Liquid Fuel Production from Woody Biomass
via Oxygen-enriched Air/CO₂ Gasification on a Bench Scale

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On a bench scale, we successfully produced 16 L/d, equal to 0.1 BPD (barrel per day), of hydrocarbon liquid fuel from woody biomass throughout a proposed biomass-to-liquid (BTL) process, which consisted of gasification, wet and dry gas cleaning, water-gas shift reaction, gas compression, and Fischer-Tropsch (FT) synthesis reaction. In the oxygen-enriched air/CO₂ gasification using a downdrift fixed-bed gasifier, the addition of CO₂ to oxygen-enriched air as a gasifying agent led to an increase in both the conversion to gas on a carbon basis and the syngas content because of the enhancement of CO₂ gasification (C + CO₂ → 2CO). The CO and H₂ contents increased to 40.8 vol%, 28.7 vol% and the N₂ content decreased to 6.9 vol% monotonously with an increase in the pure oxygen flow rate. When a mixture of 19.1/63.4/17.5 vol% of N₂/O₂/CO₂ was used as the gasifying agent, the conversion to gas on a carbon basis was 90.1 mol% and the product gas composition was 27.9 vol% H₂, 40.4 vol% CO, 21.2 vol% CO₂, 4.0 vol% CH₄, 1.0 vol% hydrocarbons with a carbon number greater than 2 (C₃+H₂C.) and 5.5 vol% N₂. Feed gas with a H₂/CO ratio appropriate for the FT synthesis reaction (57.4 vol% H₂, 28.5 vol% CO, 0.9 vol% CO₂, 5.0 vol% CH₄, 1.3 vol% C₃+H₂C., and 6.9 vol% N₂) was prepared through the water-gas shift reaction, desulfurization, CO₂ removal. In the FT synthesis reaction at 4 MPa and 290-320°C using a Ru/Mn/Al₂O₃ catalyst, the CO and H₂ conversions were 73.5% and 83.9%, respectively, and the chain growth probability was 0.82; further, the selectivity and space time yield of hydrocarbons with a carbon number greater than 5 as a liquid fuel were 81.4% and 1.793 kg/(kg-cat. h), respectively.

Key Words
Biomass, BTL, Gasification, Water-gas shift reaction, FT synthesis reaction

1. Introduction

In Japan, annually, approximately 40% of oil is used as transport fuel such as gasoline, kerosene, and light oil. In view of the global climate change and depletion of fossil fuel resources, biomass is one of the most promising renewable energy sources because it can be converted to not only liquid fuel but also materials such as plastic monomers. Some energy conversion technologies for converting biomass to first-generation biofuels (i.e., ethanol from sugarcane and vegetable oil from rapeseed) have been commercialized to address such problems. However, increasing production of the liquid fuel has led to an increase in the prices of various food products recently. Therefore, attention has been focused on second-generation biofuels derived from non-edible feedstock such as woody biomass since the feedstock does not compete with food products \[\text{1}^{\text{1}} - \text{2}\]. In particular, BTL technology has the advantage that the entire plant is transformed as feedstock, unlike conversion technologies employing saccharification and fermentation \[\text{3}\]. The technology basically consists of syngas (CO + H₂) production by gasification, gas cleaning, the FT synthesis reaction, hydrocracking of wax, and distillation. In addition to research studies on each unit operation of the process, the experimental, environmental, and economical aspects of the entire process have also been reported \[\text{4} - \text{5}\]. CHOREN has constructed a commercial BTL plant including CarboV\textsuperscript{®} gasification process at Freiberg in Germany; the annual production capacity is 18 million liters for 67500 t of biomass on a dry basis \[\text{6} - \text{6}\]. If this technology is commercially used from 2025 in Japan \[\text{10}\] although the quantity of collected biomass is smaller compared to that of the CHOREN
process, it is necessary to realize a total process with high efficiency by estimating a proposed process by simulation and enhancing liquid fuel productivity throughout the total process reciprocally.

Our research center (Biomass Technology Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Japan) has developed the total process using a bench-scale BTL plant constructed in 2007 in order to estimate the energy efficiency and CO₂ emission \(^{(13-15)}\). One of aims of the center is to increase the productivity of hydrocarbon liquid fuel corresponding to FT diesel beyond 15.9 L/d, equal to 0.1 BPD (barrel per day), at the plant by the end of FY2011. The center has already achieved a productivity of 7.8 L/d (0.05 BPD) by using a process that consists of oxygen-enriched air gasification and the FT synthesis reaction with a Co/SiO₂ catalyst \(^{(15)}\). In order to enhance both the liquid productivity and energy efficiency, it is necessary to reduce the amount of oxygen which is used as a gasifying agent, adjust the H₂/CO ratio of the feed gas in the FT synthesis reaction to 2, and enhance the catalytic performance of the FT catalyst. In this study, these requirements were satisfied at each unit operation of the process to achieve a liquid fuel productivity of 16 L/d (0.1 BPD).

### 2. Experimental

#### 2.1 Feedstock

Eucalyptus wood chips with sizes in the range of 20 to 30 mm were used as the feedstock. Table 1 shows the results of feedstock analysis.

#### 2.2 Outline of bench-scale BTL plant

Fig. 1 shows the flow diagram of the BTL plant. The BTL process proposed in the present study consists of the following steps: woody biomass gasification with oxygen-enriched air/CO₂ gas cleaning using a cyclone, a scrubber, a desulfurization tower, and two CO₂ removal towers (A and B); H₂/CO ratio adjustment using a water-gas shift converter; gas compression; and the FT synthesis reaction with a liquid phase. A mixture of oxygen-enriched air and CO₂ was supplied to the gasifier by mixing air, pure oxygen, and CO₂. For adjusting the H₂/CO ratio to a level appropriate for the FT synthesis reaction and for removing CO₂ formed during the reaction, a water-gas shift converter and CO₂ removal tower B were installed in 2010.

#### 2.3 Woody biomass gasification with oxygen-enriched air/CO₂

In the gasification step, a downdraft fixed-bed gasifier with a capacity of approximately 1 t/d was employed as

<table>
<thead>
<tr>
<th>Ultimate analysis [wt% daf basis]</th>
<th>Proximate analysis [wt%]</th>
<th>HHV (^{(c)})</th>
<th>LHV (^{(d)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>H</td>
<td>N</td>
<td>S (^{(a)})</td>
</tr>
<tr>
<td>-------</td>
<td>-------</td>
<td>------</td>
<td>---------</td>
</tr>
<tr>
<td>50.7</td>
<td>5.9</td>
<td>0.2</td>
<td>0.015</td>
</tr>
</tbody>
</table>

\(^{(a)}\) ion chromatography  \(^{(b)}\) By difference  \(^{(c)}\) Higher heating value  \(^{(d)}\) Lower heating value

![Diagram of the BTL plant](image-url)
shown in Fig. 2. Woody biomass was fed through a lock-hopper from the top of the gasifier and ignited by an ignition burner. Subsequently, air was supplied to the gasifier by using a forced fan to heat the combustion and reduction zones. During the heating, an exhaust gas leaving the cyclone was delivered to a flare stack. After both zones reached the required temperature, the forced fan was turned off and air was introduced into the gasifier using a roots blower. CO₂, which was used as a gasifying agent, was delivered to the gasifier through the gas line attached to the ignition burner, which could protect it from tarry compounds. Then pure oxygen was delivered at flow rates fixed by a mass flow controller. The product gas flow rate was adjusted by using the roots blower. In order to prevent any blockages in the gasifier, the height of the woody biomass was monitored by a level sensor, and the pressure difference (ΔP) between the points before and after the gasifier was adjusted to less than 5 kPa by changing the rotation speed of a grate at the bottom of the gasifier. The composition of the product gas was estimated by analyzing the gas collected at SP1 (Figs. 1 and 2).

The effect of pure oxygen flow rate on oxygen-enriched/CO₂ gasification was investigated in the range of 0 to 7 N m⁻³/h. The CO₂ flow rate was 1.7 N m⁻³/h. The product gas flow rate was 40 N m⁻³/h.

In order to prepare the feed gas for the FT synthesis reaction, the oxygen-enriched air/CO₂ gasification was performed for 6.5 h. The flow rates of pure oxygen and CO₂ were 7 N m⁻³/h and 2.1 N m⁻³/h, respectively. The product gas flow rate ranged from 40 to 42 N m⁻³/h. The woody biomass was fed intermittently and the average feed rate was 32 kg/h on a dry basis. After the composition of product gas collected at SP1 and temperatures and the pressure difference became stable, the product gas leaving the roots blower was delivered to the first gas compressor.

Gas, dust, wood vinegar, and char were obtained as the products (Fig. 2). The char was collected from the bottom of the gasifier intermittently. The dust in the produced gas in the gasifier was collected from the cyclone after leaving the gas using the roots blower. The wood vinegar was collected through a collection line by cooling the vapor generated in the pyrolysis zone in the gasifier.

2.4 Gas cleaning

The product gas obtained in the gasification step contained not only impurities such as sulfur compounds and tarry compounds but also CO₂, which functions as an inert gas in the FT synthesis reaction. Therefore, a scrubber, a desulfurization tower packed with commercial activated carbon (TAC4; size: 1.70-4.75 mm; 50 kg; Japan EnviroChemicals, Ltd.), and CO₂ removal towers A and B packed with commercially available activated alumina and zeolite were employed.

2.5 Adjustment of H₂/CO ratio

BTL system simulation suggested that unit operations such as methane reforming and water-gas shift reaction were needed to convert the product gas in the gasification step to the feed gas desirable for the FT synthesis reaction 15. In oxygen-enriched air gasification, the H₂/CO ratios of the product gases were almost 0.8 while CH₄ composition was less than 5 vol% regardless of the oxygen content in the

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![Fig. 2 Downdraft fixed-bed gasifier for oxygen-enriched air/CO₂ gasification](image-url)
gasifying agent. In the present study, the ratio was adjusted using a water-gas shift converter. The fixed bed reactor packed with a Cu/Zn catalyst (25 kg, MDC-7; Süd-Chemie Catalysts Japan, Inc.) was employed. A part of the cleaned gas leaving the CO$_2$ removal tower A (approximately 9 N m$^3$/h) was supplied to the reactor to promote the water-gas shift reaction (CO + H$_2$O $\rightarrow$ CO$_2$ + H$_2$) (Fig. 1). The reaction temperature was 200°C and the reaction pressure was 0.6 MPa. The steam flow rate was approximately 10 kg/h. An effluent gas from water-gas shift converter was mixed with a bypassed gas, and the gas mixture was delivered to the CO$_2$ removal tower B. The cleaned syngas leaving the removal tower was compressed and stored at 14.7 MPa in a second gas holder by using two gas compressors. The composition of the gas after the reaction was estimated by analyzing the gas collected at SP2 (Fig. 1).

2.6 FT synthesis reaction

In the FT synthesis reaction, a slurry bed reactor (length: 1500 mm; id: 100 mm) was employed because the liquid-phase FT synthesis reaction has some advantages over the gas-phase reactions in terms of the temperature control because of exothermic reaction and the wax extraction for increase in the catalyst lifetime. We have researched the enhancement of the catalytic performance in the FT synthesis reaction. On a laboratory scale, the Ru/Mn/Al$_2$O$_3$ catalyst prepared using RuCl$_3$ and Mn(NO$_3$)$_2$ as precursors by the impregnation method exhibited high and stable catalytic performance for CO conversion and high and stable space time yield for 40 h. Therefore, the Ru/Mn/Al$_2$O$_3$ catalyst (285 g, Ru content: 5 wt%) was used in the plant operation. The catalyst was reduced in situ under hydrogen atmosphere at 200°C and 2 MPa for 5 h in the FT synthesis reactor. After decreasing the temperature to room temperature and the pressure to atmospheric pressure, the catalyst was suspended in 3.5 L of hexadecane. The internal pressure of the reactor increased to 4 MPa under N$_2$ flow and the reactor started heating up. When the slurry temperature reached 100°C, we started stirring at 630 rpm. When the temperature reached 210°C, N$_2$ was replaced with syngas for 30 min by delivering syngas to the reactor at a flow rate of 1.8 N m$^3$/h. The FT synthesis reaction started when the flow rate was increased to 4.0 N m$^3$/h. The operation time was 6 h. Fractions of gasoline, kerosene, and light oil along with wax with a carbon number greater than 5 were defined as liquid fuel. The vaporous gasoline fraction and steam that left the FT reactor during the reaction were condensed in the condenser by cooling them from −1 to −3°C to obtain a liquid sample intermittently. The light oil and kerosene fractions and wax were obtained from the bottom of the reactor after the reaction. The composition of gas leaving the reactor was estimated by analyzing the gas at SP3 (Fig. 1).

2.7 Product analysis

The gas sample obtained in the gasification step was analyzed with a gas chromatograph with TCD (Micro GC 3000A; Agilent Technologies). The carbon content of the char and dust obtained in the gasification step was determined with an elemental analyzer (EA1110; CE Instruments) while that of the wood vinegar was obtained with a TOC meter (TOC-5000A; Shimadzu). The effluent gas and liquid hydrocarbons obtained in the FT synthesis reaction were analyzed with gas chromatographs with TCD (GC-8A; Shimadzu) and FID (GC2014; Shimadzu).

3. Results and Discussion

3.1 Syngas production by oxygen-enriched air/CO$_2$ gasification

The effect of the pure oxygen flow rate on the gasification behavior was investigated in the oxygen-enriched air/CO$_2$ gasification. Fig. 3 shows the change in temperatures in the gasifier and the induced air flow rate at different oxygen flow rates. Table 2 shows the product gas composition at different pure oxygen flow rates (Run-1). In Fig. 3, the induced air flow rate decreased with an increase in the pure oxygen flow rate from 0 to 7 N m$^3$/h. However, because the lower limit of the induced air flow rate in the data acquisition system was 4 N m$^3$/h, it was estimated that an air flow rate of 3.5 N m$^3$/h was induced at a pure oxygen flow rate of 7 N m$^3$/h by considering that 6.9 vol% of N$_2$ was contained in the product gas. The temperatures of the combustion and reduction zones fluctuated considerably with the oxygen flow rate; however, the average temperatures slightly increased from 900-950°C and 800-850°C, respectively. Table 2 shows that with increasing pure oxygen flow rate, the oxygen content in the gasifying agent increased from 19.5 to 63.4 vol% while the CO$_2$ content did not increase so much. It was difficult to change only the oxygen content because the product gas flow rate was fixed at 40 N m$^3$/h and the induced air flow rate changed. The CO and H$_2$ contents increased and the N$_2$ content decreased monotonously with an increase in the oxygen flow rate, and the product gas composition was 28.7 vol% H$_2$, 40.8 vol% CO, 19.1 vol% CO$_2$, 3.6 vol% CH$_4$, 0.8 vol% C$_2$H$_2$, and 6.9 vol% N$_2$ when 22.7/63.4/13.9 vol% of N$_2$/O$_2$/CO$_2$ was used as the gasifying agent. The syngas content was 69.5 vol%. In the gas compression step, high syngas content is favorable for decreasing the compres-
sion power. In this study, the oxygen-enriched air/CO₂ gasification was performed at a pure oxygen flow rate of 7 N m⁻³/h to prepare feed gas for the FT synthesis reaction.

Fig. 4 shows the change in temperatures of the combustion and reduction zones, pressure difference, and product gas flow rate with time for an oxygen flow rate of 7 N m⁻³/h and a CO₂ flow rate of 2.1 N m⁻³/h. During the run, the temperature of the reduction zone as well as the product gas flow rate and pressure difference was stable while the combustion temperature fluctuated vigorously. The average temperatures of the combustion and reduction zones were 900 and 810°C, respectively, and were similar to those inferred from Fig. 3. The product gas composition is shown as Run-2 in Table 2. In this case, the composition of the N₂/O₂/CO₂ as gasifying agent was 19.1/63.4/17.5 vol% by considering that the induced air flow rate was 2.9 N m⁻³/h and the N₂ content in the product gas was 5.5 vol%. Table 3 shows the product distribution on a carbon basis. The carbon balance was almost 100 C-mol%. For comparison, the product gas composition, product distribution, and carbon balance in the oxygen-enriched air gasifi-

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**Table 2** Product gas composition in oxygen-enriched air/CO₂ gasification

<table>
<thead>
<tr>
<th>Feed rate [Nm³/h]</th>
<th>Gasifying agent [vol%]</th>
<th>Product gas composition [vol%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Air</td>
<td>O₂</td>
</tr>
<tr>
<td>Run-1</td>
<td>22</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>7.0</td>
</tr>
<tr>
<td>Run-2</td>
<td>2.9</td>
<td>7.0</td>
</tr>
<tr>
<td>Run-3[1]</td>
<td>3.7</td>
<td>3.0</td>
</tr>
</tbody>
</table>

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**Fig. 3** Change in temperatures in the gasifier and induced air flow rate at different oxygen flow rates

**Fig. 4** Change in temperatures of the combustion and reduction zones, pressure difference, product gas flow rate with time (O₂: 7 N m⁻³/h, CO₂: 2.1 N m⁻³/h)
cation with 56.7 vol% of oxygen without CO$_2$ [14] are also shown as Run-3 in the Tables. Tables 2 and 3 indicated that the oxygen-enriched air/CO$_2$ gasification exhibited a higher conversion to gas (90.1 C-mol%) and a higher CO content (40.4 vol%) compared to those of oxygen-enriched air gasification (88.2 C-mol%, 36.5 vol%) while the H$_2$ content were almost the same. These results suggested that the addition of CO$_2$ as a gasifying agent led to the enhancement of CO$_2$ gasification (C + CO$_2$ → 2CO) even when the oxygen content remained almost unchanged.

3.2 Adjustment of H$_2$/CO ratio by water-gas shift reaction

We have previously reported the synthesis of hydrocarbon fuel from feed gas with a H$_2$/CO ratio of 0.8 via oxygen-enriched air gasification [11-14]. In the present study, the ratio in the product gas in the oxygen-enriched air/CO$_2$ gasification was 0.7 as mentioned in Table 2. Therefore, the oxygen-enriched air/CO$_2$ gasification and the water-gas shift reaction were simultaneously performed. Fig. 5 shows the change in the gas flow rates of the converter inlet and the mixture gas of the converter outlet and bypassed gas, and steam flow rate with time. Unfortunately, there was no data acquisition system recording the flow rate of the gas leaving the converter; the flow rate of the mixture of gas leaving the converter and bypassed gas is shown in Fig. 5 and the average flow rate was 25 N m$^3$/h. The average gas flow rate to the converter was 9 N m$^3$/h. The flow rates and the composition of the gas at the inlet and outlet of the converter fluctuated considerably because the water-gas shift converter was located between the CO$_2$ removal towers in the pressure swing adsorption method. Therefore, the gas stored in the second gas holder was regarded as that of which H$_2$/CO ratio was adjusted by the water-gas shift reaction. Table 4 shows the gas composition and the H$_2$/CO ratio was 2. Subsequently, the FT synthesis reaction was performed with the gas.

3.3 FT synthesis reaction

Fig. 6 shows the change in temperatures of the slurry and electric furnace, in the inlet and outlet gas flow rates, and in the reaction pressure with time in the FT synthesis reaction performed with the Ru/Mn/Al$_2$O$_3$ catalyst. First, the slurry was heated under N$_2$ flow at a furnace temperature of 450°C. The syngas was then delivered to the reactor at 1.8 N m$^3$/h with decreasing the furnace temperature to 400°C. When the slurry temperature reached 320°C after the syngas was delivered at 4.0 N m$^3$/h, the furnace temperature was gradually decreased to 320°C and the furnace was turned off. Subsequently, the slurry temperature was maintained in the range of 280 to 320°C by opening the furnace and cooling it with a fan—unfortunately, the gas was not stored in the second gas holder.

Table 3 Product distribution on a carbon basis

<table>
<thead>
<tr>
<th>Gasifying agent</th>
<th>Feed rate [Nm$^3$/h]</th>
<th>Composition [vol%]</th>
<th>Gas [C-mol%]</th>
<th>Char [C-mol%]</th>
<th>Dust [C-mol%]</th>
<th>Wood vinegar [C-mol%]</th>
<th>Loss [C-mol%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run-2</td>
<td>2.9</td>
<td>7.0</td>
<td>2.1</td>
<td>19.1</td>
<td>63.4</td>
<td>17.5</td>
<td></td>
</tr>
<tr>
<td>Run-3 [14]</td>
<td>3.7</td>
<td>3.0</td>
<td>0</td>
<td>43.3</td>
<td>56.7</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

Table 4 Composition of gas stored in the second gas holder

<table>
<thead>
<tr>
<th>H$_2$</th>
<th>CO</th>
<th>CO$_2$</th>
<th>CH$_4$</th>
<th>C$_2$+H$_2$</th>
<th>N$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>vol%</td>
<td>vol%</td>
<td>vol%</td>
<td>vol%</td>
<td>vol%</td>
<td>vol%</td>
</tr>
<tr>
<td>57.4</td>
<td>28.5</td>
<td>0.9</td>
<td>5.0</td>
<td>1.3</td>
<td>6.9</td>
</tr>
</tbody>
</table>

Fig. 5 Change in the gas flow rates of the converter inlet and the mixture gas of converter outlet and bypassed gas, and steam flow rate with time.
the reactor had no cooling system. The gas flow rates and reaction pressure were stable, except that they fluctuated slightly when the liquid sample of gasoline fraction and water was collected from the condenser intermittently. Table 5 shows the results of the FT synthesis reaction over Ru/Mn/Al2O3 catalyst. The CO and H2 conversions were 73.5% and 83.9%, respectively, and the chain growth probability was 0.82. The space time yield of hydrocarbons with a carbon number greater than 5 was 1.793 kg/(kg-cat.h). The productivity of liquid fuel was 16.0 L/d throughout the total BTL process. For comparison, the catalytic behavior of the Co/SiO2 catalyst18 is also presented in Table 5. In this case, the feed gas composition was 25.2 vol% H2, 30.8 vol% CO, 0.9 vol% CO2, 2.5 vol% CH4, and 40.6 vol% N2 derived from the wood. It is difficult to compare the catalytic behavior of the Ru/Mn/Al2O3 catalyst with that of the Co/SiO2 catalyst since the feed gas compositions were different; however, by using feed gas with an appropriate H2:CO ratio for the FT synthesis reaction, higher conversions were obtained. As a result, the space time yield in the case of the Ru/Mn/Al2O3 catalyst was higher compared to that for the Co catalyst (1.04 kg/(kg-cat.h)), while the contact time of syngas with the Ru catalyst was approximately 0.11 times the contact time with the Co catalyst. Liu reported that by using a standard gas with composition similar to that of the feed gas (60 vol% H2, 30 vol% CO, 7 vol% Ar, and 3 vol% N2), the FT synthesis reaction was performed over a Co/SiO2 catalyst at 3 MPa, 240°C, and a W/F value of 2.3 g h/mol 19. In this case, the space time yield of hydrocarbons with a carbon number greater than 5 was found to be 1.041 kg/(kg-cat.h). The Ru catalyst employed in the present study exhibited higher space time yield even for an almost identical contact time even when the feed gas derived from wood was used.

### 3.4 Improvements in the BTL process

We achieved a productivity of 16 L/d for liquid fuel from woody biomass via oxygen-enriched air/CO2 gasification and the FT synthesis reaction with the Ru/Mn/Al2O3 catalyst at the total BTL plant. The following improvements in the proposed process were considered. With respect to the yield of the liquid fuel throughout the proposed BTL process, it was found from the mass balance in Fig. 1 that although 768 kg of woody biomass on a dry basis was used to produce 960 N m3 of the product gas in the gasification step per day, only 187 N m3 of feed gas for the FT synthesis reaction was stored in the gas holder through both CO2 removal towers. When the FT synthesis reac-

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**Table 5** Results of the FT synthesis reaction over Ru/Mn/Al2O3 catalyst and productivity of liquid fuel throughout BTL process

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pressure (MPa)</th>
<th>Temp. (°C)</th>
<th>W/F (g·cat·h/mol)</th>
<th>CO conv. (%)</th>
<th>H2 conv. (%)</th>
<th>αval</th>
<th>Selectivity [mol%]</th>
<th>STY (L/d)</th>
<th>Productivity (L/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru/Mn/Al2O3</td>
<td>4.0</td>
<td>290-320</td>
<td>1.6</td>
<td>73.5</td>
<td>83.9</td>
<td>-</td>
<td>C3: 81.4</td>
<td>1.793</td>
<td>16.0</td>
</tr>
<tr>
<td>Co/SiO2: 18</td>
<td>4.0</td>
<td>280-340</td>
<td>9.3</td>
<td>36.0</td>
<td>76.4</td>
<td>-</td>
<td>C2: 87.5</td>
<td>1.040</td>
<td>7.8</td>
</tr>
</tbody>
</table>

a) Feed gas composition: H2/CO/CO2/CH4/C3+H/C + H2/N = 57.4/28.5/0.9/5.0/1.3/6.9
b) Feed gas composition: H2/CO/CO2/CH4/C3+H/C + H2/N = 25.2/30.8/0.9/2.5/0.0/40.6
c) Ratio of catalyst weight to feed gas flow rate
d) Chain growth probability
e) Space time yield of hydrocarbon with a carbon number greater than 5
f) Productivity of liquid fuel throughout BTL plant
tion is performed using all the feed gas (187 N m$^3$), 31.5 L (24.3 kg) of liquid fuel can be obtained, considering that the density of liquid fuel is 0.77 kg/L. As a result, 4.1 L (3.2 kg) of liquid fuel can be obtained from 100 kg of woody biomass on a dry basis. The conversion from woody to liquid fuel on a carbon basis corresponded to 4.4 C mol%.

Fujimoto et al. reported that 16.9 kg of liquid fuel was obtained from 100 kg of woody biomass on a dry basis by system simulation\textsuperscript{12}, which indicated that 19% of liquid fuel yield was obtained on a simulated yield basis. The use of CO$_2$ removal towers led to a drastic decrease in the syngas volume because a large part of the syngas delivered to both towers was used to regenerate saturated adsorbents in the towers. In this study, in order to remove CO$_2$ completely, two removal towers were installed before the FT synthesis reaction process. Future studies should investigate methods to enhance the yield of feed gas used in the FT synthesis reaction when only the CO$_2$ removal tower B is used.

In the gasification step, the addition of CO$_2$ to oxygen-enriched air in the gasifying agent led to an increase in the syngas content and a decrease in N$_2$, which is difficult to separate. An increase in the oxygen content of the gasifying agent leads to the input energy for producing oxygen-enriched air, while the addition of CO$_2$ in excess would lead to a decrease in the conversion to gas due to endothermic reaction. Therefore, it is necessary to optimize the composition of gasifying agent so that the maximum CO yield is achieved. Here CO$_2$ as a gasifying agent is required in the gasification method. It might be possible to recycle an exhaust gas leaving the CO$_2$ removal tower in the gasifier as a gasifying agent if CO$_2$ is effectively removed.

In this study, the H$_2$/CO ratio was adjusted to 2 for enhancing the liquid fuel yield. The water-gas shift converter was installed after the desulfurization tower and between the CO$_2$ removal towers at ambient temperature because sulfur compounds would deactivate the Cu-Zn catalyst. Therefore, the cleaned gas had to be heated to 200°C to promote the water-gas shift reaction. This configuration leads to a decrease in the energy efficiency. It is convenient to place the desulfurization unit operating at a temperature above 200°C and atmospheric pressure between the gasification step (900-1200°C) and wet gas cleaning step with the scrubber (ambient temperature). The dry gas cleaning technologies are preferable to the wet gas cleaning technology since the former technologies help in reducing the drainage disposal cost and plant size. In our proposed process, the moisture in the product gas obtained in the gasification step was removed using the scrubber. When the dry gas cleaning technology is applied to the present process, the removal of moisture is one of issues. The phenanthrene adsorption capacity of activated carbon at 150°C decreased with increasing moisture in the gas stream (steam/N$_2$/phenanthrene)\textsuperscript{21} while at room temperature the moisture in the product gas derived from wood had little effect on the adsorption capacities of light aromatic hydrocarbon tar and light PAH tar using a commercial activated carbon\textsuperscript{22}. We reported the removal of heavy tar derived from wood in the temperature range of 200 to 400°C by using activated carbons and charcoal derived through woody biomass gasification on a laboratory scale\textsuperscript{23–28} and need further studies about removal of light tar and sulfur compounds derived from wood. Moreover, the activated carbon tower downstream of the gasifier was installed on a bench scale and we will investigate the removal of tarry compounds and sulfur compounds with dry gas cleaning technology.

In the FT synthesis step, technically, the FT synthesis reactor needs a cooling system such that fresh solvent is supplied to the reactor during the run and the mixture of solvent and liquid product is collected from it for the precise control of the reaction temperature. Theoretically, in order to decrease the compression power, it is important to develop a catalyst that is highly active and selective at low pressures. In Japan, the use of equipments operated at more than 1 MPa is restricted by the high pressure gas safety law and their costs are extremely high compared to those of equipments operated at less than 1 MPa. Therefore, at a low pressure, highly active catalysts can significantly contribute to not only increasing the total energy efficiency but also decreasing the equipment cost.

BTL is a process for producing carbon-free fuel; however, in the near future, we intend thoroughly and carefully estimating the energy balance including not only the input energy for oxygen-enriched air production, gas compression, drainage disposal, steam generation, but also CO$_2$ emission, and economy throughout the total process.

4. Conclusion

We achieved a productivity of 16 L/d (0.1 BPD) of hydrocarbon throughout a BTL process that involved oxygen-enriched air/CO$_2$ gasification, water-gas shift reaction, and the FT synthesis reaction with a Ru/Mn/Al$_2$O$_3$ catalyst. In the gasification step, the CO and H$_2$ contents increased and the N$_2$ content decreased monotonously with an increase in the pure oxygen flow rate. When the composition of N$_2$/O$_2$/CO$_2$, which was used as a gasifying agent, was 19.1/63.4/17.5 vol%, the conversion to gas on a carbon basis was 90.1 C mol% and the product gas composition was 27.9 vol% H$_2$, 40.4 vol% CO, 21.2 vol% CO$_2$, 4.0

vol% CH₄, 1.0 vol% C+H₂, and 5.5 vol% N₂. The addition of CO₂ to oxygen-enriched air led to an increase in both the conversion to gas and the syngas content because of the enhancement of CO₂ gasification even when the oxygen content remained almost unchanged. Using the water gas shift converter, the H₂/CO ratio of the feed gas for the FT synthesis reaction was adjusted to 2. In the FT synthesis reaction involving the Ru/Mn/Al₂O₃ catalyst, the CO and H₂ conversions were 73.5% and 83.9%, the chain growth probability was 0.82; further, the selectivity and space time yield of hydrocarbons with a carbon number greater than 5 were 81.4% and 1.793 kg/(kg·cat. h), respectively, at 4 MPa and 290-320°C.

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References

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