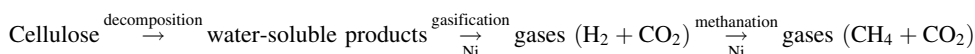# Hydrogen production from cellulose using a reduced nickel catalyst

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Abstract

Cellulose, a major component of biomass, was gasified in hot-compressed water using a reduced nickel catalyst at different reaction temperatures from 200°C to 350°C. The reaction mixture was separated to gases, oil, char and water-soluble products to discuss reaction mechanism based on the product distribution. The water-soluble products were considered as intermediates, and the obtained hydrogen was consumed by methanation reaction. The following simplified reaction scheme was proposed:

$$\text{Cellulose} \xrightarrow{\text{decomposition}} \text{water-soluble products} \xrightarrow[\text{Ni}]{\text{gasification}} \text{gases } (H_2 + CO_2) \xrightarrow[\text{Ni}]{\text{methanation}} \text{gases } (CH_4 + CO_2)$$

The effect of supports was also examined. Supports showed the strong effect on the gas yield, and the catalytic activity depended on the overall catalyst size rather than the surface area. © 1998 Elsevier Science B.V. All rights reserved.
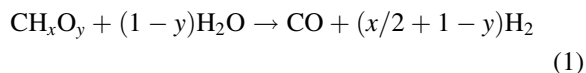
Keywords: Biomass; Cellulose; Low temperature gasification; Hydrogen production; Reduced nickel catalyst

1. Introduction

Hydrogen can be used for a clean power source of fuel cells. Since biomass is a renewable and carbon neutral resource, hydrogen production from biomass has become attractive with the global warming problem. However, biomass usually contains water and a dry feedstock is required for conventional gasification. Since a drying process is an energy intense operation, a new method by which wet biomass is directly converted to hydrogen is beneficial.

Antal and co-workers [1–3] reported that wet biomass is completely gasified to hydrogen, carbon dioxide and carbon monoxide in supercritical water at 600°C and 35 MPa. Elliott and co-workers [4–9] converted wet biomass directly to methane rich gas using a reduced nickel catalyst in supercritical and subcritical water at relatively low temperatures of 350–450°C and low pressures of 15–35 MPa. In the latter process, three major reactions, i.e., steam reforming, water-gas shift reaction and methanation, can occur.

$$CH_xO_y + (1 - y)H_2O \rightarrow CO + (x/2 + 1 - y)H_2 \tag{1}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{2}$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{3}$$

We found that hydrogen rich gas can be obtained in hot-compressed water (under supercritical condition) in which both gas and liquid phase are present [10,11].

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When the catalyst is in aqueous solution, hydrogen gas produced by steam reforming and water-gas shift reaction may move from the liquid phase to the gas phase, and, as a result, the catalyst would not be in contact with much hydrogen, thus, the methanation may be prevented. In this paper, we discuss cellulose gasification and the effect of supports. This study aims to get an insight into the reaction mechanism and the effect of support.

2. Experimental

Microcrystalline cellulose (E. Merck) was used as a starting material. It was dried at 105°C for 24 h prior to this study. A commercial nickel catalyst (Engelhard, NI-3288, ca. 50 wt% nickel on silica–alumina) was employed in the examination of reaction mechanism. It was crushed to 60–200 mesh and reduced with hydrogen gas at 350°C for 4 h, before the reaction.

The reaction was performed in a conventional stainless steel (SUS-F316L) autoclave (120 cm^3 capacity and 18 cm^3 of head-space) with a magnetic stirrer. Five grams of cellulose, 2 g of the nickel catalyst and 30 ml of water were charged into the autoclave. The residual air in the autoclave was purged with N_2 gas of which pressure was 3 MPa, to avoid vaporization of water during the reaction. Then, the reaction was started to heat the autoclave using an electric furnace. When the temperature in the autoclave reached to the desired temperature of 200–350°C, the autoclave was immediately cooled down to room temperature using an electric fan. Fig. 1 shows typical examples of the relationship between the reaction time and the temperature and pressure in the autoclave. The heating rate, as a function of time, was well reproduced in the experiments.

After cooling down to room temperature, the product gas was introduced to a sampling bag for analysis. Then, the autoclave was opened, and the reaction mixture was recovered for separation. The aqueous phase was separated by washing the reaction mixture with water and by filtration. Then, the acetone solution was separated by washing the water insoluble fraction with acetone and by filtration. The oil was obtained from the solution by evaporating acetone at 70°C. The fraction insoluble to acetone, remaining on the filter paper, was dried at 70°C to obtain the residue.
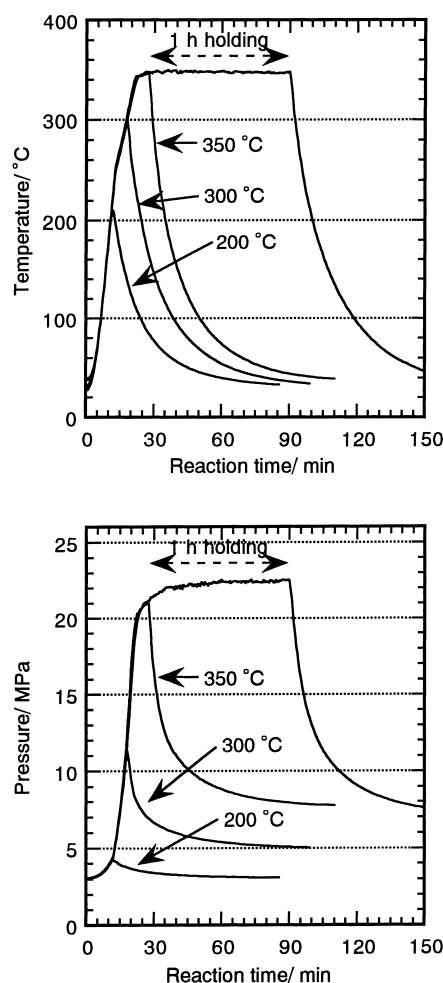

Fig. 1. (a) Temperature in the autoclave versus reaction time. (b) Pressure in the autoclave versus reaction time.

At the end of the reaction, the volume of the formed gases was measured using a gas meter (Shinagawa-sheiki, W-NK-0.5Bf), and the composition was determined with gas chromatographs (Shimadzu, GC-12A with TCD detector for inorganic gases and GC-9A with FID detector for hydrocarbon gases). The elemental composition of the oil and residue was determined by an elemental analyzer (AMCO, NA-1500). The carbon content in the aqueous phase was measured with a TOC meter (Yanaco, TOC-8L). Cellulose in the residue was hydrolyzed to glucose, and the glucose amount was measured by phenol–sulfuric acid method. The amount of cellulose was calculated by the

following equation:

Cellulose (g) = residue (g)

$$\times \frac{\text{glucose unit (g/g) in residue}}{\text{gluclose unit (g/g) in cellulose}}. \quad (4)$$

The solid products, which have no glucose-unit, in the residue (hereafter referred to as the char) were calculated by the difference. The hydrolysis procedure was referred to in the literatures [12–14]. Details were described in our previous paper [15].

Nickel catalysts with different supports were prepared by ordinary precipitation [16,17]. Sodium carbonate solution was added to a slurry of support and nickel nitrate solution to obtain the precipitate, which was then dried at 105°C for 12 h, crushed to 60–200 mesh, calcined at 350°C for 4 h and reduced with hydrogen gas at 350°C for 4 h to finally obtain the reduced nickel catalyst (50 wt% nickel to the catalyst). The supports of JRC-ALO-2, JRC-SAH-1, JRC-SAH-2, JRC-SIO-5, JRC-SIO-6 and JRC-MGO-3 were obtained from Catalyst Society of Japan. The supports of aluminum silicate and kieselguhr were obtained from Wako. The surface area of the prepared catalysts was measured by a multipoint BET method using a surface area meter (Micromeritics, Gemini 2360). The overall catalyst size was determined with a particle size analyzer (JEOL, HLOS system) after the catalyst was dispersed in water by sonication. The catalyst activity was examined in a similar manner as above; reaction temperature, 350°C, holding time 0 min, 5 g of cellulose as a feedstock, and 2 g loading of each prepared catalyst.

3. Results and discussion

3.1. Product distribution at different reaction temperatures

The product distribution on carbon basis is shown in Fig. 2. The carbon in the initial cellulose could be recovered around 100% ("Total" in Fig. 2), except at 280°C and at 350°C with 1 h holding. At 280°C, it is considered to be due to the production of C_{5+} hydrocarbon gases, which cannot be detected by GC, and the production of light oil, which can be vaporized during the separation procedure. At 350°C (1 h holding), it is considered to be due to the gas leak during the long
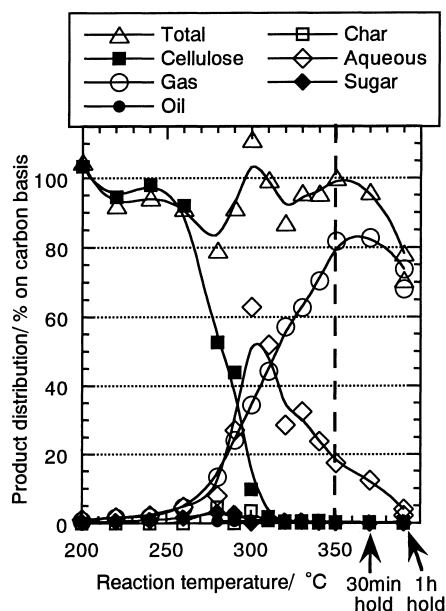

Fig. 2. Product distribution at different reaction temperatures.

holding. The cellulose decomposition occurred between 260°C and 320°C. Below 260°C, almost all cellulose remained in the reaction mixture. At 260°C, water-soluble products and gases were mainly produced, and oil and char-like residue were minor. The yield of water-soluble products was maximum at 300°C, and it decreased above 300°C. The fraction of the gas phase in the reaction mixture increased with an increase in the reaction temperature, although no cellulose remained in the autoclave. Thus, a simplified reaction scheme of the gas formation through the water-soluble products as intermediates is considered.

Cellulose → water-soluble products → gases. (5)
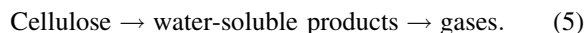
In the present study, we used much amount of the catalyst (40 wt% loading), and little oil and char was obtained. On the other hand, the oil and char were obtained as by-products under the condition of lower catalyst loading (5–10 wt% loading) [11,18]. Fig. 3 shows product distribution at different catalyst loading. The separate experiments using produced oil/char as a starting material showed that the produced oil/char was unable to be gasified. In addition, the water-soluble products were also considered as intermediates for the oil/char formation from the separate experiments under catalyst-free condition [19]. These
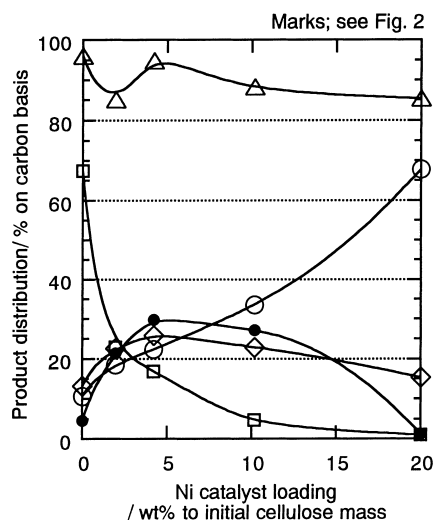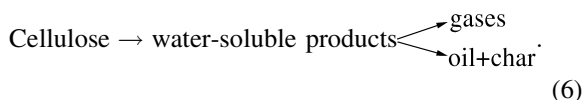
Fig. 3. Product distribution at different catalyst loading [11] (cellulose 5 g, water 30 ml, 350°C, 1 h holding).

Fig. 4. Amount of gas products at different reaction temperatures.

mean the competition between the gasification and the oil/char formation.

$$\text{Cellulose} \rightarrow \text{water-soluble products} \Big\langle \begin{array}{l} \text{gases} \\ \text{oil+char} \end{array} . \tag{6}$$

The obtained gas consisted mainly of CO_2, H_2 and CH_4. The amount of gas products at different reaction temperatures is shown in Fig. 4. Hydrogen and carbon dioxide were obtained in the highest yield at 350°C and 0 min holding, and their yields decreased during the holding. On the other hand, the yield of methane increased during the holding. Between the 0 min holding and 30 min holding at 350°C, CO_2 and H_2 decreased by 4 and 15 mmol, respectively, and CH_4 increased by 5 mmol, which is the corresponding value to the stoichiometry of methanation. Thus, the methanation through CO_2 and H_2 occurred clearly.

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \tag{7}$$
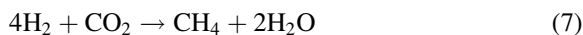
The production of methane was confirmed by the separate experiments using CO_2 and H_2 as starting materials.

3.2. Effect of supports

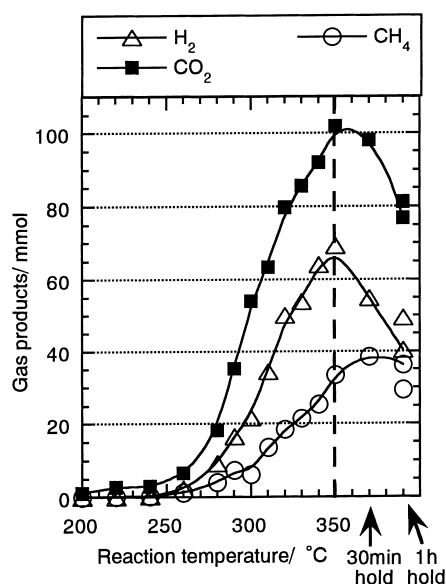Table 1 shows the support of the prepared catalysts, and their results on the gasification are shown in

Table 1
The supports and the properties of the prepared catalysts

Catalyst	Support	Surface area (m^2/g)	Overall catalyst size (μm)
A	Non	0.5	73
B	JRC-ALO-2 (alumina)	131	15.6
C	JRC-SAH-1 (silica–alumina)	252	28.0
D	JRC-SAH-2 (silica-alumina)	263	31.3
E	Aluminum silicate	193	12.8
F	Aluminum silicate	201	18.0
G	JRC-SIO-5 (silica)	179	17.7
H	JRC-SIO-6 (silica)	104	15.3
I	Kieselguhr	29	8.0
J	JRC-MGO-3 (magnesia)	107	7.7

Fig. 5. Supports showed the strong effect on the gas yield. Catalyst A without support had little catalytic activity. Therefore, any support is required for the catalyst preparation. Catalyst J with magnesia showed the highest catalytic activity, while catalyst B with alumina showed the smallest activity. This phenomenon is considered due to the acidity/basicity of supports. The highest methane yield was obtained by catalyst J, and catalyst J could catalyze more
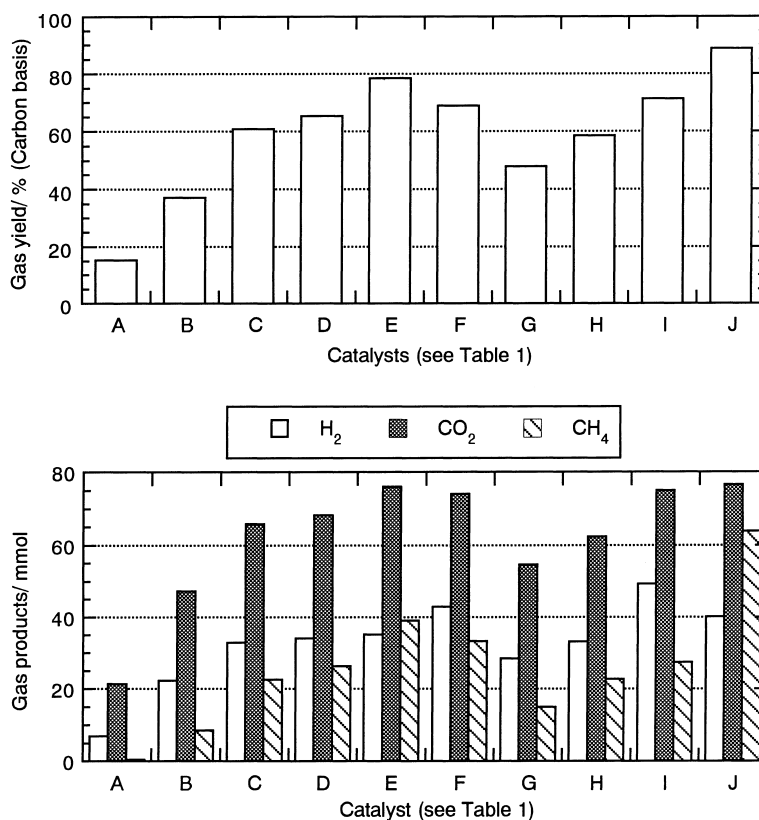
Fig. 5. Effect of support on the gasification.

methanation. Catalysts C–I with support of silica–alumina or silica showed the middle catalytic activities, but their gas yields ranged from 48% to 78%. This suggests that the catalyst activity depends not only on the kinds of support materials.

The properties of the prepared catalyst are also shown in Table 1. Fig. 6 shows the relationship between the gas yield and the catalyst properties. The surface area of the catalysts showed little effect on the gas yield, while the overall catalyst size showed the effect on the gas yield. As discussed above, cellulose, a polymer, decomposes to water-soluble products at first step, and the water-soluble products are gasified by a nickel catalyst. Since the water-soluble products such as glucose and oligomer would have big molecular sizes, the nickel particles presented on the external surface could only contribute to the gasification.
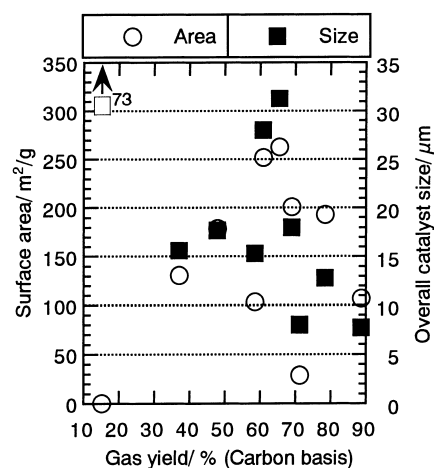

Fig. 6. Relationship between the gas yield and the properties of catalyst.

4. Conclusion

Cellulose, a major component of biomass, was gasified in hot-compressed water using a reduced nickel catalyst. The reaction mechanism was discussed based on the product distribution, and the effect of support was also examined. The following conclusions were obtained.

1. The observation indicates a simplified reaction scheme of gasification from water-soluble products as intermediates.
2. The small loading of the nickel catalyst resulted in the production of oil and char; suggesting the competition between the gasification catalyzed by the nickel catalyst and the oil/char formation by polymerization.
3. The result of distribution of gases suggests methanation from H_2 and CO_2 to CH_4.
4. The catalyst with different supports had different activity, and the activity depended not only on the kind of support materials, but also on the overall catalyst size; indicating the nickel particles presented on the external surface could only contribute to the gasification.

Acknowledgements

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