

Water Density Effect on Lignin Gasification over Supported Noble Metal Catalysts in Supercritical Water

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Gasification of lignin and 4-propylphenol, which is a model of low-molecular weight compounds from lignin, over supported metal catalysts in supercritical water was studied at 673 K. Supported ruthenium catalysts were active in supercritical water. The catalytic gasification rate was enhanced by the increase of water density. The gasification of lignin proceeded in supercritical water through two steps: (i) decomposition of lignin to low-molecular weight compounds and (ii) gasification of the low-molecular weight compounds over metal catalysts. The rate of 4-propylphenol gasification was not affected by the water density; this was different from lignin gasification. These results indicated that the first step (decomposition to low-molecular weight compounds) in the lignin gasification was enhanced by increasing the water density.

Introduction

Lignin is a component of biomass and has been found to be difficult to gasify.^{1–6} High temperatures of over 1073 K are needed for steam reforming of lignin.³ Low-temperature methods for lignin gasification are desirable, because water from industrial processes with high temperature is available.

Supercritical water ($T_c = 647.3$ K, $P_c = 22.1$ MPa) gasification is a probable technology method to reduce biomass gasification temperatures^{1,2,4–19} because of its high solubility and hydrolysis rates to reduce mass-transfer limitations of

the reactant^{20–22} and its detergent effect by washing coke precursors on the active sites.²³ Several researchers have investigated the gasification of lignin in supercritical water. The decomposition behavior of lignin in supercritical water around 673 K was reported to be that lignin was converted to alkylphenols and formaldehyde via hydrolysis,^{24–30} and then there proceeded a decomposition of the alkylphenols to gases and a cross-linking reaction between the alkylphenols and formaldehyde^{2,28–30} to produce solid materials, which are insoluble in solvents such as water and tetrahydrofuran.^{26–28}

The gasification of biomass in supercritical water around 673 K is enhanced by using metal catalysts.^{1,2,4–6,15–19} Watanabe et al. obtained below 10% of gaseous product yield over a zirconia catalyst from the gasification of lignin in supercritical water at 673 K.¹⁷ Osada et al. reported that supported ruthenium catalysts were effective for the gasification of lignin in supercritical water around 673 K.¹⁹

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(1) Matsumura, Y.; Minowa, T.; Potic, B.; Kersten, S. R. A.; Prins, W.; van Swaaij, W. P. M.; van de Beld, B.; Elliott, D. C.; Neuenschwander, G. G.; Kruse, A.; Antal, M. J. *Biomass Bioenergy* **2005**, *29*, 225–302.

(2) Osada, M.; Sato, T.; Watanabe, M.; Shirai, M.; Arai, K. *Combust. Sci. Technol.* **2006**, *178*, 537–552.

(3) Antal, M. J., Jr. *Solar Energy*; Plenum Press: New York, 1983; pp 175–255.

(4) Yoshida, T.; Matsumura, Y. *Ind. Eng. Chem. Res.* **2001**, *40*, 5469–5474.

(5) Yoshida, T.; Oshima, Y.; Matsumura, Y. *Biomass Bioenergy* **2004**, *26*, 71–78.

(6) Yoshida, T.; Oshima, Y. *Ind. Eng. Chem. Res.* **2004**, *43*, 4097–4104.

(7) Xu, X.; Matsumura, Y.; Stenberg, J.; Antal, M. J., Jr. *Ind. Eng. Chem. Res.* **1996**, *35*, 2522–2530.

(8) Xu, X.; Antal, M. J., Jr. *Environ. Prog.* **1998**, *17*, 215–220.

(9) Antal, M. J., Jr.; Allen, S. G.; Schulman, D.; Xu, X.; Divilio, R. J. *Ind. Eng. Chem. Res.* **2000**, *39*, 4040–4053.

(10) Lee, I.-G.; Kim, M.-S.; Ihm, S.-K. *Ind. Eng. Chem. Res.* **2002**, *41*, 1182–1188.

(11) Schmieder, H.; Abeln, J.; Boukis, N.; Dinjus, E.; Kruse, A.; Kluth, M.; Petrich, G.; Sadri, E.; Schacht, M. *J. Supercrit. Fluids* **2000**, *17*, 145–153.

(12) Kruse, A.; Gawlik, A. *Ind. Eng. Chem. Res.* **2003**, *42*, 267–279.

(13) Sinağ, A.; Kruse, A.; Schwarzkopf, V. *Ind. Eng. Chem. Res.* **2003**, *42*, 3516–3521.

(14) Sinağ, A.; Kruse, A.; Rathert, J. *Ind. Eng. Chem. Res.* **2004**, *43*, 502–508.

(15) Park, K. C.; Tomiyasu, H. *Chem. Commun.* **2003**, *6*, 694–695.

(16) Watanabe, M.; Inomata, H.; Arai, K. *Biomass Bioenergy* **2002**, *22*, 405–410.

(17) Watanabe, M.; Inomata, H.; Osada, M.; Sato, T.; Adschiri, T.; Arai, K. *Fuel* **2003**, *82*, 545–552.

(18) Sato, T.; Osada, M.; Watanabe, M.; Shirai, M.; Arai, K. *Ind. Eng. Chem. Res.* **2003**, *42*, 4277–4282.

(19) Osada, M.; Sato, T.; Watanabe, M.; Adschiri, T.; Arai, K. *Energy Fuels* **2004**, *18*, 327–333.

(20) Savage, P. E. *Chem. Rev.* **1999**, *99*, 603–621.

(21) Akiya, N.; Savage, P. E. *Chem. Rev.* **2002**, *102*, 2725–2750.

(22) Watanabe, M.; Sato, T.; Inomata, H.; Smith, R. L., Jr.; Arai, K.; Kruse, A.; Dinjus, E. *Chem. Rev.* **2004**, *104*, 5803–5821.

(23) Savage, P. E. *Catal. Today* **2000**, *62*, 167–173.

(24) Bobleter, O.; Consin, R. *Cellul. Chem. Technol.* **1979**, *13*, 583–593.

(25) Funazukuri, T.; Wakao, N.; Smith, J. M. *Fuel* **1990**, *69*, 349–353.

(26) Yokoyama, C.; Nishi, K.; Nakajima, A.; Seino, K. *Sekiyu Gakkaishi* **1998**, *41*, 243–250.

(27) Ehara, K.; Saka, S.; Kawamoto, H. *J. Wood Sci.* **2002**, *48*, 320–325.

(28) Saisu, M.; Sato, T.; Watanabe, M.; Adschiri, T.; Arai, K. *Energy Fuels* **2003**, *17*, 922–928.

(29) Okuda, K.; Umetsu, M.; Takami, S.; Adschiri, T. *Fuel Process. Technol.* **2004**, *85*, 803–813.

(30) Okuda, K.; Man, X.; Umetsu, M.; Takami, S.; Adschiri, T. *J. Phys.: Condens. Matter* **2004**, *16*, 1325–1330.

The gasification of lignin components in water is also enhanced using solid catalysts.^{31–36} Elliott et al.³¹ decomposed *p*-cresol, which is a model compound of lignin, in subcritical water at 623 K and reported that ruthenium, rhodium, and nickel showed higher activities than those for platinum and palladium metals based on the weight of catalyst. Also, they reported that nickel metal easily lost its activity due to sintering.³¹ Sato et al.¹⁸ conducted the gasification of alkylphenols as model compounds of lignin over supported noble metal catalysts and reported the activity of the catalyst in the order ruthenium > rhodium > platinum > palladium. These reports mean that the noble metal catalysts were effective for decomposition of the benzene ring of alkylphenols for the gasification in the presence of water.

It is reported that the product distribution in lignin conversion can be controlled by water density in the supercritical region.^{25,26,28} Yield of oil, which was defined as products dissolved in organic solvents, increased with increasing water density in lignin conversion with supercritical water at 673 K.^{25,28} Sato et al.¹⁸ reported that the yield of gas products from the gasification of alkylphenols increased as the water density increased from 0 to 0.3 g·cm⁻³ in supercritical water at 673 K. These results suggest that the yields and rates of catalytic gasification of lignin could be enhanced by controlling water density, which can be changed by temperature and pressure. In this paper, we studied the water density effect on lignin gasification with supported metal catalysts in supercritical water.

Experimental Section

Organosolv-lignin powder (lignin) was purchased from Aldrich, and its molecular formula was C_{42.39}H_{45.46}O_{12.15}, as determined by an ultimate CHNS analyzer (Perkin-Elmer, model 2400). The molecular weight was between 1000 and 1500, as determined by a gel permeation chromatography (GPC) system (Waters, GPC150C-plus). The lignin powder was completely soluble in tetrahydrofuran (THF), which was purchased from Wako Pure Chemicals Industries, Ltd. 4-Propylphenol was purchased from Tokyo Kasei Kogyo Co., Ltd and had a purity of 99%. All chemicals were used without further purification. Distilled water was obtained from a water distillation apparatus (Yamato Co., model WG-220). All catalysts tested in this study are summarized in Table 1. All catalysts were used without pretreatment of reduction. Moles of surface metal atoms of the fresh and used catalysts were determined by a carbon monoxide desorption method at 323 K (Bel Japan, Inc. BEL-CAT). It was assumed that a carbon monoxide molecule adsorbed on a surface metal atom (linear adsorption) for determining the number of surface metal atoms in a catalyst.

Catalytic gasification was conducted in a 316 stainless steel tube bomb reactor having an internal volume of 6 cm³. Certain amounts of catalyst, 0.1 g of lignin, and from 0 (no water) to 3.0 g of water were loaded into the reactor. This amount of water corresponded to a density of 0–0.5 g·cm⁻³, and the partial pressure of water at 673 K was up to 37.1 MPa. Air inside the reactor was purged with argon gas. The reactor was submerged into a sand bath (Takahashi Rica Co., model TK-3) and was maintained at the reaction

Table 1. Supported Metal Catalysts Evaluated in This Study

catalyst	manufacturer	metal (wt %)	metal dispersion (%) ^a
Ru/TiO ₂	Osaka Gas Co., Ltd.	2	27
Ru/C	N. E. CHEMCAT Co., Ltd.	5	51
Ru/Al ₂ O ₃	N. E. CHEMCAT Co., Ltd.	5	37
Rh/C	N. E. CHEMCAT Co., Ltd.	5	53
Pt/C	N. E. CHEMCAT Co., Ltd.	5	27
Pt/Al ₂ O ₃	N. E. CHEMCAT Co., Ltd.	2	33
Pd/C	N. E. CHEMCAT Co., Ltd.	5	23
Pd/Al ₂ O ₃	N. E. CHEMCAT Co., Ltd.	5	21
Ni/Al ₂ O ₃	Nissan Girdler Catalyst Co., Ltd.	17	5

^a All catalysts were pretreated under flowing hydrogen at 573 K, for 10 min. The metal dispersion was measured by a carbon monoxide adsorption at 323 K. Metal dispersion = (mol of carbon monoxide adsorbed/mol of total metal atom in a catalyst) × 100.

temperature. The reactor was heated to 673 K for 4 min. Reaction time reported here includes this heat-up time. After a given reaction time, the reactor was taken out of the sand bath and submerged in a water bath for rapid cooling to room temperature. Gaseous products were collected by a syringe through sampling loops attached to a gas chromatography–thermal conductivity detection (GC-TCD) (Shimadzu, model GC-8A) analysis. After sampling the gaseous products, the other products in the reactor were recovered with pure water and separated into water-soluble and water-insoluble fractions. The water-insoluble fraction was separated into THF-soluble and solid fractions. Because the solid fraction included supported metal catalysts used, we evaluated the amount of THF-insoluble products by subtracting the weight of the catalyst loaded from the solid fraction.

Water-soluble and THF-soluble products were analyzed with gas chromatography–flame ionization detection (GC-FID) (Hewlett-Packard, model HP-6980) and gas chromatography–mass spectroscopy (GC-MS) (JEOL, Automass 20) analyses. The molecular weight distribution of THF-soluble products was measured using GPC. Amounts of organic carbon in the water-soluble fractions were evaluated using the total organic carbon analyzer (Shimadzu, model TOC-5000A). Ultimate analysis of the solid product was conducted by the CHNS analyzer.

The product yield of the carbon (hydrogen, oxygen) basis, gas composition, and turnover number (TON) of the catalyst are defined below, respectively.

$$\text{product yield of carbon (hydrogen, oxygen) (C\% (H\%, O\%))} = \frac{\text{mol of carbon (hydrogen, oxygen) atom in product}}{\text{mol of carbon (hydrogen, oxygen) atom in reactant loaded}} \times 100 \quad (1)$$

$$\text{gas composition (\%)} = \frac{\text{mol of gaseous product}}{\text{sum of mol of gas product}} \times 100 \quad (2)$$

$$\text{TON (-)} = \frac{\text{mol of carbon atom in gaseous product}}{\text{mol of surface metal atom}} \quad (3)$$

Results and Discussion

Screening Catalysts. Table 2 shows the product yield and TON values of lignin gasification over various supported metal catalysts in supercritical water. The yields of gas products were enhanced, and solid (THF-insoluble) products were not formed, by the presence of noble metal catalysts. The TON values were the following: Ru/TiO₂ > Ru/Al₂O₃ > Ru/C, Pt/C > Pt/Al₂O₃, Rh/C > Pd/C > Pd/Al₂O₃ > Ni/Al₂O₃, indicating that supported ruthenium catalysts were very effective for gasification in water. This result also agreed with previous reports for ruthenium, rhodium, platinum, and palladium.¹⁹ Elliott et al. reported that nickel metal showed higher activities for gasification of *p*-cresol.³¹ However, they evaluated the activities of metal based on the weight of catalysts used, whereas we evaluated the

(31) Elliott, D. C.; Sealock, L. J.; Backer, E. G. *Ind. Eng. Chem. Res.* **1993**, 32, 1542–1548.

(32) Elliott, D. C.; Sealock, L. J.; Backer, E. G. *Ind. Eng. Chem. Res.* **1994**, 33, 558–565.

(33) Elliott, D. C.; Phelps, M. R.; Sealock, L. J.; Backer, E. G. *Ind. Eng. Chem. Res.* **1994**, 33, 566–574.

(34) Elliott, D. C.; Neuenschwander, G. G.; Hart, T. R.; Scott Burner, R.; Zacher, A. H.; Engelhard, M. H.; Young, J. S.; McCready, D. E. *Ind. Eng. Chem. Res.* **2004**, 43, 1999–2004.

(35) Davda, R. R.; Shabaker, J. W.; Huber, G. W.; Cortright, R. D.; Dumesic, J. A. *Appl. Catal., B* **2003**, 43, 13–26.

(36) Davda, R. R.; Shabaker, J. W.; Huber, G. W.; Cortright, R. D.; Dumesic, J. A. *Appl. Catal., B* **2005**, 56, 171–186.

Table 2. Product Yields of Catalytic Lignin Gasification in Supercritical Water^a

	metal (wt %)	amount of catalyst (g)	yield (C%)				TON (-) ^c
			gas	water- soluble	THF- insoluble	THF- soluble ^b	
without catalyst			3.7	17.2	18.4	60.7	
Ru/TiO ₂	2	0.375	39.0	12.6	0.0	45.4	108
Ru/Al ₂ O ₃	5	0.150	43.4	9.5	0.0	47.1	89
Ru/C	5	0.150	46.9	2.7	0.0	50.4	69
Rh/C	5	0.161	31.4	15.0	0.0	53.6	45
Pt/C	5	0.288	29.1	0.7	0.0	70.2	68
Pt/Al ₂ O ₃	2	0.720	20.6	11.1	0.0	68.3	47
Pd/C	5	0.158	13.9	17.5	0.0	68.6	33
Pd/Al ₂ O ₃	5	0.158	6.0	21.4	0.0	72.6	21
Ni/Al ₂ O ₃	17	0.300	4.8	21.9	0.0	73.3	6

^a Conditions: 0.1 g of lignin, 7.4×10^{-5} mol of metal atom in catalyst (8.7×10^{-4} mol for the case of Ni/Al₂O₃) at 673 K, $0.33 \text{ g}\cdot\text{cm}^{-3}$ of water density, and 15 min of reaction time. ^b THF-soluble (C%) = $100 - ((\text{gas yield (C\%)} + (\text{water-soluble yield (C\%)} + (\text{THF-insoluble (C\%)})))$. ^c TON (-) = (mol of gas carbon)/(mol of surface metal atoms).

Table 3. Gaseous Products Composition for Lignin Gasification in Supercritical Water^a

	composition of gas products (%)				
	H ₂	CH ₄	CO	CO ₂	C2~C4 gases
without catalyst	3.4	69.5	7.4	19.0	0.7
Ru/TiO ₂	10.7	40.7	0.2	46.1	2.3
Ru/Al ₂ O ₃	9.4	42.2	0.2	46.9	1.3
Ru/C	7.1	43.5	0.5	46.8	2.1
Rh/C	4.4	47.0	0.2	47.0	1.9
Pt/C	2.9	26.9	0.0	66.5	3.7
Pt/Al ₂ O ₃	14.7	27.9	0.4	50.3	6.7
Pd/C	5.2	24.9	1.2	65.1	3.6
Pd/Al ₂ O ₃	26.0	18.7	9.6	44.4	1.1
Ni/Al ₂ O ₃	18.4	18.1	4.0	58.4	1.1

^a Conditions: 0.1 g of lignin, 7.4×10^{-5} mol of metal in catalyst (8.7×10^{-4} mol for the case of Ni/Al₂O₃) at 673 K, $0.33 \text{ g}\cdot\text{cm}^{-3}$ of water density, and 15 min of reaction time.

activities based on TON values of surface metal catalysts. In our results, the activity of nickel (TON) was lower than that of other noble metal catalysts.

Table 3 summarizes the composition of gaseous products over supported metal catalysts in supercritical water. The values for selectivity to methane were in the following order, ruthenium > rhodium > platinum > palladium > nickel, and those to carbon dioxide and hydrogen were nickel > palladium > platinum > rhodium > ruthenium. The order of selectivities to methane over supported metal catalysts is the same as the ability of C–O bond cleavage of carbon monoxide;^{35,36} then, the ability of supported metal catalysts for C–O bond cleavage in oxygen-containing organic compounds in lignin would determine the selectivity of the gaseous products.

Gasification of Lignin over the Ru/TiO₂ Catalyst. Figure 1a shows the yield of products for lignin gasification in the presence of the Ru/TiO₂ catalyst, which shows the highest TON at 673 K and $0.5 \text{ g}\cdot\text{cm}^{-3}$ of water density. The gasification of lignin proceeded in supercritical water, and all lignin was gasified completely after 120 min. Compounds having hydroxyl groups, such as alkylphenols, catechol, and guaiacol, were retained as water-soluble products, and their yield decreased with increase in reaction time. THF-soluble products, which contained nonpolar aromatic compounds such as isopropyl benzene, were formed at the beginning of the reaction, but their yield decreased with increasing reaction time. The molecular weight of THF-soluble products was between 200 and 1000, which was lower than that of raw organosolv-lignin between

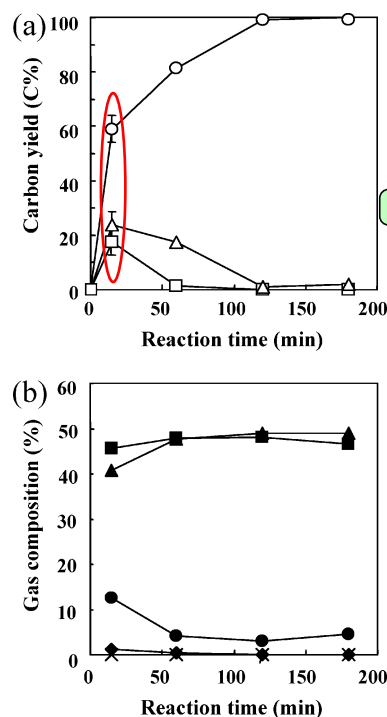


Figure 1. (a) Carbon yield and (b) gas composition for lignin gasification over Ru/TiO₂ in supercritical water at 673 K and $0.5 \text{ g}\cdot\text{cm}^{-3}$ of water density: gas (O), water-soluble (□), THF-soluble (Δ), H₂ (●), CH₄ (▲), CO (×), CO₂ (■), C2~C4 gases (◆). The amounts of Ru/TiO₂ and lignin were 0.375 and 0.1 g, respectively.

1000 and 1500. THF-insoluble product was not formed in the gasification with the Ru/TiO₂ catalyst.

The composition of gaseous products with the conversion of lignin gasification is shown in Figure 1b. At 15 min, the composition was methane 40%, carbon dioxide 40%, hydrogen 15%, and C2–C4 gases 5%. Methane yield increased with reaction time, whereas hydrogen yield decreased. After 120 min, the composition became methane 50%, carbon dioxide 45%, and hydrogen 5%, corresponding to an equilibrium composition of gas product at 673 K calculated by CHEMKIN III:³⁷ methane 49%, carbon dioxide 42%, and hydrogen 9%. Calculation results of CHEMKIN III³⁷ are based on the assumption that the gas phase is a mixture of ideal gases. One possible explanation is that carbon dioxide and hydrogen were formed at an early stage of lignin gasification, and these reacted to produce methane. Hydrogen atom yield was about 180 H% after 180 min, indicating that about half of the amount of hydrogen atoms in the gaseous products were derived from water molecules.¹⁹ Also, oxygen atom yield was about 270 O% after 180 min, indicating that two-thirds of the oxygen atoms in the gaseous products were derived from not only the lignin sample but also water.¹⁹ The ratio of hydrogen and oxygen atoms except for those from the lignin sample was about 2, suggesting that water molecules participated in the gasification as reactants. The amount of water that participated in the gasification under $0.5 \text{ g}\cdot\text{cm}^{-3}$ of water density was 0.05 g, which is 1.7% of the water loaded (3 g), indicating that water consumed in the gasification did not affect the water density in the reactor.

(37) Kee, R. J.; Rupley, F. M.; Miller, J. A.; Coltrin, M. E.; Grcar, J. F.; Meeks, E.; Moffat, H. K.; Lutz, A. E.; Dixon-Lewis, G.; Smooke, M. D.; Warnatz, J.; Evans, G. H.; Larson, R. S.; Mitchell, R. E.; Petzold, L. R.; Reynolds, W. C.; Caracotsios, M.; Stewart, W. E.; Glarborg, P.; Wang, C.; Adigun, O. *CHEMKIN Collection*, release 3.6; Reaction Design, Inc.: San Diego, CA, 2001.

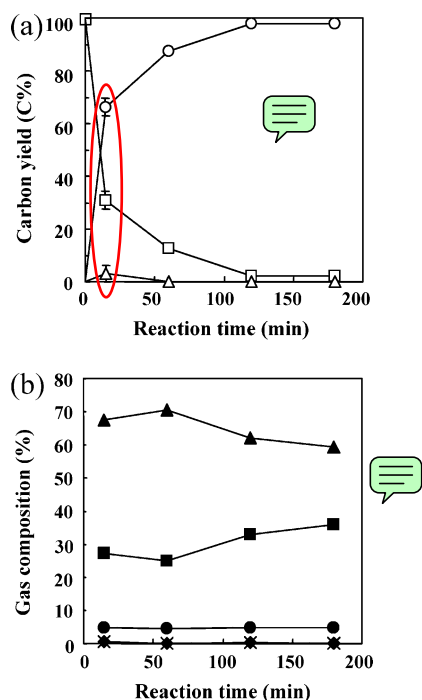


Figure 2. (a) Carbon yield and (b) gas composition for 4-propylphenol gasification over Ru/TiO₂ in supercritical water at 673 K and 0.5 g·cm⁻³ of water density: gas (○), 4-propylphenol (□), propylbenzene (△), H₂ (●), CH₄ (▲), CO (×), CO₂ (■), C₂~C₄ gases (◆). The amounts of Ru/TiO₂ and 4-propylphenol were 0.375 and 0.1 g, respectively.

Gasification of 4-Propylphenol over the Ru/TiO₂ Catalyst.

Figure 2a shows the product yield for the gasification of 4-propylphenol, which is a model of alkylphenols formed by lignin decomposition in water.¹⁸ 4-Propylphenol was stable in supercritical water at 673 K in the absence of catalyst.¹⁸ The gasification of 4-propylphenol proceeded in the presence of the Ru/TiO₂ catalyst. While a small amount of propylbenzene, a

dehydroxylated product, was formed for 15 min of treatment, 4-propylphenol was completely gasified after 120 min in supercritical water. In Figure 2b, the composition of gas products from 4-propylphenol was methane 60%, carbon dioxide 35%, and hydrogen 5%, which was a higher methane yield than that from lignin. We also calculated an equilibrium composition of gas products from the gasification of 4-propylphenol by CHEMKIN III³⁷ and obtained methane 59%, carbon dioxide 36%, and hydrogen 5%. Hydrogen and oxygen atom yields were about 190 H% and 330 O% after 180 min, respectively. The ratio of hydrogen and oxygen atoms that would be derived from water was about 2. The higher methane yield obtained in 4-propylphenol gasification than in lignin would be ascribed to the difference of the ratio of oxygen atoms to carbon (O/C) in their reactants. The O/C value of 4-propylphenol (0.11) is less than that of lignin (0.29), indicating that 4-propylphenol needs a larger amount of oxygen atoms, which could be supplied from water molecules, in supercritical water. Part of the hydrogen atoms derived from water reacted with carbon dioxide; then, the selectivity of methane in the gasification of 4-propylphenol became greater than that of lignin and that of carbon dioxide became smaller.

Water Density Effect for Products Yields. The yield of gaseous product increased with an increase in reaction time at all water densities in the presence of the Ru/TiO₂ catalyst (Figure 3a). The gasification rate also increased with increasing water density. The yields of gas products at 180 min reached about 100% above 0.33 g·cm⁻³ of water density, whereas the yields of gas products were about 60–70% at 0.1–0.2 g·cm⁻³ of water densities. Further, the yield of gas products after 180 min was only 15% in the absence of water. For the case of low water density conditions less than 0.2 g·cm⁻³, the contact efficiency between lignin and the catalyst particles would be low; then, the polymerization of lignin occurred and gasification did not proceed well. The composition of gas products was independent

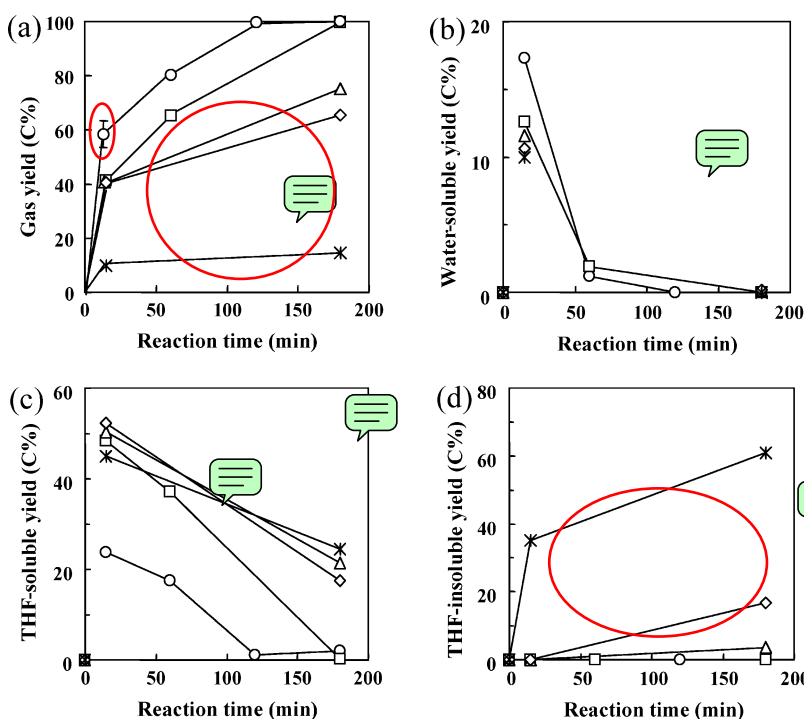


Figure 3. Water density effect on lignin gasification over Ru/TiO₂ in supercritical water at 673 K. Water densities were 0.5 g·cm⁻³ (○), 0.33 g·cm⁻³ (□), 0.2 g·cm⁻³ (△), 0.1 g·cm⁻³ (◇), and 0 g·cm⁻³ (×). The amounts of Ru/TiO₂ and lignin were 0.375 and 0.1 g, respectively. (a) Gas, (b) water-soluble, (c) THF-soluble, and (d) THF-insoluble.

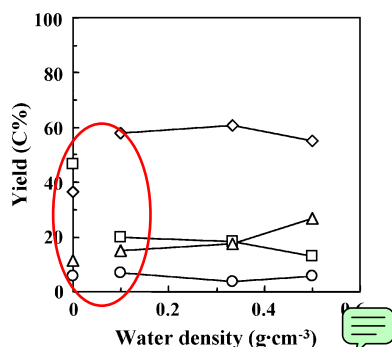


Figure 4. Dependence of product yield on water density for lignin decomposition at 673 K for 15 min: gas (○), water-soluble (□), THF-soluble (△), THF-insoluble (◇).

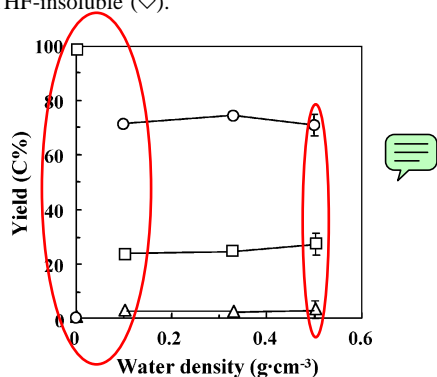


Figure 5. Water density effect on 4-propylphenol gasification over Ru/TiO₂ in supercritical water at 673 K: gas (○), 4-propylphenol (□), propylbenzene (◇). The amounts of Ru/TiO₂ and 4-propylphenol were 0.375 and 0.1 g, respectively.

of water density, which is methane 50%, carbon dioxide 45%, and hydrogen 5%.

The yields of water-soluble and THF-soluble products were high at the beginning of the reaction and decreased with reaction (Figure 3, parts b and c). Also, the initial yields for both water-soluble and THF-soluble products were higher with increasing water density.

THF-insoluble products were not formed in water above 0.33 g·cm⁻³ of water density (Figure 3d). Below 0.2 g·cm⁻³ of water density, THF-insoluble products formed and the yield increased with increase in time. The polymerization reaction of lignin would proceed under small amounts of water, because the contact efficiency between water and lignin would be too low.

Figure 4 shows the dependence of product yields on water density for lignin decomposition in the absence of a supported metal catalyst. The yields of gaseous products were very small, less than 5% regardless of water density. The yield of water-soluble products from lignin increased and that of THF-insoluble products decreased with increasing water density. Yokoyama et al.²⁶ reported that acetone-soluble products containing hydroxyl groups increased with increasing water density in the treatment of lignin in supercritical water at 648 K. The increase of water-soluble yield shown in Figure 4 would show that the hydrolysis of lignin increased with an increase of water density.

Figure 5 shows the dependence of products yields on water density for 4-propylphenol gasification in the presence of the Ru/TiO₂ catalyst. 4-Propylphenol was not decomposed on the Ru/TiO₂ catalyst without water. The yield and composition of gaseous products from 4-propylphenol were constant in water of densities between 0.1 and 0.5 g·cm⁻³, carbon dioxide 65%, methane 30%, and hydrogen 5%.

Gasification Behavior of Lignin in Supercritical Water. Lignin is a biopolymer in which hydroxyphenylpropane units

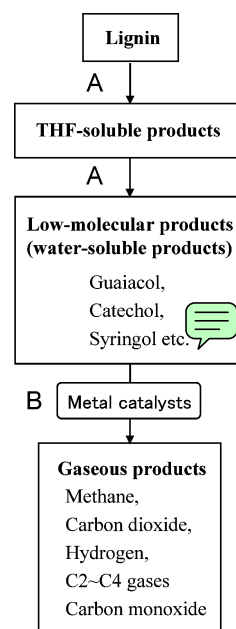


Figure 6. Reaction pathway of lignin gasification with a ruthenium catalyst in supercritical water.

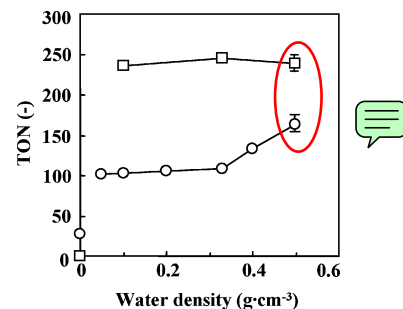


Figure 7. Water density effect for TON values of lignin and 4-propylphenol gasification over Ru/TiO₂: lignin (○), 4-propylphenol (□). The amounts of Ru/TiO₂ and lignin (or 4-propylphenol) were 0.375 and 0.1 g, respectively.

are connected with ether and carbon-carbon single bonds.³⁸ It is reported that lignin decomposition in supercritical water proceeds through hydrolysis and dealkylation (Figure 6).^{2,17-19,24-30} According to the proposed scheme, lignin was decomposed to THF-soluble products whose molecular weights were from 200 to 1000, and the THF-soluble products were converted to water-soluble products in this work (path A). In the absence of catalysts, the low-molecular weight products converted to THF-insoluble products through a cross-linking reaction.²⁸⁻³⁰ On the other hand, the low-molecular weight products were gasified to methane, carbon dioxide, hydrogen, and C2-C4 gases on metal surfaces in supercritical water (path B).^{2,18,19,32}

The yield of water-soluble products at 15 min increased with increasing water density both in the presence and absence of the Ru/TiO₂ catalyst (Figures 3a and 4). The promotion of the hydrolysis of lignin to water-soluble products (path A) enhanced with an increase of water density. On the other hand, the gasification rate of 4-propylphenol, which is a model reaction for path B, was almost constant regardless of the water density (Figure 5), indicating that path B is not affected by water density.

Figure 7 shows the TON values of the gasification of lignin and 4-propylphenol against water density. The TON values for 4-propylphenol gasification were more than 2 times higher than

(38) Dorrestijn, E.; Laarhoven, L. J. J.; Arends, I. W. C. E.; Mulder, P. J. Anal. Appl. Pyrolysis 2000, 54, 153-192.

those for lignin. The TON for 4-propylphenol gasification was almost constant regardless of water density; however, the values for lignin gasification increased from 0.33 to 0.5 g·cm⁻³. It is probable that path A is accelerated above 0.33 g·cm⁻³ of water density, and the number of water-soluble compounds, which could be easily gasified over the Ru/TiO₂ catalyst under supercritical water at high water density, increased.

Klein's group^{39,40} has already reported that the hydrolysis of guaiacol in supercritical water increased above 0.4 g·cm⁻³ of water density, whereas it was almost constant at a water density less than 0.4 g·cm⁻³. They explained the enhancement of the hydrolysis rate of ether bonds in guaiacol by the water dielectric constant. Hydrolysis of lignin also would be enhanced in supercritical water above 0.4 g·cm⁻³ of water density.

(39) Townsend, S. H.; Abraham, M. A.; Huppert, G. L.; Klein, M. T.; Paspek, S. C. *Ind. Eng. Chem. Res.* **1988**, 27, 143–149.

(40) Huppert, G. L.; Wu, B. C.; Townsend, S. H.; Klein, M. T.; Paspek, S. C. *Ind. Eng. Chem. Res.* **1989**, 28, 161–165.

Conclusion

Gasification of lignin was conducted in supercritical water in the presence of various supported metal catalysts at 673 K. The following results were obtained.

- 1 Supported ruthenium catalysts were active for gasification of lignin in supercritical water.
- 2 The rate of lignin decomposition to low-molecular weight compounds in supercritical water was enhanced by the increase of water density above 0.33 g·cm⁻³.
- 3 The gasification of low-molecular weight compounds over the supported ruthenium catalysts was not affected by water density.
- 4 The catalytic gasification rate of lignin was increased with an increase in water density above 0.33 g·cm⁻³.

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