Potential Contamination in Fuel Ethanol Production

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Ethanol can be produced from sugary, starchy, and lignocellulosic feedstocks. Each feedstock requires different procedures for its conversion to fermentable sugar. Lignocellulosic biomass requires extra pretreatment compared to sugar and starch feedstocks to disrupt the structure and improve enzymatic hydrolysis efficiency. However, the greatest concern regarding the pretreatment process is inhibitor formation, which might retard enzymatic hydrolysis and fermentation. In addition to the inhibitors from pretreatment, chemicals used during the pretreatment and fermentation of byproducts may remain in the final product if they are not removed by ethanol distillation and dehydration. Maintaining the quality of ethanol during storage is another concerning issue. Initial impurities of ethanol being stored and its nature, including hygroscopic, high oxygen and carbon dioxide solubility, influence chemical reactions during the storage period and change ethanol's characteristics (e.g., water content, ethanol content, acidity, pH, and electrical conductivity).

1. Introduction

Industrial ethanol is mostly produced for use as fuel. Ethanol is also used in many applications such as solvents, alcoholic beverages, and feedstocks for synthesizing various organic substances in the chemical industry, such as ethylene, polyethylene, 1,3-butadien, and ethyl acetate [1]. The trend of renewable energy and alleviating greenhouse gas emissions from fossil fuels has promoted greater ethanol fuel demand.

The contamination of ethanol can increase fuel corrosivity, which causes the swelling of some elastomer engine parts [2]. Thus, ethanol for gasoline blending must meet the anhydrous ethanol specification to ensure sufficient quality when it is used in vehicles, to ensure it is environmentally friendly and not harmful [3][4][5]. Certain impurities influence ethanol characteristics, such as acidity, pHe, water content, and electrical conductivity. **Table 1** compares the anhydrous and hydrated ethanol specifications of some countries, including the United States, Brazil, Thailand, and those in the European Union. It can be noticed that fuel ethanol specifications used to control ethanol quality are different due to different markets, climatic conditions, and raw materials used in ethanol production [5]. The differences in water content specification between different countries rely on ethanol–gasoline blending ratios and the methods of gasoline transportation. Only the EU has a phosphorus specification based on ethanol producers. Brazilian and Thai ethanol standards provide criteria for electrical conductivity, since conductivity can simply and quickly detect impurities in ethanol [6]. In Thailand, anhydrous ethanol specification can be categorized into three major applications: denatured ethanol for gasohol production (TIS 2324), ethanol for pharmaceutical use (TIS 640-1), and ethanol for industrial use (TIS 640-2). When compared to the EU, USA, and Brazil, Thailand does not include sulfate limitation in anhydrous ethanol for blending with gasoline. The maximum quantities of permitted sulfate in the USA, Brazil, and EU specifications are 4, 4, and 3 ppm, respectively. For the USA, 4 ppm is the sulfate limitation for E10 fuel, which is agreement with the refining, automotive, and ethanol industries. Thus, this limitation may be updated in the future due to the increasing ethanol concentration in ethanol-blended gasoline [7][8]. Hence, Thailand should include sulfate specification in the future when ethanol demand increases.

Recently, there has been more attention given to second-generation ethanol, owing to the conflict between food and fuel. However, it contains higher amounts of impurities than first-generation ethanol. Some scientific confirmation is needed to prove which impurities in lignocellulosic ethanol can cause an adverse effect on vehicle engine performance. This finding could lead to the adoption of new specifications or the revision of existing ones to make them more compatible with second-generation ethanol. According to the research, phosphorus should be limited in fuel ethanol to protect automotive catalyst systems from deactivation if ethanol is produced from non-traditional feedstocks. The phosphorus content in ethanol is affected by feedstock composition, the fertilizers used in the cultivation stage, and nutrients used in the fermentation process [6][9]. Acetic acid in ethanol has the greatest impact on ethanol acidity, causing corrosion to

automobile engines. Since the acetic content of lignocellulosic ethanol is more than that of first-generation ethanol [10], it is challenging for ethanol producers to meet the required standards. Furthermore, lignocellulosic ethanol contains a significant amount of furanic substances. The remaining furanic compounds in ethanol–gasoline blended fuel can lead to lower oxidative stability and the possibility of the formation of dangerous organic peroxides [11].

For anhydrous ethanol for pharmaceutical purposes, the limitations of non-volatile materials, benzene, acetaldehyde, acetal, and any other volatile impurities are included in the specification. If lignocellulosic ethanol is going to be used for pharmaceutical purposes, the separation technique should be improved to remove these impurities, especially acetaldehyde and acetal [12].

Habe et al. [10] reported impurities in 17 different types of bioethanol samples. They concluded that lignocellulosic-derived ethanol contains more impurities than sugar- and starch-derived ethanol because lignocellulosic feedstock requires a pretreatment to modify the lignocellulose structure and improve the accessibility of enzymes and chemicals. Lignocellulosic ethanol has high concentrations of acetic acid, acetaldehyde, methanol, and furan. On the other hand, these contaminants are lower in sugar- or starch-derived ethanol. Considering sulfur-containing compounds, dimethyl disulfide and thiazole are only found in lignocellulosic-derived ethanol. In contrast, dimethyl sulfide and dimethyl sulfoxide are sulfur-containing compounds in sugar- and starch-derived ethanol.

In addition to the type of feedstock and production process, storage procedure also has an influence on ethanol quality. Naegeli et al. [13] concluded that decreasing fuel ethanol pH over storage periods correlates with ethyl sulfate formation, which also increases ethanol conductivity. During ethanol distillation, sulfite, a fermentation byproduct, is carried over with the ethanol vapor. Then, sulfite is oxidized to sulfate during the storage period. Recently, this sulfate contamination issue has gained interest due to its effect on vehicle engines. Many studies have reported that the contamination of sulfate causes deposit formation on inlet valves in combustion chambers and on injector tips [7][8][13][14].

Although the investigation of the impurities in final fuel products has received much attention [15][16][17], there are a few studies focusing on impurities occurring throughout the production process, and only some previously published works attempting to set guidelines to control blended gasoline quality during storage periods [18][19]. The lack of collective information regarding the quality control of anhydrous ethanol from the up-stream to downstream process is a current knowledge gap, which brings about the first aim of this research—to create an understanding of the causes of impurity formation throughout the whole production process (starting from feedstock acquisition), and identify the effects on the subsequent processes (fermentation, ethanol recovery, and storage) and on the final ethanol properties. Finally, specific guidelines to control ethanol quality, from anhydrous ethanol production until the storage period, can be proposed. The strategies and methods for reducing contamination are integrated from current knowledge.

Table 1. Comparison of anhydrous and hydrated ethanol specification [20][21][22][23].

Specification	Unit		European Union prEN 15376	USA ASTM D-4806-16a	Brazil ANP Resolution nº 19	Thailand TIS 2324	TIS 640-1	TIS 640-2
Ethanol type	-	-	Anhydrous	Denatured anhydrous	Anhydrous	Denatured anhydrous	Anhydrous	Anhydrous
Ethanol	% by volume	Min.	-	-	98	-	-	-
Ethanol and higher saturated alcohols	% by volume, (% by mass)	Min.	(98.7)	92.1	(99.3)	99	99.5	99.5
Higher saturated mono-alcohols-C3-C5	% by volume, (% by mass)	Max.	(2)	-	3	2	-	-
Methanol	% by volume, (% by mass)	Max.	(1)	0.5	0.5	0.5	0.02	0.05

Specification	Unit		European Union prEN 15376	USA ASTM D-4806-16a	Brazil ANP Resolution nº 19	Thailand TIS 2324	TIS 640-1	TIS 640-2
Water content	% by volume, (% by mass)	Max.	(0.3)	1	(0.7)	0.3	-	-
Density at 20 °C	kg/m^3	Max.	-	-	791.5	-	790–793	-
Total acidity (as acetic acid)	mg/L, (% by mass)	Max.	(0.007)	56 (0.007)	30	30	30	(0.005)
Electrical conductivity	µS/m	Max.	-	-	300	500	-	-
pHe	-		-	6.5~9.0	-	6.5~9.0	-	-
Copper	mg/kg, (mg/L)	Max.	0.1	0.1	0.07	0.07	-	-
Inorganic chloride	mg/kg, (mg/L)	Max.	1.5	6.7 (5)	1	(20)	-	-
Solvent-washed gum	mg/100 mL	Max.	-	5	-	5	-	-
Sulfur	mg/kg, (ppm)	Max.	10	(30)	Report	-	-	-
Total sulfate	mg/kg	Max.	3	4	4	-	-	-
Phosphorus content	mg/L	Max.	0.15	-	-	-	-	-
Non-volatile material	mg/100 mL, (% by mass)	Max.	10	-	5	-	2.5	(0.005)
Denaturant content	vol. %	Max.	-	1.96~2.5	-	-	-	-
Iron	mg/kg	Max.	-	-	5	-	-	-
Benzene	mL/kL	Max.	-	-	-	-	2	-
Acetaldehyde and acetal (as acetaldehyde)	% by volume, (% by mass)	Max.	-	-	-	-	0.001	(0.10)
Any other volatile impurity (as 4-methylpentan-2-ol)	mL/kL	Max.	-	-	-	-	300	-
Absorbance - Lower than 240 nm - 250 to 260 nm - 270 to 340 nm		Max.	-	-	-	-	0.4 0.3 0.1	-
Sodium	% by mass	Max.	-	-	0.0002	-	-	-
Permanganate time	Minute	Min.	-	-	-	-	-	15

Specification	Unit	European Union prEN 15376	USA ASTM D-4806-16a	Brazil ANP Resolution nº 19	Thailand TIS 2324	TIS 640-1	TIS 640-2
Aspect	-	Clear and colorless	Clear and colorless	Clear and no impurities	Clear, colorless and no visible suspended solids	Clear and colorless	Corresponding to ISO 2211

2. Ethanol Production from Different Types of Feedstock

Ethanol can be produced from different feedstocks. There are two main types of ethanol production feedstock in first-generation technology: sugar-containing feedstock and starch-containing feedstock. An increase in fuel demand and concern regarding the potential negative risks of using food feedstock led to the utilization of lignocellulosic feedstock for fuel ethanol production in second-generation technology. Ethanol production processes from any feedstocks can be divided into three main steps: (1) converting feedstock into fermentable sugar; (2) the fermentation process to convert fermentable sugar to ethanol; and (3) the ethanol recovery and storage process. Although the production feedstocks are different, the fermentation and downstream processes are significantly similar. Hence, when considering different feedstocks, the difference in contamination is mainly affected by the feedstock stage involving the conversion to fermentable sugar [24].

3. Impact of Different Feedstocks on Impurities in Fuel Ethanol

As mentioned previously, the ethanol production process from each type of feedstock includes three major steps: conversion of feedstock, fermentation, and ethanol recovery. This section describes the conversion of each separate feedstock. The key to this process is to release sugar molecules from the feedstock structure. The difficulties in releasing sugar molecules depend on feedstock type, which involve different required steps to convert feedstock, and consequently result in various contamination profiles in the ethanol product.

3.1. Conversion of Sugar-Containing Feedstock

In many countries, such as Thailand, Brazil, India, and Colombia, sugarcane is cultivated for sugar production [25][26]. The valuable byproduct from sugar production is molasses, which is used in ethanol production. Besides, sugarcane juice is also utilized to produce ethanol in some countries such as Thailand [25][27][28]. Therefore, the sugar production process needs to be considered, as it determines the quality and impurities of the feedstock during ethanol production.

Attached and autonomous distilleries are two types of sugarcane-derived ethanol production plants, classified by ethanol feedstocks. The overall production process and chemical additions in each step for these two categorized sugarcane-derived ethanol production plants are shown in **Figure 1**. In the case of autonomous distilleries, the process section in the dashed–blue box can be excluded.
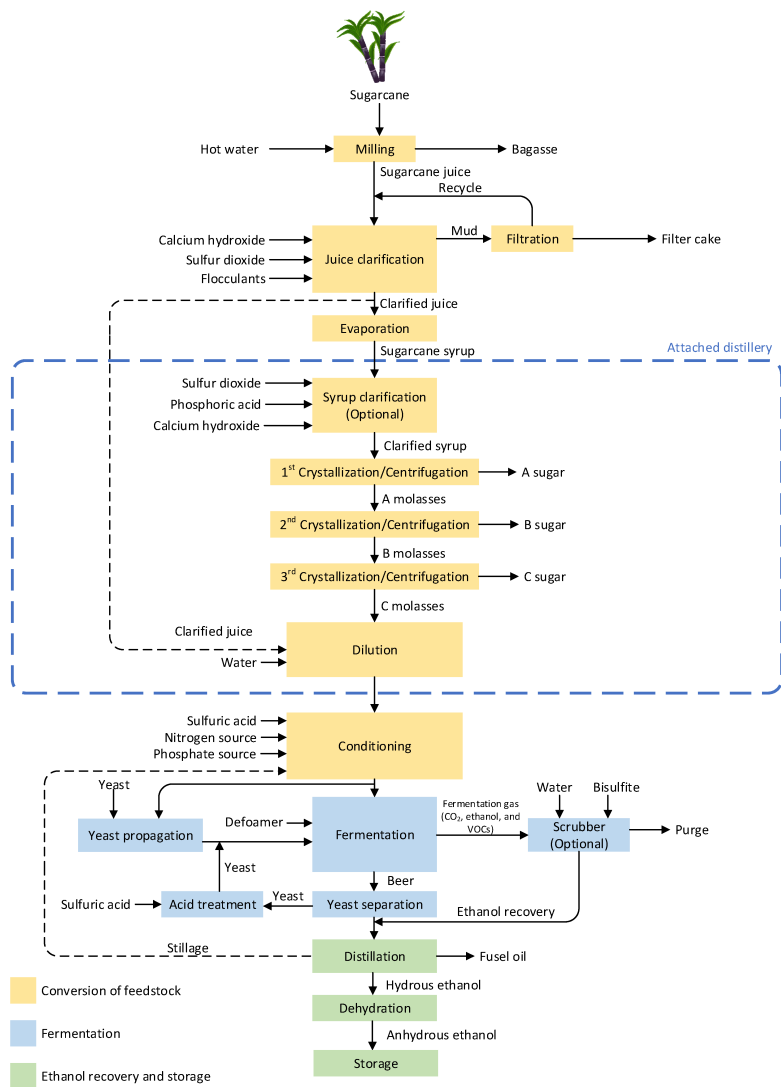
Figure 1. Type of sugarcane-derived ethanol production plant.

3.2. Conversion of Starch-Containing Feedstocks

Ethanol production from starch-containing feedstocks, such as corn kernels and cassava, can be classified into two processes: (1) the wet milling process and (2) the dry milling process, as presented in **Figure 2**. The major difference between these two methods is that the wet milling process has been developed to separate high-value products from the starchy feedstock, while the latter has not.
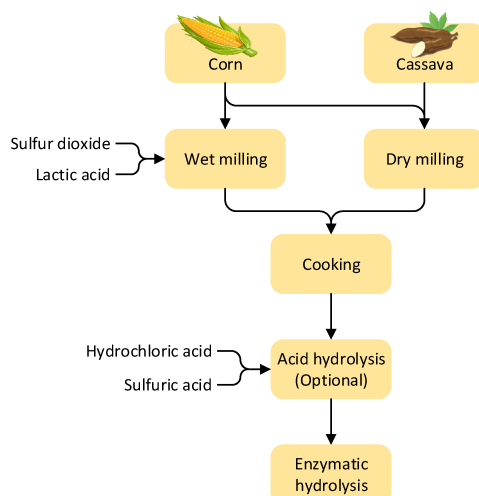

Figure 2. Conversion of starch-containing feedstock.

The wet milling process is applied for corn grain feedstock because it provides high-value products, such as corn gluten meal, corn gluten feed, and corn germ meal, which are usually applied as poultry feed. However, the drawbacks of the wet milling process include high capital cost, high energy consumption, and less ethanol yield. The dry milling process is often chosen as an alternative approach for corn grain feedstock.

The dry milling process is appropriate for cassava chip feedstock in ethanol production because cassava chips do not provide high-value components [3].

4. Ethanol Recovery

4.1. Distillation Process

In sugar and starch fermentation, other alcohols, aldehydes, ketones, fatty acids, and esters are produced as volatile byproducts, whereas cyclic and heterocyclic compounds are volatile byproducts in lignocellulosic ethanol fermentation [29]. After the fermentation process is finished, the centrifuged broth is obtained by separating the yeast from the fermented beer. The centrifuged broth containing ethanol at about 5–15 wt.% is passed to the distillation column to remove the water. The distillation column consists of two columns. The first one is called the distillation column, or the beer column. In this column, approximately 50 wt.% ethanol can be achieved. The second column is the rectifying column. Hydrous ethanol (about 93 wt.% ethanol) can be achieved in this column [30][31].

Distillation can remove some impurity from ethanol with increasing ethanol concentration. Furthermore, chemical molecules with low boiling points, or those similar to ethanol, show up in distillate because distillation is ineffective in removing them [17]. For example, volatile impurities (acetaldehyde, acetone, ester, methanol) still show up in distillate. These contaminants result in lower engine efficiency when ethanol is used as fuel [7][8][15][29][32].

4.2. Stillage Recycles

The remaining bottom liquid product after distillation of the ethanol from the beer column is called whole stillage. The whole stillage can contain ethanol up to 0.02 wt.%. Not only ethanol, but also solid particles, such as yeast cells, dissolved matter, and minerals, can be found [26][33]. After removing solid particles through a solid–liquid separation unit (e.g., centrifuge or decanter), the obtained liquid product called thin stillage can be recycled back to different process steps, e.g., fermentation or saccharification, to minimize effluent treatment cost. However, thin stillage recycling can possibly cause some drawbacks, such as the accumulation of lactic acid, minerals, and unutilized substrates [26][33][34].

The difference in the type of feedstock affects the impurities in the stillage. When stillage is recycled, it causes different contaminations. In the case of cane molasses feedstocks, whole stillage (without yeast cell separation) can be recycled in the fermentation step [26]. In the case of starch-containing feedstock, 25–75% of the thin stillage can be recycled in the fermentation or saccharification processes [26]. Other feedstocks, such as corn, wheat, and triticale, can be recycled at 75%, 60%, and 60% of thin stillage, respectively [33][35].

In Thailand, produced stillage during ethanol production from molasses or cassava is often treated and converted into methane gas. Stillage can also be distributed to farmers because stillage provides minerals for plants [36][37].

4.3. The Fate of Electrolytes during Distillation

During ethanol distillation, sulfite as sulfur dioxide can be distilled into the final ethanol product. The presence of sulfite in distilled ethanol appears to be a common experience in the distilled spirits industry [7][38]. Zhang et al. [39] reported that the distillate of chardonnay contained 12% ethanol and 176 mg/L sulfite as SO_2. After two stages of distillation, the concentration of ethanol and sulfite as SO_2 were increased to 69 vol% and 654 ppm, respectively. This phenomenon can be explained with the vapor–liquid equilibria for dilute aqueous solutions of SO_2 as volatile weak electrolyte [40].

4.4. Dehydration Process

The distillation process produces 95 vol% ethanol, approximately, because of the azeotropic mixture of ethanol and water (95.6 wt.% at 78.15 degrees Celsius). Before mixing ethanol with gasoline, it is necessary to increase the ethanol concentration to 99.3 wt.%, to make anhydrous ethanol. Anhydrous ethanol can be obtained by several dehydration methods such as molecular sieves, azeotropic distillation, and pervaporation. The molecular sieve is most commonly used because it has lower investment costs than pervaporation and requires less steam than azeotropic distillation [30][31].

The most common dehydration methods in Brazil are heterogeneous azeotropic distillation, extractive distillation, and molecular sieve adsorption [31]. The heterogeneous azeotropic distillation method requires an entrainer to increase separation. Many entrainers, such as benzene, toluene, and cyclohexane can be used to separate ethanol from water [31][41]. However, using an entrainer can cause product contamination [42][43].

Extractive distillation, as an alternative method, requires the addition of a third component to change the relative volatility of ethanol and water. The third component acts as a separating agent, such as ethylene glycol, glycerol, 1,3 diamino pentane, diethylenetriamine, or hexachlorobutadiene. The separating agent and water mixture is obtained at the bottom of the column, which is fed to the second column to recover the separating agent. Anhydrous ethanol is obtained at the top of the extractive column. Compared to azeotropic distillation, this method provides less energy consumption and less ethanol contamination [31].

In the case of molecular sieve adsorption, there is no requirement to add solvent. Ethanol vapor is fed to zeolite beds. When hydrated ethanol contacts zeolite, water molecules are absorbed. When compared to azeotropic distillation and extractive distillation, molecular sieve adsorption offers lower energy consumption and no chemical contamination [31].

Pervaporation, a membrane dehydration method, is a relatively new alternative to the dehydration process. While adsorbents need regeneration, membrane separation offers continuous operation and energy saving. Industrial applications of zeolite membranes have been reported [44].

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