Hydrogen Production from Wet Cellulose by Low Temperature Gasification Using a Reduced Nickel Catalyst

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(Received July 7, 1995)

Wet cellulose was gasified at 350 °C for 1 h in the presence of a reduced nickel catalyst under various operating pressures (8 - 18 MPa). Hydrogen was obtained specifically at high operating pressures of 17 - 18 MPa. Under the operating pressure of 18 MPa, the gas yield increased with catalyst loading and reached 91 wt% at the catalyst loading of 20 wt%. The gas consisted of hydrogen of 50 vol%, carbon dioxide of 40 vol% and methane of 10 vol%, which was equivalent to that the hydrogen of 70% in the cellulose was recovered as hydrogen gas.

Biomass is important as an alternative resource of fossil fuel, because it is renewable. Elliott et al.[1-3] of the Pacific Northwest Laboratory reported wet biomass to be directly gasified to methane rich gas using a reduced nickel catalyst at 350 - 450 °C under pressurized nitrogen. Since biomass usually has high moisture content and a drying process requires much energy to vaporize the moisture, this gasification, which requires no drying of feed stock, consumes less energy. In this gasification, high pressure is needed for methane production in terms of equilibrium. In our preceding paper,[4] wet cellulose was gasified at 400 °C under various operating pressures, and the methane production was shown to depend on the state of water around the catalyst according to the operating pressure; methane was obtained in higher yield under the steam condition of water than under the supercritical condition. In this paper, we gasified wet cellulose at 350 °C under various operating pressures, which turn water around the catalyst into steam or liquid, and found that hydrogen gas was produced in specifically high yield under the liquid condition of water.

Experiments were carried out in a similar manner as our preceding paper.[4] Cellulose, a major component of woody biomass, was used as the starting material. The cellulose sample was microcrystalline (E. Merck), and it was dried at 105 °C for 24 h prior to the experiments. The amounts of carbon, hydrogen and oxygen of the cellulose, determined by an elemental analyzer (Perkin-Elmer, 2400 CHN), were 42.5, 7.4, and 50.1%, respectively. The reduced nickel catalyst (about 50 wt% of nickel content) was prepared by ordinary precipitation.[5,6] Details were described in our preceding paper.[4] The reaction was performed in a stainless steel autoclave (100 cm^3) with a magnetic stirrer. Water (30 ml), the cellulose (3 or 5 g) and the reduced nickel catalyst (0 - 20 wt% to the cellulose) were charged into the autoclave. Nitrogen, an inert gas, was added to the desired initial pressure (0.1 - 5 MPa). The reaction was started by heating the autoclave up to 350 °C using an electric furnace. This temperature was maintained constant for 1 h. The pressure in the autoclave, monitored with a pressure transmitter, rose with temperature, and it was kept constant during the reaction at 350 °C. The operating pressure was defined as the pressure at 350 °C. Following completion of the reaction, the autoclave was cooled to room temperature using an electric fan.

The evolved gas was collected in a gas sampling bag for analysis. Its volume was measured with a gas meter (Shinagawa Seiki, W-NK-0.5Bf) and its composition was determined with a gas chromatograph (Shimadzu, GC-12A) equipped with a thermal conductivity detector and a packed column (MS-5A or Porapak Q). The reaction mixture in the autoclave was washed with water and aqueous phase was separated by filtration. The remained material was washed with acetone and the acetone solution was separated by filtration. Acetone was evaporated from the filtrate at 70 °C to obtain oil. The residue on the filter paper was dried at 70 °C for 24 h. The amount of carbon in the aqueous phase was determined by a total organic carbon meter (Yanaco, TOC-8L). The analysis of the elemental composition of the oil and the residue was done in the same manner as the cellulose.

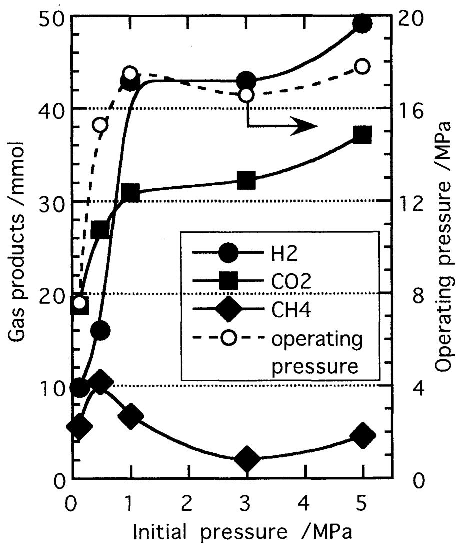

Figure 1. Effect of initial pressure on gas products. (350 °C, 1 h, cellulose 3 g, water 30 ml, Ni cat. 20 wt%)

Figure 1 shows the effect of the initial pressure on the amounts of the gas products. The initial pressure was varied from 0.1 to 5 MPa to get the various operating pressures. The operating pressures are also shown in Figure 1. The evolved gas consisted mainly of hydrogen, carbon dioxide and methane, and their amounts depended strongly on the initial pressure. The hydrogen was obtained in the specifically large amounts of 40 - 50 mmol at higher initial pressures than 1 MPa. The production of hydrogen was rapidly reduced at lower initial pressures. The behavior of the production of carbon dioxide was similar to that of hydrogen. With respect of the methane production, the largest amount of 10 mmol was obtained at the initial pressure of 0.5 MPa.

The behavior of the operating pressure was similar to that of hydrogen production; that is, the operating pressure had the high values of 17 - 18 MPa at higher initial pressures than 1 MPa, and it was rapidly reduced at lower initial pressures. Since the

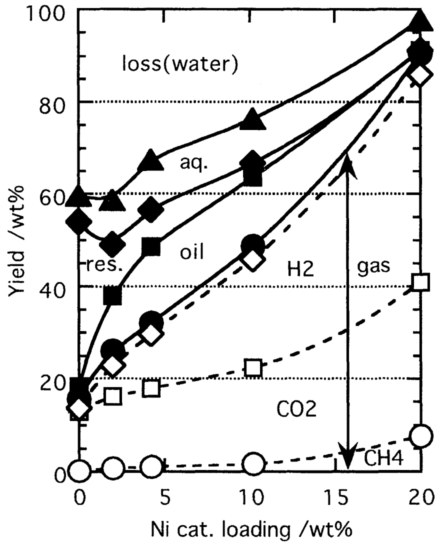

Figure 2. Effect of Ni cat. loading on product distribution. (350 °C, 18 MPa, 1 h, cellulose 5 g, water 30 ml)

saturated pressure of water is about 16.5 MPa at 350 °C, water around the catalyst should be in a liquid state at higher initial pressures than 1 MPa and in a steam state at lower initial pressures, although the state of water should change at the part of the autocalve due to the temperature slope in the autoclave. In this gasification, three major reactions would occur: steam reforming ($CH_xO_y + (1\text{-}y)H_2O \rightarrow CO + (x/2+1\text{-}y)H_2$), water-gas sift ($CO + H_2O \rightarrow O_2 + H_2$) and methanation ($CO + 3H_2 \rightarrow CH_4 + H_2O$). Methane would be formed through the methanation reaction. Although high reaction pressures are thermodynamically favorable for the methane production and unfavorable for the hydrogen production, hydrogen was produced specifically and little methane was obtained in this study. The methanation reaction, thus, was suppressed under the liquid condition of water. When the catalyst is in liquid water, the hydrogen gas produced through steam reforming and water-gas sift reaction would move to the gas phase from the liquid phase and the catalyst could contact little hydrogen; no methanation reaction, thus, would occur.

To consider the role of the nickel catalyst, the effect of catalyst loading was examined on the distribution of gas and by-products such as oil, residue and aqueous phase. The result is shown in Figure 2. The yield was defined as the weight percentage of the organics in each phase to the weight of cellulose charged. The weight of the organics in the residue was calculated by subtracting the weight of the nickel catalyst charged. Since a part of the organics in the aqueous phase can be vaporized during the drying process, which is needed to get the organics in it, the total carbon amount in the aqueous phase was regarded as the weight of the organics in it in this paper. The gas products are indicated as a mole ratio in the gas in Figure 2. Without catalyst, cellulose of about 20 wt% was converted into gas (almost carbon dioxide), about 40 wt% was into the residue, and 40 wt% was lost. With the increase of catalyst loading, the gas yield increased linearly, the sum of the yields of by-products decreased linearly, and the loss also decreased linearly. The gas yield reached 91 wt% at the catalyst loading of 20 wt%, and this gas consisted of hydrogen of 50 vol%, carbon dioxide of 40 vol%, and methane of 10 vol%, which was equivalent to that the hydrogen of 70% in the cellulose was recovered as hydrogen gas.

To clarify the reason for the loss, the balances of carbon, hydrogen and oxygen were estimated. Carbon balance was more than 90%, and the mole ratio of hydrogen loss to oxygen loss was about 2:1. The loss, thus, was due to the water production. The carbonization of cellulose ($CH_2O \rightarrow C + H_2O$) would be one of the reasons for the water production. The addition of the catalyst decreased the water production; the reaction of water production would be suppressed or water would be consumed by the reaction such as steam reforming and water-gas shift. By catalyst addition, the residue yield decreased rapidly, and the oil was obtained. Nickel catalyst is also used for the liquefaction of biomass to produce oil.[7] The oil formation would be one of the roles of the catalyst, and the oil may be an intermediate on this gasification.

In this study, we found that hydrogen could be obtained specifically from wet cellulose at low reaction temperature of 350 °C by catalytic gasification using a reduced nickel catalyst. Hydrogen is clean energy, and it is focused for fuel cells. Hydrogen is usually produced from hydrocarbon sources such as coal and natural gas by steam reforming at high reaction temperatures of 800 - 1000 °C. High reaction temperatures, however, lead to low overall thermal efficiency. Many studies have been carried out to produce hydrogen at low reaction temperatures from biomass or methane.[8,9] This gasification would be expected to be one of the hydrogen production methods which have high thermal efficiency.

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