Biomass Valorization in High-temperature Liquid Water

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Conversion of biomass resources to fuels and chemicals is a highly effective approach for a biomass valorization as a prospective alternative to petrochemical processes. Biomass conversion using water as a reaction medium is desirable because water is non-toxic and environmentally friendly. Biomass valorization techniques in high-temperature liquid water and supercritical water are reviewed, such as (i) dehydration reactions of biomass-derived polyalcohols to cyclic ethers and (ii) gasification reactions of lignin to fuel gases. (i) Cyclic ethers were produced by the intramolecular dehydration reactions of biomass-derived polyalcohols in high-temperature liquid water without acid catalysts. Addition of carbon dioxide accelerated the dehydration in high-temperature liquid water because the added carbon dioxide dissolves in water to form carbonic acid. (ii) Charcoal-supported ruthenium salts were active for lignin gasification at 673 K in supercritical water, in which ruthenium (III) species were reduced to ruthenium metal particles.

Keywords
Biomass, High-temperature liquid water, Supercritical water, Carbon dioxide, Dehydration, Gasification

1. Introduction

Conversion of biomass resources to fuels and chemicals is a highly effective approach for biomass valorization as a prospective alternative to petrochemical processes۶ ۷ ۸ ۹ ۱۰ ۱۱ ۱۲). However, “green” processes are desirable for biomass conversion, in which no hazardous acid catalyst or harmful organic solvent is used. High temperature liquid water at around 523-573 K offers an alternative to organic solvents because of the high proton concentration, which enhances the rates of acid-catalyzed reactions such as dehydration without requiring hazardous acid agents۶ ۷ ۸ ۹ ۱۰ ۱۱ ۱۲). Furthermore, addition of carbon dioxide is expected to accelerate acid catalysis in high temperature water due to the formation of carbonic acid. An acid solvent consisting of water and carbon dioxide is environmentally benign, not only because both water and carbon dioxide are non-toxic, but also because carbon dioxide can be easily removed by depressurization after the reaction, thus avoiding the need for a neutralization process. The dielectric constant of water decreases over 647 K under supercritical conditions (P > 22.1 MPa), enhancing the solubility of organic compounds.

The present review discusses biomass valorization techniques in high-temperature liquid water and supercritical water, such as dehydration reactions of biomass-derived polyalcohols to cyclic ethers and gasification reactions of lignin to fuel gases.

2. Dehydration of Biomass-derived Polyalcohols

2.1. Dehydration of Polyalcohols in High-temperature Liquid Water under High-pressure Carbon Dioxide

The dehydration of biomass-derived polyalcohols is important to obtain valuable products with useful boiling points, water solubilities, octane numbers and viscosities۶). The chemistry of the intramolecular dehydration of polyalcohols provides a key technology for developing valorization techniques. However, biomass-derived polyalcohols, such as sorbitol and fructose, contain five or six hydroxyl groups in each molecule so that the intramolecular dehydration mechanisms are complicated. At first, the dehydration behaviors of polyalcohols with two or three hydroxyl groups were investigated, as simple model compounds of biomass-derived polyalcohols, corresponding to five- or six-membered cyclic ethers in water under high-pressure carbon dioxide at 573 K.

The intramolecular dehydration of 1,2,5-pentanetriol (1,2,5-PTO) proceeded in water at 573 K and resulted in two products (Fig. 1); tetrahydrofurfuryl alcohol
(THFA) and 3-hydroxytetrahydropyran (3-HTHP) (Scheme 1)\(^7,8\). The yield of THFA was 25.6 %, about 6 times larger than that of 3-HTHP (3.9 %), after 0.17 h of reaction without carbon dioxide. The yield of THFA was increased to 35.7 % and 45.6 % after 0.17 h reaction in liquid water at 573 K by the addition of 17.7 MPa and 26.6 MPa of carbon dioxide, respectively, and the 3-HTHP yield was also increased by addition of carbon dioxide, indicating that carbonic acid from water and carbon dioxide (Scheme 2) accelerated the intramolecular dehydration. On the other hand, the final yields of THFA and 3-HTHP after 1 h of reaction were almost the same (70 % and 10 %, respectively) under these three conditions (0, 17.7, and 26.6 MPa of carbon dioxide), indicating that the added carbon dioxide enhanced the THFA and 3-HTHP formation rates to reach the equilibrium yields\(^9\).

The dehydration reactions of 1,4-butanol (1,4-BDO), 1,5-pentanol (1,5-PDO), and 1,4-pentanol (1,4-PDO) (Scheme 3) were investigated at 573 K to understand the intramolecular dehydration chemistry of polyalcohols in high-temperature liquid water with high-pressure carbon dioxide (Table 1). Initial formation rates of cyclic ethers were estimated from the initial slopes of the fitting curves of their profiles. The initial formation rates of five-membered cyclic ethers were higher than six-membered cyclic ethers, as revealed by the finding that the dehydration rate of 1,4-BDO to tetrahydrofuran (THF) \((0.68 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1})\) was larger than that of 1,5-PDO to tetrahydrofuran (THP) \((0.063 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1})\). The dehydration rate of 1,4-PDO to 2-methyltetrahydrofuran (2-MTHF) \((0.86 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1})\) was higher than that of 1,4-BDO to THF \((0.68 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1})\), indicating that the basicity of the secondary hydroxyl group in the 4-position in 1,4-PDO is higher than that of 1,4-BDO to THF.

\[
\text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{H}_2\text{CO}_3 \quad \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \quad \rightleftharpoons 2\text{H}^+ + \text{CO}_3^{2-}
\]

**Scheme 2** Formation of Carbonic Acid from Water and Carbon Dioxide

**Scheme 3** Intramolecular Dehydration Reactions of 1,4-Butanediol, 1,5-Pentanediol, and 1,4-Pentanediol

| Reactant | Product | CO₂ pressure [MPa] | Initial formation rate \([10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}]\)|
|----------|---------|-------------------|------------------|
| 1,4-BDO  | THF     | 0                 | 0.68             |
|          |         | 17.7              | 4.7              |
| 1,5-PDO  | THP     | 0                 | 0.063            |
|          |         | 17.7              | 0.42             |
| 1,4-PDO  | 2-MTHF  | 0                 | 0.86             |
|          |         | 17.7              | 10.0             |

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of the primary hydroxyl group\textsuperscript{10}). Thus, in the de-
hydration of 1,2,5-PTO, the formation rate of THFA, aive-membered heterocyclic ether formed by dehydration
between primary and secondary hydroxyl groups, is
faster than that of 3-HTHP, a six-membered hetero-
cyclic ether formed by dehydration between two primary
hydroxyl groups.

Cyclic ethers were produced by the dehydration reac-
tions of polyalcohol compounds in high temperature
liquid water, which were accelerated by the presence of
carbon dioxide dissolved in the water. The position of
the hydroxyl groups is extremely important for the de-
hydration, and suggests a new approach for conversion
of biomass derivatives to useful materials\textsuperscript{11}).

2.2. Stereoselective Dehydration in High-
temperature Liquid Water

The stereochemistry of intramolecular dehydration is
important not only to design the conversion pathway of
biomass resources but also to understand the reaction
mechanism of the dehydration of polyalcohols in high-
temperature liquid water. We investigated the intra-
molecular dehydration of chiral 2,5-hexanediol,
\((2\text{R,5R})\text{-}(-)\text{-}2,5\text{-hexanediol (2R,5R-HDO) to cis-2,5-}
dimethyльtetrahydrofuran (cis-2,5-DMTHF) or trans-2,5-
dimethyльtetrahydrofuran (trans-2,5-DMTHF) (Scheme 4) in high-temperature liquid water under
high-pressure carbon dioxide at 523 K\textsuperscript{12}). Dehy-
dration of 2R,5R-HDO proceeded slowly in water at 523 K
(Fig. 2) without adding carbon dioxide, as shown by
the 6% yield of product, 2,5-DMTHF, even after 5 h
reaction. Dehydration of 2R,5R-HDO to 2,5-DMTHF
was enhanced by the addition of high-pressure carbon
dioxide (Fig. 2). The initial formation rate of 2,5-
DMTHF by 2R,5R-HDO dehydration was increased
by more than 50 times by the addition of carbon dioxide.
The intramolecular dehydration reaction of 2,5-HDO to
2,5-DMTHF was catalyzed by the increased concentra-
tion of protons in water, which was increased by the
formation of carbonic acid under high-pressure carbon
dioxide.

The percentage of cis-2,5-DMTHF (cis selectivity) in
the 2,5-DMTHF product (sum of cis and trans forms)
from the dehydration of 2R,5R-HDO is also shown in
Fig. 2. The cis selectivity of 2,5-DMTHF was more
than 85% under all conditions of 2R,5R-HDO de-
hydration at 523 K, indicating that sterically hindered
cis-2,5-DMTHF was produced preferentially from
2R,5R-HDO in high-temperature liquid water. The high
cis selectivity of 2,5-DMTHF in the 2R,5R-HDO
dehydration demonstrated that 2,5-HDO dehydration
proceeded via an SN2 substitution of a protonated
hydroxyl group, as shown in Scheme 5. In the first

\[
\begin{align*}
\text{Scheme 4} & \quad \text{Intramolecular Dehydration Reaction of 2,5-Hexanediol} \\
\text{Scheme 5} & \quad \text{Reaction Pathway of 2,5-Hexanediol Dehydration}
\end{align*}
\]
step, a hydroxyl group was protonated, and then the oxygen atom in the unprotonated hydroxyl group attacked the carbon atom connected with the protonated hydroxyl group with simultaneous elimination of water.

2R,5R-HDO dehydration by sulfuric acid produces a mixture of cis-2,5-DMTHF (ca. 50 %) and trans-2,5-DMTHF (ca. 50 %)\(^{13,14}\). The strong acidity of sulfuric acid should cause first elimination of water and then the formation of the carbocation intermediate (SN1 reaction). The acidity of carbonic acid, formed from water and carbon dioxide, can catalyze the stereoselective dehydration of 2,5-HDO via the SN2 substitution process.

We successfully demonstrated that the combination of high-temperature liquid water and high-pressure carbon dioxide can effectively generate protons for the stereoselective intramolecular dehydration of polyalcohols.

2.3. Dehydration of Biomass-derived Sugar Alcohols in High-temperature Liquid Water

Conversion of the non-edible fraction of biomass, such as cellulose, to valuable chemicals using environmental-friendly techniques is very important. Sorbitol is a promising biomass-derived material from cellulose as an intermediate to other chemicals. Recently, sorbitol was produced by one-step cracking of cellulose using supported metal catalysts and hydrogen in water\(^{15,16}\). Sorbitol can be converted to anhydroisorbitol by monomolecular dehydration and isosorbide by bimolecular dehydration (Scheme 6). Anhydroisorbitol is a key material for producing sorbitan fatty acid esters, which are used as naturally-derived surfactants or nontoxic food additives. Isosorbide and isosorbide nitrate are pharmaceuticals used as osmotic diuretics and blood pressure-lowering agents, respectively. In addition, polyethylene terephthalate (PET) containing isosorbide has higher glass transition temperatures than pure PET, broadening the applications of polyesters\(^{17,18}\). Dehydration of sorbitol occurs with inorganic strong acid catalysts, such as sulfuric and hydrochloric acids, in the temperature range of 377-408 K\(^{19,20}\), but these reagents cause serious corrosion and require neutralization processes.

We investigated sorbitol dehydration in high-temperature liquid water without inorganic strong acid catalysts\(^{21}\). Dehydration of sorbitol proceeded at 548 K in high-temperature liquid water resulting in the formation of 1,4-anhydroisorbitol (1,4-AHSO), 2,5-anhydroisorbitol (2,5-AHSO), 1,5-anhydroisorbitol (1,5-AHSO), and isosorbide (Fig. 3). The major product of monomolecular dehydration was 1,4-AHSO with a highest yield of 55 % at 548 K for 2 h, and the yield of isosorbide from bimolecular dehydration of sorbitol increased with reaction time. On the other hand, 2,5-AHSO was obtained with a yield of 13 % at 548 K for 5 h, which did not change with reaction time for 5 h. The yield of 1,5-AHSO was always less than 1 %. The material balance, which is defined as the sum of the unreacted sorbitol and the detected products (1,4-AHSO, 2,5-AHSO, 1,5-AHSO, and isosorbide), decreased with longer reaction time and higher reaction temperature. For example, the material balance at reaction time of 5 h at 548 K was ca. 85 % based on high performance liquid chromatography (HPLC) analysis. The decrease in the material balance indicates that polymerization and/or degradation of sorbitol or anhydroisorbitol occurred in the liquid phase. Dehydration of sorbitol was also carried out at 523, 560, and 573 K in high-temperature liquid water. At all these temperatures (523-573 K), 1,4-AHSO and 2,5-AHSO were formed at the beginning of reaction. The initial formation rates of 1,4-AHSO and 2,5-AHSO increased with higher reaction temperature and the 1,4-AHSO yield was higher than the 2,5-AHSO yield at the initial stage of the sorbitol dehydration. The 1,4-AHSO yield peaked and...
then decreased with reaction time; whereas the 2,5-AHSO yield was almost constant. Isosorbide was produced later than 1,4-AHSO and 2,5-AHSO because isosorbide “1,4-3,6-dianhydro-d-sorbitol” was formed by the stepwise dehydration of 1,4-AHSO (Scheme 6).

The yields of 1,5-AHSO were always less than 1% under our experimental conditions (data not shown in Fig. 3), indicating that the formation rates of 1,4-AHSO and 2,5-AHSO (five-membered cyclic ethers) were much higher than that of 1,5-AHSO (six-membered cyclic ether). Similarly, the dehydration rate of 1,4-butanediol to tetrahydrofuran (five-membered cyclic ether) was much higher than that of 1,5-pentanediol to tetrahydropyran (six-membered cyclic ether) as shown in section 2.1. The dehydration rate of sorbitol to 1,4-AHSO was faster than that of 1,4-AHSO to isosorbide; therefore, 1,4-AHSO could be obtained as an intermediate product. Kinetic analysis of sorbitol dehydration in high-temperature liquid water showed that the maximum yield of 1,4-AHSO from the dehydration of sorbitol increased with lower reaction temperature with long reaction time (for example, 80% at 500 K for 450 h) and that the maximum yield of isosorbide was 57% at 590 K for 1 h. Therefore, 1,4-AHSO and isosorbide could be produced selectively from sorbitol dehydration in high-temperature liquid water without adding acid catalysts by controlling both reaction temperature and reaction time.

3. Gasification of Biomass Resources to Fuel Gases

3.1. Gasification of Paper Wastes

Paper usage is increasing because of the advantage of direct visual access to the information rather than stored electronic data. Used paper can be used for pulp for making recycled paper, but many important documents are shredded for confidentiality reasons. The cellulose fibers of shredded documents as well as paper recycled several times are shortened resulting in reduced quality compared with the original pulp, resulting in the formation of large amounts of paper sludge. Paper mill wastewater including short cellulose fibers is purified by costly fermentation for environmental conservation. We strongly believe that the on-site production of gaseous fuel from such nonrecyclable paper wastes is the best solution for establishing a sustainable society. Pyrolytic gasification of cellulose based on steam reforming and partial oxidation is a promising technology for the utilization of paper wastes with low water content, but high temperature (823-873 K) is required for pyrolytic gasification and the resultant tar or char formation causes deactivation of catalysts. In contrast, gasification of biomass in supercritical or subcritical water requires lower temperature with less tar or char formation. We investigated the gasification of printed paper wastes in water at low temperature (523 K) to produce methane and hydrogen.

The gasification of recycled paper and cellulose powder was studied at 523 K in water over Ru/C catalyst (Fig. 4). The recycled paper was gasified completely to methane, carbon dioxide, and hydrogen at 523 K within 3 h, a shorter time than that required for cellulose powder (5 h), indicating that the gasification rate of recycled paper was higher than that of cellulose. Figure 5 shows the X-ray diffraction (XRD) patterns of cellulose powder and recycled paper, which exhibited strong peaks at 2θ = 22.6 degree ascribed to the cellulose crystal plane (002). The intensity of the XRD peak for cellulose powder was higher than that for recy-
ried paper, indicating that the cellulose crystalline sizes in cellulose powder were larger than those in the recycled paper. The gas yield of paper or cellulose gasification over Ru/C increased with lower cellulose crystallinity.

The gas yields from both recycled paper and cellulose powder increased with ball-milling treatment for up to 24 h. The cellulose crystallinity of both recycled paper and cellulose powder was decreased by the ball-milling treatment as revealed by the XRD peak broadening at 2θ = 22.6° (Fig. 5). The crystalline size of cellulose powder was decreased from 15.4 to 9.9 nm by ball-milling treatment for 24 h and the gas yield from cellulose powder increased from 28.6 to 60.4 C% at 523 K for 0.5 h, indicating that the gas yield of cellulose gasification over Ru/C increased with lower cellulose crystallinity. Scanning electron microscope (SEM) of cellulose powder observed the fibrous structure of cellulose before ball-milling treatment, whereas the fibrous structure had collapsed and particles of cellulose (5-20 μm) were observed after ball-milling treatment, indicating that the morphological structure of cellulose powder was dramatically changed by the ball-milling treatment. The morphological structure of the recycled paper was also changed from fibrous structure to particles by ball-milling treatment. The morphological structures of the reactants might be very important in gasification. Cellulose with a small particle structure might be more easily accessible by water and catalysts than cellulose with a large fibrous structure. Gas yields depended on cellulose crystallinity for reactants with similar morphological structures. Gas yields also were changed by morphological structures if the reactants had similar cellulose crystallinity. Therefore, both cellulose crystallinity and morphological structure are important for cellulose gasification in high-temperature liquid water.

The gasification of recycled printed papers from laser monochrome printers and copy machines was also successfully achieved over Ru/C catalyst in water at 523 K, similar to fresh recycled paper, indicating that fuel gases could be produced from waste paper using catalysts in high-temperature liquid water. Such a technique could utilize paper wastes produced in office buildings.

### Table 2 Product Yield and Composition of Catalytic Lignin Gasification in Supercritical Water

| Catalyst       | Gas yield [C%] | Gas composition [%] | Water soluble [C%] | THF soluble [C%] | THF insoluble [C%] |
|----------------|----------------|---------------------|--------------------|-----------------|-------------------|
| Carbon support | 8.4            | 6.9                 | 23.6               | 15.4            | 52.8              |
| Ru/C           | 87.5           | 3.1                 | 0.7                | 47.4            | 48.2              |
| RuCl₃/C        | 24.3           | 14.6                | 0.0                | 17.1            | 65.7              |
| Ru(NO)(NO₃)₃/C | 75.4           | 3.1                 | 2.8                | 41.9            | 51.4              |

| THF soluble [C%] | THF insoluble [C%] |
|------------------|--------------------|
| 10.9             | 25.9               |
| 0.6              | 9.4                |
| 2.6              | 25.3               |
| 0.9              | 19.4               |

*Table 2* Product Yield and Composition of Catalytic Lignin Gasification in Supercritical Water*[^a]*

[^a]: Reaction conditions; lignin 0.10 g, catalyst 0.15 g, water density 0.50 g cm⁻³, 673 K, 1 h.

woody biomass, will allow efficient use of lignin as a high quality energy source. Steam reforming of lignin requires both high reaction temperature (1073-1273 K) and drying of the woody biomass. Gasification methods at low temperature are more desirable because the waste heat from industrial processes, such as iron or cement production, can be utilized. Therefore, the gasification of lignin in supercritical water is a promising technique to both reduce the lignin gasification temperature and eliminate the drying processes. Lignin gasification in supercritical water is catalyzed by metal catalysts (II).[33] Titania or carbon supported ruthenium metal catalysts are effective for lignin gasification in supercritical water at 673 K.[34,35]

Identifying the active sites of ruthenium species for lignin gasification in supercritical water is essential to develop active catalysts. We investigated the catalytic performance of charcoal-supported ruthenium salts for lignin gasification in supercritical water at 673 K and observed that the ruthenium (III) species in the supported ruthenium salts were reduced to ruthenium metal particles, which were responsible for the lignin gasification activities in supercritical water.[36,37]

Table 2 shows the product yields and gas composition of lignin gasification at 673 K for 1 h in supercritical water over the ruthenium-based catalysts (Ru 5 wt%) and charcoal catalyst without ruthenium species. The catalysts RuCl₃/C and Ru(NO)(NO₃)₃/C, which were not reduced during the preparation, showed activities for lignin gasification. Ru(NO)(NO₃)₃/C was almost as active as Ru/C (87.5 C%) for the gasification, but RuCl₃/C catalyst was much less active, as revealed by their gas yields in Table 2. Figure 6 shows the gas yields of lignin gasification in supercritical water as a function of reaction time. Lignin in the reactor was almost completely gasified over Ru(NO)(NO₃)₃/C in supercritical water at 673 K for 3 h, whereas lignin gasification over RuCl₃/C catalyst reached a plateau at about 30 C% lignin conversion after 1 h.

Figure 7 shows the XRD patterns of RuCl₃/C and Ru(NO)(NO₃)₃/C catalysts before and after lignin gasification in supercritical water for 1 h at 673 K. Four XRD peaks observed at 38.8, 42.2, 44.4, 58.4° for RuCl₃/C catalyst after lignin gasification were assigned to ruthenium metal. The XRD pattern suggested that the ruthenium metal species were formed in RuCl₃/C.
after lignin gasification, indicating that RuCl₃ was reduced to ruthenium metal during lignin gasification in supercritical water. On the other hand, these peaks assigned to ruthenium metal particles were not observed in the XRD pattern of Ru(NO)(NO₃)₃/C after lignin gasification. Inductive coupled plasma emission spectrometric analysis detected no ruthenium species in the liquid phase after lignin gasification using the catalysts RuCl₃/C and Ru(NO)(NO₃)₃/C, implying that all ruthenium species were located on the charcoal support. Extended X-ray absorption fine structure (EXAFS) spectra at the Ru K-edge of RuCl₃/C and Ru(NO)(NO₃)₃/C catalysts after lignin gasification in supercritical water for 1 h at 673 K were also studied.

Figure 8 shows Fourier transforms of k⁴-weighted EXAFS spectra for the ruthenium catalysts after lignin gasification. The peaks of Ru-Ru were observed at 0.23 nm (phase shift uncorrected) in both RuCl₃/C and Ru(NO)(NO₃)₃/C catalysts after lignin gasification, indicating that ruthenium metal particles were formed in all samples during the lignin gasification. The coordination number (CN) of the Ru-Ru bond for RuCl₃/C as determined by a curve fitting analysis was 11.3 ± 1.2, confirming that large Ru metal particles (12 nm from TEM images) were formed in RuCl₃/C, in accordance with the XRD result. On the other hand, the CN of Ru(NO)(NO₃)₃/C was 5.5 ± 0.9, which corresponds to Ru metal clusters (ca. 1.0 nm) with between 10 and 23 atoms. These findings indicate that the size of the Ru metal particles, formed by the reduction of Ru trivalent salts during lignin gasification in supercritical water, depends on the ruthenium precursors and dramatically affects the gasification activity. Lignin gasification occurs in two steps; (i) decomposition of lignin to alkylphenols and formaldehyde via hydrolysis in supercritical water without a catalyst, and (ii) gasification of alkylphenols and formaldehyde in the presence of supported ruthenium catalysts. The initial oxidation state of ruthenium species (ruthenium (III) or ruthenium metal) did not directly affect the lignin gasification activity, except indirectly through the effect on metal particle size. The ruthenium (III) species in the supported ruthenium salts were reduced to ruthenium metal particles, which were responsible for the catalytic activity for lignin gasification in supercritical water.
4. Conclusions

Biomass valorization techniques were investigated using high-temperature liquid water and supercritical water, such as (i) dehydration reactions of biomass-derived polyalcohols to cyclic ethers and (ii) gasification reactions of lignin to fuel gases. (i) Cyclic ethers were produced by the intramolecular dehydration of biomass-derived polyalcohols in high-temperature liquid water without acid catalysts, which could be accelerated by the addition of carbon dioxide. (ii) Charcoal-supported ruthenium salts were active for lignin gasification at 673 K in supercritical water, in which ruthenium (III) species were reduced to ruthenium metal particles as active sites for the gasification.

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要旨

高温高圧水を利用したバイオマス資源化技術

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環境负荷の低い新たなプロセスによって石油化学原料を代替するバイオマス資源の利用を加速するため、バイオマス資源化技術の開発が行われている。環境負荷低減のために、最も環境負荷が少なく無毒な「水」を反応媒体としたバイオマスの変換反応を行った。高温水中でバイオマス由来多価アルコールの脱水反応が進行し、有用物質への変換が可能であることを明らかにした。さらに、反応系内に二酸化炭素を添加することにより、水と二酸化炭素から炭酸が生成し、酸触媒反応がさらに促進されることが実証した。本手法では、反応後、中和プロセスや触媒を分離・回収する必要がない利点がある。また、高温水および超臨界水中で担持金属触媒を利用し、生物およびリグニンから燃料ガスへ変換可能であることを明らかにした。