1. Introduction

Lignocellulosic biomass is an abundant sustainable carbon resource with great potential to solve some of the problems posed by dwindling fossil resources and global warming\(^{1)}\). Lignocellulosic biomass mainly consists of cellulose, hemicellulose and lignin. Cellulose is a polymer of glucose units with high crystallinity, and hemicellulose is an amorphous polymer formed of several types of monosaccharide units, \(\text{i.e.}, \) glucose, xylose, mannose, arabinose, galactose and others. These monosaccharides are potential feedstocks for conversion to bioethanol\(^{4)}\) and other useful chemicals such as sugar alcohols and polymer precursors\(^{7)}\). Lignin is a polymer of alkyl phenol units\(^{10)}\) and is a potential resource for phenols formed by degradation into its monomers. However, the current pulping process separates cellulose and hemicellulose from lignin which is converted into a residue with a complicated three-dimensional structure, and the lignin residue is generally burned as a fuel to recover energy. Therefore, a novel separation technique for lignocellulose is highly desirable to obtain the valuable components of lignocellulose.

Conventional separation methods include steam explosion treatment, acid treatment, and alkaline treatment. Steam explosion treatment mainly achieves the decomposition of hemicellulose, followed by solvent extraction of hemicellulose and lignin. However, recovery of the hemicellulose and lignin often requires addition of acid in the case of softwood. Moreover, the structure of the obtained cellulose is thought to be partly destroyed by the explosive decompression, which hinders the utilization of the cellulose as pulp and fibers\(^{11)\,12)}\). Alkaline treatment is the most commonly method adopted in the pulping process\(^{12)\,14)}\). However, several inorganic reagents such as sodium hydroxide and sodium sulfide are required\(^{14)}\), which are harmful to
the environment and cause considerable chemical modification of the lignin\(^1\). In comparison, organosolv treatment uses water/organic solvent for the depolymerization of lignin and hemicellulose in raw biomass, so the milder treatment conditions are expected to form useful lignin products\(^1\).2\).

Our previous study developed a two-step process for producing phenols from organosolv lignin propionate and kraft lignin\(^1\)6,17). In the first-step reaction, the lignins were depolymerized into lower molecular-weight fractions using a solid acid catalyst in a water/1-butanol (BuOH) mixture. In the second-step reaction, catalytic cracking of the recovered lignin fractions was carried out over CeO\(_2\)-ZrO\(_2\)-Al\(_2\)O\(_3\)-FeO\(_x\), which is effective for producing useful chemicals from biomass wastes\(^1\)8,19-20). This two-step process obtained approximately 17 % of the phenols based on the amounts of aromatic rings in lignin\(^1\)7).

The present study used a water/BuOH mixture as the organosolv solvent for separating lignin fractions from raw biomass into the BuOH phase, leaving cellulose as a solid product. Subsequently, the extracted lignin fractions were used as the feedstock for conversion into phenols over CeO\(_2\)-ZrO\(_2\)-Al\(_2\)O\(_3\)-FeO\(_x\) catalyst. The reaction scheme is summarized in Fig. 1. Japanese cedar, a widely-grown forest tree in Japan, was chosen as the raw biomass feedstock.

2. Materials and Methods

2.1. Organosolv Treatment Using a Water/1-Butanol Mixture

Organosolv treatment of Japanese cedar was carried out in an autoclave reactor made of Hastelloy alloy C-276 (KH-50; Hiro Co., Ltd.) with inner volume 40 cm\(^3\) at 423-523 K for 2 h. Japanese cedar (purchased from Shimada Kowari Seizaisyo Co., Ltd.; abbreviated as JC) sieved to less than 300 μm was used as the feedstock. Silica–alumina with Si/Al = 2 (N631HN; JGC Catalysts and Chemicals Ltd.; abbreviated as SA) and a water/BuOH mixture were used as the solid acid catalyst and the solvent, respectively. The weight ratios of reactant to silica–alumina and reactant to water/BuOH mixture were fixed at 1 : 1 and 1 : 30, respectively. The molar ratio of water to BuOH was fixed at 4 : 1, which was optimized using organosolv lignin propionate and kraft lignin\(^1\)6). Distilled water and BuOH were purchased from FUJIFILM Wako Pure Chemical Corp. The inner vessel of the reactor was purged with N\(_2\) gas before the treatment, and the reactor was swung back and forth about 20 times per minute during the treatment. Treatment time was measured after the inside temperature of the reactor reached the designated temperature.

Figure 2 shows the procedure after the treatment. The mixture in the reactor was filtered to separate Japanese cedar-derived liquid products and solid products. After the Japanese cedar-derived liquid products were divided into water and BuOH phases, the phases were analyzed by gel permeation chromatography (GPC) using a HPLC system (Jasco Corp.) equipped with a KF-G and two KF-806 L columns (Showa Denko K. K.) and a UV detector at 254 nm. The eluent was 1-methyl-2-pyrrolidone including 1 wt% of lithium bromide monohydrate. Both reagents were purchased from FUJIFILM Wako Pure Chemical Corp. The molecular weight was calibrated using polystyrene standards (Varian, Inc.) with molecular weights of 162, 1530, 3790, 7210, and 19640. Moreover, the phases were analyzed using a gas chromatograph with hydrogen-flame ionization detector (GC-FID, GC-2014; Shimadzu Corp.) equipped with capillary columns (DB-5; J&W Scientific) to calculate the carbon yield of phenols based on the extracted lignin fractions. 1-Pentanol and propylene glycol were used as internal standards for the BuOH and water phases, respectively.
The solid products recovered after filtration were analyzed by an elemental analyzer (ECS 4010; Costech Instruments or JM10; J-Science Lab Co., Ltd. or CE440; Exeter Analytical) to determine carbon content. The Japanese cedar-derived liquid yields were calculated by Eq. (1).

\[
\text{Yield of JC-derived liquid } [\text{C-mol%}] = 100 \times \left(1 - \frac{\text{Carbon mols of JC-derived solid}}{\text{Carbon mols of JC}}\right) \tag{1}
\]

The carbon content of Japanese cedar was determined as 52.7 wt% by elemental analysis.

The chemical compositions of Japanese cedar and the solid products, i.e., the content of cellulose, hemicellulose and lignin, were determined in accordance with the NREL method\(^ {21}\). The obtained acid-insoluble lignin in the NREL method was measured with an elemental analyzer to calculate carbon content. Monosaccharides obtained in the NREL method were measured by a HPLC system with a RI detector (Shimadzu Corp.) and columns (SP-G 6B, SP0810; Showa Denko K. K.). Acid soluble lignin was ignored and hemicellulose was assumed to include only xylose, arabinose, mannose and galactose to simplify the calculation of each component yield.

The carbon yields of phenols based on the carbon content of the extracted lignin fractions were calculated from Eqs. (2) and (3).

\[
\begin{align*}
\text{Carbon mols of the extracted lignin} &= (\text{Carbon mols of lignin in JC}) - (\text{Carbon mols of lignin in the solid product}) \tag{2} \\
\text{Carbon yield of phenols [C-mol%]} &= \frac{\text{Carbon mols of phenols}}{\text{Carbon mols of the extracted lignin}} \tag{3}
\end{align*}
\]

### 2.2 Pyrolysis-GC-MS (Py-GC-MS) Analysis of BuOH and Water Phases

Py-GC-MS analyses of the BuOH and water phases were performed using a GC-MS (GC-17A GCMS-QP5050; Shimadzu Corp.) equipped with a DB-5 MS column and double-shot pyrolyzer (PY-2020D; Frontier Lab). The BuOH and water phases obtained from treatment at 473 K with silica-alumina catalyst were evaporated at 353 K to remove the solvents and obtain solid samples. The solids were continuously dried at 403 K for 0.5 h to obtain dried samples. Approximately 0.3 mg of each sample was used for Py-GC-MS analysis at 873 K for 3 min under He atmosphere. Gaseous products were trapped at the inlet of the column using liquid N\(_2\) during pyrolysis. Then, the liquid N\(_2\) trap was removed to start the gas chromatograph-mass spectrometer (GC-MS) analysis.

### 2.3 Catalytic Cracking of Recovered Lignin Fractions

#### 2.3.1 Preparation and Characterization of CeO\(_2\)-ZrO\(_2\)-Al\(_2\)O\(_3\)-FeO\(_x\) Catalyst

The iron oxide catalyst was prepared by the co-precipitation method\(^ {17}\). Aqueous solutions of Fe(NO\(_3\))\(_3\)·9H\(_2\)O, Ce(NO\(_3\))\(_3\)·6H\(_2\)O, Zr(NO\(_3\))\(_4\)·2H\(_2\)O, and Al(NO\(_3\))\(_3\)·9H\(_2\)O were combined and stirred for 30 min. Then, 10 wt% of NH\(_3\) aq. was added until the pH reached 7 and the mixture was stirred for 1 h. All reagents were purchased from FUJIFILM Wako Pure Chemical Corp. The precipitate was filtered and dried in an oven at 383 K overnight to obtain the catalyst precursor. Subsequently, the precursor was calcined at 773 K for 2 h in air. The content of each component in the prepared catalyst was analyzed by X-ray fluorescence spectroscopy (XRF Supermini; Rigaku Corp.) which showed that the catalyst contained 5.6 wt% of CeO\(_2\), 6.0 wt% of ZrO\(_2\), and 4.4 wt% of Al\(_2\)O\(_3\).

### 2.3.2 Catalytic Cracking over CeO\(_2\)-ZrO\(_2\)-Al\(_2\)O\(_3\)-FeO\(_x\) Catalyst

Only the BuOH phase of the Japanese cedar-derived liquid was used as a feedstock for catalytic cracking over CeO\(_2\)-ZrO\(_2\)-Al\(_2\)O\(_3\)-FeO\(_x\). The treatment was carried out using a high pressure fixed-bed flow reactor\(^ {17,22}\). The feedstock was supplied to the reactor with steam under high pressure. Before the reaction, steam preheated to the desired reaction temperature was fed into the reactor for 1 h under 15 MPa. The reaction temperature and time were fixed at 673 K and 2 h. \(W/F\) was 2.5, where \(W\) is the weight of catalyst (g), and \(F\) and \(F_{\text{H}_2\text{O}}\) are the flow rates of feedstock and steam (g/h), respectively.

After the reaction, the inner vessel of the reactor was purged with steam for 1 h at 673 K. Liquid products were collected with an ice trap and divided into a water phase and a BuOH phase. Both phases were analyzed using the same GC-FID and internal standards, and the BuOH phase was analyzed by the GPC system described in section 2.1.

#### 3. Organosolv Treatment

#### 3.1.1 Effects of Treatment Temperature on the Yields of JC-derived Liquid and MWDs of Oligomers in the BuOH Phase

To investigate the effect of the treatment temperature on the yields of Japanese cedar-derived liquid, extraction of lignin fractions from Japanese cedar was carried out in a water/BuOH mixture using SA catalyst at 423-523 K for 2 h. Figure 3 shows the yields of Japanese cedar-derived products and the chemical composition of the Japanese cedar, in which the category others includes extractives and so on. The yields of Japanese cedar-derived liquid gradually increased at higher treatment temperature, and reached approximately 97
C-mol% at 503 K. In particular, the yield significantly increased from 473 to 503 K, indicating that decomposition of cellulose began at 503 K\(^2\)\(^3\),\(^2\)\(^4\). Therefore, the most suitable treatment temperature was determined to be 473 K to separate lignin fractions from cellulose.

Chemical compositions of Japanese cedar and the solid product obtained after the reaction at 473 K with SA catalyst are shown in Fig. 4. Overall, 81.8% of cellulose could be recovered as solid product and water/BuOH treatment was effective in extracting lignin fractions and recovering solid cellulose.

**Figure 5** shows molecular weight distributions (MWDs) obtained from the reactions carried out using SA catalyst at 423, 473 and 503 K. The Japanese cedar-derived MWD showed several peaks assigned to oligomers consisted of 2-12 units of lignin monomer except at 423 K. The lignin monomer in Japanese cedar is classified as a guaiacyl-type, that is ciniferyl alcohol\(^2\)\(^5\). Additionally, carbohydrates derived from hemicellulose and cellulose generally do not absorb UV radiation. Therefore, the detected oligomers in the BuOH phase mainly consisted of aromatic rings originating from the lignin in Japanese cedar. In contrast, these oligomers were hardly detected in the water phase. These results suggested that the lignin fractions were selectively extracted in the BuOH phase. The MWD at 423 K indicated higher molecular weight fractions than at 473 K and 503 K. Moreover, the MWD at 503 K showed broader peaks compared with that at 473 K. This finding indicated that solubilized cellulose fractions in the water phase were further decomposed, and extracted into the BuOH phase.

3.1.2. Effects of SA Catalyst on the Yields of JC-derived Liquid and MWD of JC-derived Lignin Fractions in the BuOH Phase

To investigate the effects of SA catalyst on the yield of Japanese cedar-derived liquid and MWD of the BuOH phase, organosolv treatments were performed with/without SA catalyst at 473 K for 2 h. The yields of Japanese cedar-derived products obtained and the chemical composition of Japanese cedar are shown in **Fig. 6**. Using the SA catalyst, the yields of Japanese cedar-derived liquid increased by 9.0 C-mol%. At this temperature, hemicellulose and lignin were mainly depolymerized because depolymerization of hemicellulose and lignin in biomass starts at around 423-473 K, whereas this temperature was not high enough to cause depolymerization of cellulose by the hot-compressed water treatment\(^2\)\(^3\),\(^2\)\(^4\). Therefore, the SA catalyst caused the depolymerization of hemicellulose and/or lignin.

To examine the effects of the SA catalyst on degradation of the lignin fractions, the average molecular weight (\(M_a\) and \(M_w\)) of the oligomers in the BuOH phase with/without SA catalyst were calculated as shown in **Table 1**. Clearly, the SA catalyst enhanced depolymerization of lignin oligomers. Lignin mono-
mers are mainly connected via aryl-ether bonds (approximately 60 % of all interunit linkages) and condensation bonds (approximately 30 %)\(^{23,26}\). Our previous study using lignin model compounds suggested that the SA catalyst has the potential to promote cleavage of aryl-ether bonds\(^{17}\). Therefore, the SA catalyst is useful to obtain lower molecular-weight lignin fractions in the organosolv reaction, leading to facilitation of the catalytic cracking to produce phenols from the lignin fractions.

### 3.1.3. Py-GC-MS Analysis of Liquid Product Obtained at 473 K Using SA Catalyst

To investigate the specific oligomers extracted into the water/BuOH mixture from Japanese cedar, Py-GC-MS analyses of the concentrates of the BuOH and water phases were performed. Figure 7 shows the Py-GC-MS chromatograms and the detected compounds are summarized in Table 2. These compounds were

![Figure 6: Chemical Composition of Japanese Cedar and Effect of SA Catalyst on the Yields of Japanese Cedar-derived Products after Organosolv Treatments](image)

![Figure 7: Py-GC-MS Chromatograms](image)

**Table 1** Effects of SA Catalyst on the Number and Weight-average Molecular Weight (\(M_n, M_w\)) of the BuOH Phase after Organosolv at 473 K

| Catalyst     | \(M_n\) | \(M_w\) |
|--------------|---------|---------|
| No catalyst  | 990     | 2501    |
| SA catalyst  | 808     | 2060    |

Treatment conditions: water/1-butanol = 4, \(T = 473\) K, treatment time = 2 h.

**Table 2** Compounds Detected by Py-GC-MS Analyses of the BuOH and Water Phases Obtained after Organosolv at 473 K with SA Catalyst

(a) 1-Butanol phase

| Label | Compound                              | Origin | Label | Compound                              | Origin |
|-------|---------------------------------------|--------|-------|---------------------------------------|--------|
| 1     | 5-Methyl-2-furancarboxaldehyde        | C      | 15    | 4-Methyl-1,2-benzeneediol             | L      |
| 2     | Phenol                                | L      | 16    | 2-Methoxy-4-vinylphenol               | L      |
| 3     | \(\alpha\)-Cresol                      | L      | 17    | 2-Methoxy-5-(1-propenyl)-phenol       | L      |
| 4     | \(\beta\)-Cresol                       | L      | 18    | 2-Methoxy-4-propyl-phenol             | L      |
| 5     | 2-Methoxy-phenol                      | L      | 19    | Vanillin                              | L      |
| 6     | 2,4-Dimethyl-phenol                   | L      | 20    | 2-Methyl-1,3-benzenedirol             | L      |
| 7     | 2-Hydroxy-6-methyl-benzaldehyde       | L      | 21    | 2-Methoxy-4-(1-propenyl)-phenol       | L      |
| 8     | 3-Ethyl-phenol                        | L      | 22    | 3,4-Furandimethanol                   | C      |
| 9     | 2-Methoxy-6-methyl-phenol             | L      | 23    | Homovanillic acid                     | L      |
| 10    | Creosol                               | L      | 24    | Apocynin                              | L      |
| 11    | Catechol                              | L      | 25    | Coniferyl alcohol                     | L      |
| 12    | 3,4,5-Trimethyl-phenol                | L      | 26    | Butyrovanilone                        | L      |
| 13    | 3,4-Dimethoxytoluene                  | L      | 27    | 4-Hydroxy-3-methoxy-benzenepropanol   | L      |
| 14    | 4-Ethyl-2-methoxy-phenol              | L      | 28    | Coniferyl aldehyde                    | L      |

(b) Water phase

| Label | Compound                              | Origin |
|-------|---------------------------------------|--------|
| 29    | Furfural                              | C      |
| 30    | 2-Pentanol                            | U      |
| 31    | 4-Methyliden-cyclohexanone            | U      |
| 32    | 5-Methyl-2-furancarboxaldehyde        | C      |
| 33    | 2-Hydroxy-gamma-butyrolactone         | C      |

L; Lignin, C; Carbohydrate, U; Unknown.

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assigned as lignin-derived or carbohydrates-derived compounds with reference to the Py-GC-MS studies of biomass. The descriptions of the peaks labeled as 7-9, 12, and 13 in Table 2 were omitted from Fig. 7 because their relative abundance was much weaker than the other peaks. These results showed that many types of phenols were formed by pyrolysis of the BuOH phase, but not the water phase. Therefore, the lignin fractions extracted from Japanese cedar were mainly extracted in the BuOH phase, which agrees with the absence in the water phase (see section 3.1.1.). Moreover, the pyrolyzed products of the water phase contained almost no lignin-derived compounds, but were mainly identified as furan compounds, which presumably originated from carbohydrates.

3.1. Catalytic Cracking of Lignin Fractions over CeO2-ZrO2-Al2O3-FeOx Catalyst

To explore the possibility of producing phenols from Japanese cedar-derived lignin fractions, catalytic cracking of the BuOH phase obtained by organosolv treatment was performed over CeO2-ZrO2-Al2O3-FeOx. The feedstock was limited to the BuOH phase which contained the main extracted lignin fractions based on the Py-GC-MS analysis. The feedstock was supplied to the reactor with high pressure steam which is effective for suppression of coking on the catalyst and maintaining catalytic activity.

Figures 8 and 9 show the obtained yields of phenols and MWDs after organosolv treatment and catalytic cracking. The yields of phenols improved from 1.9 C-mol% to approximately 9.6 C-mol% with catalytic cracking as shown in Fig. 8. The lignin fractions in the BuOH phase after catalytic cracking were degraded into lower molecular weight compound than after only organosolv treatment as shown in Fig. 9. We previously reported that lignin monomeric and dimeric model compounds such as guaiacol, catechol, and 2-benzoxynaphthol could be decomposed to form phenol after reaction over the FeOx-based catalyst. We also reported that catalytic cracking of lignin-derived liquid over FeOx-based catalyst, was effective for converting the lignin fractions into monomeric phenols as compared with the reaction without the catalyst. Therefore, the results shown in Figs. 8 and 9 suggest that CeO2-ZrO2-Al2O3-FeOx catalyst was effective for the decomposition of substituted groups and interunit linkages of Japanese cedar-derived lignin fractions.

4. Conclusions

Organosolv of Japanese cedar wood using BuOH was investigated for separating lignin as soluble fractions from solid cellulose. The optimum temperature for separating lignin fractions from solid cellulose was around 473 K because decomposition of solid cellulose began at 503 K. The MWDs of the BuOH phase after organosolv showed that the lignin fraction consisted of oligomers of lignin units. Py-GC-MS of the liquid products revealed that the compounds in the BuOH phase were mostly alkyl-phenols derived from lignin, and no compounds were observed in the water phase. These results suggested that Japanese cedar-derived lignin fractions were selectively recovered in the BuOH phase. Next, catalytic cracking of the recovered lignin fractions to produce phenols was carried out over CeO2-ZrO2-Al2O3-FeOx catalyst. The MWDs showed decomposition of lignin fractions and 9.6 C-mol% of phenols were obtained. The organosolv reaction using 1-butanol solvent has high potential for the utilization of lignin.

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Catalytic cracking conditions: CeO2-ZrO2-Al2O3-FeOx, W/F = 0.5 h, T = 673 K, P = 15 MPa, reaction time = 2 h.

Fig. 8 Yields of Phenols Based on the Extracted Lignin Fractions after Organosolv (473 K, 2 h, with silica-alumina catalyst) and Catalytic Cracking Reactions

Fig. 9 Molecular Weight Distributions of the BuOH Phase Obtained after Organosolv and Catalytic Cracking Reactions

Catalytic cracking conditions: CeO2-ZrO2-Al2O3-FeOx, W/F = 0.5 h, T = 673 K, P = 15 MPa, reaction time = 2 h.
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要旨

1-ブタノールによるオルガノソルブ処理と酸化鉄系触媒を用いた
可溶化リグニンの接触分解によるフェノール類の製造

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本研究では、スギを原料に1-ブタノールを用いてオルガノソルブ処理をオートクレープ中、無触媒またはシリカアルミナ触媒下で実施し、構成成分であるリグニンとヘミセルロースの可溶化による固形セルロースとの分離を検討した。また、可溶化リグニンを原料に酸化鉄系触媒による接触分解を実施し、フェノール類の製造を検討した。オルガノソルブ処理では、473 K のとき無触媒条件下で可溶化リグニンの重量平均分子量が 2501 であったのに対して、シリカアルミナ触媒存在下では 2060 まで分解が促進された。さらに、503 K 以上では固形セルロースの可溶化が進行し、可溶化リグニンとの分離が困難となるため、処理温度はセルロースを固体成分として回収できる 473 K 付近が適することが分かった。分子量分布と熱分解 GC-MS の結果から、可溶化リグニンは1-ブタノール相に主に存在することが示された。そこで、可溶化リグニン成分の接触分解反応を高圧流通式反応器を用いて 673 K で実施した。その結果、可溶化リグニンに対してフェノール類を 9.6 C-mol% の収率で得た。