

Hydrogen production from lignin with supported nickel catalysts through supercritical water gasification

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ABSTRACT:

The production of hydrogen through the gasification of lignin was examined with nickel supported magnesium oxide catalysts in supercritical water at 673 K. In the absence of nickel (MgO only), the amount of gases were very low and almost all of lignin were decomposed to THF insolubles. The increase in the amount of nickel on catalyst led to the increase in the amount of gases. In this reaction, the magnesium oxide decomposed the lignin to lower molecular components. The nickel probably promoted the participation of hydrogen and oxygen atom to form gases through the gasification of lignin. The gas yield was attained almost 80% in a carbon basis at 673 K and 0.3 g/cm³ of water density. The main gas components were methane, carbon dioxide, hydrogen and these composition were about 54%, 40% and 6%, respectively. These results indicate that the biomass can be converted to gases including hydrogen by using nickel catalyst at low temperature region.

KEYWORDS : gasification, supercritical water, biomass, nickel, lignin

Introduction

The gasification of biomass is one of the important methods to obtain hydrogen for the establishment of sustainable society. Further, the low temperature is preferred to of gasification should be in a view of cold gas efficiency. Lignin is a component of woody biomass and its structure is an aromatic polymer. The conversion of lignin is a key reaction for the gasification of biomass because the gasification of lignin was difficult due to its stable structure.

Supercritical water is dense steam that has many favorable properties for gasification.¹ 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. In the case of heterogeneous catalytic reaction, 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.

The gasification of lignin has been studied in supercritical water. In particular, the activity of ruthenium catalyst was relatively higher than other catalysts. Osada et al.² 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 minutes of 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 et al.³ 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% in a carbon basis for 1 hour. Minowa et al.⁴ conducted gasification experiments of cellulose with commercial nickel catalysts in subcritical water and reported that nickel catalyzed gas formation from aqueous products that followed from the decomposition of cellulose. They also reported that the activity of magnesia support was better than those of other catalyst supports such as silica and alumina.⁵ Yoshida and Matsumura^{6,7} 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 about 20% on a carbon basis.

In this study, the production of hydrogen through the gasification of lignin was examined with nickel supported magnesium oxide catalysts in supercritical water. We evaluated the effect of the amount of nickel loaded and water density. From these results, we proposed the reaction route for the reaction of lignin with Ni/MgO catalyst in supercritical water.

Experimental

Organosolve lignin (Aldrich) was used as the lignin and its molecular formula was $C_{42.87}H_{44.15}O_{12.98}$. The lignin powder was completely soluble in tetrahydrofuran (THF). The catalysts used in this study were prepared by impregnating MgO with aqueous solutions of $Ni(NO_3)_2 \cdot 6H_2O$, 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 particles under 180 mm in diameter. The calcined catalysts are 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 (6 cm³). 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. The reactor was put into a forced convection oven that was controlled at the appropriate reaction temperature. It took about 40 minutes 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 minute to cool down 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). 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 analysis were made of the liquid fraction by GC-MS (GC-17A-QP5050A, Shimadzu). The carbon yield and hydrogen yield was determined by carbon mole and hydrogen mole in initial lignin basis, respectively.

Results and discussion

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 of water density for 120 min. The dispersion of nickel ranged from 1.3 to 2.0 between 5 and 20 wt% of nickel, and the amount of nickel metal on surface increased with increasing the amount of nickel loaded. The water-soluble products consisted of phenol and alkylphenols and the individual yield of these compounds were below 2 % and the total yield was below 5%. 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 and we mainly evaluated the gas products and THF insolubles in this study. We detected carbon monoxide, ethylene and ethane in some cases, however, these yields were below 0.1% and not shown in Table 1.

In Table 1, the sum of the carbon yield of gases was 8.3% in the absent of catalyst, which means that the lignin could be gasified in supercritical water without catalyst. The yield of methane and carbon dioxide were largest. Saisu et al.⁸ reported that the polymerization of lignin occurred without catalyst in supercritical water to form THF insolubles. 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. In the experimental results, the yield 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% yields that was significantly larger than those obtained without catalyst. The MgO catalyzed reactions to form THF insoluble. Similar results were obtained in the presence of 5wt% 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 increased with increasing nickel over 10, 15 and 20wt% Ni/MgO catalyst, respectively. 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. For Ni/MgO catalyst, both the support and the metal played a role in gasification process. The MgO catalyzed reactions led to unstable

Table 1 Carbon yield and the yield of THF insolubles for lignin gasified with Ni/MgO in supercritical water at 673 K and 0.3 g/cm³ of water density for 120 min.

	Dispersion [%]	Carbon yield [C%]			THF insolubles yield [wt%]
		CH ₄	CO ₂	Total gas	
No catalyst	-	3.2	4.9	8.3	10.0
MgO	-	0.3	4.2	4.7	99.0
5wt% Ni / MgO	2.0	2.8	5.6	8.4	84.5
10wt%Ni/ MgO	1.3	9.6	12.1	21.7	35.0
15wt%Ni/ MgO	1.8	11.8	13.2	25.1	26.9
20wt%Ni/ MgO	2.0	17.0	18.4	35.5	33.7

Table 2 Hydrogen yield for lignin gasified with Ni/MgO in supercritical water at 673 K and 0.3 g/cm³ of water density for 120 min.

	Hydrogen yield [H%]		
	H ₂	CH ₄	Total gas
No catalyst	1.5	12.3	14.1
MgO	0.4	1.3	1.9
5wt% Ni / MgO	1.9	10.9	12.9
10wt% Ni / MgO	11.7	37.2	49.2
15wt% Ni / MgO	11.0	45.6	56.8
20wt% Ni / MgO	9.3	65.9	75.5

lignin fragments which could condense to THF insoluble products such as char. Further, 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.

Table 2 shows the yields of hydrogen obtained by gasification of lignin. The total gas yield increased with increasing nickel metal loaded in the presence of catalyst. The gases formed containing hydrogen atom were mainly hydrogen and methane. For the case of more than 10wt% of 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%. Nickel catalyst promotes methanation from hydrogen and carbon dioxide to methane and water in subcritical water.^{4,5} In supercritical water, nickel also probably promoted methanation to consume hydrogen, a part of which derived from 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.²

Water density is one of the important factors for controlling the reaction kinetics of lignin-like compounds in supercritical water for both noncatalytic^{9,10} and catalytic reactions.¹¹ Figure 1(a) and (b) shows that the carbon yield and the hydrogen yield versus reaction time at 673 K and water density of 0.3 g/cm³ with 20wt% Ni/MgO catalyst, respectively. In Figure 1(a), the yield of methane and carbon dioxide increased with reaction time until 180 minutes 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 (H₂O) to form methane and carbon dioxide because the oxygen content in raw lignin was less than 13 mol%. The total gas yield increased with reaction time and attained 78% after 180 min reaction time. Most of the lignin could be gasified in several hours with 20wt% Ni/MgO catalyst in supercritical water. In the presence of water, the THF insolubles was almost 40%. In Figure 1(b), 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.² The trends of methane, carbon dioxide and hydrogen with reaction time shown in Figure 1(a) were almost the same as those obtained with Ru/TiO₂ catalyst at 673 K and 0.33g/cm³ water density.² The final values of these yields were probably governed by the equilibrium of this system.

Figure 1(c) and (d) shows the carbon yield and the hydrogen yield versus reaction time at 673 K in the absence of water with 20wt% Ni/MgO catalyst, respectively. In figure 1(c), the yields of methane and carbon dioxide were below 9% and did not seem to vary with reaction time. In figure 1(d), the hydrogen yield was below 2% and the methane yield was as high as 33%. In the absence of water, the THF insolubles were generally greater than 60%, which is significantly higher than that in the presence of water. These results clearly indicate that water promoted gasification of lignin.

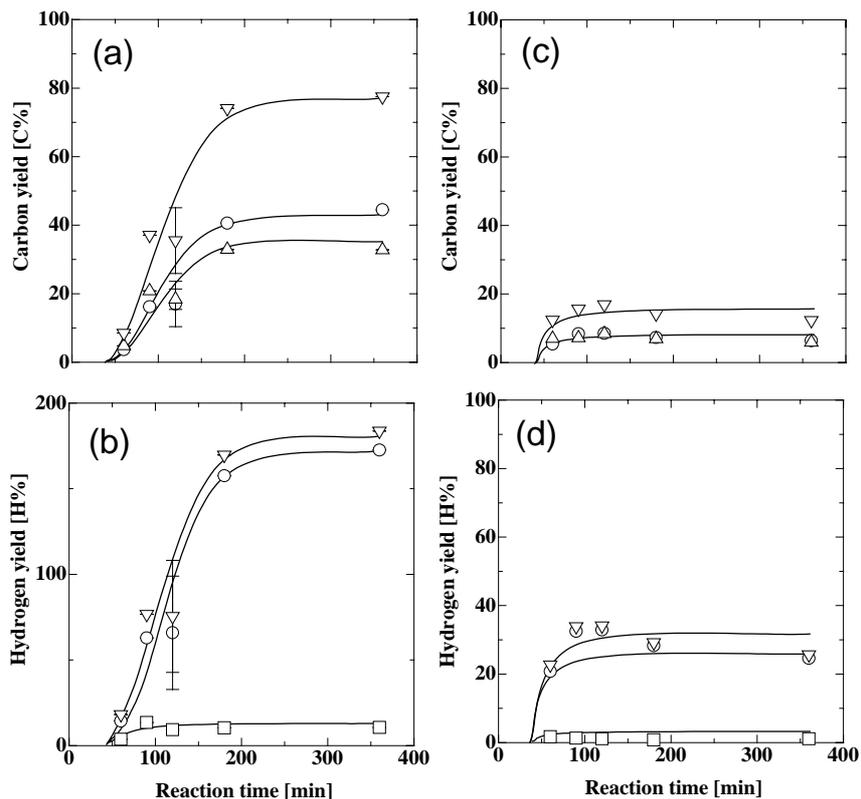


Figure 1 Product yield with reaction time with 20 wt% Ni/MgO at 673 K. () : CH₄, () : CO₂, () : H₂, (∇):Total gas (a) carbon yield for 0.3 g/cm³ of water density; (b) hydrogen yield for 0.3 g/cm³ of water density; (c) carbon yield in the absence of water; (d) hydrogen yield in the absence of water.

Conclusion

Gasification of lignin was conducted in the presence of magnesium oxide supported nickel (Ni/MgO) catalysts in sub and supercritical water without special hydrogen donor from 523 K 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 about 80% of lignin in a carbon basis could be gasified with 20 wt% Ni/MgO catalyst for 360 minutes reaction time in supercritical water at 673 K, 0.3 g/cm³ 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 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.

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