Bench-Scale Production of Hydrocarbon Liquid Fuel from Woody Biomass via Gasification

Toshiaki HANAOKA, Yanyoung LIU, Kotetsu MATSUNAGA, Satoshi HIRATA, and Kinya SAKANISHI

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The bench-scale production of hydrocarbon liquid fuel was successful from woody biomass via gasification. The production capacity of the biomass-to-liquid (BTL) plant used in this study was 1.9 L of hydrocarbon liquid from 13 kg of woody biomass per day. The BTL process involved the following steps: gasification of the woody biomass, wet and dry gas cleaning, gas compression, the removal of carbon dioxide, and the Fischer-Tropsch (FT) synthesis reaction. In the gasification step, oxygen-enriched air gasification was carried out using a downdraft fixed-bed gasifier. By increasing the oxygen content, which acts as a gasifying agent, from 21.0 to 31.5 vol%, the conversion to gas on a carbon basis increased from 91.9 to 96.3 C-mol%, while the concentrations of CO and H2 increased from 22.8 to 30.1 vol% and from 16.8 to 23.7 vol%, respectively. The product gas obtained with an oxygen content of 27.6 vol% was subsequently converted to a liquid fuel through the gas cleaning and FT synthesis reaction steps. The concentrations of H2S and COS produced in the gasification step decreased to less than 5 ppb through the scrubber and desulfurization tower for the wet and dry gas cleaning, respectively. The concentration of the syngas (CO + H2) increased from 48.1 to 56.0 vol%, while that of CO2 decreased from 12.1 to 0.6 vol% after the cleaned gas was passed through a carbon dioxide removal tower. Subsequently, the cleaned gas was compressed up to 12.6 MPa using compressors to obtain a feed gas for the FT synthesis reaction, and its composition was as follows: 30.8 vol% of CO, 25.2 vol% of H2, 0.9 vol% of CO2, 2.5 vol% of CH4, 40.6 vol% of N2, <5 ppb of H2S, and <5 ppb of COS. In the FT synthesis step, the hydrocarbon fuel was synthesized in a slurry bed reactor using hexadecane as the solvent and Co/SiO2 catalyst. The selectivity to hydrocarbon with a carbon chain length of more than 5 carbon atoms as a liquid fuel, i.e., a C5+ selectivity of 73.0% was obtained along with a chain growth probability of 0.85 under the following conditions: 3 MPa, 280 to 310°C, and when the ratio of catalyst weight to feed gas rate (W/F) was 86.9 g h/mol.

Key Words
BTL, Biomass, Gasification, Gas cleaning, Fischer-Tropsch synthesis reaction

1. Introduction
In Japan, approximately 40 million kL of diesel fuel is annually consumed as liquid fuels derived from fossil fuels. Biomass is expected to be one of the most attractive potential feedstocks for an alternative liquid fuel among renewable energies in the near future because of its carbon neutrality and abundance. Recently, the synthesis of liquid fuels such as ethanol from sugarcane and maize has led to an increase in the prices of various food products. Therefore, it is important to develop a technology to convert from woody biomass — whose consumption does not affect the price of food products — to liquid fuels. Since woody biomass has a sulfur content lower than that of fossil fuels, clean liquid fuels with low sulfur contents can be synthesized; the use of these fuels would restrict acid rain and extend the lifetime of catalysts for reducing NOx in diesel exhaust gases. The technology used for the conversion of woody biomass to liquid fuel via gasification (biomass-to-liquid; BTL) is very promising, and the process generally involves biomass gasification, gas cleaning, and the Fischer-Tropsch (FT) synthesis. Some researchers have
reported experimental studies$^{1-3}$ and their environmental and economic analyses$^4$. The FT synthesis reaction used in the gas-to-liquid (GTL) process has been investigated in Japan on a scale larger than the laboratory scale$^5$; however, the production of hydrocarbon liquid fuels such as diesel fuels from woody biomass is required on a bench scale by using the BTL process in order to apply this process to pilot- or commercial-scale plants.

In the present study, a bench-scale BTL plant was constructed as shown in Fig. 1: the following steps took place in this plant: woody biomass gasification, gas cleaning, gas compression, removal of carbon dioxide, and the FT synthesis reaction. We succeeded in the bench-scale production of a hydrocarbon liquid fuel from woody biomass via gasification and discussed the improvements with respect to the proposed BTL process.

2. Outline of bench-scale BTL plant and experimental

Eucalyptus wood chips (size: 20-30 mm) were employed as the feedstock. Table 1 shows the analytical results of the feedstock. Table 2 shows the conditions required in each step for increasing the liquid fuel yield. Fig. 2 shows the flow diagram of a bench-scale BTL plant. The BTL process proposed in the present study comprises the following steps: woody biomass gasification, first gas cleaning step using a scrubber, first gas compression step, second gas cleaning step under pressurized conditions using a desulfurization tower, removal of carbon dioxide, second gas compression step, and FT synthesis reaction.

### 2.1 Woody biomass gasification

In the gasification step, syngas must be effectively produced from woody biomass. In the present study, oxygen-enriched air gasification was carried out using a downdraft fixed-bed gasifier (capacity: 40 kg wood/h), taking the produced tar concentration, applicability to small- or medium-

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**Table 1** Analytical results of the feedstock

<table>
<thead>
<tr>
<th>Ultimate analysis [wt% daf basis]</th>
<th>Proximate analysis [wt%]</th>
<th>HHV$^v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td>50.7</td>
<td>5.9</td>
<td>0.2</td>
</tr>
</tbody>
</table>

a) Ion chromatography  
b) By difference  
c) Higher heating value

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**Table 2** Conditions required in gasification, gas cleaning and Fischer-Tropsch synthesis reaction

<table>
<thead>
<tr>
<th>Required condition</th>
<th>Gasification</th>
<th>Gas cleaning</th>
<th>Fischer-Tropsch synthesis reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>· High syngas yield</td>
<td>· Decrease in the sulfur compound concentration in the cleaned gas to less than 1 ppm</td>
<td>· Temperature control</td>
</tr>
<tr>
<td></td>
<td>· Oxygen-enriched air gasification</td>
<td>· Wet gas cleaning</td>
<td>· Catalyst lifetime extension</td>
</tr>
<tr>
<td></td>
<td>· Downdraft fixed-bed gasifier</td>
<td>· Dry gas cleaning using activated carbons</td>
<td>· Liquid-phase FT synthesis reaction</td>
</tr>
<tr>
<td></td>
<td></td>
<td>· Removal of CO$_2$ using zeolite and alumina</td>
<td>· Slurry bed reactor</td>
</tr>
</tbody>
</table>

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**Fig. 1** Photographs of a bench-scale BTL plant  
Left: Downdraft fixed-bed gasifier, Right: FT reactor (slurry bed reactor)

**Fig. 2** Flow diagram of a bench-scale BTL plant
2.2 Gas cleaning

The product gas obtained by woody biomass gasification contained sulfur compounds that would deactivate the FT catalysts\(^6\). In the gas cleaning step, in order to extend the lifetime of the FT catalysts, the sulfur compound concentration had to be decreased to less than 1 ppm. In the present study, the removal of sulfur compounds was carried out using a scrubber and a desulfurization tower that was packed with commercial activated carbons (TAC4; size: 1.70-4.75 mm; 50 kg; Japan EnviroChemicals, Ltd.). The product gas leaving the roots blower was fed into the desulfurization tower through the first compressor (Fig. 2). Subsequently, the cleaned gas was fed into a carbon dioxide removal tower packed with a mixture of commercial zeolite (Molecular Sieve 13X; size: 8×12 mm; 1.0 kg; Union Showa K.K.) and commercial alumina (TCG 205-A; size: 7×12 mm; 18 kg; Union Showa K.K.) in order to increase the syngas concentration; the resulting gas was pressurized up to 12.6 MPa through a second compressor and then it was stored in the second gas holder shown in Fig. 2.

2.3 FT synthesis reaction

The FT synthesis reaction is an exothermic reaction, and the deposition of wax, which is the product, on the surface of the catalyst during this synthesis would lead to its deactivation. Therefore, the liquid-phase FT synthesis reaction was employed; this type of reaction has advantages over the common gas-phase reactions in terms of temperature control, wax extraction, and extension of catalyst lifetime\(^6\). A slurry bed reactor (length: 1500 mm, id: 100 mm) was employed. Six hundred grams of Co/SiO\(_2\) (Co content: 20 wt%) catalyst, prepared by using an impregnation method, was introduced into the reactor and was reduced with H\(_2\) in situ at 400°C for 10 h under atmospheric pressure. After the reduction, 4 L of hexadecane was introduced as a solvent into the reactor, and the inner pressure was increased up to the desired level under a N\(_2\) flow rate of 20 NL/min. The inner temperature was increased up to 220°C by an electric furnace; further, the FT synthesis reaction was started by feeding the cleaned gas into the reactor. The operation time was approximately 5 h. The hydrocarbon liquid fuel contained fractions of gasoline, kerosene, and diesel along with wax with a carbon number greater than 5. The diesel and kerosene fractions and wax were obtained from the reactor after the FT synthesis reaction, while the vaporizable gasoline fraction and steam that left the FT reactor during the reaction were condensed by cooling at 5°C to obtain a liquid sample.

2.4 Product analysis

The gas sample obtained at each sampling port, denoted by SP in Fig. 2, was analyzed by GC-TCD (GC-8A; Shimadzu), GC-FID (GC-8A; Shimadzu), and GC-FPD (6890N; Agilent Technologies). The carbon content in the char and dust was measured by an elemental analyzer (EA1110; CE Instruments) and that in the wood vinegar was measured by a TOC meter (TOC-5000A; Shimadzu).
3. BTL plant operation

3.1 Syngas production from woody biomass by oxygen-enriched air gasification

Fig. 4 shows the time dependence of the temperatures of the combustion and reduction zones in the gasifier and the product gas flow rate for 21.0 vol% of oxygen. During the run, the temperatures of the combustion zone and reduction zone were 900-1000°C and 800-850°C, respectively, and the product gas flow rate was approximately 18 Nm³/h. For each value of oxygen content in the range of 21.0-31.5 vol%, the gasifier was steadily operated without any problems such as blockage. Table 3 shows the product distribution on a carbon basis. The result indicated that the total carbon balance for each value of oxygen content was almost 100 C-mol%. The conversion to gas on a carbon basis increased from 91.9 to 96.2 C-mol% with the oxygen content, while the conversions to char, dust, and wood vinegar were independent of the oxygen content. Tar production is an important issue pertaining to biomass gasification\(^6\). Loss would be attributed to the production of tarry compounds that were difficult to collect. A high oxygen content promotes the oxidation of tarry compounds; therefore, the conversion to gas would be increased while loss decreased. Fig. 5 shows the effect of oxygen content on the product gas composition and cold gas efficiency in oxygen-enriched air gasification. The product gas composition was estimated from the gas sample obtained at SP2, as shown in Fig. 2. With an increase in the oxygen content, the concentration of CO increased from 22.8 to 30.1 vol%, and that of H₂ also increased from 16.8 to 23.7 vol%, while that of N₂ decreased from 48.8 to 32.2 vol%. As a result, the cold gas efficiency increased from 81.3% to 87.8%. When the oxygen content was 27.6 vol%, the composition of product gas was as follows: 29.3 vol% of CO, 21.9 vol% of H₂, 11.0 vol% of CO₂, 2.0 vol% of CH₄, 0.4 vol% of C₂H₆, and 35.5 vol% of N₂. The average woody biomass feed rate on a dry basis was 8.2 kg/h, and the average product gas flow rate was 18.4 Nm³/h. In this case, the cold gas efficiency was 85.7% for the higher heating values of product gas (139.1 MJ/h) and wood (162.2 MJ/h). The CO₂ and CH₄ concentrations remained almost constant and were approximately 11 and 0.5 vol%, respectively. This trend with respect to CO₂ and CH₄ was noted in the simulation results provided by Mathieu et al\(^6\). With an increase in the oxygen content, the temperature in the reduction zone in the gasifier also increased owing to the promotion of the oxidation reaction. A high temperature in the reduction zone is favorable for promoting the reforming of hydrocarbon as tarry compounds (CnHm + CO₂ \(\rightarrow\) CO + H₂, CnHm + H₂O \(\rightarrow\) CO + H₂) with CO₂ and H₂O produced in the combustion zone, which would lead to an increase in the syngas yield with the oxygen content.

<table>
<thead>
<tr>
<th>O₂ concentration</th>
<th>Product distribution on a carbon basis [C-mol%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Vol%</td>
</tr>
<tr>
<td>------------------</td>
<td>-------</td>
</tr>
<tr>
<td>21.0</td>
<td>91.9</td>
</tr>
<tr>
<td>25.1</td>
<td>94.9</td>
</tr>
<tr>
<td>27.6</td>
<td>96.3</td>
</tr>
<tr>
<td>31.5</td>
<td>96.2</td>
</tr>
</tbody>
</table>

\(a\) SP2

\(b\) By difference

![Fig. 5 Effect of oxygen content on product gas composition and cold gas efficiency (SP2)](image)

3.2 Desulfurization and enhancement of syngas pressure by gas cleaning step

The product gas obtained at 27.6 vol% of oxygen in the gasification step was cleaned and compressed for the FT reaction. Fig. 6 shows the mass balance in this case. The product gas leaving the roots blower (18 Nm³/h) was fed into the desulfurization tower at 0.9 MPa at a flow rate of 5.5 Nm³/h through the first compressor. Fig. 7 shows the concentration of the sulfur compounds after the gasifier (SP1), scrubber (SP2), and desulfurization tower (SP3). H₂S
and COS were detected as sulfur compounds produced in the gasification. Using the scrubber, 78% of H₂S and 18.9% of COS were removed; subsequently, the concentration of both the sulfur compounds decreased to less than 5 ppb after passing through the desulfurization tower. The cleaned gas was fed into the zeolite-packed tower at 0.9 MPa at a flow rate of 5.5 Nm³/h to remove CO₂ (Fig. 6). The cleaned gas after the removal of CO₂ was fed into the first gas holder at 0.9 MPa at a flow rate of 2.0 Nm³/h. Fig. 8 shows the gas composition before (SP3) and after (SP4) the removal of CO₂. The concentration of syngas (CO + H₂) increased from 48.1 to 56.0 vol%, while that of CO₂ decreased from 12.1 to 0.6 vol% in the zeolite-packed tower. Then, the cleaned gas was compressed up to 12.6 MPa using a second compressor to obtain a feed gas for the FT synthesis reaction, whose composition at SP5 was as follows: 30.8 vol% of CO, 25.2% of H₂, 0.9 vol% of CO₂, 2.5 vol% of CH₄, 40.6 vol% of N₂, (5 ppb of H₂S, and (5 ppb of COS.

### 3.3 FT synthesis reaction using the cleaned gas

Table 4 shows the catalytic performance of the Co/SiO₂ catalyst in the FT synthesis reaction using the cleaned gas and the productivity of hydrocarbon liquid fuel in the BTL plant. The selectivity was evaluated from the compositions of the product gas collected at SP6 and obtained liquid sample. Fig. 9 shows the time dependence of temperature, pressure, and product gas flow rate in Run-2. After feeding the cleaned gas into the reactor, there was an increase in the temperature due to the exothermic reaction, while the product gas flow rate decreased until around 1300 due to the promotion of the FT reaction. After 1300, the temperature was controlled to be in the range of approximately 280-310°C; the product gas flow rate and pressure were almost stable since there were no problems such as blockage for 5 h. In both the runs, the chain growth probabili-

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**Table 4** FT synthesis reaction using cleaned gas and productivity of hydrocarbon liquid fuel in the BTL plant

<table>
<thead>
<tr>
<th>Pressure (MPa)</th>
<th>Temperature (°C)</th>
<th>W/F (mol)</th>
<th>CO Conv.</th>
<th>H₂ Conv.</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run-1</td>
<td>2.0</td>
<td>240-260</td>
<td>160.7</td>
<td>38.4</td>
<td>80.3</td>
</tr>
<tr>
<td>Run-2</td>
<td>3.0</td>
<td>280-310</td>
<td>86.9</td>
<td>36.2</td>
<td>76.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CO₂</th>
<th>CH₄</th>
<th>C₂</th>
<th>C₃</th>
<th>C₄</th>
<th>CO₂</th>
<th>L/d</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.83</td>
<td>78.0</td>
<td>5.3</td>
<td>1.3</td>
<td>1.5</td>
<td>17.2</td>
<td>1.1</td>
</tr>
<tr>
<td>0.85</td>
<td>73.0</td>
<td>8.3</td>
<td>1.3</td>
<td>1.6</td>
<td>14.6</td>
<td>1.9</td>
</tr>
</tbody>
</table>

a) The ratio of catalyst to feed gas rate  
b) Chain growth probability  
c) SP6
ties were 0.83 and 0.85, and these values were similar to those reported in the laboratory-scale results[8,11]. Table 4 shows that the reaction temperature, pressure, and ratio of the catalyst weight to the feed gas rate (W/F) would affect the catalytic performance of the Co/SiO$_2$ catalyst. In Run-2, the hydrocarbon liquid fuel was obtained from 26.6 Nm$^3$ of the cleaned gas per day for a feed gas rate of 18.5 NL/min, and the cleaned gas was produced from 13 kg of woody biomass, i.e., the production capacity of the BTL plant was 1.9 L of hydrocarbon liquid from 13 kg of woody biomass per day.

4. Improvement in the proposed BTL process

We showed the bench-scale production of a hydrocarbon liquid fuel from woody biomass via gasification. The following improvements in the proposed BTL process were considered. In the gasification step, the production of oxygen-enriched air and adjustment of the H$_2$/CO ratio are important issues. In the present study, approximately 30 vol% of oxygen-enriched air was fed into the gasifier by adding pure oxygen, whose production cost is relatively expensive, to the air flow. However, the oxygen-enriched air may be easily produced by using a commercial membrane even on a larger scale. On the contrary, the H$_2$/CO ratios obtained for each oxygen content were approximately 0.8, while a ratio of approximately 2 is favorable for obtaining high yields of the hydrocarbon fuel by the FT synthesis. The ratio can be varied by promoting a water gas shift reaction (CO + H$_2$O $\rightarrow$ CO$_2$ + H$_2$). The promotion in the gasification step at high temperatures such as 800-1000 $^\circ$C is not favorable since the reaction is exothermic and a large amount of input energy is required to elevate the steam temperature up to around 900$^\circ$C. Wilhelm et al. indicated that the introduction of a shift converter was one of the appropriate options to vary the H$_2$/CO ratio in the GTL process[12], where product gas composition was similar to that obtained in the BTL process. In our future study, we intend to introduce a shift converter after the gasifier and adjust the H$_2$/CO ratio at low temperatures such as 250-400$^\circ$C.

The wet gas cleaning process is generally employed; however, in the present study, this method was not effective for the removal of COS. On the contrary, dry gas cleaning using activated carbons under pressurized conditions led to a reduction in the concentrations of both the sulfur compounds from 2.0 ppm (COS) and 4.3 ppm (H$_2$S) to less than 5 ppb. If we consider the drain treatment and facility size, then the BTL process without the wet gas cleaning is found to be favorable. Therefore, after gasification, the tarry compounds would be mainly removed by the dry gas cleaning method using carbonaceous materials[13]. Subsequently, the sulfur compounds would be removed under pressurized conditions by passing the resulting gas through the desulfurization tower using activated carbons. Here, the regeneration of the used activated carbons is an important issue. It is thus necessary to design a BTL process that involves the regeneration of the activated carbons using the exhaust heat from the gasification and FT synthesis steps. The cleaned gas obtained in the present study contained approximately 40 vol% of N$_2$, which is inactive in the FT synthesis reaction. Conducting woody biomass gasification in the absence of air, such as CO$_2$ gasification, could be one of the feasible options since the product gas in this case would not contain nitrogen that is responsible for the decrease in the compression power and FT reaction pressure.

In the FT synthesis reaction, we showed the production of liquid fuel using the cleaned gas derived from woody biomass as a preliminary result. In the near future, we intend to systematically investigate this step in terms of

Fig. 9 Time dependence of temperature, pressure, and product gas flow rate in Run-2

Fig. 10 Photograph of liquid samples obtained by BTL plant operation

Left sample — upper phase: diesel and kerosene fractions + solvent (hexadecane), lower phase: wax
Right sample — upper phase: gasoline fraction, lower phase: water
not only the reaction conditions such as temperature, pressure, and catalyst lifetime but also the type of reactor. Fig. 10 shows a photograph of liquid samples obtained by the BTL plant operation. Since these samples were a mixture of gasoline, kerosene, diesel, wax, and water, the wax had to be converted into diesel and kerosene by hydrocracking after separating it from the mixture by distillation. The simulation result obtained using the BTL system indicated that the distillation step involved half the initial cost \(^{14}\). Therefore, in the FT synthesis reaction, it is necessary to develop a highly selective catalyst that enhances the diesel yield in order to develop a process without hydrocracking and distillation.

In this study, we demonstrated the production of a hydrocarbon liquid fuel from woody biomass on a bench scale as a preliminary result. In our future study, we will improve each step, including the estimation of liquid fuels such as diesel fuels.

5. Conclusion

Hydrocarbon liquid fuel was obtained on a bench scale from woody biomass via gasification using the bench-scale BTL plant. In oxygen-enriched air gasification, with an increase in the oxygen content from 21.0 to 31.5 vol%, the conversion to gas on a carbon basis increased from 91.9 to 96.3 C-mol%; and the concentrations of CO and H\(_2\) increased from 22.8 to 30.1 vol% and from 16.8 to 23.7 vol%, respectively. Further, the cold gas efficiency increased from 81.3 to 87.8%. When 27.6 vol% of oxygen was used as the gasifying agent, the product gas comprised 29.3 vol% of CO, 21.9 vol% of H\(_2\), 11.0 vol% of CO\(_2\), 2.0 vol% of CH\(_4\), 0.4 vol% of C\(_2\) hydrocarbon, 35.5 vol% of N\(_2\), 9.1 ppm of H\(_2\)S, and 5.3 ppm of COS. The subsequent gas cleaning and FT synthesis were carried out using the product gas. In the gas cleaning step, the concentrations of H\(_2\)S and COS decreased to less than 5 ppb after the gas was passed through a scrubber and desulfurization tower. During the removal of carbon dioxide, the concentration of syngas (CO + H\(_2\)) increased from 48.1 to 56.0 vol%, while that of CO decreased from 12.1 to 0.6 vol% when a tower packed with a mixture of zeolite and alumina was employed. The cleaned gas was compressed up to 12.6 MPa to obtain the feed gas for the FT synthesis, whose composition was 30.8 vol% of CO, 25.2% of H\(_2\), 0.9 vol% of CO\(_2\), 2.5 vol% of CH\(_4\), 40.6 vol% of N\(_2\), (5 ppb of H\(_2\)S and 5 ppb of COS. In the FT synthesis reaction step, a C\(_2\)- selectivity of 73.0% and chain growth probability of 0.85 was obtained at 3 MPa, 280-310°C, and a W/F of 86.9 g h/mol. The production capacity of the BTL plant was 1.9 L of hydrocarbon liquid from 13 kg of woody biomass per day.

Acknowledgement

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