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Gasification of Alkylphenols with Supported Noble Metal Catalysts in Supercritical Water

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Gasification of alkylphenols as lignin model compounds was examined in the presence of supported noble metal catalysts in supercritical water without hydrogen donor at 673 K. The activity of the catalyst was in the order of Ru/γ-alumina > Ru/carbon, Rh/carbon > Pt/γ-alumina, Pd/carbon, and Pd/γ-alumina. The effect of water density with the Ru/γ-alumina catalyst was examined in detail. The main gas products were methane, carbon dioxide, and hydrogen. The yield of gases and the ratio of methane increased with increasing water density. The gasification of the isomers of propylphenols was also examined with the Ru/γ-alumina catalyst. The reactivities of *o*- and *p*-propylphenols were relatively higher than those of *m*-propylphenols.

Introduction

The alkylphenol unit is a basic structure of phenolic resources such as lignin, coal, and phenol resin.[1–3] In particular, lignin is one of the main components in the biomass together with cellulose and hemicellulose. Lignin is a biopolymer in which hydroxyphenylpropane units such as *trans-p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol are connected with ether and carbon–carbon linkages and has various oxygen functional groups such as hydroxyl, carboxyl, and carbonyl groups and bonds such as ether and ester bonds.[1] It is probable to say that lignin is a biopolymer of mainly methoxy- and dimethoxy-propylphenols and *p*-propylphenol is a useful model.

Gasification is a useful method for obtaining fuel gases from lignin. The effective recovery of energy from lignin can be achieved by developing a method of decomposition of stable propylphenols, especially *p*-propylphenol. Phenolic resources are often converted to liquid products by hydrogenation using hydrogen donor solvents or catalysts; however, the use of organic solvents is expected to be limited and nonpreferable for green chemistry.

Supercritical water (T_c = 647.3 K and P_c = 22.1 MPa) is a dense steam and has received attention as an environmentally friendly reaction solvent because of its unique properties as described below. Supercritical water is miscible with light gases and hydrocarbons, and its dielectric constant is from 2 to 20, near the critical point, which is similar to that of polar organic solvents at room temperature.[4,5] Some organic reactions such as hydrolysis[6,7] and Friedel–Crafts reaction,[8,9] proceed without a catalyst in supercritical water. In these reactions, water can sometimes participate in the reaction as a reactant.[5] Further, the rate and equilibrium of the reaction can be controlled by manipulating temperature and pressure because of the changing of solvent properties such as dielectric constant.[5]

The noncatalytic conversion of alkylphenols and alkylbenzene has been studied in high-temperature water including supercritical conditions. Katritzky et al.[10,11] reported that alkylphenols (2-, 3-, 4-cresols, 4-ethylphenol, 4-propylphenol, 4-isopropylphenol, and 4-*tert*-butylphenol) were almost stable at 523 K. Ederer et al.[12] conducted the decomposition of *tert*-butylbenzene in supercritical water at 773–813 K without catalyst and revealed that the increase of water density affected the reaction rate and product distribution. They analyzed the detailed reaction mechanism by a radical elementary reaction model, which suggests that cage effect and pressure effect are important. Martino et al.[13] reported that the decomposition of cresols in supercritical water at 733 K was 10% at about less than 10 seconds and phenol was the main product. Adschiri et al.[14] reported the decomposition of bisphenol A, which contains two phenolic units, in supercritical water at 673 K occurred to produce phenol. Tagaya et al.[15] reported that bisphenol-F decomposed to phenol, cresols, and some polymerization products in supercritical water at 703 K. These results indicate that supercritical water is a good tool for the cleavage of carbon–carbon bonds, while aromatic rings remain unchanged as they are. We have examined the decomposition of 4-isopropylphenol as a model compound of lignin and reported that 4-isopropylphenol was extremely stable in supercritical water at 673 K, indicating that *p*-propylphenols were very stable, even in supercritical water.[9,16]

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The conversion process with heterogeneous catalysts in supercritical water is also useful.[17,18] High solvent solubility of supercritical water can eliminate mass-transfer transport limitations. Supercritical water allows in situ extraction of coke precursors to prevent coking on a catalyst. Further, water density can be controlled by temperature and pressure in the supercritical region. The water density affects the interaction between catalysts and reactants; thus, rates and equilibrium of the reaction can be controlled, indicating that the reactivity of catalysts can be enhanced by changing the water density in supercritical water. There are some studies about catalytic gasification of biomass resources in supercritical water. Antal et al.[19] reported that corn starch was almost completely gasified at around 927 K. Watanabe et al.[20] reported that lignin was gasified with a zinc oxide catalyst at 673 K in supercritical water and the yield of gases was below 10% in a carbon basis. Yoshida and Matsumura[21] conducted the gasification of a lignin−cellulose mixture at 673 K with a nickel catalyst. They reported that the gasification of lignin was influenced in the presence of cellulose because the yield of gas product did not change proportionally with the ratio of cellulose.

The decomposition of alkylphenols with heterogeneous catalysts has been studied in steam and subcritical water, although studies in supercritical temperature water were limited. Assafi and Duprez[22] treated *m*-cresol with steam in the presence of a nickel or a rhodium catalyst at 733 K and found that dealkylation was the main reaction pathway. Elliott et al.[23−25] gasified cresols with various heterogeneous catalysts in subcritical water at 623 K. They reported that noble metal catalysts such as ruthenium and rhodium had high activity over 89% of the decomposition for 90 min of reaction time, and nickel also had high activity but easily lost activity due to sintering. Their results mean that the noble metal catalysts were effective for decomposition of the benzene ring of alkylphenols for the gasification in the presence of water.

In this paper, we report the gasification of various alkylphenols with noble metal catalysts over a wide range of water density in supercritical water. We also discuss the effect of water density and structure of alkylphenols for gasification.

Experimental Section

Chemicals 2-isopropylphenol, 4-isopropylphenol, 2-propylphenol, and 4-propylphenol were purchased from Tokyo Kasei and had a purity of +98%, +99%, 98%, and 99%, respectively. The 3-isopropylphenol was purchased from Aldrich Chemicals. Phenol (+99.8%), tetrahydrofuran (THF, +97%), with 2,6-di-*tert*-butyl-4-methylphenol inhibitor and naphthalene (+99%) were obtained from Wako Chemical. All chemicals were used without further purification. The catalysts tested were summarized in Table 1. All catalysts were purchased from N.E. Chemcat Corporation (Tokyo).

Experiments were conducted with 6 cm³ of stainless steel 316 tube bomb reactors with a thermocouple and a high-pressure valve. A certain amount of catalyst and 0.3 g of alkylphenol were loaded. Water from 0 (no water) to 1.8 g was also introduced into a reactor. This amount of water corresponded to 0−0.3 g/cm³ of density and the partial pressure of water at 673 K was up to 28.8 MPa.[26] After loading substrates, the reactor was purged by argon gas and then submerged into a sand

Table 1. Noble Metal Catalysts Tested in This Study

catalyst	form	mean diameter (μm)	water content (wt %)	specific surface area (m²/g)
5% Ru/γ-alumina	powder	20		80−100
2% Pt/γ-alumina	powder	20		80−100
5% Pd/γ-alumina	powder	20		80−100
5% Ru/carbon (wet)	powder	30	50.26	900−1300
5% Rh/carbon (wet)	powder	30	51.20	1000−1300
5% Pd/carbon (wet)	powder	25	57.89	900−1300

bath (Takabayashirika, model TK-3) that was maintained at 673 K. The reactor was heated to 673 K for 4 min. Reaction time reported here included this heat-up time. After a given reaction period, 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 gas chromatographs and analyzed with two gas chromatographs with a thermal conductivity detector, GC-TCD (Hitachi GC-163 and Shimadzu, model GC-7A). Hydrogen, carbon monoxide, and methane were analyzed with a molecular sieve 13X column and Ar carrier by GC-163. Carbon dioxide and C2−C4 hydrocarbons were analyzed by a Porapak Q column with He carrier by GC-7A.

After sampling the gases, liquid products were extracted with THF from the catalyst. This solution was filtered with a 10.0-μm filter and separated from the catalyst. The products dissolved in THF were defined as liquid products. The aromatics in liquid products were analyzed by gas chromatography with a flame ionization detector (Hewlett-Packard, model 5890, series II) with a HP-5 column and gas chromatography-mass spectrometry, (Japan Electron Optics Laboratory, model Automass 20) with a HP-5MS column.

The product yield of the carbon basis, gas composition, and liquid composition are defined as below, respectively.

$$\text{yield [C mol \%]} = \frac{\text{mol of carbon atom in reactant or product}}{\text{mol of carbon atom in reactant loaded}} \times 100 \tag{1}$$

$$\text{gas composition [\%]} = \frac{\text{mol of gaseous product}}{\text{sum of mol of gas product}} \times 100 \tag{2}$$

$$\text{liquid composition [\%]} = \frac{\text{mol of product}}{\text{sum of mol of liquid product}} \times 100 \tag{3}$$

Results and Discussion

Table 2 shows the product yield from 4-propylphenol (4PP) decomposition with various catalysts at 673 K, 0.3 g/cm³ of water density after 15 min. The amount of metal loaded was 3.69×10^{-5} mol in every case. This amount of metal corresponded to the molar ratio of metal to 4-propylphenol being 0.017. The carbon balance was above 83.5% and the reactant that still remained was 72.8−87.0% of the yield. In this condition, the solid material was not formed. The low yield would be due to the formation of high molecular weight products that could not be detected by GC analysis.

The yield of gaseous materials was in the order of Ru/γ-alumina > Ru/carbon, Rh/carbon > Pt/γ-alumina, Pd/

Table 2. Yield of Products for 4-Propylphenol Decomposition with Noble Metal Catalysts at 673 K and 0.3 g/cm³ of Water Density for 15 min

	product yield (C mol %)		reactant (C mol %)	carbon balance (C mol %)
catalyst[a]	gas	liquid		
Ru/γ-alumina	14.7	5.0	74.4	94.1
Ru/carbon	5.1	9.5	68.9	83.5
Rh/carbon	3.5	10.2	72.8	86.5
Pt/γ-alumina	0.9	3.1	85.1	89.1
Pd/carbon	0.4	2.0	87.0	89.4
Pd/γ-alumina	0.2	0.3	86.9	87.4

[a] The molar ratio of metal to 4-propylphenol is 0.017.

Table 3. Composition of Gas Products for 4-Propylphenol Decomposition with Noble Metal Catalysts at 673 K and 0.3 g/cm³ of Water Density for 15 min

	composition of gas products (mol %)						
catalyst[a]	CH_4	CO_2	H_2	C_2H_6	C_3H_6	C_3H_8	C_4
Ru/γ-alumina	60.7	26.2	11.7	0.9	0.0	0.3	0.2
Ru/carbon	53.8	29.7	13.7	2.8	0.0	0.0	0.0
Rh/carbon	65.8	20.4	9.2	4.1	0.0	0.5	0.0
Pt/γ-alumina	25.1	28.2	24.4	17.4	0.0	4.9	0.0
Pd/carbon	38.8	32.4	24.0	4.8	0.0	0.0	0.0
Pd/γ-alumina	33.8	12.2	50.3	3.7	0.0	0.0	0.0

[a] The molar ratio of metal to 4-propylphenol is 0.017.

carbon, and Pd/γ-alumina. For gasification, the activity of the Ru/γ-alumina catalyst was the highest among supported noble metal catalysts used and the activities of supported platinum and palladium catalysts were significantly low. Both gaseous and liquid products were below 0.1% of the yield without a catalyst in supercritical water. Elliott et al.[23] reported that the activity of the decomposition of 4-cresol in subcritical water at 623 K was in order of Ru/γ-alumina > Rh/carbon, Ru/carbon > Pt/γ-alumina, Pd/γ-alumina, and Pd/carbon. Further, they pointed out that γ-alumina is not a useful catalyst support for more than a few hours in aqueous systems because γ-alumina will not survive in long-term processing.

In supercritical water, the order of the activity of metal and that of support for Ru catalyst were almost the same as that in subcritical water. The yield of liquid was larger than that of gaseous materials for the decomposition of 4PP except for the Ru/γ-alumina catalyst. The activities for gasification over Rh/carbon, Ru/carbon, Pt/γ-alumina, Pd/γ-alumina, and Pd/carbon catalysts were lower than that of the Ru/γ-alumina catalyst and the formation of liquid was preferred to gaseous materials.

Table 3 shows the composition of gas products. The gas products detected were methane, carbon dioxide, ethane, propene, propane, and C4 compounds (butanes and butenes). For Ru/γ-alumina, Ru/carbon, and Rh/

carbon catalysts, methane that was obtained was approximately 60% whereas hydrogen was about 10%. For Pt and Pd catalysts, the composition of hydrogen was quite larger than those for Ru and Rh catalysts. The composition of hydrogen was about 50% for the Pd/γ-alumina catalyst. These results show the same trend as the previous results in subcritical water by Elliott et al.[23]

Table 4 summarizes the composition of liquid products for each catalyst. The liquid products detected were benzene, toluene, ethylbenzene, propylbenzene, phenol, methyl-ethylbenzenes, 4-cresol, 4-ethylphenol, and methyl-propylphenols. The yield of liquid product was lower than 11% and the amount of each product was very small. Further, the yield of detected liquid products was smaller than that of unknown products as shown in Table 2. It is difficult to determine the major reaction path accurately; however, the distribution of liquid products was characteristic for noble metals. For Ru and Pt catalysts, the main product was propylbenzene derived from dehydroxylation of 4PP. For Rh/carbon, Pd/carbon, and Pd/γ-alumina catalysts, the sum of composition of 4-cresol and 4-ethylphenol derived from dealkylation were above 66% whereas the composition of propylbenzene was lower than 10%. These results indicate that supported Rh and Pd catalysts were more active for the cleavage of carbon−carbon bonds in alkyl chains of alkylphenols than supported Ru and Pt catalysts.

We also evaluated the effect of the amount of catalyst and the reaction time for the Ru/γ-alumina catalyst that showed the highest activity for gasification among the catalysts in this study. Figure 1 shows that the product yield against the molar ratio of ruthenuim in the Ru/γ-alumina catalyst to alkylphenol loaded at 0.3 g/cm³ of water density and for 15 min of reaction time. The gaseous and liquid materials were not produced in the absence of the catalyst, which indicates that 4PP was stable in supercritical water at 673 K. The yields of both methane and carbon dioxide increased with increasing amount of catalyst. The yield of liquid products slightly increased with increase of the weight of catalyst because gasification is a major reaction pathway.

Figure 2 shows the product yield against reaction time at the molar ratio of ruthenium on γ-alumina to alkylphenol being 0.017, 673 K, and 0.3 g/cm³ of water density. Methane and carbon dioxide were the main products and propylbenzene was a minor one. The yield of methane and carbon dioxide increased with reaction time, while the yield of reactant, namely, 4PP, decreased with reaction time. At 15 min of reaction time as discussed in Table 1, this reaction did not attain equilibrium. At early reaction times, the yield of methane was larger than that of carbon dioxide; however,

Table 4. Composition of Liquid Products for 4-Propylphenol Decomposition with Noble Metal Catalysts at 673 K and 0.3 g/cm³ of Water Density for 15 min

	composition of liquid products (C mol %)								
catalyst[a]	benzene	toluene	ethyl benzene	propyl benzene	phenol	methyl propyl benzenes	4-cresol	4-ethylphenol	methyl propyl phenols
Ru/γ-alumina	1.3	5.9	1.9	56.7	0.0	2.3	7.5	6.9	17.5
Ru/carbon	2.1	7.3	3.5	50.4	0.0	1.9	10.0	12.9	11.9
Rh/carbon	2.3	3.8	1.4	8.3	9.4	1.4	33.0	33.4	7.0
Pt/γ-alumina	4.1	4.4	0.0	54.6	0.0	6.9	14.5	15.5	0.0
Pd/carbon	0.0	0.0	0.0	10.0	3.6	0.0	10.3	64.1	12.0
Pd/γ-alumina	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.0	0.0

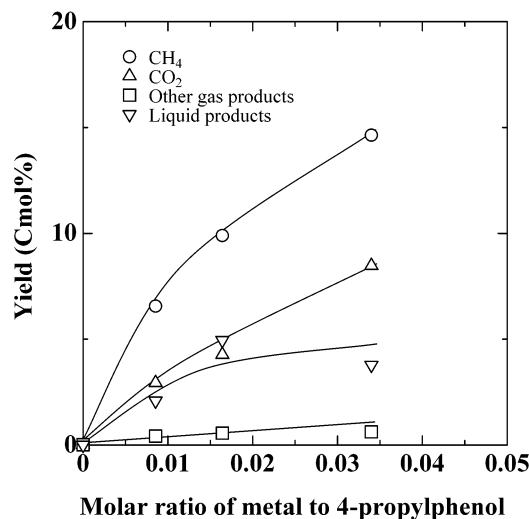[a] The molar ratio of metal to 4-propylphenol is 0.017.

Figure 1. Effect of the amount of catalyst for 4-propylphenol decomposition with Ru/γ-alumina at 673 K and 0.3 g/cm^3 of water density for 15 min.
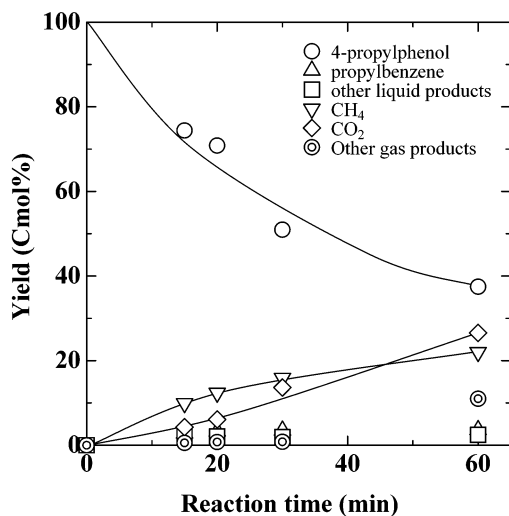

Figure 2. Product yield with reaction time for 4-propylphenol decomposition with Ru/γ-alumina at 673 K and 0.3 g/cm^3 of water density. The molar ratio of metal to 4-propylphenol is 0.017.

Figure 3. Dependence of product yield on water density for 4-propylphenol decomposition with Ru/γ-alumina at 673 K for 15 min. The molar ratio of metal to 4-propylphenol is 0.017.

Figure 4. Dependence of the composition of gas products on water density for 4-propylphenol decomposition with Ru/γ-alumina at 673 K for 15 min. The molar ratio of metal to 4-propylphenol is 0.017.

the yield of carbon dioxide was larger than that of methane with increasing reaction time.

The density of supercritical water can be greatly changed with manipulating pressure, which is a different characteristic from that in subcritical water. The effect of water density on the gasification was studied in supercritical water. Figure 3 shows the yield against water density at the molar ratio of ruthenium on γ-alumina to alkylphenol being 0.017 for 15 min. In the absence of water, methane and carbon dioxide were almost not formed. The yield of liquid products increased with increasing water density up to 9.6% below 0.1 g/cm^3 of water density and then decreased with increasing water density. The composition of liquid products was almost the same in the presence of water regardless of water density and the main product was propylbenzene of approximately 60% of the composition. The yields of methane and carbon dioxide clearly increased in proportion to water density and were almost constant above 0.2 g/cm^3 of water density. From this result, we can suggest that water promoted the gasification of liquid products such as propybenzene to methane and carbon dioxide above 0.2 g/cm^3 of water density.
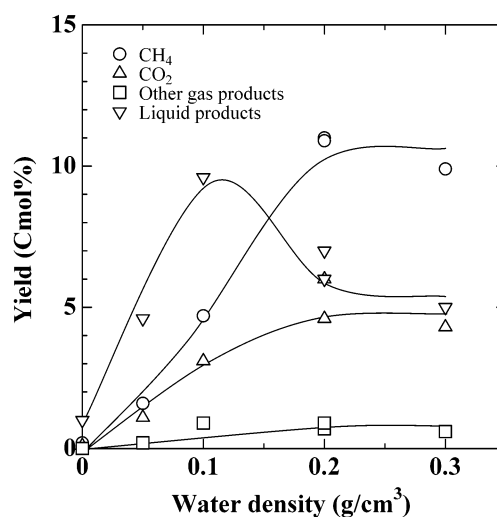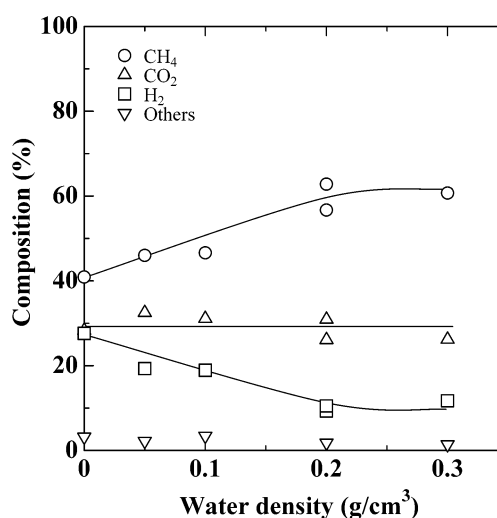
Figure 4 shows the gas composition with water density at the molar ratio of ruthenium on γ-alumina to alkylphenol being 0.017 and 0.3 g/cm^3 of water density for 15 min. The composition of carbon dioxide was almost constant, and methane increased with increasing water density, corresponding to the decrease of the yield of hydrogen.

In the dehydroxylation and gasification, hydrogen and oxygen atoms required for the reaction are supplied from the water molecule. The reactant 4PP was almost stable without water, even in the presence of catalyst, because of insufficiency of hydrogen and oxygen donor. In the low water density region (0.05−0.1 g/cm^3), the yield of liquid product was high and propylbenzene derived from dehydroxylation was the largest composition. The dehydroxylation of 4PP to propylbenzene requires two hydrogen atoms to form one water molecule and one propylbenzene one. The formation of methane and carbon dioxide proceeded well in the high water density region because the amount of water molecules was enough. The formation of methane and carbon dioxide from alkylphenol or alkylbenzene requires more
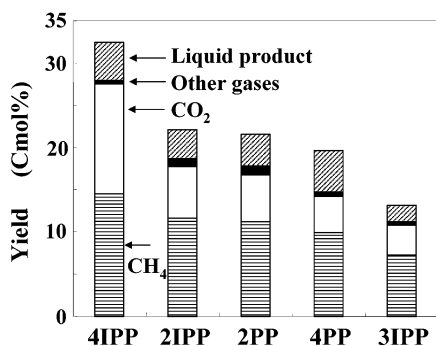
Figure 5. Product yield with Ru/γ-alumina at 673 K and 0.3 g/cm^3 of water density for 15 min (4IPP, 4-isopropylphenol; 2IPP, 2-isoproylphenol; 2PP, 2-propylphenol; 4PP, 4-propylphenol; 3IPP, 3-isopropylphenol). The molar ratio of metal to 4-propylphenol is 0.017.

hydrogen and oxygen atoms than those in dehydroxylation. Claeys and Steen[27] conducted Fischer–Tropsch synthesis with a ruthenium catalyst in steam under partial pressure of water up to 0.5 MPa. They reported that the reaction promoted with increasing partial pressure of water because water supplied surface hydrogen atoms. In the case of steam dealkylation with ruthenium, water molecules could be dissociated and adsorbed on metal to form hydroxy groups.[22] The partial pressure of water in this study was up to 28.8 MPa. Water probably supplied the active hydrogen atoms on the catalyst.

We evaluated the reactivity of various alkylphenols in the presence of Ru/γ-alumina in supercritical water. The molar ratio of ruthenium on γ-alumina to alkylphenol was 0.017. The alkylphenols treated were 4-isopropylphenol (4IPP), 2-isopropylphenol (2IPP), 2-propylphenol (2PP), 4-propylphenol (4PP), and 3-isopropylphenol (3IPP). Figure 5 shows the yield of gas and liquid in the presence of the Ru/γ-alumina catalyst at 673 K and 0.3 g/cm^3 of water density for 15 min. The carbon balance of these experiments was above 88.2%. The sum of the yield of methane and carbon dioxide was above 10%. The yield of liquid product was below 5% in every case. The gasification using the Ru/γ-alumina catalyst proceeded in all the alkylphenols. The yield of gas was in the order of 4IPP > 2IPP, 2PP > 4PP > 3IPP. 3IPP, whose alkyl side chain is attached to the meta position of the hydroxy group, showed the lowest reactivity for gasification. Nesterova et al.[28] measured the equilibrium of o-, m-, and p-isopropylphenols at 523 K and reported that 3IPP was more stable than 2IPP and 4IPP. m-Alkylphenols were also more stable than o- and p-alkylphenols in supercritical water.

Figure 6 shows the composition of gas products in the presence of the Ru/γ-alumina catalyst at 673 K and 0.3 g/cm^3 of water density for 15 min. The methane, carbon dioxide, and hydrogen were the main gas components and about 50–60%, 30–40%, and 10% of composition, respectively. The composition of gas was almost the same regardless of the kinds of alkylphenols.

Table 5 shows the composition of liquid products in the presence of Ru/γ-alumina at 673 K and 0.3 g/cm^3 of water density for 15 min. The formation of methylpropylphenols might be due to the reaction of the methyl group and alkylphenols remaining; however, the reaction mechanism is not clear. For the case of 4IPP, 4PP, and 3IPP, propylbenzene or isopropylbenzene was the main product and approximately 60% of composition.
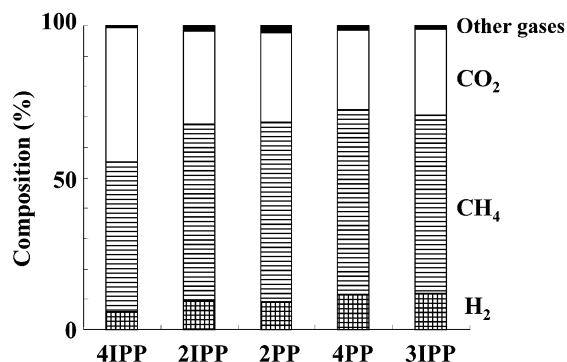

Figure 6. Composition of gas products with Ru/γ-alumina at 673 K and 0.3 g/cm^3 of water density for 15 min (4IPP, 4-isopropylphenol; 2IPP, 2-isopropylphenol; 2PP, 2-propylphenol; 4PP, 4-propylphenol; 3IPP, 3-isopropylphenol). The molar ratio of metal to alkylphenol is 0.017.

Table 5. Composition of Liquid Products with Ru/γ-Alumina at 673 K and 0.3 g/cm^3 of Water Density for 15 min (4IPP, 4-Isopropylphenol, 2IPP, 2-Isoproylphenol; 2PP, 2-Propylphenol; 4PP, 4-Propylphenol; 3IPP, 3-Isopropylphenol)^a

composition of liquid products (C mol %)	reactant				
	4IPP	2IPP	2PP	4PP	3IPP
benzene	1.2	3.9	4.0	1.3	1.8
toluene	6.0	8.5	7.5	5.9	6.2
ethylbenzene	2.3	1.8	2.0	1.9	1.3
isopropylbenzene	60.6	15.2	11.8	56.7	64.3
propylbenzene	0.0	0.0	11.8	56.7	0.0
methylpropylbenzenes	0.0	0.0	2.0	2.3	0.0
phenol	0.0	0.0	1.6	0.0	0.0
2-cresol	0.0	16.4	38.0	0.0	0.0
4-cresol	0.0	0.0	0.0	7.5	0.0
2-ethylphenol	0.0	20.1	8.6	0.0	0.0
3-ethylphenol	0.0	0.0	0.0	0.0	7.6
4-ethylphenol	13.5	0.0	0.0	6.9	0.0
2-isopropylphenol	0.0		7.8	0.0	0.0
2-propylphenol	0.0	31.2		0.0	0.0
methylpropylphenols	16.4	2.9	16.7	17.5	18.8

^{a} The molar ratio of metal to alkylphenol is 0.017.

The main liquid products were alkylbenzenes derived from dehydroxylation and the alkylphenols were not formed so much. On the other hand, for gasification of 2IPP and 2PP, the sum of the composition of 2-cresol and 2-ethylphenol was above 36.5% while the composition of propylbenzenes was below 15.2%. The alkylphenols were the main products instead of alkylbenzenes. In the decomposition of o-alkylphenols, the dehydroxylation was suppressed because the alkyl side chain would prevent contact of hydroxy group with the metal particle surface. The steric interaction between catalyst and reactant should be an important factor for determining the product distribution.

Conclusion

Gasification of alkylphenols was conducted in supercritical water in the presence of various supported metal catalysts at 673 K. The main gas products were methane, carbon dioxide, and hydrogen. The analysis of liquid products showed that dehydroxylation occurred easier than dealkylation for supported ruthenium and rhodium catalysts. The sum of the yield of gases and the ratio of methane from 4-propylphenol with a Ru/γ-alumina catalyst increased with increasing water density, while the yield of liquid products showed a maximum at 0.1 g/cm^3. The gasification of various alkyl-

phenols was investigated over a Ru/γ-alumina catalyst at 673 K and 0.3 g/cm^3 of water density for 15 min. The yield of gas was above 10% and in the order of 4-isopropylphenol > 2-isopropylphenol, 2-propylphenol > 4-propylphenol > 3-isopropylphenol. The composition of gas was 50−60% of methane, 30−40% of carbon dioxide, and 10% of hydrogen. The reactivities of o- and p-alkylphenols were relatively higher than those of m-alkylphenol.

Literature Cited

(1) Dorrstijn, E.; Laarhoven, L. J. J.; Arends, I. W. C. E.; Mulder, P. The occurrence and reactivity of phenoxyl linkages in lignin and low rank coal. *J. Anal. Appl. Pyrolysis* **2000**, *54*, 153.

(2) Dong, J.-Z.; Ouchi, K. Geochemical origin of long chain alkyl aromatics in coal. *Fuel* **1989**, *68*, 710.

(3) Kroschwitz, J. I.; Mary, H.-G. *Kirk−Othmer, Encyclopedia of Chemical Technology*, Fourth Edition; A Wiley-Interscience Publication: New York, 1991.

(4) Savage, P. E. Organic Chemical Reactions in Supercritical Water. *Chem. Rev.* **1999**, *99*, 603.

(5) Akiya, N.; Savage, P. E. Roles of Water for Chemical Reactions in High-Temperature Water. *Chem. Rev.* **2002**, *102*, 2725.

(6) Townsend, S. H.; Abraham, M. A.; Huppert, G. L.; Klein, M. T.; Paspek, S. C. Solvent Effects during Reactions in Supercritical Water. *Ind. Eng. Chem. Res.* **1988**, *27*, 143.

(7) Lawson, J. R.; Klein, M. T. Influence of Water on Guaiacol Pyrolysis. *Ind. Eng. Chem. Fundam.* **1985**, *24*, 203.

(8) Sato, T.; Sekiguchi, G.; Adschiri, T.; Arai, K. Non-catalytic and selective alkylation of phenol with propan-2-ol in supercritical water. *Chem. Commun.* **2001**, *17*, 1566.

(9) Sato, T.; Sekiguchi, G.; Adschiri, T.; Arai, K. Ortho Selective Alkylation of Phenol with 2-Propanol without Catalyst in Supercritical Water. *Ind. Eng. Chem. Res.* **2002**, *41*, 3064.

(10) Katritzky, A. R.; Murugan, R.; Siskin, M. Aqueous High-Temperature Chemistry of Carbo- and Heterocycles. 8. Aquathermolysis of Para-Substituted Phenols in the Presence and Absence of Sodium Bisulfite. *Energy Fuels* **1990**, *4*, 531.

(11) Katritzky, A. R.; Murugan, R.; Siskin, M. Aqueous High-Temperature Chemistry of Carbo- and Heterocycles. 9. Aquathermolysis of Ortho-Substituted, Meta-Substituted, and Multisubstituted Phenols in the Presence and Absence of Sodium Bisulfite. *Energy Fuels* **1990**, *4*, 538.

(12) Ederer, H. J.; Kruse, A.; Mas, C.; Ebert, K. H. Modelling of the pyrolysis of tert-butylbenzene in supercritical water. *J. Supercrit. Fluids* **1999**, *15*, 191.

(13) Martino, C. J.; Savage, P. E. Thermal decomposition of substituted phenols in supercritical water. *Ind. Eng. Chem. Res.* **1997**, *36*, 1385.

(14) Adschiri, T.; Shibata, R.; Arai, K. Phenol recovery by BPA tar hydrolysis in supercritical water. *Sekiyu Gakkaishi* **1997**, *4*, 291.

(15) Tagaya, T.; Suzuki, Y.; Kadokawa, J.; Karatsu, M.; Chiba, K. Decomposition of model compounds of phenol resin waste with supercritical water. *Chem. Lett.* **1997**, 47.

(16) Sato, T.; Sekiguchi, G.; Saisu, M.; Watanabe, M.; Adschiri, T.; Arai, K. Dealkylation and Rearrangement Kinetics of 2-Isopropylphenol in Supercritical Water. *Ind. Eng. Chem. Res.* **2002**, *41*, 3124.

(17) Savage, P. E. Heterogeneous catalysis in supercritical water. *Catal. Today* **2000**, *62*, 167.

(18) Ding, Z. Y.; Frisch, M. A.; Li, L.; Gloyna, E. F. Catalytic oxidation in supercritical water. *Ind. Eng. Chem. Res.* **1996**, *35*, 3257.

(19) Antal, M. J., Jr.; Allen, S. G.; Schulman, D.; Xu, X.; Divilio, R. J. Biomass Gasification in Supercritical Water. *Ind. Eng. Chem. Res.* **2000**, *39*, 4040.

(20) Watanabe, M.; Inomata, H.; Osada, M.; Sato, T.; Adschiri, T.; Arai, K. Catalytic effects of NaOH and ZrO$_2$ for partial oxidative gasification of n-hexadecane and lignin in supercritical water. *Fuel* **2003**, *82* (5), 545.

(21) Yoshida, T.; Matsumura, Y. Gasification of cellulose, xylan, and lignin mixtures in supercritical water. *Ind. Eng. Chem. Res.* **2001**, *40*, 5469.

(22) Assafi, M.; Duprez, D. Steam-dealkylation and hydrodealkylation of meta-cresol on potassium-promoted rhodium and nickel catalysts. *Appl. Catal., A* **1992**, *80*, 23.

(23) Elliott, D. C.; Sealock, L. W. J., Jr.; Backer, E. G. Chemical Processing in High-Pressure Aqueous Environments. 2. Development of Catalyst for Gasification. *Ind. Eng. Chem. Res.* **1993**, *32*, 1542.

(24) Elliott, D. C.; Sealock, L. J., Jr.; Backer, E. G. Chemical Processing in High-Pressure Aqueous Environments. 3. Batch Reactor Process Development Experiments for Organics Destruction. *Ind. Eng. Chem. Res.* **1994**, *33*, 558.

(25) Elliott, D. C.; Phelps, M. R.; Sealock, L. J., Jr.; Backer, E. G. Chemical Processing in High-Pressure Aqueous Environments. 4. Continuous-Flow Reactor Process Development Experiments for Organics Destruction. *Ind. Eng. Chem. Res.* **1994**, *33*, 566.

(26) Lemmon, E. W.; McLinden, M. O.; Friend, D. G. Thermophysical properties of fluid systems in NIST Chemistry WebBook, NIST Standard reference database number 69; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, July 2001 (http://webbook.nist.gov).

(27) Claeys, M.; Steen, E. On the effect of water during Fischer−Tropsch synthesis with a ruthenium catalyst. *Catal. Today* **2002**, *71*, 419.

(28) Nesterova, T. N.; Pilyshchikov, V. A.; Rozhnov, A. M. Chemical equilibrium in the system isopropylphnols-phenol. *Zh. Prikl. Khim.* **1983**, *6*, 1338.