process of conversion of it to fermentable sugars is often a very expensive pretreatment step using enzymes [5, 6]. Starch-containing substrates must be hydrolyzed by enzymes or acid to simple sugars and can be used for the production of ethanol. The carbon, hydrogen, and oxygen are normally provided by a complex carbohydrate source such as cane or beet molasses in industries. Vitamins and minerals may be added as additional nutrients. The sources of nitrogen are generally ammonium sulfate and urea, but they require biotin for effective utilization [7]. Other cheaper raw materials such as spent sulfite liquors, and whey also are sources of fermentable sugars. The sugar concentration in the above-mentioned industrial effluents is very much lower than in usual starchy and cellulosic substrates. Spent sulfite liquors contain 20–30 gL^{-1} of hexose while whey contains 40–50 gL^{-1} of lactose. Cellulosic raw materials on acid or enzyme hydrolysis give a maximum sugar concentration of around 40–60 gL^{-1} [8]. Ammonium or potassium phosphate provides the potassium and phosphorous required for growth of yeast. The magnesium sulfate, chloride and biotin can be provided as additional supplements [8, 9]. In a study by Qureshi and Manderson [10] four renewable agricultural resources were considered, namely wood, molasses, whey permeate, and starch. He reported that molasses sugars were cheaper than sugars derived from the other raw materials.

The simultaneous saccharification and fermentation (SSF) process was conceptualized in the late 1970s by Wright et al., Takagi et al., and Blotkamp et al. [11, 12]. This process employs fermentative microorganisms in combination with amylolytic enzymes in a single fermenter. Sugar accumulation in the fermenter is minimized in this process that favors increased hydrolysis and ethanol yield when compared to separate hydrolysis and fermentation. The main advantage process over separate hydrolysis and fermentation is that high substrate concentration, long residence time and high enzyme concentration can be used in same reactor. Optimization of process variables namely substrate concentration, enzyme concentration, pH and temperature are important to maximize the ethanol yield.

Starches that can be used for ethanol production by fermentation, includes grains, cassava (manioc, tapioca), sweet potato, sweet sorghum, and Jerusalem artichoke, corn, wheat, rice, potatoes, and sugar beets are the mostly used feedstocks in Europe and North America, sugarcane, molasses, cassava, babassu nuts, and sweet potatoes appear to provide the most promising feed for ethanol for countries such as Brazil.

1.1 Substrates for ethanol production using SSF process

1.1.1 Corn

According to Miranowski [13], corn is the most viable feedstock for ethanol production. The main factors are high yield, broad geographical cultivation range and available at cheaper cost. Annual production of corn biomass is about 300×10^6 tons (dry basis), about 40% of which are residues which is suitable for ethanol production. Extremely efficient systems are already in place for corn production from seed at very low cost. In evaluating the potential of corn (and any other food crop) for the production of energy, the moral issue of food vs. fuel must be considered. Approximately 66% of the grain produced consumed as food. The proportion of grain that are unsuitable for food production is about 5% of the annual grain production and it is suitable for alcohol production. In many countries corn is used as a raw material. The suitability of corn for ethanol production using SSF process depends on the contents of starch. A high content of horny endosperm leads to problems in ethanol production using SSF processes. The starch isolated from horny endosperm is difficult to gelatinize, and has low swelling, swelling value, and α-amylase digestibility is very less when compared to floury endosperm. Pretreatment of horny endosperm is difficult and requires more enzyme concentration.

1.1.2 Wheat

Wheat is mostly used in distilleries, because it yields a mild and smooth distillate. The starch content of wheat is usually about 60%. Wheat containing more than 13% raw protein causes problems in fermentation. Wheat mashes with high protein forms foam during fermentation and the use of antifoam agent (e.g., silicone anti-foam) is necessary. **Table 1** shows the composition of key components in wheat grain and **Table 2** shows the average composition of wheat.

Components	Protein	Ash	Carbohydrates	Fat
Seed coat	7–12	5–6	80–85	1.0
Aleurone layer	24–26	10–12	52–58	1.8
Endosperm	4–6	0.4–0.6	80–84	8–10

Table 1.
Composition of wheat components in % dry solids.

Components	Composition in g/100 g of flour
water	13.2
Crude protein	11.7
Crude fat	2.0
Starch	69.3
Crude fiber	2.0
Ash	1.8

Table 2.
Average composition of wheat.

1.1.3 Cassava

Cassava (*Manihot esculenta*), is cultivated widely in many tropical countries and used as food in African countries. Brazil, Indonesia, and Zaire are the major producers in the world. Cassava roots have 20–35 wt.% starch and 1–2 wt.% protein [14]. The composition of cassava is shown in **Table 3**. At a productivity level of 30 tons ha^{-1} of Cassava with 25 wt.% starch, 70% conversion to ethanol has been reported [15].

Components	Composition in g/100 g of flour
Reducing sugars	0.1
protein	2.1
Fat	0.2
Starch	80
Crude fiber	2.0
Ash	0.9
Total sugars	3.6

Table 3.
Average composition of cassava.

1.1.4 Sweet potato

Sweet potato (*Ipomoea batatas*) represents a fuel crop of significant potential [16] and has a starch content of 64.4% on a dry basis. SSF process is used to get a maximum ethanol yield from sweet potato tubers and stalk using combination of enzymes and microbes in a single reactor.

1.1.5 Sweet sorghum

Sweet sorghum (*Sorghum saccharatum*) is a valuable energy crop containing both starches and sugars. More than 17,000 types of sorghum are known to exist in world. Ethanol production of 3500 L ha^{-1} can be obtained from the fermentable sugars alone. An additional 1600–1900 L is derived from stalk fibers using SSF process. With hybrid strains, the yield may be increased 30% above present levels [17].

The adaptability to the majority of the world's agricultural regions, its resistance to draught, and its efficient utilization of nutrients make it as a viable raw material for ethanol production using SSF process [18].

1.1.6 Barley

Barley is mostly used as malting grain in ethanol production. It is also an interesting raw material in ethanol production using SSF process. The disadvantages of barley as a feed stock in distilleries are the husks surrounding the kernels and the content of glucans that leads to high viscosities in mashes. Therefore, special pretreatment step before SSF process is necessary in preparing mashes from barley. **Table 4** shows an average analysis of barley. Barley with 55% starch is also a major feedstock for beer production. Potable distillates produced from barley are smooth, but they have a more powerful grain taste.

Components	Composition in g/100 g of flour
Protein	11.8
Fat	2.3
Starch	63.2
Crude fiber	5.3
Ash	2.8

Table 4.
Average composition of barley.

1.2 Pre-treatment of substrates used in SSF process

1.2.1 Enzymatic liquefaction of starch in SSF process

It is essential to liquefy the starch as a pretreatment step before using the substrate SSF process. Liquefying enzymes are virtually all α-amylases (α-l, 4-glucane 4-glucanohydroase, E.C. 3.2.1.1) that split α-1,4 bonds in amylose and amylopectin that are basically derived from plants, bacteria and fungi. Liquefying enzymes may be classified as endo-acting enzymes and exo-acting enzymes. The α-1,6 glycosidic bonds are not hydrolyzed by alpha amylase since they are endo-acting enzymes. The enzyme activity of α-amylase is majorly dependent on the type of microorganisms or plants from which it is synthesized. α-Amylases rapidly decrease the viscosity due to its endo-acting nature and is used in simultaneous saccharification and fermentation process for pretreatment.

1.2.2 Treatment with α-amylase of Bacillus licheniformis (TBA)

The optimum conditions of pH for enzyme hydrolysis of starch using TBA is between 6 and 7 and the optimum temperature is in the range of 85–90°C [18]. The hydrolysis of corn starch with TBA, mainly produces maltotriose, maltopentaose, and maltohexaose. TBA enzyme is highly unstable and degrade at temperatures above 65°C in absence of Calcium ions and substrate. Senn [19] established an optimum pH range from 6.2 to 7.5, and pH values below 5.6 lead to a rapid decrease in enzyme activity. Enzyme activity is influenced greatly by the proportion of horny to floury endosperm present in the corn feed stock. Liquefaction of corn mashes using TBA yields mainly starch fragments with a maltotriose as well as maltose and glucose.

1.2.3 Treatment with α-amylase of Bacillus subtilis (BAA)

BAA synthesized using *Bacillus subtilis* is found to have an optimum pH value between 5.3 and 6.4, and an optimum temperature of 50°C [20]. Fogarty and Kelly [21] reported that with starch as substrate BAA produces limit dextrins. BAA enzyme produces limit dextrins that cannot be hydrolyzed using glucoamylase obtained from mold *A. niger* and starch degradation often remains incomplete BAA is unsuitable for SSF process which mainly uses glucoamylase enzyme. The BAA enzyme activity reaches a maximum for a pH between 5.8 and 6.8 and a temperature of 55–60°C, when corn is used a substrate [22, 23].

1.2.4 Treatment with α-amylase expressed by Bacillus licheniformis (BAB)

BAB, a new technical enzyme produced with a genetically engineered strain of *B. licheniformis* (Liquozyme, NOVO Nordisk, Denmark) [24] for its tolerant even at low pH values down to 4.8–5. But BAB is used to liquefy cereal mashes and is very effective. This enzyme express it activity up to 90°C and is used in pretreatment step for liquefying substrate in SSF process.

1.2.5 Treatment with fungal α-amylase of Aspergillus oryzae (FAA)

Fogarty and Kelly [21], reported that FAA contains only a few amino acid residues and is highly stable in acidic pH. The enzyme activity is maximum in a pH between 5.5–5.9 and at a temperature of 40°C. FAA can hydrolyze starch granules at a pH of 7.2 and temperature of 37°C and only 40% of starch was dextrinized in pretreatment step after 60 hour. The optimum pH ranges from 5.0 to 6.0 while corn is used as a substrate. The optimum temperature is reported between 50 and 57°C. FAA reduces the viscosity which is desirable for saccharification and is more effective in producing dextrins.

1.2.6 Enzymes for starch saccharification in SSF process

Glucoamylase (EC 3.2.1.3) enzyme, hydrolyzes α-1,4, α-1,6, and α-1,3 glycosidic linkages of starch molecules. Hydrolysis rate of starch is based upon the size and structure of the molecules [21].

1.2.7 Treatment with glucoamylase of Aspergillus niger (GAA)

Glucoamylases from *Aspergillus niger*, have been characterized by Fogarty and Kelly, 1979 The suitable pH for GAA is found to be in the range of 4.5–5.0 and an optimum temperature of GAA is 60°C. When corn mash was used as substrate, the optimum range of pH value reaches from 5.0 down to 3.4 [22, 25]. Thus, GAA is stable during fermentation. GAA was stable up to 70°C with an optimum at 65°C.

1.2.8 Treatment with glucoamylase of Rhizopus sp. (GAR)

GAR enzyme shows a maximum activity at temperature of 40°C and a pH value of 4.5–6.3 [21]. Glucoamylase 1 exhibits maximum debranching activity and totally degrades starchy materials to fermentable sugars in SSF process. Saccharification using GAR was carried out in a temperature range of 55–60°C and a pH of 4.4–5.4 [23]; GAR was also stable in acidic pH while corn is used as substrate.

1.2.9 Enzyme combinations in saccharification process

Single enzymes are rarely used for saccharification process. Enzymes may be combined successfully in mashing processes and fermentation. As reported by [24], different combinations of technical enzymes may exhibit either complementary or inhibitory effects. “OPTIMALT” is an industrially used enzyme combination off GAR GAA and FAA [28]. The concentration of fermentable sugars in mashes rises rapidly when enzyme combination is used in SSF process.

1.3 Microorganisms for ethanol production using SSF process

The yeast species mainly *S. cerevisiae, S. uvarum, Schizosaccharomyces pombe, Kluyveromyces marxianus and Candida utilis* are used for industrial alcohol production using SSF process [29]. *Saccharomyces cerevisiae* is the common microbe used for industrial ethanol production owing to its use for long time food industry. *Kluyveromyces marxianus* yeast grows well even up to 40°C [30]. This species is mainly used for production of alcohol from cellulosic, starch and saccharine substrates using SSF process. The activity of the yeast is very high at high temperatures and results in high ethanol production in less fermentation time.

Yeasts can utilize a variety of substrates. In general, they are able to grow and efficiently ferment in a pH between 3.5–6.0 and temperature in the range of 28–35°C. The overall productivity of the fermentation was less due to ethanol product inhibition and substrate inhibition [26]. This drawback of substrate inhibition can be overcome in SSF process where simultaneous utilization of substrate by microbes and synthesis of glucose by enzymes at faster rates.

Yeast, under anaerobic conditions, converts glucose to ethanol by the Embden-Meyerhof pathway and is shown in **Figure 1**. 2 mol of ethanol, CO_2, and ATP per mol of glucose fermented were synthesized in this pathway with a yield coefficient of 0.51 g alcohol [27].

1.4 Simultaneous saccharification and fermentation (SSF) process and key variables

Simultaneous saccharification and fermentation SSF is a process in which sugars from the liquefied substrates are saccharified and fermented in a single fermenter using enzyme and yeast. The drawback of SSF of cellulose using enzymes is feedback inhibition by the product. Separate Hydrolysis and Fermentation uses different temperature for hydrolysis and fermentation but the main disadvantage is the end product inhibition of glucose that accumulates in the hydrolysis step [31]. SSF process overcomes this difficulty of accumulation of sugars inside the fermenter by simultaneous fermentation of sugar by suitable yeast [32, 34]. The flow sheet of the SSF process using corn starch is shown in **Figure 2**.

Verma et al. [35] studied the conversion of starch to ethanol in a SSF process using co culture of amylolytic yeast and *S. cerevisiae*. The optimum temperature was reported as 30°C. Banerjee et al. [36] reported an optimum temperature of 37°C for *S. diastaticus* using soluble starch as a substrate. Saha and Ueda et al. [37] reported that 38°C gave a maximum ethanol yield by *S. cerevisiae* in a fermentation of glucoamylase treated starch. Bandaru et al. [38] had optimized the operating variables of fermentation for the production of ethanol using sago starch using co-immobilized glucoamylase and *Z. mobilis* and he reported an optimum temperature of 32.4°C and desirable pH at 4.93.

Amutha et al. [39] studied the ethanol from pretreated cassava starch by co-immobilized cells of *Z. mobilis* and *S. diastaticus* in batch and continuous fermentation. Pretreatment of substrate was carried out using BAB at 75°C for 1 hour. The

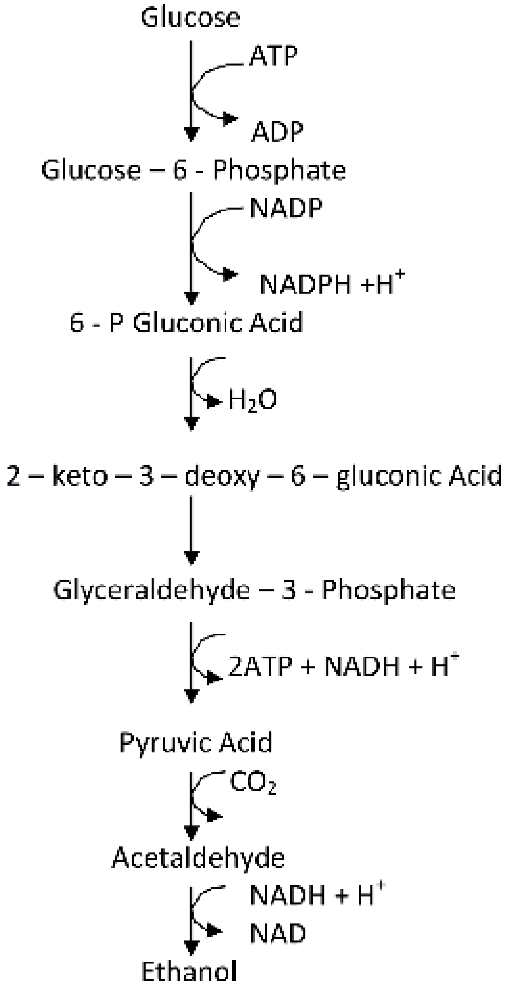

Figure 1.
EMP pathway for glucose to ethanol.

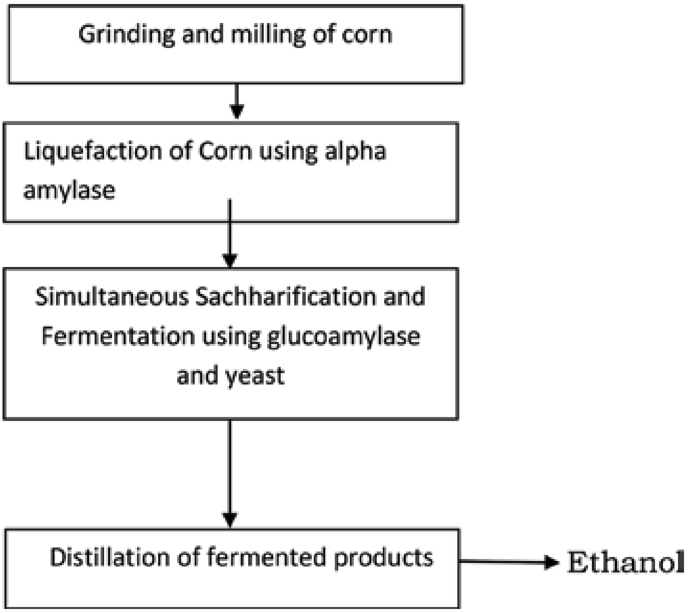

Figure 2.
Flow sheet for simultaneous saccharification and fermentation.

batch fermentation was carried out at a temperature of 30°C and at an initial pH of 6.0. 37.5 gL^{-1} of ethanol production was reported using free cells in mixed culture fermentation and 46.7 gL^{-1} using co-immobilized cells in batch fermentation.

Neves et al. [40] studied the ethanol production from wheat flour by SSF process. SSF process was conducted at 5°C and a controlled pH of 4.5 using glucoamylase 200 U/g of flour and *S. cerevisiae* in a batch fermenter. The fermentation time was 72 hour. 38.76 gL^{-1} of ethanol production was reported.

Davis et al. [41] studied the production of ethanol using waste starch stream by SSF process using *Z. mobilis* and *S. cerevisiae*. The operating conditions for SSF process were a controlled pH of 5.0 and temperature at 30°C. A maximum ethanol production of 39 gL^{-1} was reported.

Nakumara et al 1997 [42] studied the production from raw wheat flour using glucoamylase and *S. cerevisiae*. The pre-treatment of starch was carried out by adding 0.02 g of Termamyl/kg of starch and at a temperature of 95°C for 2 hour. Ethanol concentration of 67 gL^{-1} was reported using SSF process at a controlled temperature of 35°C and controlled pH of 4.5. The alcoholic fermentation of whey using K. marxianus yeast immobilized on delignified cellulose material. The optimum pH value was reported as 4.5. The optimum temperature for fermentation was reported as 37°C.

Pavla et al. [43] had studied the SSF process using wheat bran as substrate. Wheat bran was pre-treated with FAA followed by saccharification using glucoamylase. Pre-treatment temperature for FAA was 55°C and pH 6.0 for 4 hour and saccharification at 55°C for 48 hour to ensure the total hydrolysis of starch. The fermentation of filtrates resulting from pre-treatment using *S. cerevisiae* was carried out with initial pH of 5.5 and 30°C. The ethanol yield reported was 0.41 g/g of glucose fermented.

Reddy et al. [44] had studied the direct fermentation of potato starch to ethanol by co culture of *A. niger* and *S. cerevisiae*. The optimum pH for maximum ethanol production was reported as 5 to 6. The temperature of the fermentation medium was controlled at 30°C.

SSF process using maize starch as substrate by glucoamylase and *S. cerevisiae* at 35°C with the initial pH 5.5 was carried out. A maximum ethanol productivity of 1.23 $gL^{-1}h^{-1}$ was reported.

Kadam and Newman [33] evaluated several industrially available nutrient sources for their effectiveness in the SSF of pretreated starch with *Saccharomyces cerevisiae* D5A. Ethanol production was found to increase for a combination of 0.3% CSL and 2.5 mM $MgSO_4.7H_2O$ Hence, it is more industrially relevant medium than the medium containing rich nutrients.

The pH and temperature of the medium plays a vital role in all types of fermentation processes. As temperature increases the rate of biological reactions also increases upto a certain temperature and further increase in temperature may result in lesser product formation. That temperature was always chosen as the optimum temperature for the fermentation. This characteristic is similar to chemical reaction. This increase in rate of biological reaction may be due to more production of required enzymes at the faster rate. The ethanol producing microorganisms such as *S. cerevisiae, K. marxianus, S. diastaticus* prefer to grow best at 30°C [47]. Most of the microorganisms prefer to grow at neutral pH and hence we have more contamination at that pH. Ethanol producing yeast prefer to grow and metabolize in the pH

Culture	Source of starch	Process and fermentation conditions	Ethanol concentration gL^{-1}	Ethanol productivity $gL^{-1}h^{-1}$	Ethanol yield g/g of starch	Reference
Glucoamylase + yeast	cassava	batch fermentation	16.5	0.14	0.49	Ueda et al. [37]
Co-immobilized *Aspergillus niger*, and yeast	Rice	Mini jar fermenter	40	0.18	0.48	Lee et al. [45]
A. niger and *S. cerevisiae*	Potato	SSF pH—5.5, T—30°C, S—100 gL^{-1}	13.5	0.18	0.135	Reddy et al. [44]
Glucoamylase + *S. cerevisiae*	Raw wheat flour	SSF process pH—4.5, T—35°C, S—150 gL^{-1}	60	9.5	0.40	Nakumara et al 1997 [42]
Co-immobilized *Z. mobilis* + *S. diastaticus*	liquefied cassava	continuous fermentation pH—6.0, T—30°C, S—150 gL^{-1}	69.6	0.99	0.46	Amutha et al. [39]
A. awamori and *S. cerevisiae*	Cassava	SSF pH—5.5, T—30°C	90	0.5	0.45	Roble et al., (2002)
Glucoamylase + *S. cerevisiae*	Raw starch	Fed-batch fermentation pH—5.0, T—30°C	20–30	0.60	0.35	Konda et al. [2]
Mutant *A. niger* + *S. cerevisiae*	Raw starch	SSF pH—5.5, T—35°C, S—150 gL^{-1}	50	1.42	0.33	Rajoka et al [46]
Co-immobilized glucoamylase + *Z. mobilis*	Sago starch	SSF pH—4.9, T—32°C, S—150 gL^{-1}	55.3	0.98	0.36	Bantaru et al. [38]

Table 5.
Production of ethanol from starch sources using SSF process.

5–6 and a controlled pH environment is always preferred for maximum ethanol production. Very low pH is also not preferred as the rate of growth was very less. Hence an optimum pH of 5–6 must be maintained in the medium. In addition to that the medium should have optimum mineral concentration which provides more biomass and in turn more ethanol yield **Table 5**.

2. Conclusion

SSF process is found to be a promising technology for industrial ethanol production from cheaper substrates like cellulose and starchy substrates. The success of the SSF process depends mainly on pre-treatment step using suitable enzymes for cellulose hydrolysis and starch hydrolysis. Starchy substrates can be easily liquefied using low cost commercially available alpha amylase enzymes at optimum conditions and can be utilized in SSF process. But the pre-treatment steps in cellulosic materials are more challenging because of the presence of lignin and hemicelluloses. A suitable pre-treatment steps to separate cellulose from naturally occurring lignin and hemicelluloses substrates involves energy intensive process. Furthermore, presence of inhibitory end products from hemicelluloses may hinder the SSF process. SSF process using starch substrates are more promising and also commercial industrial production is feasible in many countries. The advantages of the process are reduction in investment by having single fermenter for both saccharification and fermentation. The feedback inhibition of sugars is greatly reduced. The fermentation time is very less in SSF process.

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Chapter 6

Structural Integrity of Materials in Fuel Ethanol Environments

Olufunmilayo O. Joseph

Abstract

Nowadays, the use of liquid fuels is prevalent in the transport sector due to ease of storage. There are two different fuel types namely, fuels obtained from fossil resources and biofuels made from renewable resources. Typical biofuels in industry use include pure plant oil (PPO), biodiesel, ethyl tertiary butyl ether (ETBE), biobutanol and fuel ethanol. Studies carried out have shown that fuel ethanol can substitute petrol. In addition, ethanol can be blended with gasoline at any ratio depending on the circumstances and the desired fuel. Typical fuel ethanol blends in use are: E5, E10, E20, E25, E70, E85, E95 and E100. Remarkably, there have been evidences of stress corrosion cracking (SCC) of steel storage tanks and associated piping used in fuel ethanol service during the past decade. This chapter is therefore, centered on a description of structural integrity issues related to metallic and non-metallic materials in fuel ethanol environments. Prior research on the corrosion and stress corrosion cracking behavior of ethanol-gasoline blends are also reviewed.

Keywords: fuel ethanol, materials, structural integrity, fracture, corrosion

1. Introduction

There is often a great deal of corrosion data on a number of engineered materials. However, much of the available data is clustered in a limited number of environments, full immersion environments in particular. The report of the National Research Council in the United States (US) [1] revealed that the limited number of environments for corrosion research has resulted in inability to create a meaningful national database of corrosion data useful to industry, government and academia. Aside from the issue of full immersion, atmospheric and alternate immersion aqueous environments, there are also completely different environments such as non-aqueous and high-temperature environments. Ethanol is an example of non-aqueous environments for which a better ability to predict its influence on various engineering materials is paramount due to its planned widespread use.

One of the key drivers for the development of biofuels globally is the concern about universal climate change, which is mainly instigated by combustion of fossil fuels. Considerable scientific evidence abounds indicating greenhouse gas (GHG) emissions as the reason for accelerating global warming. Biofuels are not only renewable and viable energy sources but are toxic-free and so more environmentally friendly than conventional petroleum-based fuels [2, 3]. Biofuels are also biodegradable and therefore their inadvertent spillage is of no significant environmental hazard [2–4]. While biodiesel and PPO are appropriate for diesel engines,

Fuel	Density	Viscosity	Flashpoint	Calorie value	Calorie value	Octane number	Fuel equivalence
	kg/L	mm^2/s	°C	at 20°C MJ/kg	MJ/l	RON	l
Petrol	0.76	0.6	<21	42.7	32.45	92	1
Fuel ethanol	0.79	1.5	<21	26.8	21.17	>100	0.65

Table 1.
Parameters of fuel ethanol in comparison with petrol [6].

fuel ethanol can replace petrol [5–7]. The properties of fuel ethanol are shown in **Table 1** and compared with the properties of fossil petrol.

The anti-knocking property of the fuel is influenced by the octane number while its energy yield is about one third lower than petrol. Ethanol, also known as ethyl alcohol (CH_3CH_2OH) is a volatile, flammable, colorless liquid obtained from some energy crop that comprises high quantities of sugar or substance that can be converted into sugar like starch or cellulose from grains [6]. In the US the most common source is from corn and grain. In Brazil, it is sourced from sugarcane [8].

However, ethanol can also be produced naturally (fermented) from any carbohydrate source, such as wheat, cane, beet and fruits like grapes and apples [8]. While grain and synthetic alcohols are technically the same (the molecule is identical), there are differences in the amounts of contaminants (butanol, acetone, methanol, organic acids) in each. According to Paul and Kemnitz [9], for ethanol to be used as fuel, water must be removed. If fuel ethanol is vended with zero water content, it would be referred to as anhydrous ethanol. Typically, denatured alcohol holds about 1% water besides additional constituents. Fuel ethanol with <0.5% water is considered "anhydrous ethanol" [8]. Ethanol with higher water content is usually referred to as "hydrated ethanol". Such hydrated ethanol is uncommon in the US but has been used as a fuel in Brazil.

During the past 8 years, a substantial testing effort on the structural integrity of metallic and non-metallic materials in fuel ethanol has been undertaken by various organizations. Though SCC has not been extensive, it has caused several failures in a number of user facilities. Various factors have been associated with ethanol SCC of carbon steels which include: conditions that promote crack initiation and growth, dissolved oxygen concentration levels, chloride concentration, corrosion potential, water content, and the chemical species of the ethanol itself.

There have been a substantial number of notched slow-strain rate (N-SSR) tests conducted with the aim of studying stress corrosion crack initiation (SCCI) and propagation mechanisms in fuel ethanol [10]. It is worth noting that significant concerns currently exist regarding the SCC behavior of pipeline steels as well as terminal facilities used to handle fuel ethanol.

2. Stress corrosion cracking in fuel ethanol environments

A corrosion failure such as stress corrosion cracking is an insidious form of corrosion which has far more adverse effects. Usually there is no prior warning before failure due to SCC. A 2004 survey of causes for failure in refining and petrochemical plants in Japan shows that a majority of the failures were due to corrosion, with the highest percentage due to SCC [11, 12]. The chart in **Figure 1** shows percentages of failures by type of material of construction [11]. Stress-corrosion failures can affect public health as in pollution due to escaping product from corroded

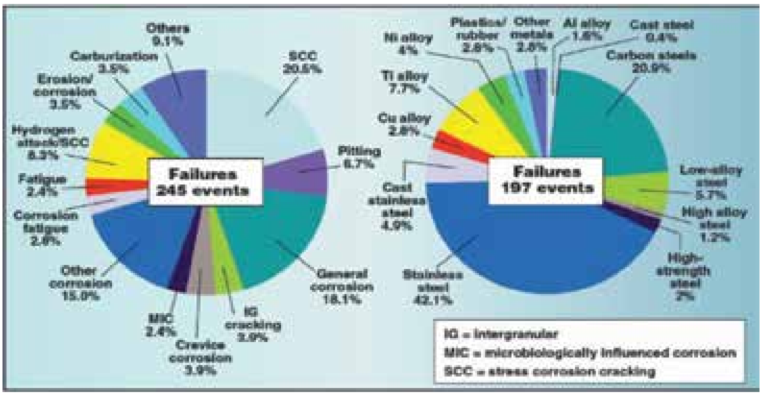

Figure 1.
Component failure frequencies [12].

equipment or due to the corrosion product itself. Sudden failure could result into fire, explosion, release of toxic products and construction collapse [1, 12, 13].

Commencing just about 2002, a number of ethanol storage tanks at blending terminals which have been used for a period of <2 years suffered leaks owing to SCC [14, 15]. Afterwards, more than 35 incidences of SCC failures in tanks, associated piping, and fittings have been discovered by an industry survey [14]. All failures so far have been in blending terminals, occurring in several regions in the United States. No SCC case has been reported by ethanol producers, transportation trucks, service stations and rail cars. Brazil has manufactured and distributed ethanol for quite a few years and has not likewise reported any SCC. Because of these failures, there was concern about the ability of pipelines to safely transport ethanol to and from blending terminals.

2.1 Supply chain of fuel ethanol

As soon as fuel ethanol is produced at a manufacturer's facility, it is held in storage tanks pending its release for distribution. Generally, manufacturers add the denaturant before or in the course of onsite storage. In addition, an inhibitor is added during storage or just preceding discharge of the shipment for supply. This may be one reason for SCC experience at some downstream facilities and no reported failures at manufacturer facilities. On entering the distribution system, fuel ethanol can be transported by numerous means, which include pipeline, barge, tanker truck and railroad tanker car [16].

The duration that fuel ethanol spends in the sequence can fluctuate significantly from days to months, subject to several factors: the obtainability of intermediate distribution storage, the site of the manufacturing facility, the transportation mode used, and the location of gasoline blending terminals. Fuel ethanol is held in storage tanks as soon as it comes into a gasoline blending facility. Contingent on usage and traffic requirements, the residence period in these tanks also differs. In certain cases, it can be held for months in the course of a period of dormancy [16].

However, in certain instances, at gasoline blending facilities, the residence period in the storage tank is relatively short as incoming ethanol supplies and outgoing shipments of blended gasoline are a proximate frequent process. Nevertheless, observations of SCC have been restricted to the lot of the supply chain encompassing the intermediate liquids storage through the gasoline blending facility and possibly will be linked to circumstances that develop in the distribution system or variations that transpire in the fuel ethanol [16].

2.2 Documented cases of SCC in fuel ethanol

Research carried out by the American Petroleum Institute (API) has shown that SCC of steel in fuel ethanol environment is a subject matter where awareness of the issue is growing dynamically as a result of documentation of experiences and research works in progress. Findings by API point out that documented catastrophes of ethanol process equipment dates back to no less than the early 1990s. Establishments undergoing what they contemplate as cases of SCC in fuel ethanol have been stimulated to confirm these issues through appraisal and documentation of service conditions, along with metallurgical examination of the failed or cracked components.

The appearance of cracks caused by other cracking environments is similar to SCC cracks of steel in fuel ethanol. Instances of SCC in steel equipment exposed to fuel ethanol are presented in **Figures 2–4**. The cracks are characteristically branched and may possibly be transgranular, intergranular or mixed mode.

Both transgranular and intergranular cracking may well occur in laboratory testing subject to the composition of ethanol. However, greater number of cracks documented from field failures display intergranular cracking. While analyzing a field catastrophe, intergranular cracking suggests ethanol SCC, but transgranular or mixed mode cracking might likewise be present [16].

Instances of SCC of steel components in fuel ethanol have been conveyed in the following kinds of equipment in gasoline blending facilities and fuel ethanol distribution:

a. Welds and adjacent metal in tank bottoms, detached roofs besides related seal components;

b. Fittings, facility rack piping, and accompanying equipment (for example, air eliminators);

c. Nozzle welds and vertical seam in lower tank shells situated off bottom;

d. Pipeline used to convey fuel ethanol from terminal to end user facility.

The blend of low cost and strength brands carbon steel as the principal material of construction for equipment used in the conveyance, handling and storage of fuel ethanol [16]. Generally, carbon steel is thought as compatible with fuel ethanol from the perspective of corrosion since its corrosion rates are characteristically low. On the other hand, the corrosion rate can occasionally escalate with agitation, the presence of contaminants, and the level of dissolved oxygen content of the ethanol. In the API program, the field corrosion rate measurements in fuel ethanol point out that the corrosion rates of carbon steel were typically very low.

Figure 2.
Locations of ethanol SCC near fillet welds used to make the branch connections to piping B [17].

Figure 3.
Photograph of cracked steel elbow welded to the flange [17].

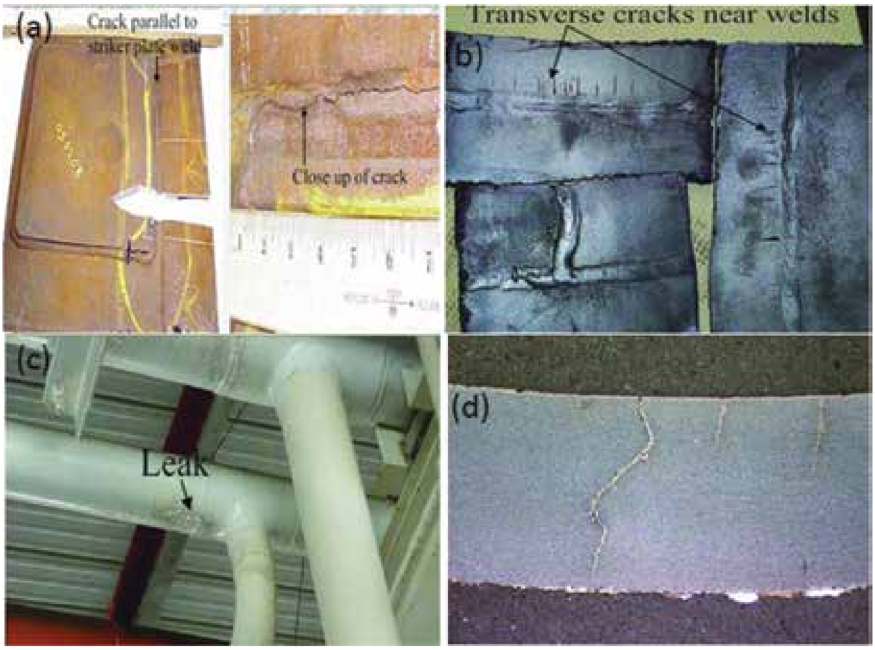

Figure 4.
SCC failures showing (a) SCC in steel tank bottom, (b) SCC in steel air eliminator vessel, (c) leak in piping resulting from a crack adjacent to the weld, (d) multiple crack initiations and through-thickness propagation in piping [8, 16].

2.3 Structural integrity of materials in fuel ethanol environments, previous research and current trends

Investigation of the corrosion and stress corrosion cracking (SCC) mechanism of steel in fuel ethanol is still in the early stages and several countries are considering increasing biofuel production as an approach to secure future energy supplies and mitigate global warming. When these come to the market, the infrastructure will play a key role in ensuring safe, reliable, and efficient distribution of these fuels to the end users [14]. Pipeline is the most effective transportation method in meeting these requirements. Hence, there is dire need of evaluating and predicting the influence of fuel ethanol on various steel grades which can be used for such pipelines.

A most recent study [18], jointly funded by API and Renewable Fuels Association (RFA), using the slow strain rate test method (SSRT), found that SCC of steel can take place in fuel ethanol meeting the ASTM D4806 standard specification (see **Table 2**). From the study, the inhibitor, Octel DC1-11 was discovered to lower the corrosion rate of steel in ethanol but had no effect on SCC. In addition, the team found that in addition to water, the most important factor that caused SCC in fuel ethanol appeared to be dissolved oxygen. When dissolved oxygen was minimized through nitrogen purging, no SCC occurred in the presence of all other species at their maximum levels. But on introducing oxygen, the reverse occurred. Furthermore, corrosion potential was used to monitor the potential for SCC of steel exposed to ethanol. One short coming of the study was that the results obtained are limited to fuel ethanol of ASTM D4806 standard and the study of the effect of stress level on SCC was left out. Hence, parameters for estimating risk of SCC from known defects in the studied environment were not obtained.

Other studies include those of Beavers et al. [19] and Lou et al. [20]. While [19] examined pitting corrosion in simulated fuel grade ethanol (SFGE) solutions on carbon steel, [20] examined the addition of chemical additives to SFGE to provide scavenging of oxygen in solution or inhibition of SCC in fuel grade ethanol (FGE) using slow strain rate (SSR) techniques. The latter study found a dependence of ethanol SCC on electrochemical potential that was consistent with observations from previous API studies (i.e., increased susceptibility to SCC with increasing corrosion potential). Based on this study, three active techniques of non-chemical deaeration were recognized. Altogether, the three methods reduced the corrosion potential below −100 mV Ag/AgCl EtOH and alleviated SCC.

Also, Beavers and Gui [21] summarized the results of research studies involving factors affecting ethanol SCC of carbon steel as water content, level of aeration, aging during storage, blend ratio with gasoline, steel type and welding. In addition, Gui et al. [22] carried out studies on the influence of ethanol composition on SCC susceptibility of carbon steel by evaluating ethanol SCC in field FGE samples and correlating the results in terms of SCC severity to compositional differences in the FGE samples. Carbon steel was found to be susceptible in all FGE samples conducted in two laboratories but with a varied degree of susceptibility in one FGE sample compared with the others.

Furthermore, Venkatesh et al. [10] evaluated the SCC behavior of pipeline steel in multiple ethanol environments. The program used N-SSR testing and field samples of FGE obtained from Brazilian sources. Severity of cracking was assessed

Property	**Units**	**Specification**	**ASTM designation**
Ethanol	%v min	92.1	D5501
Methanol	%v max	0.5	—
Solvent-washed gum	mg/100 ml max	5	D381
Water content	%v max	1	E203
Denaturant content	%v min, %v max	1.96, 5.00	D4806
Inorganic chloride	ppm (mg/l) max	40 (32)	E512
Copper content	Mg/kg max	0.1	D1688
Acidity as acetic acid	%m (mg/l)	0.007 (56)	D1613
pH	–	6.5–9.0	D6423
Appearance	Visibly free of suspended or precipitated contaminants (e.g., clear and bright)		

Table 2.
Quality specifications of fuel ethanol per ASTM D4806 [16].

based on crack growth rates determined from N-SSR testing and K_{ISCC} values based on a fracture mechanics treatment of the N-SSR test data. In another study [23], the effects of inorganic chloride in ethanolic solutions on the SCC behavior of carbon steels was assessed by varying the inorganic chloride concentrations between 0 and 70 mg/L using additions of sodium chloride (NaCl) to SFGE. The results indicated that both crack density and crack growth rate increased with chloride concentration. Two laboratory testing programs were used to evaluate the SCC behavior of steel in fuel ethanol and butanol [24]. The first part of the program revealed that cracking of API 5L X42 carbon steel compact tension specimens in FGE solutions (client supplied and synthetically prepared) required high K (stress intensity) values to initiate cracks. Highest crack growth rates were observed in SSR tests and in tests conducted in SFGE and under aerated conditions. Fracture mechanics tests and tests involving an actual field sample of FGE resulted in lower crack growth rates.

The second part of the program evaluated ASTM A36 carbon steel for SCC in the reagent grade butanol and anhydrous butanol solutions using SSR testing. The tests showed no evidence of SCC. Likewise, Cao [25] studied the corrosion and stress corrosion cracking of carbon steel in simulated fuel grade ethanol using SSR techniques and accurately controlled fracture mechanics conditions. Goodman and Singh [26] evaluated the influences of chemical composition of ethanol fuel on carbon steel pipelines using SSR testing on carbon steel samples in five FGE environments. SCC was discovered in two of the as-received FGE environments and in FGE environments to which NaCl was added.

Furthermore, substantial information has been gathered from reviews, reports and summaries of studies investigating the compatibility of fuel ethanol with metallic materials. Nevertheless, care must be taken in interpretation of the information [27]. Examples are:

a. a Concawe [28] report recommending carbon steel and aluminum for ethanol/petrol handling situations; and

b. a laboratory study conducted by Minnesota Pollution Control Agency [29] evaluated 19 metallic species, including four types of aluminum alloy and brass in E10 and E20 blends, three aluminum alloys were adjudged as satisfactory as was brass.

Unfortunately, it is known from field experience that E10 blends can severely corrode aluminum components, leading to catastrophic failure [27, 30]. Also, carbon steel can suffer severe corrosive attack if the fuel contains water [27, 31]. Likewise, brass components in carburetors are known to corrode when exposed to E10. The carburetor manufacturer who reported this, conducted compatibility testing of its products with petrol/ethanol blends and has identified corrosion of metallic components as an issue, requiring replacement of brass components with more resistant, but more expensive, alloys.

Qinetiq reports the Brazilian experience with ethanol blends [27, 32]. According to Stephen [27], in order to make vehicles more durable when employing ethanol blends, various fuel system components require modifications among which are:

a. zinc steel alloy fuel lines changed to cadmium brass;

b. tin and lead coatings (terne plate) of fuel tanks changed to pure tin; and

c. cast iron valve housings changed to iron cobalt alloy (QINETIQ, 2010).

Beavers et al. [33] carried out a recent research that was funded by the Pipeline Research Council, in which methods for prevention of internal SCC in ethanol pipelines were evaluated. The methods assessed include the addition of inhibitors and oxygen scavengers to ethanol and other ways and means of deaeration. On the other hand, Beavers et al. [34] studied the effects of ethanol-gasoline blends, metallurgical variables, inhibitors and dissolved oxygen on the stress-corrosion cracking of carbon steel in ethanol. Slow strain rate (SSR) and fatigue precracked compact tension (CT) tests were employed to characterize the influence of environmental and metallurgical variables on SCC of carbon steel. Metallurgical factors, including steel grade within a range of pipeline grades, welds, and heat-affected zone, do not seem to have a noteworthy effect on the degree or frequency of SCC. In terms of environmental factors, it was observed that SCC of carbon steel does not take place even in a completely aerated state, if the ethanol-gasoline blends contain below approximately 15 vol.% ethanol; susceptibility to SCC and crack growth rate are greater in 50 vol.% ethanol gasoline blend (E-50) than in either lower or higher ethanol concentration blends; oxygen scavenging can be an effective method to inhibit SCC; water content exceeding 4.5 wt.% prevents SCC in ethanol; and fatigue precracked CT tests display comparable inclinations to SCC susceptibility as SSR tests.

Maldonado and Kane [35] studied the stress corrosion cracking of carbon steel in fuel ethanol service and postulated that the hygroscopic nature of ethanol is an important aspect with potential relevance to its corrosivity. Also, ethanol possesses high potential for oxygen solubility; therefore, the availability of oxygen for involvement in the corrosion reaction is anticipated to be largely greater.

The authors in [36] presented an evaluation of fatigue crack propagation in three steels namely; A36, X52 and X70 steels in a SFGE. By using a fracture mechanics approach to determine crack propagation rates, all the three materials were found to be prone to enhanced fatigue damage in fuel-grade ethanol environments. **Figure 5** shows a macroscopic view of the fracture surface of X52 steel after testing in SFGE. A model for determining crack growth rates in ethanol fuel was further proposed by the authors.

A recent study [37] investigated the corrosion of martensitic stainless steel in ethanol-containing gasoline mixture as a function of water, chloride and acetic acid concentrations. The results obtained showed that, water and chloride ions (Cl^-) are the primary corrosion causing factors in EtOH/gasoline mixtures; critical water

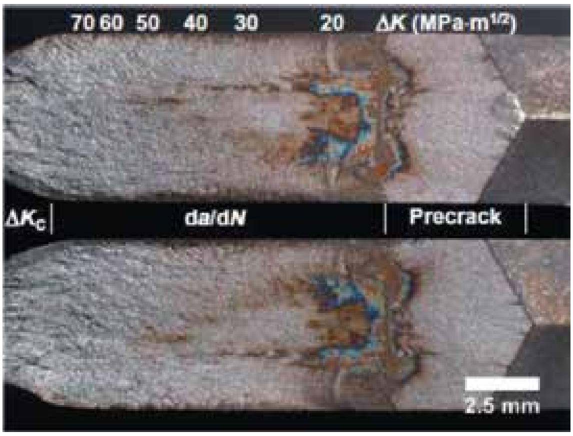

Figure 5.
Macroscopic view of X52 fracture surface after testing in SFGE [36].

content depends on EtOH/gasoline-ratio; pitting corrosion occurred at tremendously low chloride concentrations; increasing chloride concentration enhanced pit propagation, with slight influence on pit densities and higher concentrations of acetic acid lead to a greater attacked area, with negligible impact on the depth of pit propagation.

Another study [38] investigated the influence and role of minor constituents (organic acids, water and chloride) of fuel grade ethanol on corrosion behavior of carbon steel using X-ray photoelectron spectroscopy (XPS), auger electron spectroscopy (AES) and electrochemical experiments. The results showed that iron (II) acetate is generated on oxide film due to its high solubility in FGE environments. Chloride stimulated anodic dissolution at those sites where iron (II) acetate occurred.

Also, in 2016, Rangel et al. [39] carried out a study on the SCC susceptibility of API X-80 pipeline steel in SFGE. Water contents of 0, 1, 5, 10 and 20 vol.% and chloride content of 0, 10 and 32 g/L were investigated. Results have shown that X-80 carbon steel in the as-received condition was susceptible only when 5% water and 10 g/L NaCl were present. Heat treatments suppressed this susceptibility. Conditions that increased the corrosion rate also increased the SCC susceptibility, which, together with metallographic observations and noise in current measurements, indicated that SCC in this environment is caused by a film rupture, dissolution mechanism.

Recently, an investigation on the fracture behavior of micro-alloyed steel and API-5L X65 steel in simulated fuel ethanol environment was carried out [40]. Micro-alloyed steel was found to exhibit better fracture resistance than API-5L X65 steel in air and in solution. API-5L X65 in solution showed faster crack extension than MAS-in solution. It was also observed that J_{str} (fracture toughness derived from stretch zone geometry) obtained for the two steels shows a similar trend with J_i (initiation fracture toughness) which is found at the parting of the blunting line on their J-R curves and as a result appropriate for signifying the initiation toughness of the two steels in solution. On the whole, fuel ethanol decreases fracture resistance in X65 and micro-alloyed steels (**Figure 6**).

All of the findings point to the fact that SCC of metals do occur in FGE environment, whether simulated or field FGE due to several factors which have been mentioned. Most of the SCC tests were carried out using SSR techniques to assess the fracture toughness of the materials in fuel ethanol environment.

Ethanol fuels have gradually developed into a remarkable alternate energy source. Ethanol-based biofuel can be used to power engines and run cars, hence it is now the main alternative to automotive fossil fuels. The combination of gasoline

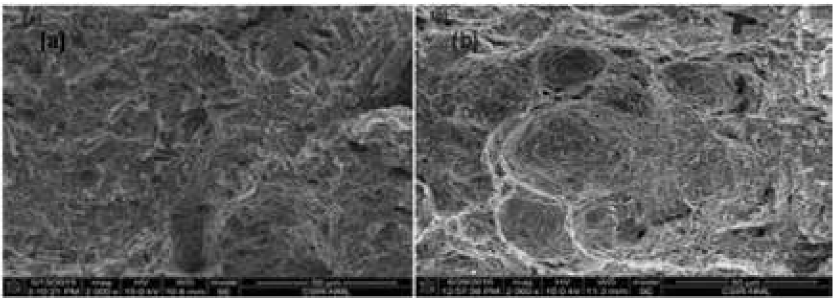

Figure 6.
Fracture surface of micro-alloyed steel and API-5L X65 steel after J tests in E20 SFGE [40].

with ethanol results into the fuel currently called "**Gasohol**" [4]. Despite the documented cases of corrosion and stress-corrosion failures in fuel ethanol, corrosion rates are typically low and recommendations regarding compatible materials are currently in literature [7, 40, 41]. These materials include carbon steels; micro-alloyed steel; unplated steel; stainless steel; black iron; bronze; polypropylene; Teflon; neoprene rubber; thermoplastic piping; thermoset reinforced fiberglass; nitrile and viton among many others. Hence, ethanol fuel is still the best possible alternative to fossil fuels.

Most of the gasoline sold in the United States contain some percentages of ethanol.

3. Conclusions

The kinetics of corrosion behavior, fracture behavior and crack growth depends on the material-environment system. It is important to state that function, material, shape and process do interact. The specification of process limits the materials you can use and the shapes they can take. In other words, the process of employing fuel ethanol in the fuel industry and its associated corrosion and stress corrosion failures has invariably placed a limit on the materials that can be used as pipes, storage tanks and the required automotive parts.

The structural integrity assessments carried out in fuel ethanol is of optimal benefit to designers in the fuel, automotive, aviation, and chemical industries. Material compatibility with fuel ethanol, based on corrosion rates, stress intensity factor, fracture toughness and crack propagation resistance, amongst others have been reviewed. A designer must give considerable attention to these parameters in order to ensure reliable performance of materials.

Requirements for design, materials and inspection are then established in a conventional manner relative to the estimates of progressive crack extension behavior presented in literature.

Acknowledgements

My thanks go to Professor John Ade Ajayi for helping me find a career path in Failure Analysis and Structural Integrity. The mentorship role of Professor C.A. Loto in my career cannot be overemphasized.

Covenant University is gratefully acknowledged for open access funding.

Conflict of interest

The author declares no conflict of interest.

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Chapter 7

Recent Application of Bio-Alcohol: Bio-Jet Fuel

Gi Bo Han, Jung Hee Jang, Min Hwei Ahn and Byung Hun Jung

Abstract

Recently, the biomass-based energy production has been actively studied as a research and development area for reducing carbon emissions as a solution to global warming caused by the increase of carbon dioxide emissions. Especially, as the energy consumption in the air transportation field increases, the carbon dioxide emissions increase simultaneously. Therefore, the bio-jet fuel production technology is being actively developed to solve this problem. The bio-jet fuel manufacturing process is a process of manufacturing biomass-derived jet fuel that can replace the existing petroleum-based jet fuel. It includes an alcohol-to-jet (ATJ) process using bio-alcohol such as bio-butanol and bio-ethanol, oil-to-jet (OTJ) process using vegetable oil, and an F-T process using syngas obtained from gasification of biomass-based raw materials.

Keywords: bio-alcohol, bio-ethanol, bio-jet fuel, manufacturing technology, greenhouse gas reduction, alcohol-to-jet (ATJ) process

1. Introduction

Bio-alcohol is an environment-friendly clean fuel for transportation application and convertible to various other fuel compounds. It is also a means of reducing greenhouse gas and fossil fuel consumption. Bio-alcohol includes various formulas such as bio-ethanol and bio-butanol. R & D for commercialization of bio-butanol is currently active which can replace existing petroleum fuel or can be converted to other forms of fuel. Bio-ethanol is collectively called as bio-alcohol in view of worldwide total production volume and quantity in use. Bio-ethanol among other bio-alcohols is mainly considered in the present survey, especially related to its current trend of conversion technology to other fuel formulas. Korean domestic bio-alcohol technology boasts of its long history in alcohol liquor industries. However, its food-based raw material casts a negative perspective, and technical solution for diversion to nonfood-based raw material is to be sought after. As an example, bio-alcohol production from cellulosic biomass as raw material involves the introduction of breaking method for the strong chemical bonding of cellulosic biomass to improve conversion efficiency, which was made possible by pre-treatment technology. However, high production cost incurred from pre-treatment process technology and high enzyme cost for bio-treatment process are another technical barrier, and it has to be overcome by overall process and energy cost reduction.

About 100 billion liters (5 million TOE) of bio-ethanol is produced worldwide in 2014. The USA consumes 14.4 billion gallons of bio-ethanol per annum, the most significant quantity in the world. This is also manifested in **Figure 1** where most of the bio-ethanol production is consumed in North and South America with comparatively similar amount consumed in Europe and China. As for bio-ethanol production, the USA and South America, especially Brazil, are well known for bio-ethanol production. Brazil was ranked first as a bio-ethanol exporter before 2010, but the USA surpassed Brazil as a prime exporter of bio-ethanol thereafter (**Figure 2**). This is attributed to significant growth in number of bio-ethanol producers such as

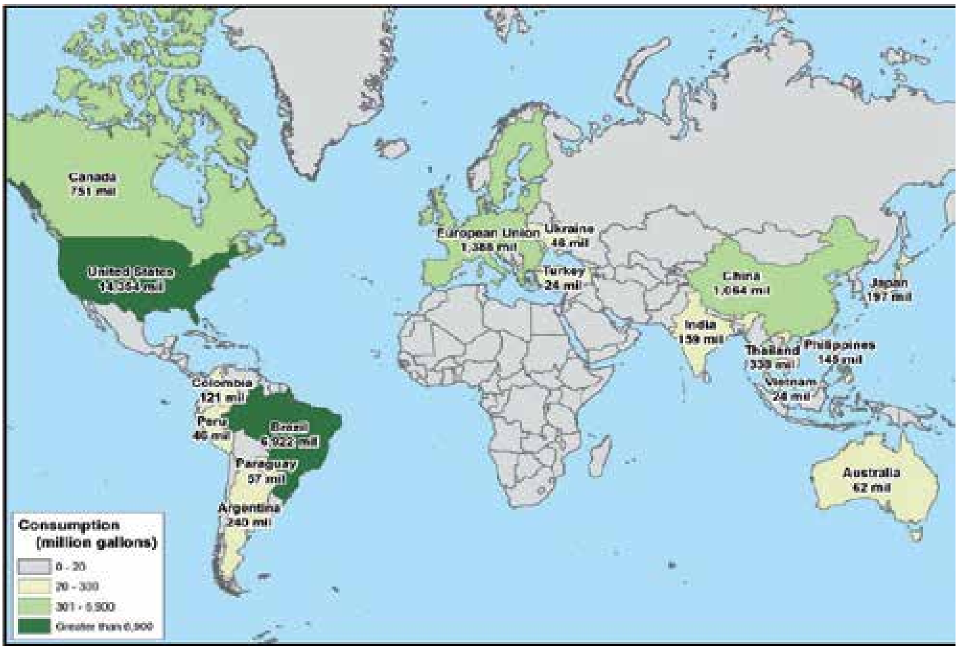
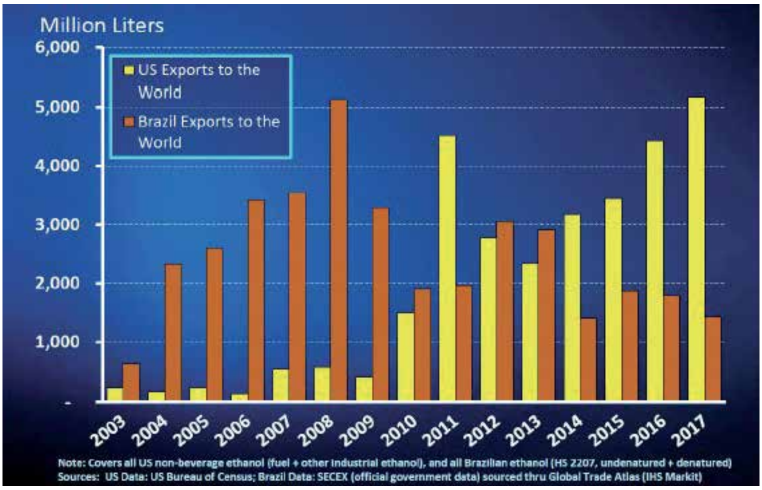


Figure 1.
Global ethanol consumption for transportation fuel in 2016 [1].



Note: Covers all US non-beverage ethanol (fuel + other industrial ethanol), and all Brazilian ethanol (HS 2207, undenatured + denatured)
Sources: US Data: US Bureau of Census; Brazil Data: SECEX (official government data) sourced thru Global Trade Atlas (IHS Markit)

Figure 2.
Yearly variation in export of US and Brazilian bio-ethanol based on nonfood-based ethanol [2].

Producers	Production quantities
Archer Daniels Midland Co. (ADM)	6.44 billion liters
POET Ltd	6.06 billion liters
Green Plains	5.68 billion liters
Valero	5.3 billion liters
Flint Hills	3.03 billion liters
Others	33.31 billion liters

Table 1.
Bio-ethanol production by major US domestic producers.

ADM, POET Ltd., and Green Plains. **Table 1** shows production scale of US bio-ethanol production companies.

Bio-ethanol is well known for its direct application for transportation fuel as well as for various other fuels after conversion. The use of bio-ethanol is currently sought after as a fuel source for renewable energy such as hydrogen production and bio-jet fuel production. Worldwide attention is directed to efficient conversion of bio-ethanol to environment-friendly hydrogen and bio-jet fuel. Conversion of bio-ethanol to hydrogen and bio-jet fuel is surveyed.

2. Necessity for bio-jet fuel

Recent fuel consumption survey shows that 12% of transportation fuel is accounted for by aviation industry and it contributes 2% of greenhouse gas to environment pollution and global warming. To comply with 2015 Paris Climate Change Accord, improved energy efficiency and increased low-carbon bio-energy and fuel utilization (rate) in aviation industries are expected, and such efforts are in progress in various related fields. As examples of such efforts, airlines and aircraft manufacturers voluntarily set goals for carbon-neutral growth, and 50% reduction of greenhouse gases by 2050 with respect to 2005 criteria and various concrete ways are implemented. Ordinarily, electricity, solar energy, and hydrogen fuel are mentioned as means of low-carbon energy utilization in transportation fields [3]. As for aviation industries, the only technically viable means is limited to bio-jet fuel and its utilization. Therefore, long-term carbon reduction is only made possible by increased utilization of bio-jet fuel. **Figure 3** shows IRENA's future prospect for carbon emission by aviation industries. As shown in **Figure 3**, it was known that the 1.5% reduction of greenhouse gas is reportedly possible by both the utilization of bio-jet fuel and the increase in the energy efficiency resulting from aircraft design improvement, optimization of airport facility, and flight paths.

The most representative way to reduce carbon emissions is to develop the biomass-based fuels such as bio-aviation oil with low carbon emission and their production technologies. Also, many international airlines have launched pilot projects for their application feasibility. However, it is difficult to secure economic feasibility in various cost aspects. In order to overcome these problems such as securing economic feasibility, developing bio-air fuels as well as setting international standards and providing incentives for the use of bio-fuels, which can be the basis for establishing carbon emission goals and policies of international airlines. In order to overcome such problems as securing economic feasibility, the international standards that can be the basis for establishing carbon emissions goals and

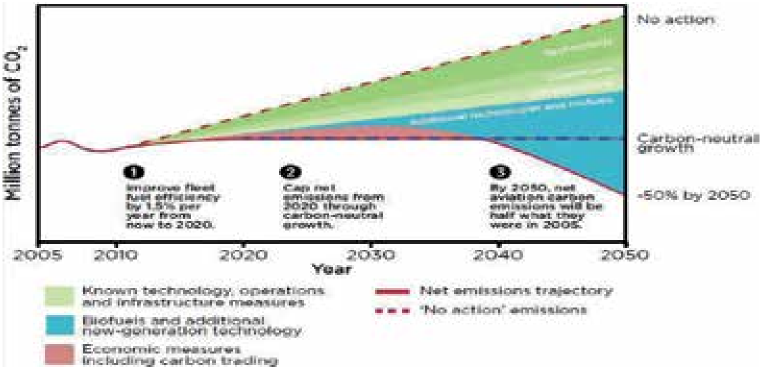


Figure 3.
Future prospect for carbon emission from aviation industries (unit: million tons of CO_2) [4].

policies for international airlines should be established, and the bio-jet fuel market should be activated by securing technologies for developing bio-jet fuel fuels in addition to providing incentives for the use of bio-jet fuels. In order to achieve this goal, the ICAO established the Commission for Aviation Environment Protection (CAEP), and efforts to reduce aviation greenhouse gas emissions have been increasing, especially for ICAO. Developments are emerging, and countries and international organizations are stepping up their aviation bio-fuel development policies. The 38th ICAO General Assembly resolution approved the importance of aviation biofuels as a medium-to-long term GHG reduction measure, established a global framework, the possibility of sustainable drop-in aviation biofuel technology, and emphasis is placed on the need to introduce policies and incentives from a perspective of accelerating wide utilization. The IATA announces continued use of renewable energy as the most reliable way to meet its greenhouse gas reduction targets and requires by 2020 to replace 6% of aviation fuel demand with renewables. The various bio-fuel support policies are being promoted by spreading awareness that bio-fuels can contribute to greenhouse gas emission reduction, energy security enhancement, rural income, and new market development. These support policies include tax exemptions for bio-fuels in most countries, including budgetary support (tax exemption or direct subsidies to bio-fuel producers, sellers, and users), minimum mix ratios, and import tariffs on imported bio-fuels. In addition, subsidies are being used to support bio-fuel dissemination, resulting in $ 20 billion in grants from governments around the world in 2009, mostly in the US and EU countries. The Korean government subsidies are expected to increase to US$ 37.5 million annually from 2010 to 2020 and to US$ 70.8 million annually from 2021 to 2035.

3. Production technologies for bio-jet fuel

Representative production technologies for bio-jet fuel include alcohol-to-jet (ATJ), oil-to-jet (OTJ), gas-to-jet (GTJ), and sugar-to-jet (STJ) process. OTJ process produces bio-jet fuel from animal or plant tallow such as waste vegetable oil, beef tallow, and microalgae. More specifically, hydrotreated esters and fatty acid (HEFA) technology, a kind of OTJ process, encompasses hydrotreated renewable jet (HRJ) process among HEFA technologies, catalytic hydro-thermolysis (CH), and rapid thermal decomposition process (HDCJ). STJ process involves catalytic upgrading and conversion of glucose- or starch-based raw material to hydrocarbons or biological conversion to bio-jet fuel via direct sugar to hydrocarbons (DSHC) and catalytic upgrading. ATJ process involves production of bio-jet fuel via hydrolysis of wooden fiber biomass or glucose into intermediate alcohols (methanol, ethanol, butanol, and fatty acid alcohols) and their dehydration and oligomerization. It is divided into ethanol-to-jet or butanol-to-jet technologies, depending on alcohol involved. GTJ process involves biogas, natural gas, or syngas from wood fiber biomass to bio-jet fuel via bio-chemical or thermos-chemical routes such as gas fermentation and Fischer-Tropsch processes. **Table 2** shows the production technologies for bio-jet fuel.

Figure 4 shows the production process-wise raw material and technology overview for bio-jet fuel. Among many classification methods, bio-jet fuel is divided via production pathways: fermentation, deoxidation, or thermal decomposition. As of 2016, ASTM 7566 dictates five production processes (Fischer-Tropsch Synthetic Kerosene with Aromatics (FT-SPK), HEFA, Synthesized Iso-Paraffins (SIP), ATJ) as means to produce commercially viable bio-jet fuels. It simultaneously regulates product quality criteria as per 100% assay as well as mixing proportion in existing

Technologies	Production processes
Alcohol to jet	Ethanol to jet
	N-butanol to jet
	Iso-butanol to jet
	Methanol to jet
Oil to jet	Hydro-processed renewable jet
	Catalytic hydro-thermolysis
	Hydrotreated depolymerized cellulosic jet
Gas to jet	Fischer-Tropsch synthesis
	Gas fermentation
Sugar to jet	Direct sugar to hydrocarbons
	Catalytic upgrading

Table 2.
Production technologies for bio-jet fuel [5].

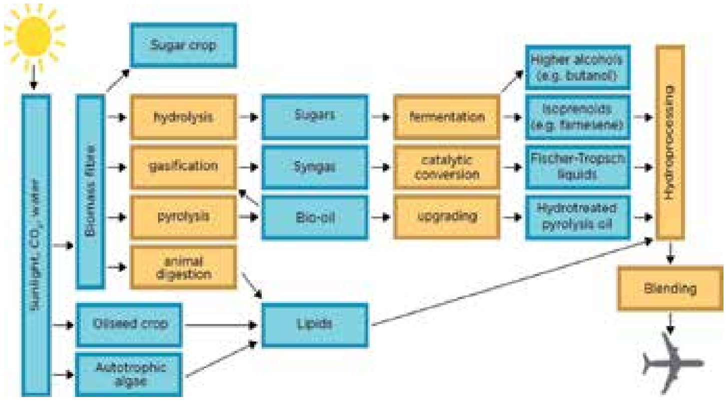


Figure 4.
Production process-wise raw material and technology overview for bio-jet fuel [6].

Production process	Developer/manufacturer	Raw materials	Aromatic content	ASTM review stage and max. Mixing proportions
FT-SPK	Sasol, Shell, Syntroleum	Coal, natural gas, biomass	Low	(2009)-50% Approved
HEFA	Honeywell UOP, Neste Oil, Dynamic Fuels, EERC	Vegetable oil, animal fat, recycled vegetable oil	Low	(2011)-50% Approved
SIP	Amyris, Total	Sugar	Low	(2014)-10% Approved
ATJ-SPK	Gevo, Cobalt, Honeywell UOP, LanzaTech, Swedish Biofuels, Byogy	Starch, sugar, cellulose-based biomass	Low	(2016)-30% Approved
FT-SKA	Sasol	Coal, natural gas, biomass	High	Under review by committee
HDO-SK	Virent	Starch, sugar, cellulose-based biomass	Low	Investigation report submitted
HDO-SAK	Virent	Starch, sugar, cellulose-based biomass	High	Investigation report under review
HDCJ	Honeywell UOP, Licella, KiOR	Cellulose-based biomass	High	Supplement to investigation report received
CH	Chevron Lummus Global, Applied Research Associates, Blue Sun Energy	Vegetable oil, animal fat, recycled vegetable oil	Low	Investigation report under review

Table 3.
Production process-wise classification of bio-jet fuel production process [7].

petroleum-based aviation fuel. Many other production processes are also used to produce bio-jet fuel, and the following technologies are under review by ASTM for approval. **Table 3** shows production process-wise classification of bio-jet fuel production process.

4. Bio-alcohol-based bio-jet fuel production technologies

Figure 5 shows current worldwide production and consumption trend of bio-jet fuel. Bio-ethanol is widely commercialized as sustainable source of energy for use in transportation with worldwide production of 104 million m^3 and 80% of its utilization as transportation fuel. The USA and Brazil accounted for 51.8 and 2.77 million m^3 production, respectively. Worldwide bio-jet fuel amounted to 30 billion m^3. On the other hand, Korean domestic petroleum-based aviation fuel products totaled 13% (20.66 million m^3) in 2013, which is similar to gasoline products (13.5%) and 44% of light oil products (29.7%).

Possible raw material for ATJ process includes methanol, ethanol, and butanol. Such alcohol-based raw material is converted to bio-jet fuel via polymerization and upgrading technology. Among these alcohols, bio-ethanol utilization is promising in view of its current production and consumption and worldwide use. At present,

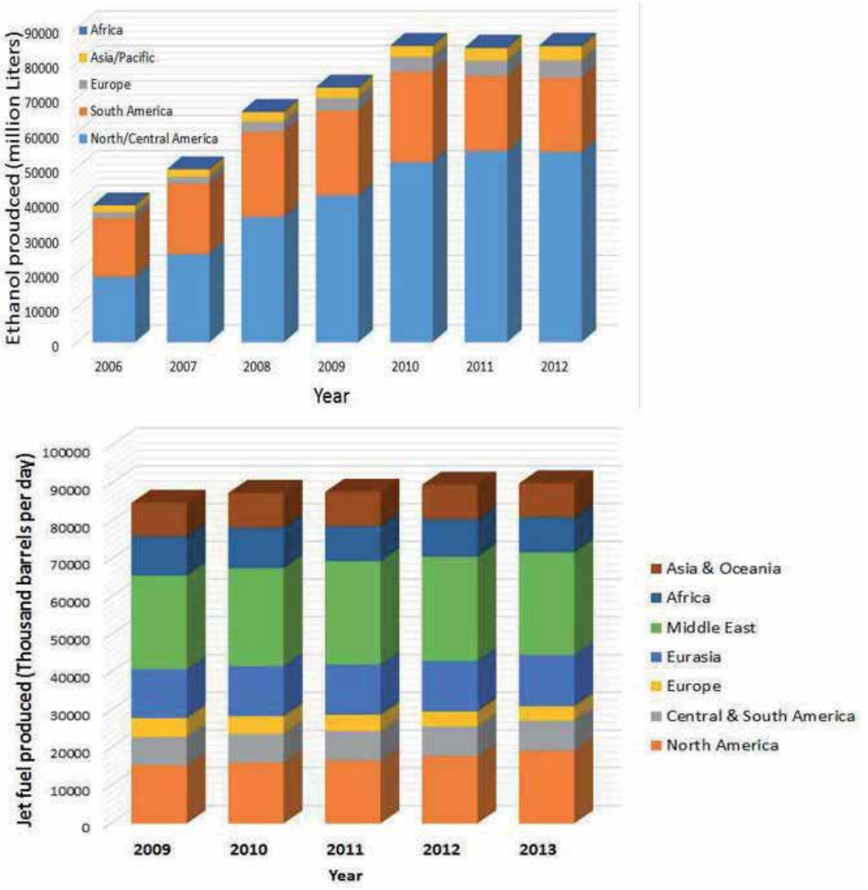


Figure 5.
Worldwide bio-ethanol production and consumption of aviation fuel.

bio-ethanol is mixed to maximum 10~15% with gasoline. Although potential market of ethanol for mixing with gasoline seems limited for expansion, conversion to bio-jet fuel via bio-ethanol upgrading shows possibility of replacing existing petroleum-based aviation fuel.

For conversion of bio-ethanol to bio-jet fuel, physicochemical properties of bio-ethanol should be compatible with petroleum-based aviation fuel. The USA is utilizing advanced ATJ technology to make physicochemical properties of bio-ethanol compatible with those of existing petroleum-based fuel. More specifically, 99.5~99.9% of anhydrous ethanol is mixed with existing fuel or converted to bio-jet fuel. High purity ethanol is used as raw material in the process for upgrading physicochemical properties of bio-jet fuel. Such ATJ process is based on bio-ethanol for production of bio-jet fuel, and oxygen contents of bio-ethanol is removed by dehydration, polymerization for access of carbon atoms from existing petroleum-based aviation fuel, and hydrogenation reaction for optimization of physicochemical properties. **Figure 6** shows technical overview of ATJ process for production of bio-jet fuel from bio-ethanol [8].

The most efficient method of reducing carbon emission is low carbon bio-jet fuel, relevant technology to produce it and its commercialization. Many international airlines initiated small-scale projects, but so far economic viability has not been demonstrated, and possible remedy is under consideration. To accomplish such economic viability, international standards for carbon emission objective and related policy on the part of airlines have to be established as well as monetary

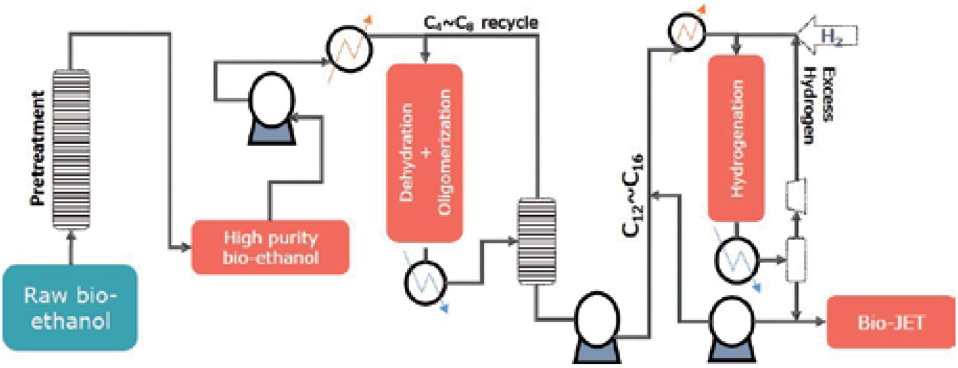


Figure 6.
Technical overview of ATJ process for production of bio-jet fuel from bio-ethanol.

incentive for bio-jet fuel utilization. To initiate economic drive for bio-jet fuel market, mass production-capable technology for bio-jet fuel production has to be developed. For carbon-neutral growth by 2050, international carbon emission reduction objective has been set by the ICAO with respect to greenhouse gas emission of 2005. For this, the CAEP has been established within the ICAO, and the ICAO is playing a central role to reduce aviation-induced greenhouse gas emission by intensive efforts. Development of aviation bio-jet fuel is taken as a pivotal means for greenhouse gas reduction, and many nations and international organizations are actively initiating aviation bio-jet fuel development. The ICAO 38th general meeting resolution approved aviation bio-jet fuel as vitally important intermediate to long-term means of greenhouse gas reduction, thus establishing fundamental frame of reference. More specifically, possibility of sustainable drop-in bio-jet fuel technology and related long-term policy as well as monetary incentive is also emphasized. Furthermore, IATA announced that sustainable and renewable energy utilization is the most reliable means to achieve established objective of greenhouse gas reduction and requested 6% replacement of aviation fuel with renewable energy by 2020. Bio-fuel is regarded as efficient and economical means of greenhouse gas reduction, energy security, new source of income, and market development for farm products in rural areas. Therefore, bio-fuel drive is supported as a national policy. Bio-fuel is supported by national policy in many nations via budget support (bio-fuel producers, vendors, and users are exempt from taxation or subsidy is given), minimum mixing proportion regulation, and import duty levied on foreign bio-fuel for wide distribution of bio-fuel. Altogether, worldwide monetary subsidy for bio-fuel totaled 20 billion US dollars in 2009 which was supported by US and EU nations. The Korean government subsidy will increase by 4.5 billion KRW every year during 2010~2020. This will be augmented by 8.5 billion KRW during 2021~2035.

To convert ordinary alcohol to fundamental aviation fuel element of hydrocarbon, oxygen contents have to be removed by dehydration via catalytic upgrading process. Alumina, transition metal oxides, and zeolite derivatives of SAPO, H-ZSM-5, and heterogeneous acid catalyst 0.5%La-2%P/H-ZSM-5 with acid sites [9]. Conversion rate was close to 100% at 250°C. Selectivity of ethylene was nearly 99.9% which was obtained by removal of oxygen via dehydration [10]. Such ethylene is converted to another reaction intermediate of alpha-olefin by polymerization called oligomerization. This is approximately equivalent to existing aviation fuel compound and intended to increase distribution of carbons. Candidate catalysts include Ziegler-Natta-based, homogeneous chromium-diphosphine-based, and heterogeneous zeolite-based catalysts. Oligomerization reaction took place at 90~110°C and 89 bar, where alpha-olefin with C4~C20 carbon numbers was synthesized with 96~97% of yield. Commercial oligomerization reaction involves 200°C and 250 bar with relatively wide range of carbon distribution of 5% C4, 50% C6~C10, 30% C12~C14, and 12% C16~C18 [11]. Such wide range of carbon numbers enables separation by selective distillation to light oil and aviation fuel. Hydrocarbons with low carbon numbers of C4~C8 separated by selective distillation process are reintroduced into oligomerization process and further synthesized into hydrocarbons with relatively high carbon numbers. Existing petroleum-based aviation fuel consists of hydrocarbons with C6~C16 range of high carbon numbers which require upgrading process. Such upgrading process necessitates hydrogenation reaction under hydrogen atmosphere and 370°C, WHSV of 3 h^{-1}, using 5% Pd/C or 5% Pt/C catalysts [12, 13].

5. Technological overview of bio-jet fuel based on bio-alcohol

Bio-jet fuel is currently being developed and commercialized with various degrees of technology development readiness with various production processes

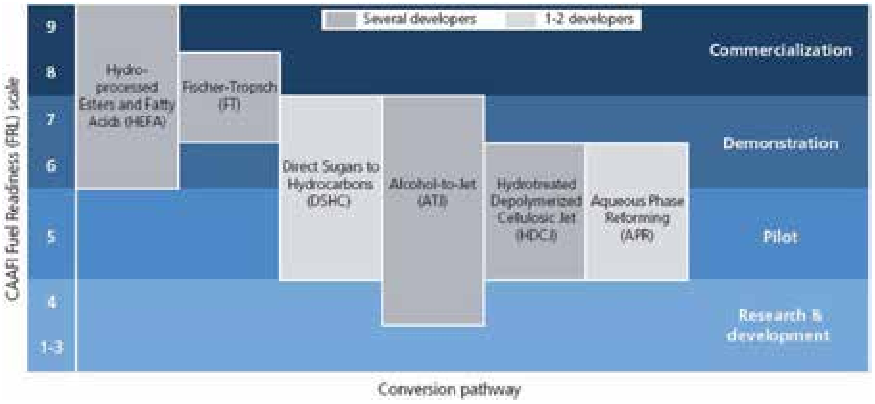


Figure 7.
Process technology-wise fuel readiness level (FRL) for bio-jet fuel [14].

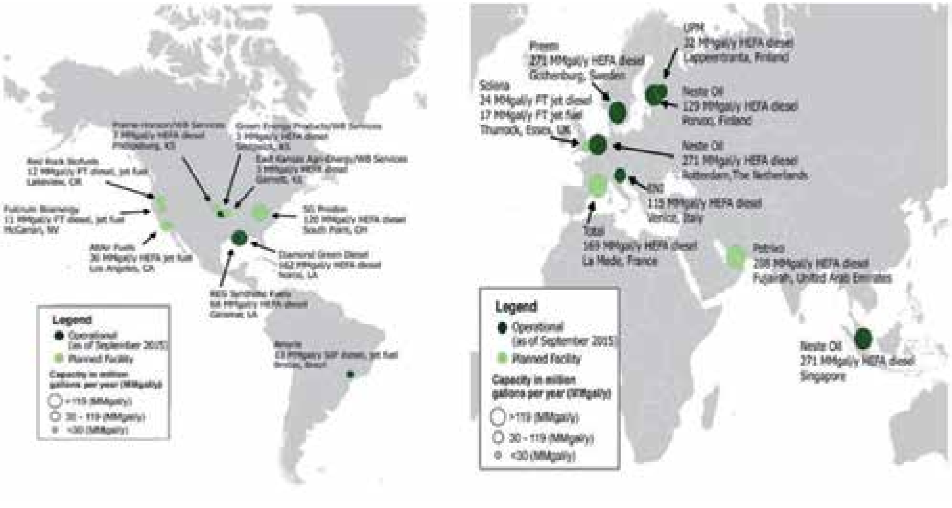


Figure 8.
Worldwide bio-jet fuel production facility and scale [15].

Airlines	**United**	**Cathay**	**FedEx/ Southwest**	**United**	**JetBlue**	**GE Aviation**	**Gulf Stream**	**KLM**	**Lufthansa**
Providers	Altair	Fulcrum	Red Rock	Fulcrum	SG Preston	D' Arcinoff	World Fuel Services (Altair)	Altair	Gevo
(t/yr)Supply	17,000	100,000	10,000	270,000+	33,500	17,000	—	—	270,000+
Major raw material	Waste fat oil	Waste	Forest residue	Waste	Vegetable oil	Cellulosic biomass	Waste fatty oil	Waste vegetable oil	Wood waste
Duration	3 years	10 years	8 years	10 years	10 years	10 years	3 years	3 years	5 years
Introduced	2016	2019	2017	2019	2019	—	2016	—	—
Contract year	2013	2014	2014	2015	2016	2013	2015	2016	2016

Table 4.
Current status of bio-jet fuel production and utilization [16].

employed for different raw materials. **Figure 7** shows the process technology-wise fuel readiness level (FRL) for bio-jet fuel. In view of the fuel readiness level (FRL), the bio-jet fuel production process close to technology development completion is HEFA process which was commercialized by UOP, AltAir, and Neste Oil companies as a kind of OJT process. On the other hand, FT, DSHC, and ATJ processes involving gasification of biomass, fermentation of glucose and catalytic conversion, and alcohol conversion, respectively, are also actively studied, but they are not as economically viable as HEFA/HRJ process from practical standpoint. As for major bio-ethanol upgrading companies, Terrabon and ZeaChem produce organic acid-derived hydrocarbon fuels, and Gevo and Vertimass produce alcohol-derived hydrocarbon fuels, the latter company utilizing ORNL technology. However, none of these companies have accomplished commercialization capability.

Figure 8 shows the worldwide bio-jet fuel production facility and scale. According to published data of ATAG and EIA in 2017 and 2015, annual US consumption of jet fuel and production of bio-jet fuel amounted to 8 billion and 200 million gallons, respectively. Approximately 190 million gallons of the bio-jet fuel was commercially produced by HEFA process, which is attributed to similarity to green diesel or hydrotreated vegetable oil (HVO) facility which produces automobile light oil using biomass. Sweden, the Netherlands, Singapore, and UAE are in possession of 50% of the production facility, while the USA produced 20% of them in eight regions. Representative bio-jet fuel producers include AltAir Fuels Refinery which was established in 2013 and introduced Honeywell UOP technology. Neste oil is operating production facility in Finland, Singapore, and the Netherlands, totaling 2 million gallons per annum. Other bio-jet fuel producers and airline consumers are listed in **Table 4**.

Apart from this, short-term test flight using bio-jet fuel is also actively performed by major airlines. Japan Airlines was tested by supplying 50% bio-jet fuel mixture to one of the four jet engines in January, 2009. Singapore Airlines also

Airlines	**Aircraft**	**Manufacturer/partners**	**Year**	**Raw material**	**Mixing proportion of bio-jet fuel**
Virgin Atlantic	B747–400	Boeing, GE Aviation	2008	Coconut babassu	20%
Air New Zealand	B747–400	Boeing Rolls-Royce, UOP	2008	*Jatropha*	50%
Continental Airlines	B737–800	Boeing, GE Aviation, CFM, Honeywell UOP	2009	2.5% Algae, 47.5% *Jatropha*	50%
JAL	B747–400	Boeing, Pratt & Whitney, Honeywell UOP, Nikki-Universal	2009	42% *Camelina*, 8% *Jatropha*, <0.5% algae	50%
KLM	B747–400	GE, Honeywell UOP	2009	*Camelina*	50%
KLM	B737–800	SkyNRG, Dynamic Fuels	2011	Waste cooking oil	50%
TAM Airlines	A-320	Airbus, CFM	2010	*Jatropha*	50%

Boeing	B747-8F		2011	*Camelina*	15%
Air France	A-321	SkyNRG	2011	Waste cooking oil	50%
Gulfstream Aerospace	Gulfstream G450	Honeywell, NBAA	2012	*Camelina*	50%
Air China	B747–400	Boeing, PetroChina	2012	*Jatropha*	50%
Alaska Airlines	B737, Bombardier Q400	Dynamic fuels, Horizon air	2011	Algae and waste cooking oil	20%
Paramus Flying Club	Cessna 182	SkyNRG	2013	Waste cooking oil	50%
LAN	A-320	Honeywell	2013	*Camelina*	30%
Thai Airways	Boeing-777	SkyNRG	2012	Waste cooking oil	50%
NRC Canada	Falcon 20, T-33	Aemetis, AFRL, Rolls-Royce, FAA-CLEEN, Agrisoma Biosciences, Applied Research Assoc., Chevron Lummus Global	2012	Carinata	100%
Military aircraft	**Aircraft**	**Manufacturer/partners**	**Year**	**Raw materials**	**Mixing proportion of bio-jet fuel**
US Navy	F/A-18	Honeywell UOP	2010	*Camelina*	50%
US Air Force	A-10c	Honeywell UOP	2010	*Camelina*, waste cooking oil	50%
US Air Force	F-22	Honeywell UOP	2011	*Camelina*	50%
US Navy	MH60S Seahawk Helicopter	Honeywell UOP, Bozeman	2010	*Camelina*	50%
US Navy	MH60S Seahawk Helicopter	Solazyme	2011	Algae	50%
Netherlands Air Force	AH-64D Apache Helicopter	Honeywell UOP	2010	Waste cooking oil and algae	50%
US Army	Sikorsky UH-60 Black Hawk helicopter	Gevo	2013	Cellulose-derived alcohol	50%
US Air Force	B-52	Syntroleum	2006	Natural gas	50%

Table 5.
Representative civil and military test flights using bio-jet fuel [17].

performed 12 test flights for 3 months from May, 2017, using bio-jet fuel mixture from waste vegetable oil. According to the ICAO, 40,000 or more flights were successfully performed by using bio-jet fuel, and US Air Force and Navy aircraft were also separately tested for possibility of using bio-jet fuel as a contingency plan for replacement fuel. Representative test flight data for civil and military aircraft are listed in **Table 5**.

6. Summary

Recently the Brisbane Airport of Australia made a partnership with Virgin Australia and the US fuel company of Gevo for a 2-year supply of bio-jet fuel produced by ATJ process to Virgin Australia and other Brisbane Airport-departing airlines, which approximately reached commercialization-capable level. However, economical feasibility is a prime concern before commercialization of bio-jet fuel and unit production cost is a major such index. For this, unit production cost of bio-alcohol is very important for its subsequent utilization as raw material of bio-jet fuel. As of 2011, unit retail price of ethanol produced by bio-chemical process from biomass was $4.18/GGE (gallon for gasoline equivalent). On the other hand, minimum unit retail price for ethanol produced by thermochemical process was $3.8 GGE. Butanol's unit retail price was $0.34/kg produced by ABE fermentation process from corn of $79.23/ton, while cellulosic raw material resulted in $4.1/GGE. For proper assessment of economic feasibility for ATJ conversion process, commercial production facility, upgrading process, and product distribution are primary considerations, which require intensive efforts for process upgrading.

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Edited by Yongseung Yun

Alcohol fuels must remain as an essential component for the realization of a sustainable low-carbon society. Use of locally available, under-utilized feedstock becomes important for local energy security as well as an option for distributed energy infrastructure. Utilizing the available feedstock that has not been properly regarded as a legitimate resource due to economic and social reasons should be the focal point in the search for possible resources for alcohol fuels. Lignocellulosic biomass and algal species are feedstocks that suit the purpose. This book can provide a brief introduction regarding the recent advances in the alcohol fuel field that is in constant challenge from recent issues on CO_2, shale oil, power-to-gas, and hydrogen.

Published in London, UK

IntechOpen

ISBN 978-1-78985-654-5