RECENT ADVANCES AND IMPROVEMENT IN BIOETHANOL TECHNOLOGY

Introduction

The 21st Century has been characterized by environmental consciousness and global efforts towards biofuels. One promising alternative is bioethanol, which is already incorporated in gasoline blends worldwide. In the United States, up to 98% of gasoline contains 10% ethanol (E10). Most bioethanol production in the US is from corn grain starch at approximately 94% [1]. There are several different methods for producing ethanol as well as various feedstocks, which differ from country to country.

History

Ethanol is in use because of its ability to increase the octane ratings in gasoline and has replaced several predecessors due to their environmental and health detriments. In the 1900s, gasoline in the United States used lead as a primary additive but was phased out due to health risks until its full ban in 1990 by the Environmental Protection Agency (EPA). Following the ban, alternative additives became popular like methyl tertiary butyl ether (MTBE) and the hydrocarbon mixture BTEX (benzene, toluene, ethylbenzene, and xylene). Later research found associated health risks, leading to discontinuation of these additives. Currently, bioethanol is being used since it is considered cleaner [2]. The Renewable Fuel Standard (RFS1) was created by the EPA in 2005 which mandated at least 4 billion gallons of renewable fuel. RFS1 was implemented to reduce greenhouse gas emissions, as well as expand the alternative fuels sector to promote widespread environmental protections. RFS1 was amended in 2010, referred to as RFS2, which expanded the standard to 36 billion gallons of biofuel that would be in use by 2022. Within this amended standard, the EPA defined that no more than 15 billion gallons of biofuel was to be from corn grain ethanol and no less than 16 billion from cellulosic biofuel [3]. As of 2023, the EPA has defined a target production of 840 million barrels of cellulosic biofuel, and a total renewable biofuel output of 20.94 billion barrels [4]. While vastly undershooting total output, the RFS is implemented to promote alternative fuel industries, specifically biofuels, for better emissions output.

Ethanol in the US

In the US, about 90% of all ethanol production is done through dry milling, and 10% through wet milling [5]. The primary difference between these methods is how the corn grain is prepared. During dry milling, corn grain is first ground up with no separation of its components. It is then mixed with water, where it is cooked with enzymes to induce its starch to undergo saccharification into glucose. Yeast gets added to the mixture to ferment and forms the ethanol. Finally, separation is used to purify the ethanol mixture and remove unwanted products. In wet milling, corn grain is first separated into its components: Starch, fiber, germ, and gluten, through seeping corn grain in a water and sulfur dioxide mixture [6]. Figures 1 and 2 below show the wet and dry milling processes, respectively; both diagrams show their primary products, along with the unit operations required. Dry mills are often favored due to lower energy requirements. However, they primarily produce ethanol and animal feed, while wet mills also make food-grade ethanol. There is a much larger range of by-products that wet milling can produce. This is because wet milling is able to accomplish less amount of impurities in the ethanol due to properties in its separation[6].

EFFECTS OF BIOETHANOL

Air Quality

There has been much concern over whether or not ethanol is the safest choice as a potential gasoline alternative. Globally, countries have adopted different standards for ethanol-gasoline fuel percentages. An assessment was conducted in 2010 simulating certain emissions by 2022, using the RSF from the same year. The researchers assumed in this model that 15 billion gallons of corn grain ethanol and 16 billion gallons of cellulosic ethanol [3] would be used by this year, as mandated by the standard. Results indicated that particle matter (PM) and ground-level ozone were expected to increase over areas including the Midwest, but also expected to decrease in crowded cities. Corn fertilization and harvesting are responsible for this trend, while the tailpipe emissions from utilizing ethanol decrease the ambient PM and ozone in vehicle-dense cities. Sulfur dioxide levels were also found to increase due to the agricultural portion of ethanol production [8]. Figure 3 below visualizes the changes in ozone design values, modeled for 2022 in 2012 [8].Another simulation conducted in 2014 saw similar results despite utilizing a different methodology. In this simulation, the researchers used an estimation of the miles traveled by cars in 2020 all using E10 fuel, while the 2010 study used the RFS2 fuel predictions directly. Spikes in ambient PM2.5 in the "corn belt" areas of the Midwest are visible under corn grain ethanol predictions, affecting local air quality [9].

A more recent model from 2019 calculated emissions based on certain proposed ethanol standards in China, with predictions for 2030 [10]. Unlike previous studies, this simulation showed a decrease of PM2.5 emissions from 10% to 16% across certain Chinese regions, as well as the amount of aromatics and olefins present in the fuel modeled. However, researchers did not consider the upstream processes of ethanol production since the corn would be imported under Chinese standards. This accounts for the disagreement between studies since these emissions primarily come from corn grain cultivation. As for carbon emissions, both black carbon [10] and carbon monoxide [8] were predicted to be reduced. Results from a second study regarding China's fuel program saw a 7-38% decrease in black carbon emissions in ethanol fuel blends in comparison to traditional gasoline [11]. Emission levels for nitrogen oxides (NOx) and volatile organic compounds (VOCs) have been inconsistent across research most likely due to differences in engines and automotive technologies used for testing. These emissions depend on the vehicle's technology [8].

Health Effects

One of the biggest concerns over ethanol usage in fuel is the increased risk of adverse health effects. Emissions of ethanol increase the formation of formaldehyde and acetaldehyde [8,12,10]. Formaldehyde is a known human carcinogen and acetaldehyde is a possible carcinogen [13]. In Brazil, until the early 2000s, there were many cars running on pure or high-percentage ethanol-gasoline blends [9]. As of 2023, the mandatory fuel blend percentage of ethanol in Brazil has decreased to be between 20% and 27% indicating that biofuel is still prevalent, albeit in decreased amounts [14]. Peak ethanol fuel program usage occurred during the 1980s and data has shown that ambient acetaldehyde and formaldehyde levels have decreased since then [12].

Improvements to Bioethanol

Most bioethanol produced worldwide is first-generation at more than 99% of the total supply. First-generation bioethanol is produced from sugar and starches, typically from sugarcane, wheat, and corn [15]. As previously mentioned, the US predominantly produces ethanol from corn grain, classifying it as first-generation [1]. The drawbacks of using first-generation ethanol include high PM emissions and ground-level ozone spikes in areas where corn grain is cultivated [9]. In addition, food security concerns remain prevalent since many first-generation ethanol plants double as food sources [16]. In the US, corn prices

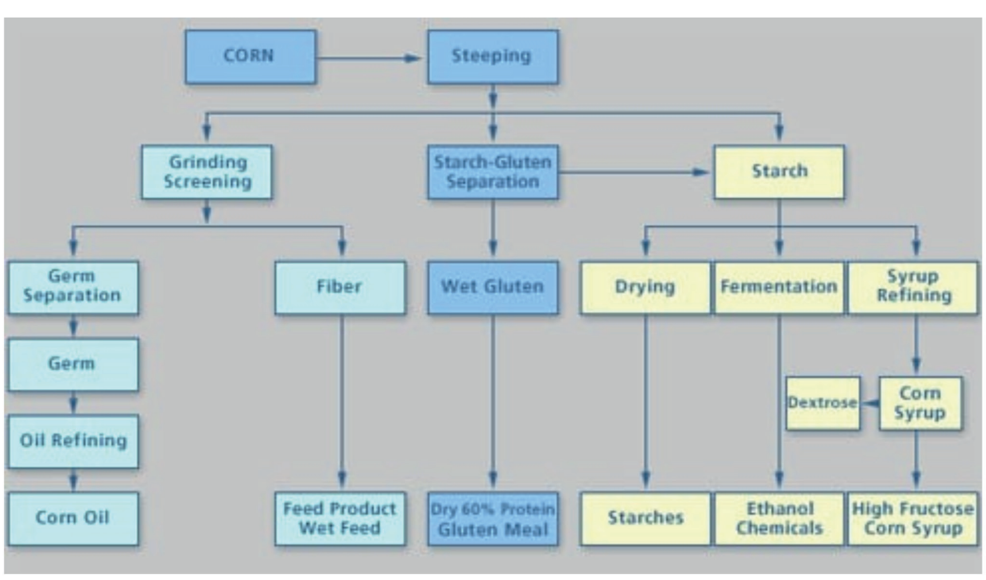

Figure 1 (left): Depicts the wet milling process of corn [7].

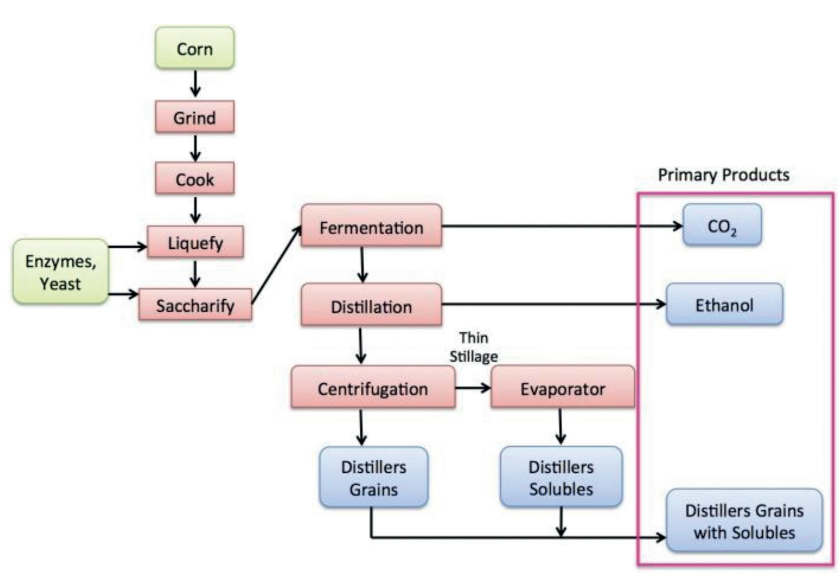

Figure 2 (right): Depicts the dry milling process of corn [7].

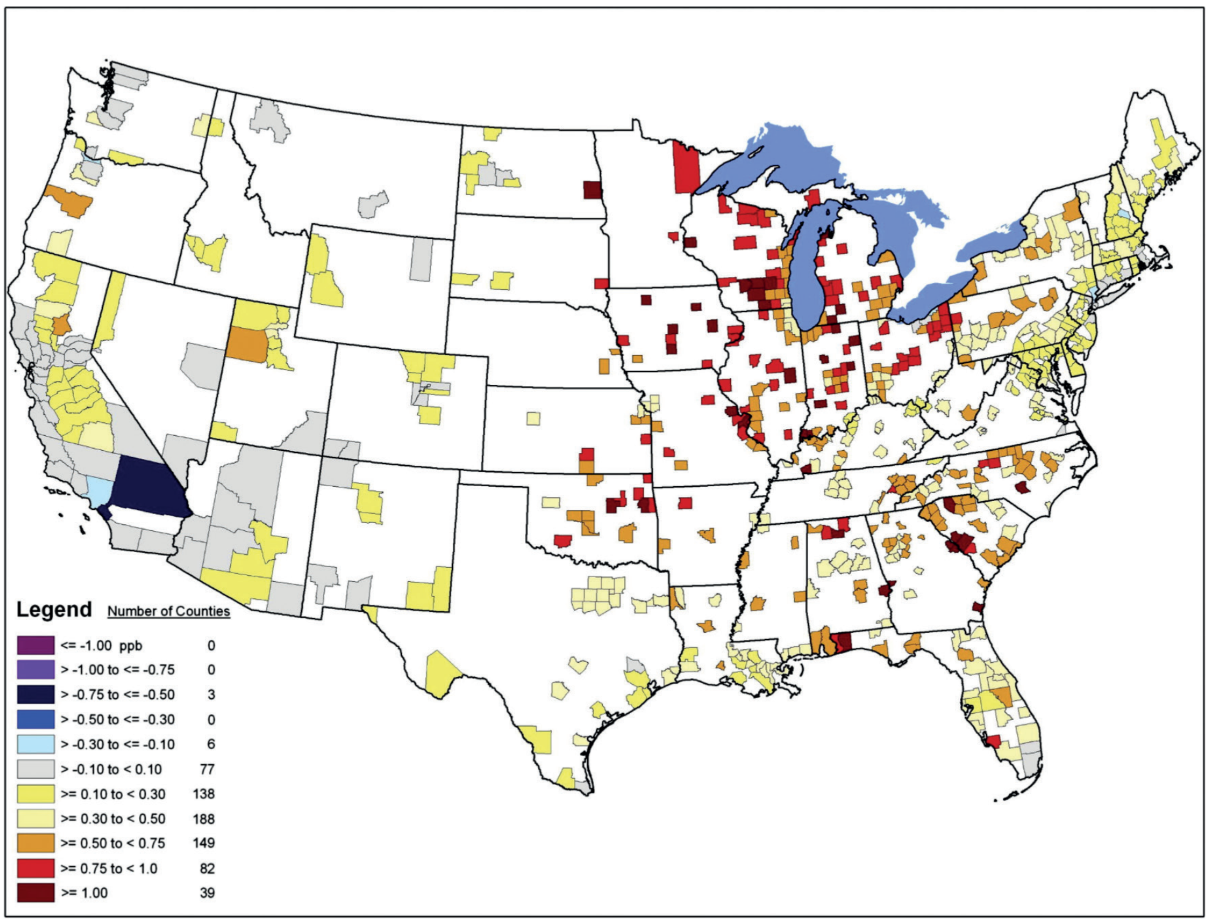

Figure 3: Changes in 2022 8-hour ozone design values for nonattainment areas between the RFS2 scenario and the RFS1 scenario [8].

per bushel have been predicted to increase due to the rise of ethanol production [3]. Second-generation ethanol is considered an improvement to first-generation ethanol. Also known as cellulosic ethanol, second-generation ethanol is sourced from biowaste [17] rather than crop sugars or starches. This type of ethanol allows for biofuel production without affecting food sources. In the US, instead of corn grain, corn stover could be used for cellulosic ethanol production [18]. Corn stover includes the leaves and stalk of a corn, which is then used as the basis for second-generation ethanol. Depending on the method and feedstock used, cellulosic ethanol could result in a larger carbon reduction than first-generation bioethanol [19]. Although the EPA mandated at least 16 billion gallons of cellulosic biofuel, there is currently no commercial cellulosic bioethanol production in the US due to technological and economic challenges [17, 3]. Such challenges include finding efficient pretreatment methods as well as production methods that can make cellulosic ethanol more economically viable.

Cellulosic Ethanol Production Methods

The process in which cellulosic ethanol is made differs significantly from first-generation ethanol. Instead of fermenting plant starches directly into ethanol, hydrolysis is the primary method. Brazil, the second largest producer of ethanol worldwide, uses sugarcane as its primary feedstock [20]. Although most of its production is first-generation, the country is home to the only plant in the world that commercially produces cellulosic ethanol [1]. Making cellulosic ethanol is a more complicated process than conventional first-generation ethanol because the cellulose must first be broken down into sugars before starting fermentation. These free sugar molecules, through hydrolysis, then can be fermented for ethanol production [21]. One vital step, however, is the pretreatment of the feedstock. Known as first-stage hydrolysis, it aims to break down the lignin and hemicellulose that surround the feedstock cellulose [22]. One of the most common pretreatments, acid hydrolysis, is performed by soaking the feedstock in a dilute acid solution and heating the mixture [21,22]. Enzymatic hydrolysis, a second pretreatment also known as second-stage hydrolysis, introduces a cellulose-degrading enzyme that converts the complex carbohydrate into sugars for fermentation [21]. Cellulosic bioethanol requires complex methods, which is partially why many countries are reluctant to incorporate it into their commercial biofuel production.

Recently, there have been efforts to make cellulosic ethanol production more favorable by potentially mitigating the amount of pre-processing requirements needed for the feedstock. A potential idea that is being researched is the incorporation of biological microorganisms into pre-treatments. Microorganisms play an important role in the fermentation process in common cellulosic production systems, but they are rarely used in the saccharification stage. Consolidated bioprocessing (CBP) is an approach that aims to merge both the saccharification stage with the fermentation stage by using a single organism to convert the material to sugars as well as ferment it to ethanol. By combining these processes, the costs of breaking down the cellulose could be reduced by avoiding the usage of expensive commercial enzymes [23]. CBP organisms have also been the target of genetic modification in order to increase ethanol yield. Some of the organisms researched for engineering include various yeasts, bacteria, and fungi and it has been predicted that a consortium of microbials could make the process even more robust [24].

The International Energy Agency (IEA) Bioenergy Organization has created a classification that aims to quantifiably measure the readiness of a system for commercial deployment, the Technology Readiness Level (TRL) which uses values 1 to 9 [25]. When measuring both the feedstock and the concept of specific biofuel refineries, it was found that while conventional (first-generation) biorefineries have a readiness of 9, lignocellulosic biorefineries only have a TRL of 6-8. One way researchers are aiming to make cellulosic bioethanol production more economically viable is by finding ways to utilize the lignin component of cellulosic material that would have otherwise been discarded as residue, also known as valorization. Due to the specific structure of lignin and certain features it possesses such as high reactive groups and hydrophobicity, it has the potential to be made into many types of chemicals and materials. Some of these include carbon fibers, oleo-gels, polymer blends, and phenols which have applications in industries like pharmaceutical, cosmetics, and fuels [26]. Economic analyses have been conducted on the impact of lignin valorization on bioethanol product economics. In one model of a specific industrial process, researchers analyzed the economic impact of two potential co-products of cellulosic ethanol production: Compressed natural gas (CNG) and lignin plastic composite material (LPCM) both of which have various applications apart from bioethanol. In this model, it was found that by including CNG and LPCM as co-products, the capital costs could be distributed among these products, resulting in a feedstock cost decrease of 19.4% [27]. Instead of discarding the byproducts of second-generation bioethanol production, valorization could help make the industry more competitive and economically viable.

Third-Generation Ethanol

Cellulosic ethanol does not come without its drawbacks. Despite not being a food source, cultivation still produces harmful emissions and other environmental detriments. Harvesting excessive stover from corn, for example, can harm the soil, lead to increased levels of erosion and water pollution [18]. In addition, cellulosic ethanol can be costly and requires advanced technologies in order to facilitate the complicated process. A newer feedstock for ethanol is being researched and the results are promising: third-generation bioethanol. Third-generation bioethanol uses algae as its feedstock- a remarkable feat. Algae is a promising alternative due to its high lipid and carbohydrate content, low land usage, and low levels of lignin and hemicellulose [28]. The low levels of lignin and hemicellulose make this option more attractive than second-generation ethanol since the main obstacle for cellulosic ethanol production is that advanced technology needed for substance breakdown.

Third-generation bioethanol is still being researched and there are still no commercial producers of it. Currently, the main drawback is the large amount of energy needed to cultivate it. For this reason, the net energy return is lower than what is needed to compete with fossil fuels [29]. Different species of algae as well as cultivation and fermentation methods are being researched so that algal bioethanol could become more economically attractive. Various algae species have different carbohydrate contents, and ones with higher carbohydrate percentages may have higher conversion into biofuel [30]. There are two main types of algae: microalgae and macroalgae, which include seaweed. Researchers propose that seaweed has the most potential due to its low lignin composition. Because of this, the greatest potential for investment in third-generation ethanol is in eastern Asian countries, where 98.9% of the world's macroalgae cultivation occurs a there [28]

The algal-ethanol process is similar to cellulosic production in the sense that both have to undergo pretreatment, fermentation, and purification. Discovering appropriate algae species for cultivation is important, but research is also being conducted on different pretreatment and hydrolysis methods [31]. One study was done on a fungal pretreatment method for the algae K.alvarezii and G.amansii which are potentially suitable for bioethanol

Figure 4: Global seaweed distributions across the different regions of the world [28].

production due to their high percentage of carbohydrates. It was found that the fungal pretreatment resulted in a 2.3-fold increase in sugar yield from the unpretreated algae [32]. In another study, a chemoenzymatic method which is an acid pretreatment, was tested for the hydrolysis microalgae Chlorella sorokiniana, Tetraselmis sp., and Slkeletonema sp. The results were promising, showing that ethanol yields were close to the theoretical maximum [33]. Many components go into the conversion process of algae feedstock to third-generation bioethanol, all of which are being actively studied in order to make the process efficient and economical.

The Future of Bioethanol

When discussing the future of bioethanol and whether or not it should be promoted, it is important to understand the distinctions between all the different methods and feedstocks involved in the process. The biggest challenge for the incorporation of bioethanol into society is finding ways to increase its attractiveness in comparison to traditional fuels. Although it succeeds in aspects such as improving tailpipe emissions, it also falls short in other ways. All over the world, researchers are constantly discovering new methods and technologies to make bioethanol more competitive. This involves finding appropriate feedstock, ones that don't interfere with human food sources, have high conversion rates, and have high potential for cultivation. This also involves creating methods for pretreatment and fermentation that aid in making ethanol production more economically viable and efficient.

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