Effect of Operating Parameters on Hydrothermal Liquefaction of Agricultural Waste

○Joko Sulistyo Yekti1, Teppei Nunoura2, Fumiyuki Nakajima2, Kazuo Yamamoto2
1) Department of Urban Engineering, the University of Tokyo, Japan
2) Environmental Science Center, the University of Tokyo, Japan

1. Introduction

Sustainable energy production from agricultural waste is one of the great focuses nowadays. Hydrogen production by supercritical water gasification (SCWG) is one promising process. At supercritical condition (T > 374°C and P > 22.1 MPa), water acts as homogenous non-polar solvent of high diffusivity and high transport properties, thus it is able to dissolve organic compounds and gases. However, there are still some technical challenges of SCWG. Difficulty in continuous supply of solid biomass into the reactor is one of the challenges, while the other is the formation of chars and tars from complex chemical mechanism during direct heating of lignocellulosic biomass.

The use of hydrothermal liquefaction process as pretreatment of SCWG is important, not only to make solid biomass into fluid phase, but to extract hemicellulose, cellulose, and lignin separately. It is known that gasification efficiency of SCWG process becomes worse when these compounds are gasified together. The fact that these compounds can be liquefied separately depending on the operating conditions makes this hydrothermal liquefaction technically applicable as the pretreatment process.

This study was carried out to determine the effect of operating parameters (temperature, pressure and heating rate) on the liquefaction of biomass compounds. Experiments were conducted at pressure of 5-25 MPa, temperature range of 200-300°C with different heating rate using semi-continuous flow reactor system.

2. Experimental Procedures

2.1. Apparatus and Operating Procedures

Figure 1 shows the apparatus for the hydrothermal liquefaction experiment. Rice hull was used as a representative agricultural waste. 1.00 g (dry mass) of rice hulls was manually inserted into SUS316 stainless steel reactor tube with 10 cm length and inner diameter of 10.1 mm. At both ends of the reactor, metal screen was placed to prevent the outflow of rice hulls. After the reactor was set, deionized water with flow rate of 2 mL/min was flown to the reactor and the system was pressurized to desired level by using a back pressure regulator. Subsequently, the reactor was put into the heater. Two types of heater were used in this experiment to identify the effect of heating rate:

1. Tubular furnace. The reactor was put inside the furnace and the time needed to reach 200, 250 and 270°C from 25°C was measured to be 8, 10 and 12 min, respectively.
2. Salt bath heater. The reactor was immersed in the molten salt bath, which was already heated to the desired temperature. Time needed to reach 220°C from room temperature was measured to be 30 s.

When the reactor reached the desired temperature, it was regarded as “0 min of time-on-stream” in the experiments; and the effluent from the reactor was collected until 90 min of heating.

[Figure 1. Experimental Set-up using Salt Bath Heater]

P: Pressure Gauge; TC: Thermocouple; BPR: Back Pressure Regulator; PRV: Pressure Relief Valve

[Corresponding author]: Teppei Nunoura, Kashiwanoha 5-1-5, Kashiwa, Chiba 277-8581, Japan, Environmental Science Center, The University of Tokyo  Tel: 81-4-7136-5701, Fax: 81-4-7136-4204; Email: nunoura@esc.u-tokyo.ac.jp

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time-on-stream for most of the runs. In the two-step liquefaction experiment (Run H in Table 1), however, the effluent from the reactor at 220°C (in the salt bath) was collected for 70 min, and then the bath temperature was increased to 300°C with continuing the sampling for another 90 min (in total, 160 min). The time needed to reach 300°C from 220°C was 28 min.

At the sampling point, all the liquid products were collected, with changing a vial every 10 min. The gaseous products were collected using aluminum sampling bags.

At the end of the experiment, water pump was turned off and the system was depressurized. The reactor was taken out from the heater, and suddenly cooled down using a water bath. The solid residue inside the reactor was collected, dried, and analyzed for its carbon content. The system line itself was cleaned by flowing water, acetone and then water again sequentially by using the pump. For each run, the reactor and the tubing line were replaced with brand new ones to remove possible contamination from the previous runs.

2.2. Run Condition

Table 1 shows the reaction conditions. The flow rate of water fed into the reactor was 2 mL/min. Runs A to F were conducted by using the tubular furnace with slow heating rate, while the salt bath was used as a heater with high heating rate for runs G and H.

2.3. Analyses

Total carbon analysis for solid residue after each run as well as for raw rice hulls, was conducted using Shimadzu TOC-5000A, coupled with the Solid Sample Module. Lignin content of the residues was analyzed following the ASTM E-1758-01 procedure using a spectrophotometer. All the liquid products, including the liquid obtained from the cleaning process were analyzed for their TOC content using Shimadzu TOC-V and for their sugar contents by the HPLC (Shimadzu LC-10Advp) use a Transgenomic\textsuperscript{TM} CARBOSep Coregel 87P column with a diode array detector, Shimadzu SPD-M10Avp. As for gas products, it was analyzed by using Shimadzu GC-TCD 2014 with argon gas as the carrier.

Table 1. Experimental Conditions

<table>
<thead>
<tr>
<th>Run Code</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
</tr>
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<td>250°C</td>
<td>270°C</td>
<td>220°C</td>
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<td>10 MPa</td>
<td>15 MPa</td>
<td>25 MPa</td>
<td>5 MPa</td>
<td>5 MPa</td>
<td>23.5 MPa</td>
<td>23.5 MPa</td>
</tr>
<tr>
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<td>90 min</td>
<td>90 min</td>
<td>90 min</td>
<td>90 min</td>
<td>90 min</td>
<td>90 min</td>
<td>160 min</td>
</tr>
</tbody>
</table>

3. Results and Discussions

The TOC concentrations of the liquid effluent from all runs showed almost similar time profiles. Figure 2 is an example obtained from run G. The TOC reached a maximum at 15 min of time-on-stream, and then started to decrease. 90 min reaction time was set because there was no longer significant decrement in TOC values. Total carbon of 1.00 g raw rice hulls was measured to be 0.527 g. Solid residues after the liquefaction runs retained 4.5 % to 9.1 % of initial carbon, while carbon contained in gaseous product was only 0.003 % in average, and the remaining part was all liquefied with maximum carbon recovery of 98 % for run H.

Figures 3 and 4 show the effects of temperature and pressure on the amount of carbon in solid residue, respectively. Temperature increase did not show clear correlation to the carbon content, while the increase of pressure at constant temperature 200°C gave smaller carbon amounts in the solid residue. The increase of water density at higher pressure, which in turn increased the accessibility of water to biomass, seems to be the reason [1], while the increase of temperature that would reduce the viscosity of water did not show clear correlations in the reaction with biomass.
From the HPLC analysis of the effluents from runs A-F, five sugars listed in Table 2 were detected, covering 48 to 85 % of the TOC amount. The largest portion of the sugars was cellobiose, which was followed by glucose, xylose, mannose, and galactose. The unidentified compounds are supposed to include derived products of lignin, because lignin was not detected from the solid residue. Gas product was detected in the runs C to F, but in very small amounts. The main component of the gas was CO₂, which could be the product of biomass pyrolysis as well as the water-gas shift reaction as CO + H₂O $\rightarrow$ CO₂ + H₂. The other gases detected were H₂ and CO but both were below the quantifiable limit.

The two-step dissolution experiment (Run H), gave a 1.65-fold higher amount of TOC in the liquid products compared with the result from liquefaction at a single temperature of 220°C (Run G). Note that prolongation of run G until 160 min of time-on-stream would not give as high TOC amount as observed in run H, because the TOC concentration in the effluent of run G was expected to decrease monotonically after 90 min (Figure 2). The reason of much larger extent of liquefaction in run H is the dissolution of the crystalline part of cellulose, which is known to dissolve at higher temperatures than hemicelluloses and lignin, as can be seen in Figure 5. This TOC profile suggests that separate delivery of cellulose and other components of biomass into the SCWG reactor is possible through the hydrothermal liquefaction pretreatment.

4. Conclusions

The effect of operating parameters on hydrothermal liquefaction of rice hulls was studied within 200-300°C at pressure of 5-25 MPa. Very trivial amount of gaseous products (mainly CO₂) were detected. Carbon content in lignin-free solid residue was accounted to be 4.5-9.1 %, while the rest of carbon was liquefied. Five sugars which are beneficial for SCWG process were detected as the main components in the liquid products, with cellobiose as the highest portion. Temperature increase did not show clear correlation to carbon content in solid residue, while the increase of pressure gave smaller carbon residue amounts (i.e., larger extent of liquefaction). Finally, two-step liquefaction experiment gave an increase of TOC amount in liquid product compared with single-step liquefaction at 220°C.

References