Supercritical Water Gasification Staged at Intervals for Hydrogen Fermentation Residue of Food Waste

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To circumvent the problem of reactor plugging in supercritical water gasification (SCWG), we proposed an SCWG process operated at intervals with a continuous-flow system (10 kg/d) configured to feed water and feedstock in alternate steps. Hydrogen fermentation residues of soybean fiber and restaurant food waste (SFHFR and RWFR, respectively) were employed as feedstock, and fine activated carbon was used as catalyst. Feedstocks of 2.0-10.0% SFHFR were gasified in a tubular reactor at 600°C, 25 MPa with a residence time of 60-105 s. An 8% concentration SFHSR was gasified with a carbon gasification efficiency of 0.75 without plugging. A 4% RWFR, a feedstock composed of more diverse substances, was gasified with a carbon gasification efficiency of 0.57.

Key Words
Supercritical water gasification, Fermentation residue, Activated carbon catalyst, Interval operation, Biomass

1. Introduction

Society nowadays need new and better ways to reduce and recycle food wastes. The Japanese population discharges about 20 Tg of food waste annually, of which 16 Tg is disposed of unused1. The “Food Recycling Law,” a legislation enforced in 2001 and revised in 2007, seeks to reduce these levels by mandating recycling, heat recovery, control of discharge amounts, and volume reductions for food waste in the food sector. While heat recovery appears to be the most promising option for the processing of food waste, the high water content of food waste (usually more than 80%) poses challenges. The large energy consumption required to produce the heat for evaporation lowers the efficiency of the system.

To remedy this situation, a method has been proposed for the recycling of food waste into fuel gas through a combined process of hydrogen fermentation, methane fermentation, and supercritical water gasification 2: First, food waste is treated by hydrogen fermentation to collect hydrogen gas. Next, the solid residue is gasified by supercritical water gasification to retrieve energy while the waste water is treated by methane fermentation.

Supercritical water gasification has been a recent subject of focus as a promising technique for energy recovery from biomasses with high moisture content. Organic compounds in supercritical water are gasified easily into gases such as hydrogen, methane, and carbon dioxide. Many earlier studies have investigated the supercritical water gasification of biomass 3. Real biomass feedstocks have included diverse substances such as potato 4, baby food 5, sawdust 6, and sewage sludge 7. The catalyst tested for efficient supercritical water gasification has also been diverse, ranging from carbon 4, and alkali 5 to nickel 9 and ruthenium 10. One of the latest approaches is to use fine activated carbon 8. Suspended fine activated carbon holds particular promise as a catalyst, as it helps to prevent plugging of the reactor in addition to attaining high gasification efficiency. It does not, however, wholly eliminate the plugging. In this study we propose a method for preventing reactor plugging through an operation staged at intervals by supplying water at a high flow rate alternately between feedstock supplies.

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There have been no earlier reports on this type of supercritical water gasification staged at intervals. The purpose of this study is to confirm the effectiveness with which this operation circumvents reactor plugging.

2. Experimental

2.1 Experimental apparatus
We developed a continuous flow system (10 kg/d) for gasifying food waste hydrogen fermentation residue in supercritical water with a fine activated carbon catalyst. Fig. 1 shows the experimental apparatus. The system is composed of a feedstock tank equipped with a mixer, two syringe pumps (syringe volume, 0.5 L), an interval pump (Nihon Seimitsu Kagaku Co., Ltd.), a heat exchanger (length, 1.3 m; inner tube diameter, 3/8 mm; outer tube diameter, 8/14 mm), a tubular reactor (length, 15.5 m; diameter, 4/8 mm; stainless steel), a cooler, two solid-liquid separators, a back pressure regulator, and a gas-liquid separator. Temperatures and pressures are measured at the positions shown in Fig. 1.

The feedstock is initially heated to about 390°C with the heat exchanger, then immediately heated to 600°C in the reactor. The reactor effluent is cooled twice, first with the heat exchanger and then with the cooler. Next, the effluent passes through the solid-liquid separator and is separated into gas and liquid in the gas-liquid separator. The gasification temperature and pressure are 600°C and 25 MPa, respectively.

2.2 Non-interval operation
The system was run in continuous operation without interval staging for comparison with the staged operation at intervals. The process was tested the gasification of soybean fiber hydrogen fermentation residue (SFHFR). The syringe pump supplied feedstock at a rate of 7 cm³/min without the alternate supply of water.

2.3 Interval operation
The equipment was operated by supplying water and feedstock alternately. The syringe pump supplied feedstock at a rate of 7 cm³/min and the supply time was changed from 0.5 to 6 min. The interval water was supplied in an amount necessary to prevent the feedstock from stagnation in the low-temperature position of the heat exchanger. The volume of the inner tube of the heat exchanger was 9.2 cm³ and the water supplied by the interval pump was at almost an equal volume. The average temperature of the inner tube was about 210°C and the corresponding water density was about 900 kg/m³. The interval water supply times were set at 0.3 and 0.4 min, the periods necessary to supply interval water in actual volumes of 9.05 and 13.1 cm³, respectively. The syringe pumps and the interval pump were operated in alternate stages. The average flow rate of the total flow of water and feedstock ranged from 7.98 to 13.9 cm³/min. The residence time in the reactor was 120 s when the feedstock supply rate was 7 cm³/min. The average residence time in the reactor calculated from the average supply flow rate of the interval operation ranged from 105 to 60 s. Both SFHFR and RWHFR were gasified in this operation.

2.3.1 Influence of water supply time
We examined the influence of the water supply time in the interval operation with a 2% solid concentration SFHFR. Two water supply times were tested, 0.3 and 0.4 min. The feedstock supply time was changed from 2 to 6 min. Under these conditions, the average residence time in the reactor ranged from 78 to 105 s.

2.3.2 Influence of feedstock supply time and feedstock concentration
Next, we examined how the feedstock supply time and feedstock concentration influenced the effective supply of SFHFR feedstock to the reactor. The actual feedstock solid concentrations were set at 2, 4, 8, and 10%. The levels corresponded to the feedstock solid concentrations of the reactor of 0.9, 1.7, 3.5, and 4.4% in the reactor, assuming plug flow for the interval operation. The interval pump supplied water for 0.3 min. The feedstock supply time was adjusted between 0.5, 1, and 2 min, which corresponded to the average flow rates of 13.9, 11.5, and 9.6 cm³/min, respectively.

2.3.3 Gasification of RWHFR
Our next experiment was to gasify a 4% RWHFR feedstock. The gas composition, gas generation, TOC removal (η), and carbon gasification efficiency (γ) were compared with those obtained in the gasification of a 4% SFHFR feed-
stock. The water supply time was 0.3 min, the feedstock supply rate was 7 cm³/min, and the feedstock supply time was 1 min.

2.4 Analysis

The amount of carbon in the gas (C₇) was calculated based measurements by a meter (Shinagawa Co) and an analysis of the gas composition (H₂, CH₄, CO₂, C₂H₆, C₃H₆, and CO) by a gas chromatograph (Shimadzu GC-8A). The amounts of carbon in the TOC (C) and IC (C) of the effluent water were determined with a TOC analyzer (Shimadzu TOC-5000A). The measurements and analysis of the gas was conducted after the gas generation rate reached steady state.

2.5 Feedstock

Hydrogen fermentation residues of soybean fiber and restaurant food waste (SFHFR and RWHFR, respectively) were supplied from Sapporo Beer Co., Ltd. Feedstock solid concentration was adjusted and activated carbon (74 μm pass > 90%, Kuraray Chemical CO., LTD) was added to the feedstock by a 1 wt% of its total weight. The SFHFR and RWHFR were analyzed with an elemental analyzer (Perkin-Elmer 2400D). The Carbon, the nitrogen, the hydrogen, and the oxygen in SFHFR and RWHFR were used to determine the carbon content of the supplied feedstock (C₇) and to calculate the rate of TOC removal (ηₗ) and efficiency of carbon gasification(ηₑ), as defined by Eqs. 1 and 2, respectively. Table 1 shows the results of the elemental analysis of SFHFR and RWHFR.

\[ \etaₗ = 1 - C / C₇ \]  
\[ \etaₑ = (C₇ + C) / C₇ \]

3. Results and Discussion

3.1 Non-interval operation

In the test operation without intervals, we observed pressure rises induced by plugging at the low-temperature position even with the 2% concentration feedstock. This pressure rise was observed after about 1 h from start of supplying feedstock. While, in the case of supplying 1 wt% activated carbon without feedstock, plugging was not observed in less than 6 h. Cellulose decomposes rapidly at around 250°C to form water-soluble product without catalyst. Noting this, we speculated that the un-solubilized feedstock at low temperature may have caused the plugging.

3.1.1 Influence of water supply time

Fig. 2 shows the amount of gas generated with the water supply times set to 0.3 and 0.4 min. A change of the feedstock supply time changes the residence time in the reactor even when the water supply is the same (as shown in the abscissa). More gas was generated as the residence time increased, but no large difference was found in the extent of the increase in gas generation between the test operations at water supply times of 0.3 and 0.4 min. Fig. 3 shows the corresponding carbon gasification efficiency. The carbon gasification efficiency also increased as the residence time grew longer, and again, no large difference was found between the water supply times of 0.3 and 0.4 min. These results suggest that the average residence time is the main determinant of the gasification efficiency in the operation staged at intervals. The carbon gasification efficiency reached 0.8, but only for the residence time of 105 s. A longer residence time was necessary for the complete gasification of SFHFR. TOC removal was 0.9 for all cases.
implying tarry material production.

3.1.2 Influences of feedstock supply time and feedstock concentration

Figs. 4 and 5 show how the feedstock supply time and feedstock concentration influenced the amount of gas generation and the carbon gasification efficiency ($\eta_c$), respectively. The 1 min feedstock supply time yielded the highest $\eta_c$ in this study. The carbon gasification efficiency began to decline at concentrations higher than 8% and reached an efficiency of 0.56 at the 10% concentration. The tarry material produced in the experiments was likely to have been a result of the high feedstock concentration. The brownish color of the liquid effluent observed at this high concentration supports this. Less gas was generated at a feed supply time of 2 min than at 1 min, and plugging occurred at the entrance of the reactor when the 8% concentration feedstock was supplied for 2 min. A longer feedstock supply time results in a decline in the average flow rate in this kind of system, which in turn leads to a slower feedstock heating rate in the heat exchanger. A slow heating rate, meanwhile, is known to enhance the tarry material production, which in turn reduces the gas generation rate. This mechanism explains the lower gas generation for the 2 min feed supply time in our experiments. In our test at the 0.5 min supply time, the amount of gas generation and carbon gasification efficiency were both low. This may have been due to the short residence time. Fig. 6 summarizes above. Though carbon gasification efficiency lowered with each reason, only in the case of the 2 min supply time, the plugging occurred. This fact suggests that the low average flow rate also influenced plugging.

Fig. 7 shows how the feedstock concentration in the reactor influenced the gas composition in the test operation with the water supply and feedstock supply times set at 0.3 min and 1 min, respectively. An increase in the feedstock concentration led to an increase in the CH$_4$ fraction, while the H$_2$ fraction was approximately constant.

Fig. 8 shows the theoretical gas composition calculated by STANJAN$^{14}$, an application used for calculating chemi-
tatural equilibrium. The pattern of increasing CH$_4$ at higher 
feedstock concentrations agrees with the result shown in 
Fig. 7, while the H$_2$ fraction decreased against experimen-
tal data of Fig.7. Additionally, the values themselves are 
very different. These results clearly demonstrate that no 
chemical equilibrium was reached, because of lack of resi-
dence time. This meant that the relatively poor hydrogen 
production from methane was also responsible for the de-
crease in gas generation in the operation with a high feed-
stock concentration.

Figs. 9 shows gas yields in the experiments and in the 
calculations by STANJAN, respectively. The gas yields of 
H$_2$ differed markedly. The actual CH$_4$ yield, meanwhile, 
was higher than the thermodynamic prediction, implying 
that the CH$_4$ was initially formed and converted into H$_2$ 
afterwards. Thus, large difference of the amount of gas gen-
eration between experimental and calculated values should 
have been caused by the insufficient conversion of CH$_4$ into 
H$_2$. No CO was detected in the experiment. This is usual 
for supercritical water gasification and consistent with the 
thermodynamic prediction.

3.1.3 Gasification of RWHFR

Table 2 shows the result of gasification of a 4% concen-
tration RWHFR compared with that of SFHFR at the same 
concentration. The former generated almost the same 
amount of gas as the latter, but with a much lower carbon 
gasification efficiency. SFHFR is mainly composed of soy-
bean fiber. RWHFR contains substances other than fiber, 
such as fat and proteins. The lower gasification efficiency 
of RWHFR is unsurprising. Supercritical water gasification 
of sugars or sugar polymers are reported to interact with 
other compounds such as fat, protein, lignin $^{[2]}$, and we 
confirmed decrease of gas generation from food waste model 
compared with glucose in supercritical water $^{[6]}$, thus this 
interaction can sometimes reduce the gasification efficiency.

<table>
<thead>
<tr>
<th>Gas composition</th>
<th>4% SHSRF</th>
<th>4% RWHFR</th>
</tr>
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<tbody>
<tr>
<td>H$_2$ [-]</td>
<td>0.35</td>
<td>0.43</td>
</tr>
<tr>
<td>CH$_4$ [-]</td>
<td>0.18</td>
<td>0.19</td>
</tr>
<tr>
<td>CO$_2$ [-]</td>
<td>0.39</td>
<td>0.29</td>
</tr>
<tr>
<td>C$_2$H$_4$ [-]</td>
<td>0.016</td>
<td>0.012</td>
</tr>
<tr>
<td>C$_2$H$_6$ [-]</td>
<td>0.06</td>
<td>0.08</td>
</tr>
<tr>
<td>Gas generation [L/h]</td>
<td>10.7</td>
<td>9.9</td>
</tr>
<tr>
<td>$\eta_1$ [-]</td>
<td>0.92</td>
<td>0.95</td>
</tr>
<tr>
<td>$\eta_2$ [-]</td>
<td>0.77</td>
<td>0.57</td>
</tr>
</tbody>
</table>

4. Conclusion

In this study we proposed and investigated a process for 
the supercritical water gasification of SFHFR staged inter-
vals. We also discussed the effectiveness with which this 
interval operation prevents reactor plugging. The follow-
ing findings were obtained.

- The Feedstock before solubilization at low temperature 
  seems to be the cause of the reactor plugging in gasifi-
cation without staging at intervals.
- The staged operation in intervals effectively prevents 
  reactor plugging.
- The average residence time is the main determinant of 
  the gasification efficiency in the staged operations in 
  intervals.
- A short residence time due to a longer water supply time 
  results in a low gasification efficiency.
- An 8% concentration feedstock was successfully gasified 
  with a carbon gasification efficiency of 0.75 using equip-
  ment configured to operate at intervals.
- A 4% RWHFR was gasified continuously, but with a 
  lower carbon gasification efficiency than the gasification 
  of SFHFR at the same concentration.

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