[Technical Report]

Chemical Analysis of Impurities in Diverse Bioethanol Samples

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Bioethanol has recently become an important resource for chemical industries. The chemical compositions of 17 different types of bioethanol were investigated with a focus on impurities that could affect catalytic performances in the downstream chemical processes. Lignocellulosic ethanol contained higher concentrations and a greater variety of organic impurities compared to sugar- or starch-derived bioethanol. Twenty-nine impurities were identified in lignocellulosic ethanol, whereas 16 impurities were in sugar- or starch-derived bioethanol. Lignocellulosic ethanol contained high concentrations of acetic acid, acetaldehyde, methanol, and furan-related compounds such as furfural. In contrast, with the exception of molasses-derived bioethanol obtained by crude distillation, the concentrations of these components were lower in sugar- or starch-derived bioethanol samples. Lignocellulosic ethanol contained dimethyl disulfide and thiazole, whereas the only organosulfur compounds found in sugar- or starch-derived bioethanol were dimethyl sulfide and dimethyl sulfoxide. These sulfur-containing impurities can cause catalyst deactivation in the bioethanol transformation processes. In lignocellulosic ethanol, more than 0.1 μg/mL of Si was detected.

Keywords
Biorefinery, Bioethanol, Impurity, Sulfur compound, Chemical composition

1. Introduction

Biofuels are important renewable resources that facilitate the sustainable development of society. The environmental advantages of biofuels, for example, the replacement of petroleum fuels and resultant mitigation of greenhouse gases, are many. Bioethanol is a liquid energy source and fuel additive and is the most common biofuel in use worldwide 1).

Bioethanol can be produced by fermentation using various types of microorganisms. A variety of natural resources can provide sugars for the production of ethanol via fermentation, including sucrose-containing feedstocks such as sugarcane, starchy feedstocks such as corn, and lignocellulosic biomass such as wood and straw. First generation biofuels, for example, bioethanol from sugar or starch-containing feedstocks, are produced from raw materials that can be used as foodstuffs. Second generation biofuels such as lignocellulosic bioethanol are produced from inedible raw materials such as wood and straw. Possible shortages of food in the future require a worldwide shift from first- to second-generation biofuels. Toward this end, technologies for bioethanol production from inedible feedstocks have been investigated over the past two decades. With regard to the quality standardization of ethanol used as a biofuel in Japan, the Japanese Automotive Standards Organization (JASO) M361 “Automotive Fuels—Ethanol as Blend Stock” (Table 1) was established in 2006 by the Society of Automotive Engineers of Japan (JSAE) 2).

Bioethanol has recently become an important resource for chemical industries 3)～5). For example, ethylene and ethylene glycol (EG) can be chemically produced from bioethanol 6). Bio-based ethylene and EG can in turn be used to produce polyethylene and polyethylene terephthalate. Propylene, which is the second largest platform chemical after ethylene, is also an important target to be produced from bioethanol 4).

As shown in Table 1, bioethanol that is to be blended with gasoline should contain more than 99.5 % (v/v) alcohol. However, if bioethanol is to be used as a resource for chemical industries, high purity is not necessarily needed. Lower grades of bioethanol contain less ethanol and more impurities, but may satisfy the requirements for the above use, because the desired purity of bioethanol depends on both energy and processing costs required to produce the final chemical products. Clarifying the properties and concentrations of impurities in low-grade bioethanol sample and determining to what extent these impurities affect the downstream chemical processes, for example, catalytic performances, is important. At present, JASO M361
Table 1: Japanese Quality Standard of Bioethanol for Blending with Gasoline (JASO M361)\(^{2)}\)

| Item                     | Unit            | Limit         | Test method\(^a)\) |
|--------------------------|-----------------|---------------|--------------------|
| Appearance               | [-]             | Transparent, No-turbidity | Visual inspection |
| Alcohol                  | [vol%]          | ≥99.5         | JAA S 001, 6.2     |
| Methanol                 | [g/L]           | ≤4.0          | JAA S 001, 6.4     |
| Water                    | [wt%]           | ≤0.70         | JIS K 8101         |
| Organic impurities       | [g/L]           | ≤10           | JAA S 001, 6.4     |
| (except methanol)        |                 |               |                    |
| Electric conductivity    | [μS/m]          | ≤500          | JIS K 0130         |
| Evaporated residues      | [mg/100 mL]     | ≤5.0          | JAA S 001, 6.3     |
| Copper                   | [mg/kg]         | ≤0.10         | JIS K 0101, 51.2 or 51.3 |
| Acidity (as acetic acid) | [wt%]           | ≤0.0070       | ISO 1388/2         |
| pH                       | [-]             | 7.0 ± 1.0     | ASTM D 6423        |
| Sulfur                   | [mg/kg]         | ≤10           | JIS K 2541-6 or 2541-7 |

\(^{a}\) Abbreviations: JASO, Japanese Automotive Standards Organization; JAA, Japan Alcohol Association; JIS, Japanese Industrial Standards; ISO, International Organization for Standardization; ASTM, American Society of Testing and Materials.

Table 2: Properties of 17 Bioethanol Samples Used in This Study

| Sample name | Feedstock (sugar) | Country of origin | Alcohol by volume\(^a)\) [%] | Water content\(^b)\) [%] |
|-------------|-------------------|-------------------|-----------------------------|-------------------------|
| T08-1       | Sugarcane (sucrose) | Thailand          | 95.8                        | 6.72                    |
| T08-2       | Sugarcane (sucrose) | Thailand          | 96.3                        | 5.68                    |
| C08-1       | Corn (starch)     | China             | 95.2                        | 7.13                    |
| P08-1       | Sugarcane (sucrose) | Pakistan         | 96.4                        | 5.87                    |
| B08-1       | Sugarcane (sucrose) | Brazil           | 95.6                        | 6.75                    |
| B08-2       | Sugarcane (sucrose) | Brazil           | 95.6                        | 6.74                    |
| B09-1       | Sugarcane (sucrose) | Brazil           | 95.6                        | 6.24                    |
| B09-2       | Sugarcane (sucrose) | Brazil           | 95.6                        | 6.26                    |
| B09-3       | Sugarcane (sucrose) | Brazil           | 95.7                        | 5.80                    |
| B09-4       | Sugarcane (sucrose) | Brazil           | 95.4                        | 6.33                    |
| T09-1       | Sugarcane (sucrose) | Thailand         | 96.1                        | 6.76                    |
| C09-1       | Corn (starch)     | China             | 95.3                        | 6.71                    |
| Miyako      | Molasses (sucrose) | Japan            | 88.0\(^c)\)                | 13.80                   |
| Hinoki      | Chamaecyparis obtusa (cellulose) | Japan          | Dehydrated (99.7)          | 0.40                    |
| Eucalypt    | Eucalyptus (cellulose) | Australia and China (mixed sample) | Dehydrated (99.5) | 0.45                    |
| Pine        | Douglas fir (cellulose) | Canada          | Dehydrated (99.5)          | 0.67                    |
| Straw       | Rice straw (cellulose) | Japan           | Dehydrated (99.5)          | 0.50                    |

\(^{a}\) The values of alcohol by volume were provided by the supplier of each sample.  
\(^{b}\) We determined water content of the samples with a Karl Fischer Coulometer DL39 (Mettler Toledo).  
\(^{c}\) The value is not alcohol by volume but ethanol content shown in Ref. 6).

\(\text{(Table 1)}\) specifies limited numbers of impurities such as water, methanol, and copper. In this regards, there have been no available information on important impurities such as organic and organosulfur compounds that would affect the downstream chemical processes.

The properties and concentrations of impurities in bioethanol depend on multiple variables including feedstocks, fermentative microorganisms, and purification methods, and hence, these are different among diverse bioethanol samples. In this paper, we report the chemical compositions of 17 diverse bioethanol samples with a particular focus on low-concentration organic and ionic impurities. This information will be important when the bioethanol in question is to be used as a resource for chemical industries.

2. Experiments and Results

2.1. Bioethanol Samples and Their Water Contents

Seventeen bioethanol samples, shown in Table 2, were analyzed with regard to impurities. The upper 11 samples given in Table 2 are imported crude ethanol samples without azeotropic distillation, and a sample named Miyako is a crude ethanol sample just before membrane-dehydration in a pilot-scale ethanol plant\(^{6)}\). The bottom four samples are second-generation biofuels produced in a bench-scale ethanol plant of AIST\(^{7,8)}\). The upper 13 samples were kindly provided by private companies. As a result, all that was known of the samples prior to analysis were the country of origin, type of feedstock, and ethanol concentration. The production processes, including pretreatment methods and...
fermentative microorganisms, are considered trade secrets for the imported crude ethanol samples.

Water content in each of the bioethanol samples was determined with a Karl Fischer Coulometer DL39 (Mettler Toledo) (Table 2). The values provided are the average of a minimum of three replicate measurements. Compared to the alcohol by volume, as provided by the supplier, of the 17 bioethanol samples summarized in Table 2, these results of water content are nearly consistent.

### 2.2. Organic Acids

Qualitative analysis of organic acids was performed by Sumika Chemical Analysis Service, Ltd. using both a capillary electrophoretic (CE) system (Agilent Technologies) and a CE time-of-flight mass spectrometry (TOF-MS), the CE/MSD TOF system (Agilent Technologies). Both systems employed fused silica capillaries (ϕ50μm × 70-104 cm). The background electrolyte for CE contained 20 mM (1 M = 1 mol dm⁻³) 2,6-pyridinedicarboxylic acid and 0.5 mM n-hexadecyltrimethylammonium hydroxide (pH 5.8). An electrolyte of 20 mM ammonium formate (pH 10) was used for CE-TOF-MS. CE-TOF-MS data were acquired over m/z 20-1000 in ESI-negative mode. As a result, formic acid, acetic acid, and propionic acid were detected in all of the bioethanol samples by both CE and CE-TOF-MS.

These organic ions (formate, acetate, propionate, and n-butyrate) were quantified using an IC-2001 ion chromatograph (IC; Tohso) equipped with two tandem-linked Super IC-AP columns (ϕ4.6 mm × 150 mm) (Table 3). A mobile phase of 0.6 mM Na₂CO₃ and 0.6 mM NaHCO₃ was chosen as the eluent. The flow rate was 0.8 mL/min. The column temperature was maintained at 40 °C during analyses. The Miyako sample and four of the lignocellulosic bioethanol samples contained relatively high amounts of acetic acid (41.75 μg/mL and 37.99-91.59 μg/mL, respectively). As described above, since the Miyako sample was only purified by crude distillation, the acetic acid likely came through with the distillate. In contrast, the pretreatment processes used to produce lignocellulosic ethanol are designed to breakdown cellulose, hemicelluloses, and lignin, releasing simple polysaccharides for enzymatic digestion. The pretreatment processes such as acid pretreatment and autohydrolysis are used and result in residual acetic acid at concentrations of e.g., 10,000-20,000 ppm⁹,¹⁰). Although the original concentrations of acetic acid in the fermentation broth are unknown, relatively high amounts of acetic acid may have remained in the bioethanol samples even after distillation and membrane dehydration.

### 2.3. Other Organic Compounds (except sulfur compounds)

Both qualitative and quantitative analyses of organic compounds, other than the aforementioned organic acids and aftermentioned organosulfur compounds, were performed using a Shimadzu GC1700 with a hydrogen-flame ionization detector (FID) or an Agilent Technologies HP-6890/5973MSD GC-mass spectrometry (MS) system. As shown in Table 4, the choice of column type and temperature program varied for the respective samples and target compounds.

### Table 3 Concentrations of Organic Acids in Bioethanol Samples

| Sample name | Concentration [μg/mL] |
|-------------|----------------------|
|             | Formic acid | Acetic acid | Propionic acid | n-Butyric acid |
| T08-1       | 0.29        | 0.36        | ND            | ND            |
| T08-2       | <0.05       | 0.07        | ND            | ND            |
| C08-1       | 0.18        | 1.17        | ND            | ND            |
| P08-1       | <0.05       | <0.05       | ND            | ND            |
| B08-1       | 0.25        | 3.82        | 0.30          | ND            |
| B08-2       | 0.23        | 4.84        | 0.36          | ND            |
| B09-1       | 0.39        | 12.47       | 1.20          | ND            |
| B09-2       | 0.16        | 4.35        | 0.24          | ND            |
| B09-3       | 0.46        | 2.99        | 0.10          | ND            |
| B09-4       | 0.09        | 5.06        | 0.38          | ND            |
| T09-1       | 0.06        | 0.16        | 0.03          | ND            |
| C09-1       | 0.08        | 1.17        | 0.09          | ND            |
| Miyako      | 1.42        | 41.75       | 3.35          | ND            |
| Hinoki      | 0.52        | 37.99       | 1.30          | 0.21          |
| Eucalypt    | 4.01        | 86.35       | 0.26          | <0.05         |
| Pine        | 3.92        | 40.98       | 2.52          | 2.05          |
| Straw       | 0.43        | 91.59       | 2.07          | 0.05          |

a) Organic acids were quantified by IC.
b) ND means ‘Not Detected.’
Table 4  Analytical Conditions of GC-MS and GC-FID for Determining Organic Compounds in Bioethanol Samples

| Equipment | Agilent Technologies HP-6890/5973MSD | Shimadzu GC-1700<sup>α</sup> |
|-----------|--------------------------------------|-------------------------------|
| Column    | DB-WAX (Agilent Technologies), 0.25 mm x 50 m, 0.5 μm film thickness | TC-WAX (GL Science), 0.25 mm x 30 m, 0.5 μm film thickness |
|           | Pora BOND Q (Varian), 0.25 mm x 25 m, 0.3 μm film thickness | DB-WAX (Agilent Technologies), 0.25 mm x 25 m, 0.5 μm film thickness |
|           | CP-WAX 57CB (Agilent Technologies), 0.25 mm x 25 m, 0.2 μm film thickness | Pora BOND Q (Varian), 0.25 mm x 100 m, 0.5 μm film thickness |
|           | (GL Science), 0.30 m, 0.25 mm film thickness | TC-WAX (GL Science), 0.30 m, 0.25 mm film thickness |

| Column temperature | (1) 40 °C (5 min) → 60 °C (5 min) → 100 °C (15 min) | (1) 40 °C (5 min) → 60 °C (5 min) → 100 °C (15 min) |
|                   | (2) 40 °C (5 min) → 80 °C (10 min) → 150 °C (10 min) | (2) 40 °C (5 min) → 80 °C (10 min) → 150 °C (10 min) |

| Injection temperature | (1) 200 °C (2) 250 °C | (1) 200 °C (2) 250 °C |
|                       | 200 °C | 240 °C |
|                       | 250 °C | 240 °C |
|                       | 240 °C | 240 °C |

| Split ratio | 10 | 10 | 10 | 10 | 1 |

| Bioethanol samples | T08-1, T08-2, C08-1, P08-1, B08-1, B08-2, Miyako, Hinoki, Eucalypt, Pine, Straw | T08-1, T08-2, C08-1, P08-1, B08-1, B08-2, Miyako, Hinoki, Eucalypt, Pine, Straw | T08-1, T08-2, C08-1, P08-1, B08-1, B08-2, Miyako, Hinoki, Eucalypt, Pine, Straw | T08-1, T08-2, C08-1, P08-1, B08-1, B08-2, Miyako, Hinoki, Eucalypt, Pine, Straw | T08-1, T08-2, C08-1, P08-1, B08-1, B08-2, Miyako, Hinoki, Eucalypt, Pine, Straw |
|-------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                   | 10 | 10 | 10 | 10 | 10 |
|                   | 10 | 10 | 10 | 10 | 10 |

a) Results obtained with a hydrogen-flame ionization detector (FID).

Table 5  Quantitative Analyses of Various Organic Compounds (other than organic acids and sulfur compounds) in Bioethanol Samples from Sugar- or Starch-containing Feedstocks

| Compounds | Methanol (C1) | Acetaldehyde (C2) | 1-Propanol (C3) | Ethyl acetate (C4) | 1-Butanol (C4) | 2-Butanol (C4) | 2-Methyl-1-propanol (C4) | 2-Methyl-1-butanol (C5) | 2-Methyl-1-butanol (C5) | 3-Methyl-1-butanol (C5) | Acetal (C6) | Isoamyl acetate (C7) | Ethyl hexoate (C8) | Ethyl octoate (C10) | Ethyl caprate (C12) | Miyako |
|-----------|--------------|-----------------|-----------------|-------------------|----------------|----------------|------------------------|------------------------|------------------------|-----------------------|-----------|--------------------|------------------|-----------------|-----------------|---------|
|           | T08-1 | [μg/mL] | T08-2 | [μg/mL] | C08-1 | [μg/mL] | P08-1 | [μg/mL] | B08-1 | [μg/mL] | B08-2 | [μg/mL] | B08-3 | [μg/mL] | B08-4 | [μg/mL] | T09-1 | [μg/mL] | C09-1 | [μg/mL] |
| Methanol (C1) | 39 | 7 | 21 | <1 | 42 | 39 | 40 | 56 | ND<sup>α</sup> | 44 | 22 | 28 | 23 |
| Acetaldehyde (C2) | 6 | <1 | 2 | <1 | 39 | 21 | 52 | 19 | ND | 44 | 1 | 65 | 184 |
| 1-Propanol (C3) | 61 | <1 | 10 | <1 | 49 | 19 | 17 | 19 | ND | 13 | 16 | 75 | 15 |
| Ethyl acetate (C4) | 1 | 5 | 6 | <1 | 10 | 3 | 1 | 1 | 1 | 7 | 6 | 16 | 10 |
| 1-Butanol (C4) | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 |
| 2-Butanol (C4) | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 |
| 2-Methyl-1-propanol (C4) | 4 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 |
| 2-Methyl-1-butanol (C5) | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 |
| 3-Methyl-1-butanol (C5) | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 |
| Acetal (C6) | 30 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 |
| Isoamyl acetate (C7) | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 |
| Ethyl hexoate (C8) | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 |
| Ethyl octoate (C10) | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 |
| Ethyl caprate (C12) | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 |

a) ND means 'Not Detected.'
starch-derived ethanol (Table 5) and lignocellulosic ethanol (Table 6), respectively.

In sugar- or starch-derived ethanol, common impurities such as methanol, acetaldehyde, 1-propanol, ethyl acetate, 2-methyl-1-propanol, and acetal (acetaldehyde diethyl acetal) were detected at relatively high amounts (Table 5). In addition to common impurities described above, higher concentrations of both 2-methyl-1-butanol and 3-methyl-1-butanol were found in lignocellulosic ethanol. In some of the lignocellulosic ethanol samples, furan-related compounds such as furfural, dihydro-2-methyl-3-franone, 2-acetylfuran, and 5-methyl-furfural were detected (Table 6). The acid pretreatment process of lignocelluloses gives not only acetic acid but also furan-related compounds with concentrations ranging from 10,000 to 30,000 ppm. Thus, these impurities may be characteristic of lignocellulosic ethanol.

2.4. Sulfur Compounds

The total sulfur content of each bioethanol sample was measured by Sumika Chemical Analysis Service, Ltd. A Wickbold combustion (WC)-IC method was applied in accordance with JIS K 2541-1 and an ultra-violet fluorescence (UVF) analysis was applied in accordance with JIS K 2541-6. A strong correlation was observed between these two methods (Table 7).

### Table 6 Quantitative Analyses of Various Organic Compounds (other than organic acids and sulfur compounds) in Lignocellulosic Ethanol Samples

| Compounds                  | Hinoki [µg/mL] | Eucalypt [µg/mL] | Pine [µg/mL] | Straw [µg/mL] |
|----------------------------|---------------|------------------|--------------|--------------|
| Methanol (C1)              | 2322          | 4360             | 8027         | 3060         |
| Acetalddehyde (C2)         | 837           | 123              | 344          | 359          |
| 1-Propanol (C3)            | 784           | 947              | 431          | 653          |
| 2-Propanol (C3)            | ND            | 20               | 16           | 26           |
| Ethyl formate (C3)         | ND            | ND               | 32           | ND           |
| Acetone (C3)               | 42            | 65               | 386          | 141          |
| Allyl alcohol (C3)         | 2             | 98               | 23           | 4            |
| Ethyl acetate (C4)         | 31            | 115              | 98           | 72           |
| 1-Butanol (C4)             | 15            | 105              | 1            | 26           |
| 2-Butanone (C4)            | ND            | ND               | 21           | 13           |
| 2,3-Butandione (C4)        | 24            | ND               | ND           | 28           |
| 2-Methyl-1-propanol (C4)   | 2490          | 831              | 1740         | 2106         |
| Methoxyacetone (C4)        | 10            | 50               | 22           | 11           |
| 2-Methyl-1-butanol (C5)    | 930           | 219              | 53           | 911          |
| 3-Methyl-1-butanol (C5)    | 4027          | 1079             | 147          | 3685         |
| Furfural (C5)              | 164           | 37               | ND           | 144          |
| 2-Cyclopentanone (C5)      | 6             | 3                | ND           | 9            |
| Cyclopentanone (C5)        | 54            | 10               | 45           | 46           |
| 3-Methyl-3-butanol (C5)    | 2             | 1                | ND           | 3            |
| Dihydo-2-methyl-3-furanone (C5) | 22 | ND | ND | 47 |
| Pyridine (C5)              | 6             | ND               | ND           | 12           |
| Acetal (C6)                | 148           | 1651             | 10           | 535          |
| 2-Acetylferan (C6)         | 20            | ND               | ND           | 27           |
| 5-Methylfurfural (C6)      | 5             | ND               | ND           | 4            |
| Isoamyl acetate (C7)       | 1             | 11               | ND           | ND           |
| Benzaldehyde (C7)          | 16            | ND               | ND           | 5            |
| 2-Methoxyphenol (C7)       | 4             | ND               | ND           | 4            |
| 2-Heptanone (C7)           | 9             | ND               | ND           | ND           |
| 2-Furuldehyde diethyl acetal (C9) | 26 | 206 | ND | 234 |

a) ND means ‘Not Detected.’

In both cases, sample B08-1 contained the highest amount of total sulfur (9.5 wt ppm).

The amounts of specific organosulfur compounds [i.e., dimethyl sulfide (DMS), dimethyl sulfoxide (DMSO), and the sum of dimethyl disulfide (DMDS) and thiazole] were quantified using a Shimadzu GC2010 gas chromatograph (GC) equipped with an Antek7090s sulfur chemiluminescence detector (SCD; Antek Instruments, Inc.) and a DB-624 column (0.32 mm x 60 m, 1.8 µm film thickness; Agilent Technologies). Each sample was injected into the column at 40 °C with a split ratio of five. After 5 min at 40 °C, the column temperature was increased at 10 °C/min to 250 °C and was kept at 250 °C for 4 min. The head pressure of the helium carrier gas was 150 kPa. Quantitative analysis of thiazole was performed by Sumika Chemical Analysis Service, Ltd. using a GC with a flame photometric detector (FPD).

The GC-SCD results showed the presence of DMS and DMSO in several of the bioethanol samples made from saccharine or starchy feedstocks (Table 7). Considering that no organosulfur compounds other than DMS and DMSO were detected in GC-SCD analyses, most of the sulfur in these bioethanol samples derived from DMS and DMSO. In contrast, neither DMS nor DMSO was detected in the four lignocellulosic ethanol
samples by GC-SCD, however, a large peak did indicate the presence of another organosulfur species (Fig. 1). By comparing retention times with several authentic organosulfur compounds, the peak was identified as a mixture of DMDS and thiazole. The thiazole concentration was then determined independently by GC-FPD. The concentration of DMDS was then calculated by subtracting the thiazole concentration obtained by GC-FPD from the sum of DMDS and thiazole concentrations obtained by GC-SCD after calculating the respective values as total sulfur.

| Sample name | Total sulfur concentration [wt ppm] | DMS concentration [wt ppm] | DMSO concentration [wt ppm] | DMDS concentration [wt ppm] | Thiazole concentration [wt ppm] |
|-------------|------------------------------------|-----------------------------|-------------------------------|-----------------------------|-------------------------------|
|             | WC-IC | UVF | GC-SCD | GC-SCD | GC-SCD | GC-SCD | GC-FPD |
| T08-1       | 0.1   | <0.1 | 0.03   | ND   | ND   | ND   | ND     |
| T08-2       | 0.1   | 0.1  | ND     | ND   | ND   | ND   | ND     |
| C08-1       | 0.1   | <0.1 | ND     | ND   | ND   | ND   | ND     |
| P08-2       | 0.1   | <0.1 | ND     | ND   | ND   | ND   | ND     |
| B08-1       | 9.5   | 9.2  | 24.07  | 2.42 | ND   | ND   | ND     |
| B08-2       | 2.0   | 1.8  | 2.20   | 3.03 | ND   | ND   | ND     |
| B09-1       | 2.5   | 2.4  | 0.034  | 3.654| ND   | ND   | ND     |
| B09-2       | 0.4   | 0.5  | 0.066  | 0.399| ND   | ND   | ND     |
| B09-3       | 0.1   | 0.1  | ND     | ND   | ND   | ND   | ND     |
| B09-4       | 0.7   | 0.7  | 0.298  | 1.108| ND   | ND   | ND     |
| T09-1       | 0.2   | 0.2  | ND     | ND   | ND   | ND   | ND     |
| C09-1       | 2.6   | 2.1  | 2.650  | 0.155| ND   | ND   | ND     |
| Miyako      | 0.2   | 0.3  | ND     | 0.25 | ND   | ND   | ND     |
| Hinoki      | 0.9   | 1.0  | ND     | ND   | 0.6  | 0.5  | ND     |
| Eucalypt    | 0.5   | 0.5  | ND     | ND   | ND   | 0.7  | ND     |
| Pine        | 2.2   | 2.2  | ND     | ND   | 0.8  | <0.2 | ND     |
| Straw       | 2.1   | 2.1  | ND     | ND   | 0.8  | 1.3  | ND     |

a) Abbreviations: WC-IC, Wickbold combustion-ion chromatography; UVF, ultraviolet fluorescence; ICP-AES, inductively coupled plasma-atomic emission spectrometry; DMS, dimethyl sulfide; DMSO, dimethyl sulfoxide; DMDS, sum of dimethyl disulfide + thiazole.
b) GC-SCD, gas chromatography with sulfur chemiluminescence detector.
c) GC-FPD, gas chromatography with flame photometric detector.
d) The concentrations of DMDS were calculated by subtracting the thiazole concentration obtained by GC-FPD from the sum of DMDS and thiazole concentrations obtained by GC-SCD after calculating the respective values as total sulfur.
e) ND means 'Not Detected.'

The vertical axis shows abundance, and the horizontal axis retention time (min).

Fig. 1 GC-SCD Chromatograms of Samples B08-1 (bioethanol derived from sugarcane, A) and Straw (lignocellulosic ethanol, B)
Table 8  Quantitative Analyses of Cations and Anions in Bioethanol Samples

| Sample name | Na | K  | Mg | Ca | Al | Si | P  | Mn | Fe | Ca | As | Li | NH₄ | F  | Cl | Br | NO₃ | PO₄ | SO₄ |
|-------------|----|----|----|----|----|----|----|----|----|----|----|----|-----|----|----|----|-----|-----|-----|
| T08-1       | 0.84 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | 0.02 | <0.01 | 0.03 | <0.01 | 0.02 | <0.01 |
| T08-2       | 0.49 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | 0.01 | <0.01 | 0.01 | <0.01 | 0.02 | <0.01 |
| C08-1       | 1.5 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | 0.01 | <0.01 | 0.01 | <0.01 | 0.02 | <0.01 |
| P08-1       | 1.7 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | 0.01 | <0.01 | 0.02 | <0.01 | 0.06 | <0.01 |
| B08-1       | 0.97 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | 0.01 | <0.01 | 0.09 | <0.01 | 0.05 | <0.01 |
| B08-2       | 1.1 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | 0.01 | <0.01 | 0.29 | <0.01 | 0.09 | <0.01 |
| B09-1       | 4.7 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | 0.01 | <0.01 | 0.02 | <0.01 | 0.15 | 0.12 |
| B09-2       | 2.6 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | 0.01 | <0.01 | 0.74 | <0.01 | 0.05 | <0.01 |
| B09-3       | 0.54 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | 0.01 | <0.01 | 0.01 | <0.01 | 0.14 | 0.02 |
| B09-4       | 1.2 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | 0.01 | <0.01 | 0.17 | <0.01 | 0.09 | <0.01 |
| T09-1       | 0.79 | <0.05 | <0.05 | 0.14 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | 0.01 | <0.01 | 0.02 | <0.01 | 0.26 | <0.01 |
| C09-1       | 0.64 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | 0.01 | <0.01 | 0.69 | <0.01 | 0.16 | <0.01 |
| Miyako      | 0.06 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | 0.09 | <0.01 | 0.11 | <0.01 | 0.11 | <0.01 |
| Himoki      | 0.48 | <0.05 | <0.05 | <0.05 | <0.05 | 1.9 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | ND<sup>3</sup> | ND | <0.01 | 0.04 | <0.01 | 0.13 | <0.01 |
| <i>Eucalyptus</i> | 0.16 | <0.05 | <0.05 | <0.05 | <0.05 | 0.44 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | ND | <0.01 | 0.03 | <0.01 | 0.10 | <0.01 |
| Pine        | 0.09 | <0.05 | <0.05 | <0.05 | 0.31 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | ND | <0.01 | 0.01 | <0.01 | 0.10 | <0.01 |
| Straw       | 0.14 | <0.05 | <0.05 | <0.05 | 1.45 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | ND | <0.01 | 0.04 | <0.01 | 0.07 | <0.01 |

a) Inorganic cations were measured by ICP-AES; both Li<sup>+</sup> and NH₄<sup>+</sup> were quantified by IC.
b) Inorganic anions were measured by IC.
c) ND indicates ‘(could) Not be Determined.’ These results were likely due to impurity-induced damage to the IC column, which prevented the acquisition of suitable chromatograms.
the respective values as the total sulfur concentration. In addition, several unidentified peaks of organosulfur compounds were also detected (Fig. 1). Thus, differences in sulfur impurities may be considered characteristic differences between sugar or starch-derived ethanol and lignocellulosic ethanol.

2.5. Cationic and Anionic Impurities

Forty-seven elements (Li, Be, B, Na, Mg, Al, Si, P, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Pd, Ag, Cd, Sn, Sb, Ba, La, Ce, Hf, Ta, W, Pt, Au, Hg, Pb, Bi, and S) in the bioethanol samples were measured by Sumika Chemical Analysis Service, Ltd. using an SPS-5520 (Hitachi High-Tech Science) or ICPS-8100 (Shimadzu) inductively coupled plasma (ICP)-atomic emission spectrometer (AES). Eleven of these elements (Na, Mg, Al, Si, P, K, Ca, Mn, Fe, Cu, and As) were quantified using the same method. Lithium ion (Li⁺) and ammonium ion (NH₄⁺) were quantified by IC analyses with an IC-2001 (Tohso) equipped with a Super IC-CR column (φ4.6 mm × 150 mm). A mobile phase of 2.2 mM methansulfonic acid and 1.0 mM 18-crown-6 was chosen as the eluent at a flow rate of 0.7 mL/min. The column temperature was maintained at 40 °C during analyses. As shown in Table 8, more than 0.1 mg/mL of Na was identified in almost all of the bioethanol samples, but some amounts of Na might be derived from glass containers used for keeping of ethanol samples in refrigerator. In lignocellulosic ethanol, more than 0.1 mg/mL of Si was also detected. Both wooden and herbaceous plants contain approximately 0.5-5 % ash, which is composed largely of silica.

Inorganic anions (F⁻, Cl⁻, Br⁻, NO₃⁻, PO₄³⁻, and SO₄²⁻) were quantified using an IC-2001 (Tohso) equipped with a Super IC-AP column (φ4.6 mm × 150 mm). A mobile phase of 1.8 mM NaHCO₃ and 1.7 mM NaHCO₃ was chosen as the eluent at a flow rate of 0.8 mL/min. The column temperature was maintained at 40 °C during analyses. As shown in Table 8, most of the bioethanol samples contained only small amounts of Cl⁻, NO₃⁻, PO₄³⁻, and SO₄²⁻. The C09-1 sample contained a relatively high 2 μg/mL of SO₄²⁻.

3. Conclusions

Catalyst deactivation by impurities in bioethanol would be a serious problem that limits the use of bioethanol for the chemical industries. Therefore, it is crucial to clarify the nature of impurities in low-grade bioethanol and their effect(s) on downstream chemical processes. This study examined the chemical composition of 17 bioethanol samples with regard to chemical impurities and organosulfur compounds in particular. Clear differences were observed between lignocellulosic ethanol and sugar- or starch-derived bioethanol samples. The lignocellulosic ethanol samples contained a greater variety and higher concentrations of organic impurities, likely due to the pretreatment of feedstocks. Concerning organosulfur compounds, lignocellulosic ethanol contained DMDS and thiazole, whereas sugar- or starch-derived bioethanol contained DMS and DMSO. Some of the most severe poisoning encountered in metallic catalytic systems is attributable to sulfur. Therefore, knowledge of the type and amount of sulfur in bioethanol is extremely important. Further studies to clarifying the effect of these impurities on the following process are needed for evaluating the applicability of bioethanol as a resource for chemical industries.

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要目

各種バイオエタノールサンプル中の不純物分析

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近年、バイオエタノールが化学品製造における重要な原料となっている。バイオエタノール中の不純物が、下流の化学品製造プロセスで使用する触媒の性能に影響を及ぼす可能性があるため、17種のバイオエタノールサンプルについて不純物の分析を行った。リグノセルロース系バイオエタノールは、糖・デンプン系バイオエタノールと比較して、高濃度かつ多種類の有機不純物を含んでいた。特に、リグノセルロース系バイオエタノールは、高濃度の酢酸、アセトアルデヒド、メタノールおよびフルフラールのようなフラン系化合物を含んでいた。また、リグノセルロース系バイオエタノールは、有機硫黄系不純物としてジメチルジスルフィドおよびチアゾールを含んでいたのに対し、糖・デンプン系バイオエタノールからは、ジメチルジスルフィドおよびジメチルジスルフォキシドが検出された。加えて、リグノセルロース系バイオエタノールからは、0.1 μg/mL 以上の Si が検出された。