

# Hydrothermal conversion of municipal organic waste into resources

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## Abstract

Sub- and supercritical water have been focused on as an environmentally attractive reaction media where organic materials can be decomposed into smaller molecules. We applied a hydrothermal reaction in subcritical water to the treatment of rabbit food as a model municipal solid waste. The reaction was carried out in a batch reactor at the temperature range of 473–623 K or in a semi-continuous reactor with the temperature profile from 473 to 573 K. The liquid reaction products were separated into water-soluble and water-insoluble parts. The water-soluble part was analyzed in terms of glucose and organic acids. For the batch reactor, the largest amount of water-soluble component was approximately 50%. Major organic acids detected were acetic acid and lactic acid. The largest yields were 2.6% for acetic acid and 3.2% for lactic acid. The largest yield of glucose was 33% at 523 K. For the semi-continuous reactor, the glucose yields were 11.5%, 3.9% and 8.7% in each fraction obtained at 473, 523, and 573 K, respectively. © 2003 Elsevier Ltd. All rights reserved.

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## 1. Introduction

Waste treatment is one of the most important and urgent problems in environmental management. A zero emission process for the efficient treatment of biomass waste should be developed. Biomass is an important source of energy and chemicals, which are synthesized from carbon dioxide and water using solar energy. The development of a process that could recover chemical resources from biomass waste to control the circulation of carbon in the biosphere is desirable.

Water near its critical condition (647 K, 22.1 MPa) has been tested as environmentally friendly reaction media. Sub- and supercritical waters have unique features with respect to density, dielectric constant, ion product, viscosity, diffusivity, electric conductance, and solvent ability. Two major reactions in sub- or supercritical water are oxidation and hydrolysis. Supercritical water oxidation, a process that converts organic materials completely into carbon dioxide, water, and nitro-

gen, has been extensively studied (Goto et al., 1997, 1998) and commercialized.

Another important process is the hydrothermal conversion of organic materials into useful chemicals through hydrolysis or pyrolysis in sub- or supercritical water (Arai, 1995). In these reactions, the ion product and dielectric constant play an important role. Below the critical point the ion product of water increases to  $6.34 \times 10^{-12}$  at approximately 523 K, then decreases to  $1.86 \times 10^{-16}$  at the critical point (Marshall and Franck, 1981).

Biomass is a useful feed material for energy and chemical resources. The hydrolysis of cellulose has been studied in sub- and supercritical water (Bobleter, 1994, Mok and Antal, 1992, Sasaki et al., 1998, 2000). Cellulose can be converted to glucose, which is then further converted into valuable components through chemical or bioprocesses. Organic acids are also produced in the reaction of the organic materials in biomass. Among organic acids, lactic acid is considered a useful chemical for the production of polymeric lactic acid in biodegradable plastics. Sakaki et al. (1996, 2002) and Ando et al. (2000) examined the hydrothermal decomposition of cellulose and plant biomass in subcritical water using batch or semi-batch reactors. The conversion of fish

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meat to useful chemicals has also been studied and the organic acids and amino acids produced were analyzed (Yoshida et al., 1999).

In the present study, the authors investigated the decomposition of municipal organic waste in subcritical water. Municipal wastes often contain cellulosic materials could be converted to glucose. Rabbit food was selected as a model municipal waste containing cellulose. A batch reactor and a semi-continuous reactor were used. The products were analyzed to determine organic acid and glucose content. The effects of temperature and reaction time on the decomposition of rabbit food were also investigated.

## 2. Methods

The main constituents of the rabbit food used as a feed material (as provided by the manufacturer, Easter Co., Ltd.) were: protein (>18%), fat (>2%), fiber (<16%), and ash (<9%), with calcium (>1.2%), phosphorous (>0.5%), and several minor elements. Initially, the rabbit food was ground thoroughly to a powder and then dried overnight in an oven at 323 K.

The decomposition experiment was carried out in a batch reactor, or in a semi-continuous reactor (Ando et al., 2000). The batch reactor was a stainless steel tube (SUS316, 7.53 mm i.d., 5.34 ml capacity) sealed with Swagelok caps. The reactor, charged with the pretreated rabbit food and distilled water, was heated in a molten salt bath to the desired temperature of 473–623 K. After a defined reaction time, the reactor was cooled to room temperature by immersion in a cool water bath. The liquid and solid contents in the reactor were collected

and the remaining material in the reactor was washed out with water.

The semi-continuous reactor is illustrated in Fig. 1. The reactor (SUS316, 30 ml capacity) was capped with gasket filters (average pore size, 5  $\mu\text{m}$ ) at the reactor inlet and outlet. A sample was packed in the reactor and the whole system was pressurized with nitrogen gas. Distilled water was continuously delivered into the reactor by a high-pressure pump through a heat-exchange coil. The pressure was controlled by a back-pressure regulator. When the effluent water became clear and colorless after approximately 5 min of cold water flow, the pre-heater coil was immersed in a molten salt bath to heat the water flowing into the reactor.

The reaction mixture was analyzed to determine the water-soluble and water-insoluble fractions as follows. The sample was filtered using a glass filter. The water in the filtrate was evaporated under vacuum, and the water-soluble (WS) fraction was recovered. The filtered residue, a mixture of the unreacted substrate and the char-like residue, was determined to be the water-insoluble (WI) fraction. The WS and WI fractions were weighed, and each product yield was calculated based on the dry substrate. The weight loss, including the yield of gaseous products (G), was calculated by determining the difference between the charged and recovered weights of solids.

The liquid phase products were also analyzed for organic acids and glucose. The organic acids were analyzed and quantified by HPLC (column: Shim-pack SCR-102H, Shimadzu) with a UV-VIS detector using perchloric acid as a solvent by means of the BTB method. Glucose content was determined by HPLC (column: SEC-W12 and SEC-W13 in series, Hewlett

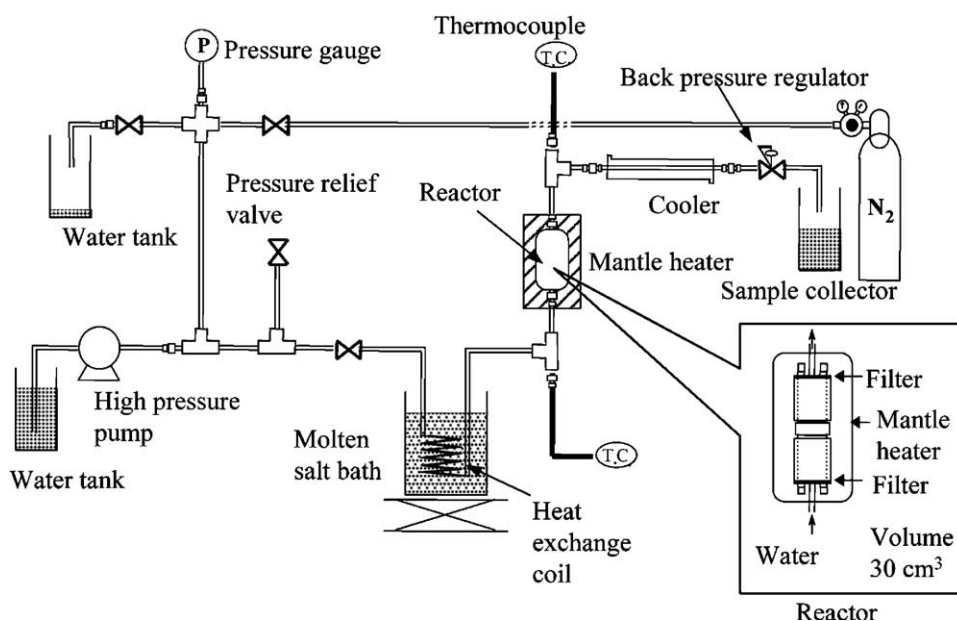


Fig. 1. Schematic diagram of experimental setup of the semi-continuous reactor.

Packard) with a RI detector using water/acetonitrile (7/3) as the solvent. Glucose content was also determined by GC-MS (column: HP-5MS, Hewlett Packard) via silylation with TMSI-C. Some typical runs were repeated twice to check the reproducibility of the experiment. Most of the runs were carried out one time for each condition.

### 3. Results and discussion

#### 3.1. Batch reactor results

##### 3.1.1. Water-soluble and water-insoluble amounts

The amounts of WS components and WI components in the product are shown in Fig. 2 for reactions at 523 and 573 K. The temperature history of the reactor is also shown in the figure. A fibrous material was observed in the reaction product at 523 K after a short time, but with an increased reaction time, the fibrous material disappeared and the WI color became darker. At both temperatures, the amount of WI did not change distinctly with reaction time, whereas the amount of WS decreased with reaction time.

The amount of WI was 48% and 33%, on average, at 523 and 573 K, respectively. The largest amount of WS was 48% in 50 s at 523 K, and 51% in 20 s at 573 K. The amount of WI at 573 K was approximately 2/3 of that observed at 523 K. The remaining part was a gas-phase product that was not measured in the present work. As reaction time proceeded, WS components were converted into gas-phase components. Some part of WS may be converted to WI through carbonization. Sakaki et al. (2002) reported that for decomposition of cellulose, 81 wt% of WS and 18 wt% of WI were obtained at 568 K in 12 min.

##### 3.1.2. Organic acids

Various organic acids were produced in subcritical water from organic wastes. The major components were

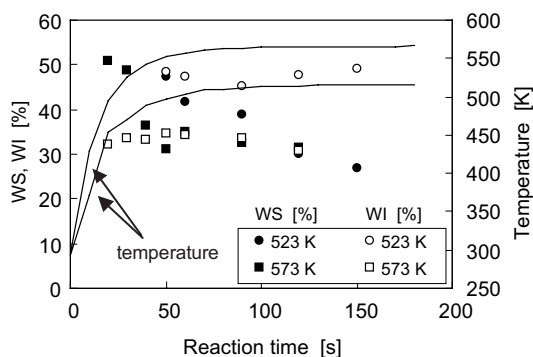


Fig. 2. Amounts of WS and WI as a function of reaction time for a batch reactor.

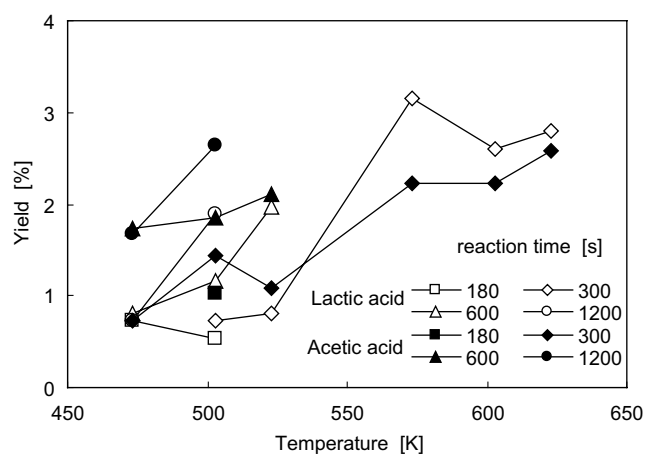


Fig. 3. Yields of organic acids at various reaction temperature for a batch reactor.

acetic acid and lactic acid. Fig. 3 shows the amounts of acetic acid and lactic acid observed in the WS components. Amounts of both acetic and lactic acids were low at temperatures below 523 K, whereas at 573 K, quantities of both increased suddenly. The largest yield for acetic acid was 2.6% at 503 K and 1200 s and at 623 K and 300 s. The yield of lactic acid was largest (3.2%) at 573 K, than gradually decreased at higher temperatures due to further decomposition.

At the lowest temperature, 473 K, the yield of lactic acid did not increase with the reaction time. For acetic acid, the yields at 600 and 1200 s were almost same. This indicates that the reaction temperature of 473 K was not sufficient to produce organic acid even with a longer reaction time. At the temperature of 503 K, both acetic and lactic acids increased with reaction time. However, the maximum amounts of both acids were observed at 523 K at 600 s, and then decreased with further reaction time owing to secondary decomposition.

##### 3.1.3. Glucose

Municipal organic wastes may contain cellulose that originated from biomass. When cellulose could be converted to various saccharides by scission of the glucoside bond in the consecutive reactions: cellulose  $\rightarrow$  oligosaccharides (cellotriase, cellobiose)  $\rightarrow$  hexose (glucose, fructose). Further decomposition to 5-hydroxymethylfurfural (5-HMF), erythrose, glyceraldehydes may be achieved through pyrolysis. Among these components, glucose is often considered a useful chemical resource that could be used as a starting material in chemical or biochemical reactions. Since glucose is an intermediate product that further decomposes to secondary products such as 5-HMF, it is important to optimize the reaction condition to maximize the glucose yield. Reactions under subcritical conditions are often control much more easily because the conversion from cellulose to glucose

in supercritical water proceeds rapidly in reaction time from millisecond to second (Sasaki et al., 1998).

The glucose concentration in the reaction product was analyzed by HPLC with an UV and RI detector. Several peaks were observed in the HPLC chromatogram. As an example, the chromatogram for the 90 s reaction product at 523 K is shown in Fig. 4. Glucose and 5-HMF are detected in most of the reaction products. Since 5-HMF is a consecutive product of glucose, the existence of 5-HMF indicates the existence of glucose. The peaks eluted earlier than glucose may be oligosaccharides. These peaks became smaller in the reaction products at higher temperatures.

Fig. 5 shows the glucose yield as a function of reaction time. The glucose yield is defined as the glucose amount in the liquid phase product divided by the cellulose content in the feed material. The cellulose content in the rabbit food was determined to be 16%. The glu-

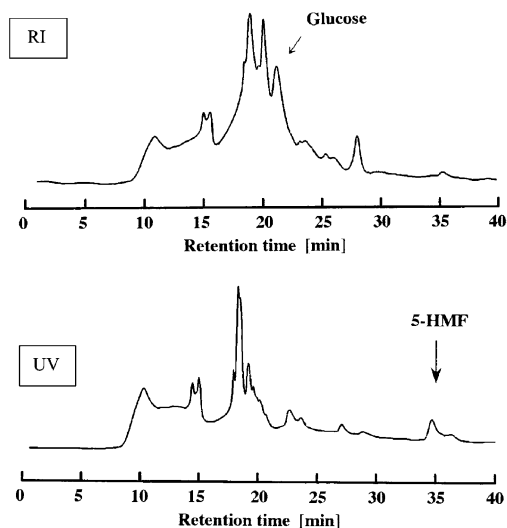


Fig. 4. HPLC chromatogram of reaction products for a bath reactor (90 s, 523 K).

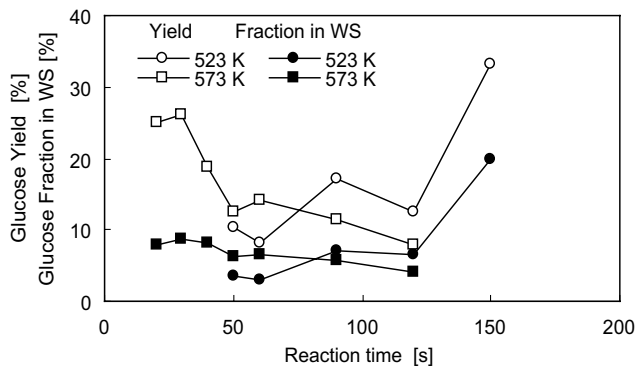


Fig. 5. Glucose yield and glucose fraction in WS for a batch reactor.

ucose content in WS, is also shown in the figure. The glucose yield increased with reaction time at 523 K and the highest yield, 33.2%, was obtained at 150 s. The glucose content in WS reached approximately 20% at 150 s.

In contrast, the change in glucose amount with time was reversed at a higher temperature, 573 K. The WS glucose yield and the glucose content decreased with reaction time after 30 s. The highest glucose yield was 26.3% at 30 s, which corresponds to 8.7% of the WS glucose content. These results indicate that conversion to glucose from higher molecules still proceeds even at 150 s and 523 K, whereas the secondary degradation of glucose is dominant at 573 K.

### 3.2. Results for a semi-continuous reactor

The temperature history of the reactor is shown in Fig. 6. Samples are collected into four fractions: sample #1 (at 473 K); sample #2 (during heating from 473 to 523 K); sample #3 (at 523 K); and, sample #4 (during heating from 523 to 573 and at 573 K). The effluents from the reactor were unclear and the liquid was brown in color regardless of the reaction temperature. The glucose content was evaluated by HPLC with a RI detector. The existence of glucose was also confirmed by GC-MS.

The chromatograms of HPLC for samples #3 and #4 are shown in Fig. 7. The GC-MS chromatogram for sample #3 is also shown in Fig. 7. The glucose peak in the HPLC chromatogram was observed for every sample. The peak for 5-HMF, a degradation product of glucose, was observed in samples #3 and #4. The existence of 5-HMF was more evident in the HPLC chromatogram with a UV detector. The amount of 5-HMF increased with reaction time, indicating the degradation of glucose.

The glucose content and the amount of WS component in each sample are shown in Fig. 8. The glucose

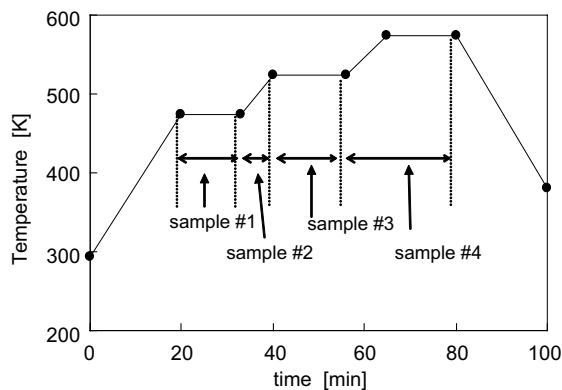


Fig. 6. Temperature history in a semi-continuous reactor during a run.

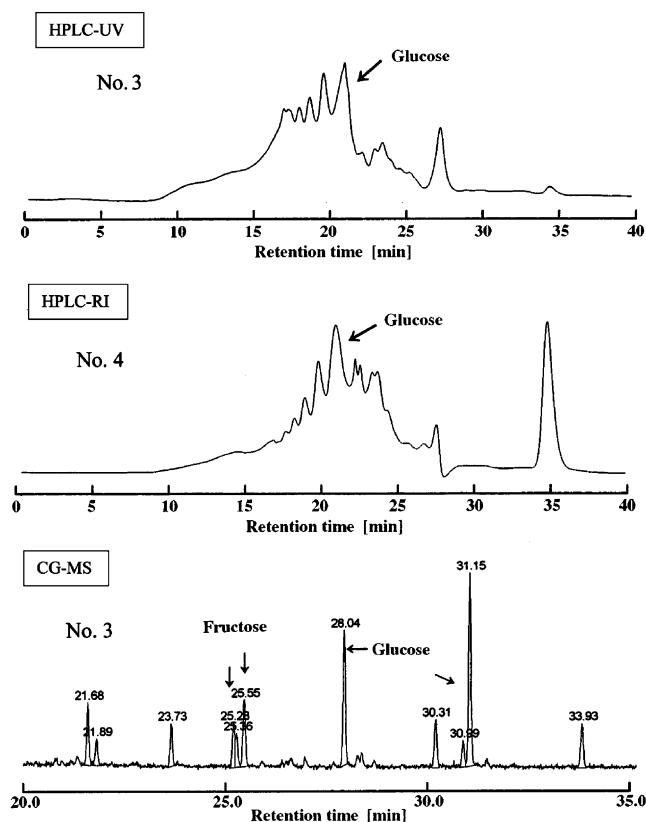


Fig. 7. HPLC and GC-MS chromatogram of reaction products for a semi-continuous reactor.

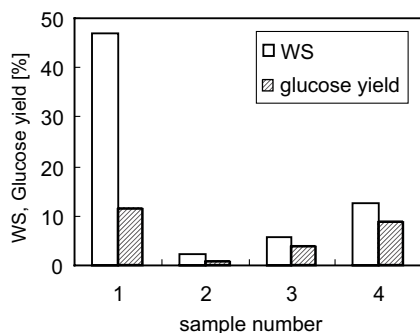


Fig. 8. Amount of WS and glucose yield for a semi-continuous reactor.

yield was 11.5% in sample #1 and was obtained at 473 K, while in samples #3 and #4 the glucose yields, obtained at 523 and 573 K, were 3.9% and 8.7%, respectively. The yields, converted to the value of fraction in water-soluble component, are 3.9%, 10.3%, and 11.0% in samples #1, #3, and #4, respectively.

Thus, the glucose content in the water-soluble component increased with reaction temperature. However, the 5-HMF content also increased with reaction temperature. This indicates that the glucose produced

decomposed to 5-HMF at a higher temperature. The large amount of water-soluble component and the low content of glucose in sample #1 at 473 K indicate that the hydrolysis did not sufficiently proceed to produce glucose. The products from cellulose may be oligosaccharides such as cellobiose (bisaccharide) or cellotriose (trisaccharide).

#### 4. Conclusions

Rabbit food was used as model municipal garbage for hydrothermal decomposition in subcritical water. The reaction product was analyzed in terms of water-soluble and water-insoluble components, organic acids, and glucose. For the batch reactor, the amount of water-insoluble component was an average 48% and 33% at 523 and 573 K, respectively, independent of reaction time. The largest amount of water-soluble component was 48% in 50 s at 523 K and 51% in 20 s at 573 K. The major organic acids detected were acetic acid and lactic acid. The largest yields were 2.6% for acetic acid and 3.2% for lactic acid. The largest yield of glucose was 33% at 523 K. For the semi-continuous reactor, the glucose yields were 11.5%, 3.9% and 8.7% in each fraction obtained at 473, 523, and 573 K, respectively.

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