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Effect of Water Density on the Gasification of Lignin with Magnesium Oxide Supported Nickel Catalysts in Supercritical Water

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Gasification of lignin biomass model compounds was examined in the presence of magnesium oxide supported nickel catalysts (Ni/MgO) in sub- and supercritical water from 523 to 673 K. The main gas products were methane, carbon dioxide, and hydrogen. The amount of gases produced increased with an increase in nickel loading on magnesium oxide. The highest total gas yield in a carbon basis was 78% with 20 wt % Ni/MgO catalyst at 673 K and 0.3 g/cm^3 water density. In this system, the metal and support of Ni/MgO probably play different roles in gasification that MgO decomposed lignin to reactive intermediates and nickel promoted reaction between intermediates and water to form gases. The yield of methane and carbon dioxide increased with increasing water density but then decreased and leveled out to constant values, which indicates that water density affected the reaction kinetics.

Introduction

Gasification of wood biomass is expected to produce fuel gas for sustainable society,[1,2] because wood biomass closes the carbon cycle through solar energy and photosynthesis. In general, wood biomass consists of about 50 wt % cellulose, 20 wt % hemicellulose, and 30 wt % lignin. Lignin is a biopolymer in which (*p*-hydroxymethoxyphenyl)propane units such as *trans-p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol are connected with ether and carbon−carbon linkages.[3] While the lignin is a potentially large energy source, it is difficult to convert the lignin to syngas,[4] which may be due to the existence of stable (*p*-hydroxymethoxyphenyl)propane units. Therefore, gasification of lignin is probably a key technology for achieving sustainable fuel sources. For biomass gasification, the lower temperature region (523−673 K) is preferred to high temperature routes due to the increase cold gas efficiency. Steam reforming of biomass in steam gasification process is usually endothermic. For this type of process, waste heat from high-temperature processes can be used and the energy can be recovered as a binding energy for gases including hydrogen and methane.[5]

A gasification process based on nickel catalyst should be economically advantageous rather than noble metal catalysts. In a biomass gasification process, nickel catalysts can be applied to the catalytic hot gas cleaning to suppress tar formation in the secondary reactor attached to the downstream of the main gasification reactor. Caballero et al.[6] tested commercial nickel-based catalysts for hot gas cleanup in biomass gasification in a pilot-scale level plant at around 1113 K and reported that their system achieved about 10 mg/m^3 tar content without catalyst deactivation for 65 h. Corella et al.[7,8] studied nickel-based monoliths for catalytic hot gas cleaning on the pilot-plant scale from 1093 to 1229 K.[9,10] Rapagná et al.[11] reported that trimetallic and LaNiFe catalysts were effective for conversion of tar in catalytic steam gasification at 1073 K.

Furusawa and Tsutsumi[12] conducted the gasification of naphthalene as a tar model compound derived from biomass gasification with magnesium oxide supported nickel (Ni/MgO) catalysts by steam re-forming from 873 to 1173 K. Interestingly, they reported that carbon conversion to gas was several percent and that water molecules might have become activated on the catalyst during steam re-forming.

Supercritical water is dense steam that has many favorable properties for gasification.[13−15] It is miscible with inorganic gases such as hydrogen and oxygen and low molecular weight hydrocarbons such as methane and ethane. Further, it is homogeneous with organic compounds such as aromatics by a proper choice of temperature and pressure. Physical properties of supercritical water such as the dielectric constant and ion products can be varied significantly by manipulating temperature and pressure or density. Various organic reactions proceed without catalyst in supercritical water.[13−15] Further, being able to vary solvent properties can enhance the stability of transition-state compounds and products, which allows the formation of substances that are kinetically limited.

The noncatalytic decomposition of biomass has been performed in sub- and supercritical water. Kruse et al.[16,17] examined the conversion of biomass in supercritical water. They identified the key compounds in biomass conversion as being phenols, furfurals, acids, and aldehydes and analyzed the reaction kinetics. Karagöz et al.[18] converted various forms of biomass in water at 553 K and reported that the reactivity of lignin was lower than that of cellulose, sawdust, and rice risk. Sasaki et al.[19,20] studied the decomposition of cellulose in sub- and supercritical water and summarized the detailed kinetics. They reported that the decomposition of cellulose gave around 70% yield of hydrolysis products without catalyst. Saisu et al.[21] conducted the conversion of lignin in supercritical water without catalyst at 673 K and reported that high molecular weight fragments were produced. In biomass decomposition, the decomposition of lignin to light molecular weight products such as gases is probably more difficult than those of other components in supercritical water.

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Heterogeneous catalytic reactions can also be performed in supercritical fluids including water.[22,23] High solvent solubility and high diffusivities of supercritical water can eliminate mass-transfer limitations. Supercritical water can reduce coke formation on catalyst since it also acts as an in-situ extraction solvent of coke precursors. In heterogeneous reactions, the change of solvent properties also influences the reaction rate because water affects the interaction between reactant and catalyst.

Heterogeneous catalysis of biomass in supercritical water has almost been studied exclusively for the purpose of gasification.[24] Antal et al.[25] reported that corn starch was almost completely gasified at around 923 K in supercritical water with carbon catalyst. Watanabe et al.[26] conducted gasification of lignin with a zinc oxide catalyst at 673 K in supercritical water and reported that gas yield was below 10% on a carbon basis. Ruthenium catalysts are effective for gasification in supercritical water in the lower temperature region around 673 K.[5,27] Park and Tomiyasu[27] reported that cellulose as well as many other polymers such as polyethylene could be gasified with ruthenium oxide in supercritical water at 723 K for 120 min. Osada et al.[5] conducted gasification studies on cellulose, lignin, and model compounds in supercritical water at 673 K. They obtained almost 80% gas yield for lignin with 180 min reaction time using a titanium oxide supported ruthenium catalyst.

The gasification of biomass with nickel catalyst has been performed in sub- and supercritical water. Elliott and Sealock[28,29] initially examined the gasification of lignin with commercial nickel catalysts in sub- and supercritical water at 653−753 K. The yield of gases was up to about 20% on a carbon basis for 1 h. Minowa et al.[30] conducted gasification experiments of cellulose with commercial nickel catalysts in subcritical water and reported nickel catalyzed gas formation from aqueous products that followed from the decomposition of cellulose. They also evaluated the effect of support for nickel catalyst on cellulose gasification and found that the activity of magnesia support was better than those of other catalyst supports such as silica and alumina.[31] Yoshida and Matsumura[32,33] examined the gasification of lignin mixtures in supercritical water at 673 K with commercial nickel catalyst to elucidate the interaction of biomass components. They reported that the gas amount for lignin conversion had a gas yield as high as 22% on a carbon basis. In considering application of catalysts, the activity of nickel catalyst has been relatively low for lignin gasification. However, nickel catalysts could be alternative catalysts for biomass gasification in supercritical water if they could be suitably modified.

In this work, we applied Ni/MgO catalyst to the gasification of lignin over a wide water density region in sub- and supercritical water at 523−673 K. At first, we evaluate catalytic activities, especially the amount of nickel on the support, and analyze the dependence of water density on the gasification. Next, we test the performance of catalyst with respect to temperature and stability. From these results, we discuss the role of Ni/MgO catalyst in supercritical water.

Experimental Section

Organosolve lignin that is one of the processed lignins purchased from Aldrich was used as the lignin, and its molecular formula was $C_{42.87}H_{44.15}O_{12.98}$, as determined by an ultimate CHN analysis. The lignin powder was completely soluble in tetrahydrofuran (THF). Water was obtained from a water distillation apparatus (Yamato Co., model WG-222). The catalysts used in this study were prepared by impregnating MgO (JRC-MGO-4 500A, 28−38 $m^2 g^{-1}$) with aqueous solutions of

$Ni(NO_3)_2 \cdot 6H_2O$ (Kanto Co.), followed by drying at 383 K overnight. The MgO treated was then calcined in air for 8 h at 873 K. The synthesized catalysts were formed into pellets and were crushed. The powder obtained from the crushing was segregated into particles under 180 μm in diameter and between 355 and 500 μm in diameter and used in the experiments. The calcined catalysts are denoted as a certain wt % Ni(O)/MgO, and reduced catalysts at 1173 K with hydrogen are denoted as a corresponding wt % Ni/MgO. The exposed metal surface area of the reduced catalyst was determined by CO pulse adsorption at room temperature, assuming a 1/1 stoichiometry.

Experiments were conducted in stainless steel tube bomb reactors whose internal volume was 6 cm³. The reactors were made of stainless steel (length = 105 mm, i.d. = 8.5 mm, o.d. = 12.7 mm) and Swagelok unions (model SS-810-6-1ZV). One end of the reactor was fitted with a high-pressure valve for analysis of gas products and a thermocouple was inserted into the other end. In the initial experiments, the loaded amount of sample was 0.1 g of lignin, 0−3 g of water, and 0.1 g of catalyst. After the samples were loaded, air in the reactor was purged with argon several times and the reactor was pressurized to about 1.5 MPa to make the recovering of gases easier. The reactor was put into a forced convection oven (MTS-CH202030, Tokyo Motoyama Syokai Co. Ltd.) that was controlled at the appropriate reaction temperature. It took about 40 min to reach reaction temperature for temperatures between 523 and 673 K. The reaction time included this heat-up time. After a given reaction time, the reactor was taken out of the oven and rapidly quenched in a water bath. It took about 1 min to cool the reactor to room temperature. The gases in the reactor were collected into a syringe via sampling valve and its volume was measured.

The gas products were analyzed by GC-TCD (Shimadzu, GC-2014) with a Shincarbon-ST (Shimadzu) column. After the gas was recovered, the products in the reactor were recovered with distilled water and separated into water-soluble and water-insoluble fractions. The water-insoluble fractions were extracted with THF and separated into THF solubles and THF insolubles and catalyst. The THF insolubles were calculated by the subtraction of the weight of catalyst from that of the recovered material that contained THF insolubles and catalyst. Qualitative and quantitative analyses were made of the liquid fraction by GC-MS (GC-17A-QP5050A, Shimadzu).

The product yield on a carbon basis, the gas composition, and liquid compositions were defined as below:

product yield (C or H %) =
$$\frac{\text{moles of carbon or hydrogen atom in product}}{\text{moles of carbon or hydrogen atom in lignin loaded}} \times 100$$

(1)

$$\text{gas composition (\%)} = \frac{\text{moles of gas product}}{\text{sum of moles of gas product}} \times 100$$

(2)

$$\text{THF insolubles (wt \%)} = \frac{\text{weight of THF insolubles}}{\text{weight of lignin loaded}} \times 100$$

(3)

Results and Discussion

Effect of Catalyst. Table 1 shows the carbon yield and the yield of THF insolubles for gasification of lignin with Ni/MgO catalysts in supercritical water at 673 K and 0.3 g/cm³ water density for 120 min. The water-soluble products consisted of phenol, cresols, ethylphenols, and propylphenols, the individual

Table 1. Carbon Yield and the Yield of THF Insolubles for Lignin Gasified with Ni/MgO in Supercritical Water[a,b]

| | dispersion (%) | Ni surface area (m²/g) | carbon yield (C %) | | | | | | THF insolubles yield (wt %) |
			CO	CH₄	CO₂	C₂H₄	C₂H₆	Total gas	
no catalyst			0.1	3.2	4.9	<0.1	0.1	8.3	10.0
MgO			0	0.3	4.2	0	0	4.7	99.0
5 wt % Ni/MgO	2.0	1.9	0	2.8	5.6	0	0	8.4	84.5
10 wt % Ni/MgO	1.3	2.5	0	9.6	12.1	0	0.1	21.7	35.0
15 wt % Ni/MgO	1.8	5.2	0	11.8	13.2	0	0.1	25.1	26.9
20 wt % Ni/MgO[c]	2.0	7.5	0	17.0	18.4	0	0.1	35.5	33.7

[a] Reaction temperature, 673 K; water density, 0.3 g/cm³; reaction time, 120 min; lignin 0.1 g; catalyst, 0.1 g. [b] Water-soluble products less than 2% in most cases. [c] Average of three data.

yields of these compounds were below 2%, and the total yield was below 5%; in most cases it was below 2%. No compound was detected by GC analysis of THF solubles. Water solubles and THF solubles probably involved larger molecular weight compounds that cannot be detected by GC. The lack of mass balance was probably due to these components. Because of the low yield of aqueous and THF soluble products by GC analysis, the gas products and THF insolubles were mainly evaluated in this study.

Here, the carbon balance of this study was evaluated. The yield of THF insolubles in weight basis represents the carbon yield of THF insolubles if the ratio of carbon for THF insolubles is the same as that for the original lignin. We calculated the sum of the carbon yield of gases, the yield of THF insolubles, and the carbon yield of liquid products (not shown). This sum value is the lowest mass balance considerably because the actual ratio of carbon for THF insolubles is probably higher than that for the original lignin. This sum value was 18.7% in the absence of catalyst. In the presence of catalyst, the sum values were 49.4% at a minimum and above 70% in most cases. In the presence of catalyst, 70% of carbon existed as gases and THF insolubles in most cases. In the absence of catalyst, about 80% of carbon possibly existed as water solubles and THF solubles.

In Table 1, the sum of the carbon yield of gases was 8.3% in the absence of catalyst, which means that the lignin could be gasified in supercritical water without catalyst. Methane and carbon dioxide were formed in the largest quantities. On the other hand, the THF insolubles formed were most likely due to the formation of higher molecular weight fragments because raw lignin completely dissolves in THF. Saisu et al.[21] reported that the polymerization of lignin occurred without catalyst in supercritical water. The 10% yield of THF insolubles is strong evidence that the polymerization occurred in parallel with gasification.

The conversion of lignin to both gases and THF insolubles was promoted with Ni/MgO catalyst. The dispersion of Ni on support and the surface area of nickel for fresh catalysts are shown in Table 1. The surface area of nickel on support increased with an increasing amount of nickel, which shows that the amount of nickel reflects the amount of nickel metal on the surface of the catalyst. In the experimental results, the yields of gases were strongly dependent on the amount of Ni metal. In the presence of MgO only, the total gas yield was below 5%, whereas THF insolubles were formed at 99% yield that was significantly larger than those obtained without catalyst. The MgO catalyzed reactions led to the formation of THF insoluble. Similar results were obtained in the presence of 5 wt % Ni/MgO catalyst with the yield of gas attained being 8.4% and the yield of THF insolubles being over 80%. The yield of gases increased with an increase in the amount of metal supported on the catalyst. The total gas yields were 21.7, 25.1, and 35.5% over 10, 15, and 20 wt % Ni/MgO catalyst, respectively.

Table 2. Hydrogen Yield for Lignin Gasified with Ni/MgO in Supercritical Water[a]

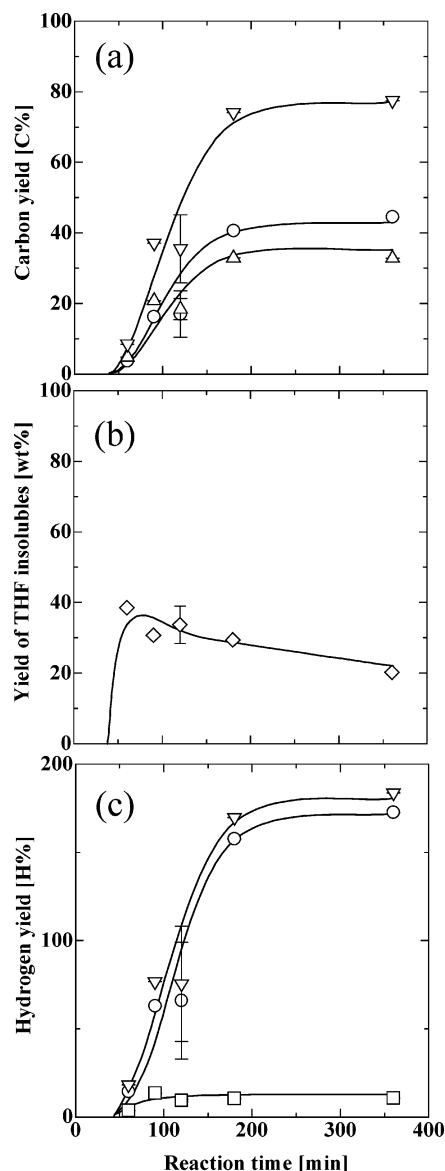| | hydrogen yield (H %) | | | | |
	H₂	CH₄	C₂H₄	C₂H₆	total gas
no catalyst	1.5	12.3	0.1	0.2	14.1
MgO	0.4	1.3	0.1	0.1	1.9
5 wt % Ni/MgO	1.9	10.9	0	0.1	12.9
10 wt % Ni/MgO	11.7	37.2	0	0.2	49.2
15 wt % Ni/MgO	11.0	45.6	0	0.2	56.8
20 wt % Ni/MgO[b]	9.3	65.9	0	0.3	75.5

[a] Reaction temperature, 673 K; water density, 0.3 g/cm³; reaction time, 120 min; lignin 0.1 g; catalyst, 0.1 g. [b] Average of three data.

The produced gases that contained carbon atoms were mainly methane and carbon dioxide. Carbon monoxide was not present, probably because nickel catalyst promotes the water gas shift reaction to form carbon dioxide and hydrogen from carbon monoxide and water. Further, the formation of THF insolubles was suppressed under 35% yield in the presence of 10−20 wt % of Ni/MgO catalyst. The increase in the amount of nickel metal suppressed the formation of heavier components such as char.

Table 2 shows the yields of hydrogen obtained by gasification of lignin. The total gas yield was below 14% for the case of MgO, 5 wt % Ni/MgO, and no catalyst and increased with increasing amounts of nickel on the catalyst. The gases formed containing hydrogen atom were mainly hydrogen and methane. For the case of more than 10 wt % nickel on the catalyst, the total gas yield was over 49%. The hydrogen yield was relatively insensitive to amounts of nickel on the catalyst for amounts of nickel greater than 10 wt % or so. Nickel catalyst promotes methanation from hydrogen and carbon dioxide to methane and water in subcritical water.[30,31] In supercritical water, nickel also probably promoted methanation to consume hydrogen, a part of which derived from a water gas shift reaction. Methane was the main product that contained atomic hydrogen, and its yield was larger than that of hydrogen, which was the same trend as in the case of lignin gasification with ruthenium catalyst in supercritical water at 673 K.[5]

Effect of Water Density. Water density is one of the important factors for controlling the reaction kinetics of lignin-like compounds in supercritical water for both noncatalytic[35,36] and catalytic reactions.[37] We performed the gasification of lignin with and without water at 673 K, because the water density greatly changes with pressure near the critical temperature. Parts a and b of Figure 1 show the carbon yield and the yield of THF insolubles versus reaction time at 673 K and water density of 0.3 g/cm³ with 20 wt % Ni/MgO catalyst, respectively. The yield of ethane is not shown because it was below 1%. In biomass conversion in supercritical water, the heating rate by a molten salt bath is approximately 370 K/min,[33,34] that by a sand bath is about 123 K/min,[5,26] and that by a autoclave type large reactor is 1 or 3 K/min.[17] The heating rate of this study was approximately 13 K/min before 30 min of reaction time, which
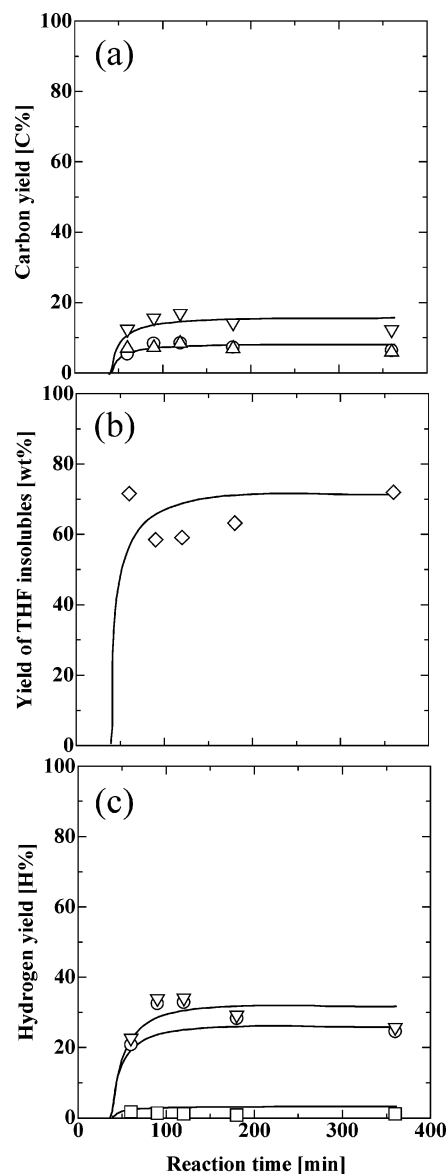
Figure 1. Product yield with reaction time with 20 wt % Ni/MgO at 673 K and 0.3 g/cm^3 water density: (a) carbon yield ($\bigcirc$, CH$_4$; $\triangle$, CO$_2$; $\triangledown$, total gas); (b) yield of THF insolubles; (c) hydrogen yield ($\bigcirc$, CH$_4$; $\square$, H$_2$; $\triangledown$, total gas).

Figure 2. Product yield with reaction time with 20 wt % Ni/MgO at 673 K in the absence of water: (a) carbon yield ($\bigcirc$, CH$_4$; $\triangle$, CO$_2$, $\triangledown$, total gas); (b) yield of THF insolubles; (c) hydrogen yield ($\bigcirc$, CH$_4$; $\square$, H$_2$; $\triangledown$, total gas).

corresponds to the heating rate between by a sand bath and by an autoclave type reactor. Judging from these facts and the results in this study, we consider that the trends of gasification obtained with the 40 min heat-up time can be discussed.

The yield of methane and carbon dioxide increased with reaction time until 180 min and then reached a plateau at around 45 and 35%, respectively. The trends of gas yields for methane and carbon dioxide were similar, which indicates that lignin most likely reacted with water (H$_2$O) to form methane and carbon dioxide because the oxygen content in raw lignin was less than 13 mol %. There are two possible pathways to form methane: the one is direct reaction lignin with water and the other is through methanation; however, it is difficult to evaluate which reaction was dominant. The total gas yield attained was 78% after 180 min reaction time. Most of the lignin could be gasified in several hours with 20 wt % Ni/MgO catalyst in supercritical water. The THF insolubles rapidly increased up to 39% in the early stage of the reaction and then slightly decreased. The decomposition of THF insolubles proceeded slowly in the presence of water and catalyst.
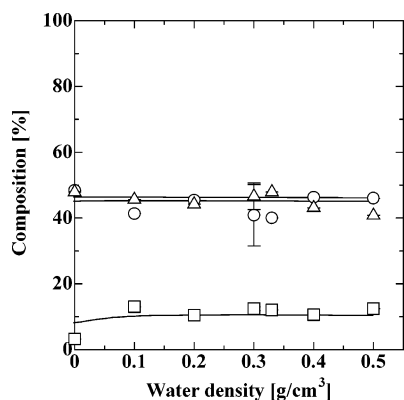
Figure 1c shows the hydrogen yield at conditions corresponding to those of Figure 1a. The yield of hydrogen was almost constant, while that of methane increased with reaction time. The sum of the hydrogen yield was over 100% after 180 min, which means that the hydrogen atom was supplied from water for the gasification of lignin.[5,27] The trends of methane, carbon dioxide, and hydrogen with reaction time shown in Figure 1a,c were almost the same as those obtained with Ru/TiO$_2$ catalyst at 673 K and 0.33 g/cm^3 water density.[5] The final values of these yields were probably governed by the equilibrium of this system.[5]

Parts a and b of Figure 2 show the carbon yield and the yield of THF insolubles versus reaction time at 673 K in the absence of water with 20 wt % Ni/MgO catalyst, respectively. The yield of ethane is not shown because it was below 1%. The yields of methane and carbon dioxide were below 9% and did not seem to vary with reaction time. The THF insolubles were generally greater than 60%, which is significantly higher than that in the presence of water. The results shown in Figure 1 and Figure 2a,b clearly indicate that water suppressed the formation of THF
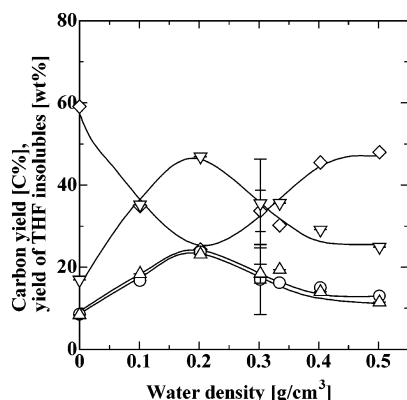
Figure 3. Carbon yield and the yield of THF insolubles with water density for gasification of lignin with 20 wt % Ni/MgO at 673 K for 120 min of reaction time (○, CH₄; △, CO₂; ▽, total gas; ◇, THF insolubles).

Figure 4. Gas composition with water density for gasification of lignin with 20 wt % Ni/MgO at 673 K for 120 min of reaction time (○, CH₄; △, CO₂; □, H₂).

insolubles, that is, heavier components such as char. Figure 2c shows the hydrogen yield at conditions corresponding to those Figure 2a. The hydrogen yield was below 2%, and the methane yield was as high as 33%. These yields did not vary over the longer reaction times (40−360 min) studied. The decomposition of lignin probably proceeded rapidly during initial heating and then slowed. We analyzed the effect of water density on this reaction in detail.

Figures 3 and 4 indicate the effect of water on product distribution in detail at constant temperature. Figure 3 shows the carbon yield and the yield of THF insolubles against water density at 673 K for 120 min with 20 wt % Ni/MgO catalyst. The yield of ethane was below 1% and is not shown. The yield of methane and carbon dioxide increased to about 25% with increasing water density under 0.2 g/cm³ but then decreased and leveled out to constant values at water densities greater than 0.4 g/cm³ or so. The total gas yield had the same trend as the methane and carbon dioxide yields. The maximal total gas yield was 47% at 0.2 g/cm³ water density. On the other hand, the trend of THF insolubles was contrary to the trend observed for the total gas yield.

Figure 4 shows the gas composition against water density at 673 K for 120 min with 20 wt % Ni/MgO catalyst. The gas composition did not seem to vary with water density. The hydrogen, methane, and carbon dioxide yields were roughly 12, 45, and 43%, respectively.

The water density affected the yield of gases and THF insolubles. The decomposition mechanism of lignin in supercritical water without catalyst has been reported. At first, the decomposition of lignin by hydrolysis and dealkylation yields

low molecular weight fragments that have reactive functional groups and phenolic compounds. Then, cross-linking reaction between these fragments and residual lignin gives higher molecular weight fragments.[21] In catalytic gasification, low molecular weight fragments that yielded gases were probably stable as gases; however, the fragments that had not been gasified rapidly probably participated in a cross-linking reaction to give high molecular weight fragments. Here, we discuss the effect of water based on this kinetics.

The increase in water density should increase the amount of reactants, that is, hydrogen donors for gasification, which should enhance the gasification of low molecular weight fragments. For example, an increase in water density accelerated the gasification of alkylphenols with Ru/Al₂O₃ catalyst from 0 to 0.3 g/cm³ water density at 673 K.[37] As a result, THF insolubles should decrease. On the other hand, reaction pressure increased corresponding to the water density. For example, the increase in water density from 0.1 to 0.5 g/cm³ corresponds the increase in pressure from 20.0 to 37.3 MPa.[38] In general, a reaction that increases the number of molecules is inhibited in the high-pressure region according to Le Chatelier's principle. The experimental data obtained here were not completely kinetic and should imply the effect of equilibrium. Gasification of lignin should increase the number of molecules, which would possibly inhibit gasification at high pressures. In addition, the solvent−solid or reactant−solid interaction is important in catalysis in supercritical fluids.[22,37] In a higher water density region, water molecules that are strongly adsorbed on the nickel or support would possibly have lower reactivity or restrict transport to and from the catalyst active site, which leads to the decrease of the reaction rate. Further, it has been noted that the cross-linking reaction of fragments is enhanced with increasing water density in the absence of catalyst.[21] Judging from these findings, the extent of gasification is probably a result of the balance of acceleratory and inhibitory factors, which lead to a maximum yield in the total yield of gases with respect to the water density.

Role of Ni/MgO Catalyst. For Ni/MgO catalyst, both the support and the metal played a role in the gasification process. In supercritical water, the yield of THF insolubles with both MgO only and with 5 wt % Ni/MgO were significantly higher than those in the absence of catalyst, as shown in Table 1. Further, the yield of THF insolubles was high for Ni/MgO in the absence of water, as shown in Figure 2b. The MgO catalyzed reactions led to unstable lignin fragments which could condense to THF insoluble products such as char regardless of the existence of water. The MgO did not promote the formation of lower molecular weight components such as gases. On the other hand, the total gas yield increased with an increase in the amount of nickel on the support in the presence of water. The increase in gas with increasing nickel loading is the same trend in cellulose gasification in subcritical water.[31] For the case of dense water and sufficient amounts of nickel, the nickel promoted the gasification of reactive fragments derived from lignin with water; otherwise, the reactive species probably would have been bound to each other to form larger molecular weight components. Next, we evaluated the effect of temperature for the gasification of lignin with Ni/MgO catalyst.

Figure 5 shows the carbon yield and the yield of THF insolubles for lignin gasification with 20 wt % Ni/MgO for 120 min and 0.3 g/cm³ total water density. We use the term of total water density, because water separates into two phases from 523 to 623 K under subcritical condition and the saturated water density was 0.80, 0.71, and 0.57 g/cm³ for 523, 573, and 623
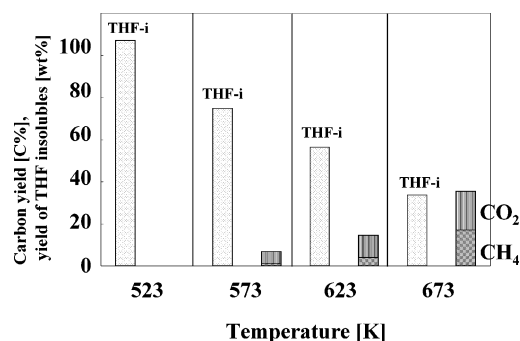
Figure 5. Carbon yield and the yield of THF insolubles with temperature for gasification of lignin with 20 wt % Ni/MgO at 0.3 g/cm^3 total water density for 120 min of reaction time.
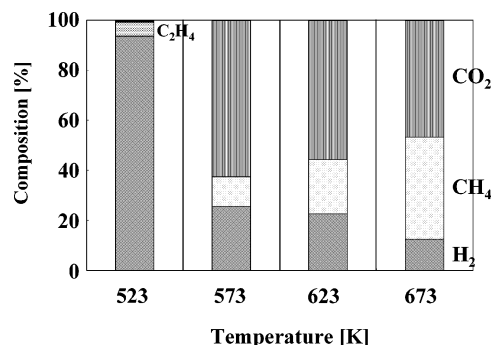
Figure 6. Gas composition with temperature for gasification of lignin with 20 wt % Ni/MgO at 0.3 g/cm^3 total water density for 120 min of reaction time.

K, respectively.[38] The yields of methane and carbon dioxide increased significantly with increasing temperature. The yield of ethane was below 0.1%. For the case of lignin conversion with Ru/C catalyst in high-temperature water, the amount of gases increased with increasing temperature from 523 to 673 K.[5] THF insolubles formed regardless of temperature. The yield of THF insolubles was greater than 100% at 523 K, which makes it clear that much THF insolubles were formed even in view of the experimental error. Considering the role of Ni/MgO catalyst, the MgO effectively promoted the decomposition of lignin to high molecular weight fragments, even in the lower temperature region (523−623 K). The yield of THF insolubles decreased with increasing temperature, which corresponded to an increase in the yield of gases. The high-temperature region was preferred for reaction between species derived from lignin and water to form gases on nickel.

Figure 6 shows the gas composition for experiments with 20 wt % Ni/MgO for 120 min and 0.3 g/cm^3 total water density. At 523 K, the gas products were mainly hydrogen because the gasification of carbon atom in lignin scarcely proceeded. The composition of methane increased with increasing temperature, and those of hydrogen and carbon dioxide decreased at temperatures higher than 573 K. Below 623 K, the reaction probably occurred in liquid phase where the solubility of hydrogen is much lower than the supercritical state, which could inhibit methanation. Judging from these results, methanation was preferred to proceed in the high-temperature region.

We evaluated the effect of the particle size of the catalyst by conducting experiments with large diameter catalysts at 673 K and 0.3 g/cm^3 water density. Table 3 shows the carbon yield and the yield of THF insolubles of this experiment. By comparing the results for under 180 μm of diameter (first use) with that for 355−500 μm, the yield of methane and carbon

Table 3. Carbon Yield and the Yield of THF Insolubles for the Effect of Catalyst Size and Reuse in Lignin Gasification with Ni/MgO in Supercritical Water[a]

	carbon yield (C %)				THF insolubles yield (wt %)
	CH$_4$	CO$_2$	C$_2$H$_6$	total gas	
first use[b]	17.0	18.4	0.1	35.5	33.7
second use	10.9	13.6	0.1	24.6	
third use	4.4	9.9	0.1	14.4	
large particle[c]	6.9	8.2	0.0	15.2	56.4

[a] Reaction temperature, 673 K; water density, 0.3 g/cm^3; reaction time, 120 min; lignin 0.1 g; initial catalyst, 0.1 g. [b] Under 180 μm of particle diameter. [c] 355−500 μm of particle diameter.

Table 4. Hydrogen Yield for the Effect of Catalyst Size and Reuse in Lignin Gasification with Ni/MgO in Supercritical Water[a]

	hydrogen yield (H %)			
	H$_2$	CH$_4$	C$_2$H$_6$	total gas
first use[b]	9.3	65.9	0.3	75.5
second use	2.9	42.5	0.2	45.6
third use	7.1	16.9	0.2	24.2
large particle[c]	8.4	26.9	0.1	35.4

[a] Reaction temperature, 673 K; water density, 0.3 g/cm^3; reaction time, 120 min; lignin 0.1 g; initial catalyst, 0.1 g. [b] Under 180 μm of particle diameter. [c] 355−500 μm of particle diameter.

dioxide with large catalyst particles were almost half as much as those obtained for small catalyst particles. The yields of THF insolubles for the large catalyst particles were higher than those obtained for small catalyst particles. Table 4 shows the hydrogen yield. The yield of hydrogen was almost the same between these two catalysts, and the yield of methane for small catalyst particles was higher than that for the large catalyst particles. These results mean that the contact between catalyst and reactant is important in this system as well as in the gasification of cellulose in subcritical water[31] because the surface area of the small catalyst particles was larger than that of large catalyst particles and the surface area of catalyst probably reflected the amount of nickel on the catalyst surface.

The stability of Ni/MgO catalyst was also studied by reusing the same catalyst several times at 673 K and 0.3 g/cm^3 water density. Table 3 shows the results for the carbon yield. After the experiment, the mixture of the catalyst and THF insolubles became difficult to separate from each other. Therefore, we used the mixture of the catalyst and THF insolubles obtained in the previous run as a catalyst for the second run and the third run, and the yield of THF insolubles in the second and the third run was not evaluated. The yield of methane and carbon dioxide considerably dropped after the catalyst was used successively three times. Table 4 provides the hydrogen yield of these experiments, which shows that the yield of hydrogen was always below 10% and the yield of methane decreased with the reuse of catalyst. It is reported that the nickel is stable in high-temperature water.[39] On the other hand, the agglomeration of nickel occurs in high-temperature water.[40] Further, THF insolubles always formed after a reaction in supercritical water for 120 min with Ni/MgO as explained before. In the reuse experiments of catalyst, THF insolubles such as heavier comments or char probably formed in each run. Judging from these facts, the deactivation of catalyst during reuse was probably because of the agglomeration of nickel and the formation of char-like carbonaceous products on the surface of the catalyst. Improving the stability of the Ni/MgO catalyst will be a future work.

Conclusion

Gasification of lignin was conducted in the presence of magnesium oxide supported nickel (Ni/MgO) catalysts in sub- and supercritical water without a special hydrogen donor from 523 to 673 K. The main gas products were methane, carbon dioxide, and hydrogen. The amount of gases produced increased with an increase in nickel loading on magnesium oxide. The 78% of lignin on a carbon basis could be gasified with 20 wt % Ni/MgO catalyst for a 360 min reaction time in supercritical water at 673 K and 0.3 g/cm^3 water density. The yield of THF insolubles in the presence of MgO was higher than that in the absence of MgO, and the yield of gases increased with increasing amounts of nickel on the MgO catalyst. These results indicate that the support and metal of the catalyst played different roles in the lignin gasification. The MgO catalyzed reactions led to unstable lignin fragments which could condense to THF insoluble products, and nickel probably promoted reaction between intermediates and water to form gases.

Water density greatly affected gasification. The yield of methane and carbon dioxide increased up to about 25% with increasing water density under 0.2 g/cm^3 but then decreased and leveled out to constant values at water densities greater than 0.4 g/cm^3 or so at 673 K for 120 min. This is probably due to a balance of the reaction promoting factors such as higher reactant concentration and inhibitory factors such as chemical equilibrium at high pressures to suppress gas formation and the restriction of reactants to active sites by water.

It is revealed that the supported nickel catalyst can be used for the effective gasification of lignin by choosing MgO as a support, although the extension of their life is necessary in the next step.

Acknowledgment

Literature Cited

(1) McKendry, P. Energy production from biomass (part 2): Conversion technologies. *Bioresour. Technol.* **2002**, *83*, 47−54.

(2) McKendry, P. Energy production from biomass (part 3): Gasification technologies. *Bioresource Technol.* **2002**, *83*, 55−63.

(3) 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*, 153−192.

(4) McKendry, P. Energy production from biomass (part 1): Overview of biomass. *Bioresour. Technol.* **2002**, *83*, 37−46.

(5) Osada, M.; Sato, T.; Watanabe, M.; Adschiri T.; Arai, K. Low-temperature catalytic gasification of lignin and cellulose with a ruthenium catalyst in supercritical water. *Energy Fuels* **2004**, *18*, 327−333.

(6) Caballero, M. A.; Corella, J.; Aznar, M.-P.; Gil, J. Biomass gasification with air in fluidized bed. Hot gas cleanup with selected commercial and full-size nickel-based catalysts. *Ind. Eng. Chem. Res.* **2000**, *39*, 1143−1154.

(7) Corella, J.; Toledo, J. M.; Padilla, R. Catalytic hot gas cleaning with monoliths in biomass gasification in fluidized beds. 1. Their effectiveness for tar elimination. *Ind. Eng. Chem. Res.* **2004**, *43*, 2433−2445.

(8) Corella, J.; Toledo, J. M.; Padilla, R. Catalytic gas cleaning with monoliths in biomass gasification in fluidized beds. 3. Their effectiveness for ammonia elimination. *Ind. Eng. Chem. Res.* **2005**, *44*, 2036−2045.

(9) Corella, J.; Toledo, J. M.; Aznar, M.-P. Improving the modeling of the kinetics of the catalytic tar elimination in biomass gasification. *Ind. Eng. Chem. Res.* **2002**, *41*, 3351−3356.

(10) Corella, J.; Toledo, J. M.; Padilla, R. Catalytic hot gas cleaning with monoliths in biomass gasification in fluidized beds. 2. Modeling of the monolithic reactor. *Ind. Eng. Chem. Res.* **2004**, *43*, 8207−8216.

(11) Rapagná, S.; Provendier, H.; Petit, C.; Kiennemann, A.; Foscolo, P. U. Development of catalysts suitable for hydrogen or syn-gas production from biomass gasification. *Biomass Bioenergy* **2002**, *22*, 377−388.

(12) Furusawa, T.; Tsutsumi, A. Comparison of Co/MgO and Ni/MgO catalysts for the steam reforming of naphthalene as a model compound of tar derived from biomass gasification. *Appl. Catal., A* **2005**, *278*, 207−212.

(13) Savage, P. E. Organic chemical reactions in supercritical water. *Chem. Rev.* **1999**, *99*, 603−621.

(14) Akiya, N.; Savage, P. E. Roles of water for chemical reactions in high-temperature water. *Chem. Rev.* **2002**, *102*, 2725−2750.

(15) Watanabe, M.; Sato, T.; Inomata, H.; Smith, R. L., Jr.; Arai, K.; Kruse, A.; Dinjus, E. Chemical reactions of C1 compounds in sub- and supercritical water. *Chem. Rev.* **2004**, *104*, 5803−5821.

(16) Kruse, A.; Gawlik, A. Biomass conversion in water at 330−410 °C and 30−50 MPa. Identification of key compounds for indicating different chemical reaction pathways. *Ind. Eng. Chem. Res.* **2003**, *42*, 267−279.

(17) Kruse, A.; Henningsen, T.; Sinag, A.; Pfeiffer, J. Biomass gasification in supercritical water: Influence of the dry matter content and the formation of phenols. *Ind. Eng. Chem. Res.* **2003**, *42*, 3711−3717.

(18) Karagöz, S.; Bhaskar, T.; Muto, A.; Sakata, Y. Comparative studies of oil compositions produced from sawdust rice husk, lignin and cellulose by hydrothermal treatment. *Fuel* **2005**, *84*, 875−884.

(19) Sasaki, M.; Adschiri, T.; Arai, K. Kinetics of cellulose conversion at 25 Mpa in sub- and supercritical water. *AIChE J.* **2004**, *50*, 192−202.

(20) Sasaki, M.; Fang, Z.; Fukushima, Y.; Adschiri, T.; Arai, K. Dissolution and hydrolysis of cellulose in subcritical and supercritical water. *Ind. Eng. Chem. Res.* **2000**, *39*, 2883−2890.

(21) Saisu, M.; Sato, T.; Watanabe, M.; Adschiri, T.; Arai, K. Conversion of lignin with supercritical water−phenol mixtures. *Energy Fuels* **2003**, *17*, 922−928.

(22) Baiker, A. Supercritical fluids in heterogeneous catalysis. *Chem. Rev.* **1999**, *99*, 453−473.

(23) Savage, P. E. Heterogeneous catalysis in supercritical water. *Catal. Today* **2000**, *62*, 167−173.

(24) Calzavara, Y.; Joussot-Dubien, C.; Boissonnet, G.; Sarrade, S. Evaluation of biomass gasification in supercritical water process for hydrogen production. *Energy Convers. Manage.* **2005**, *46*, 615−631.

(25) 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*, 4040−4053.

(26) 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*, 545−552.

(27) Park, K. C.; Tomiyasu, H. Gasification reaction of organic compounds catalyzed by RuO$_2$ in supercritical water. *Chem Commun.* **2003**, *6*, 694−695.

(28) Elliott, D. C.; Sealock, L. J., Jr. Low-temperature gasification of biomass under pressure. In *Fundermentals of Thermochemical Biomass Conversion*; Overend, R. P., Milne, T. A., Mudge, L. K., Eds.; Elsevier: London, 1985; pp 937−950.

(29) Sealock, L. J., Jr.; Elliott, D. C. U.S. Patent 5,019,135, 1991.

(30) Minowa, T.; Zhen, F.; Ogi, T. Cellulose decomposition in hot-compressed water with alkali or nickel catalyst. *J. Supercrit. Fluids* **1998**, *13*, 253−259.

(31) Minowa, T.; Ogi, T. Hydrogen production from cellulose using a reduced nickel catalyst. *Catal. Today* **1998**, *45*, 411−426.

(32) Yoshida, T.; Matsumura, Y. Gasification of cellulose, xylan, and lignin mixtures in supercritical water. *Ind. Eng. Chem. Res.* **2001**, *40*, 5469−5474.

(33) Yoshida, T.; Oshima, Y.; Matsumura, Y. Gasification of biomass model compounds and real biomass in supercritical water. *Biomass Bioenergy* **2004**, *26*, 71−78.

(34) Yoshida, T.; Oshima, Y. Partial oxidative and catalytic biomass gasification in supercritical water: A promising flow reactor system. *Ind. Eng. Chem. Res.* **2004**, *43*, 4097−4104.

(35) 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*, 3124−3130.

(36) Sato, T.; Haryu, E.; Adschiri, T.; Arai, K. Noncatalytic recovery of phenol through decomposition of 2-isopropylphenol in supercritical water. *Chem. Eng. Sci.* **2004**, *59*, 1247−1253.

(37) Sato, T.; Osada, M.; Watabnabe, M.; Shirai, M.; Arai, K. Gasification of alkylphenols with supported noble metal catalysts in supercritical water. *Ind. Eng. Chem. Res.* **2003**, *42*, 4277−4282.

(38) Wagner, W.; Pruss, A. The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use. *J. Phys. Chem. Ref. Data* **2002**, *31*, 387−535.

(39) Elliott, D. C.; Sealock, L. J., Jr.; Baker, E. G. Chemical processing in high-pressure aqueous environments. 2. Development of catalysts for gasification. *Ind. Eng. Chem. Res.* **1993**, *32*, 1542−1548.

(40) Elliott, D. C.; Phelps, M. R.; Sealock, L. J., Jr.; Baker, 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*, 566−574.