

# Utilization of Biomass for Fuel and Energy Productions Using Large-scale Plants with Sub- and Supercritical Water

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## ABSTRACT

Utilization of large amount of waste biomass is very important in 21<sup>st</sup> century. Environmentally friendly sub- and supercritical water was used for the conversion of waste biomass to useful fuels and clean energy with large-scale plants.

The first topic is the production of thermal energy from bad-smelling waste biomass. 2-step subcritical water oxidation process was developed to incinerate large amount of livestock excrement or sewage sludge completely and safely to carbon dioxide, water and nitrogen gas. The thermal energy was recovered using high-pressure heat exchanger efficiently.

The second topic is the gasification and hydrogen production from wet waste biomass. Hydrogen gas was produced from waste biomass using subcritical water. Waste biomass could be converted to a gaseous mixture of hydrogen, methane, carbon dioxide and others rapidly and completely. Furthermore subcritical water itself decomposed to hydrogen and the hydrogen yield increased much.

The third topic is the production of bioethanol from paper sludge. Effective bioethanol production was developed using combined process of subcritical water hydrolysis and enzymatic saccharization. This process realized more than 80 % of high glucose yield and no production of furfural compounds, which are inhibitors of ethanol fermentation.

The last topic is the production of powder fuel from the mixture of garbage and waste plastics. New technique using subcritical water was developed to convert refractory waste mixture to high quality and sulfur-free fuel with high heat of combustion.

## INTRODUCTION

Recently the recycling of wastes is expected strongly from the viewpoint of the environmental defense and the effective use of resources. Among many kinds of wastes, waste biomass is focused the spotlight of attention as a renewable resource because they are produced much and carbon neutral for use. Sub- and supercritical water (critical temperature=374°C and critical pressure=22.1MPa) is a promising benign solvent for the decomposition of organic substances and is suitable for the treatment of waste biomass because the biomass contains around 80% moisture [1-2].

In this work, we investigated the applicability of sub- and supercritical water to the conversion of wet waste biomass to high quality and clean fuels or energy[3-4].

## MATERIALS AND METHODS

### 1. Production of thermal energy

We constructed a pilot-scale plant for the complete and clean combustion in subcritical water and the recovery of thermal energy from waste biomass. Figure 1 shows the flow diagram of the plant. The waste-treatment capacity was 30kg/h. The first reactor was made of

SUS316 with 82L of the inner volume and the three-cascaded second reactors were made of SUS316 with 5L of the inner volume. The first reactor was empty and the second reactor was packed with manganese dioxide catalyst. Waste biomass slurry was charged into the first reactor using high-pressure double syringe pumps continuously. The

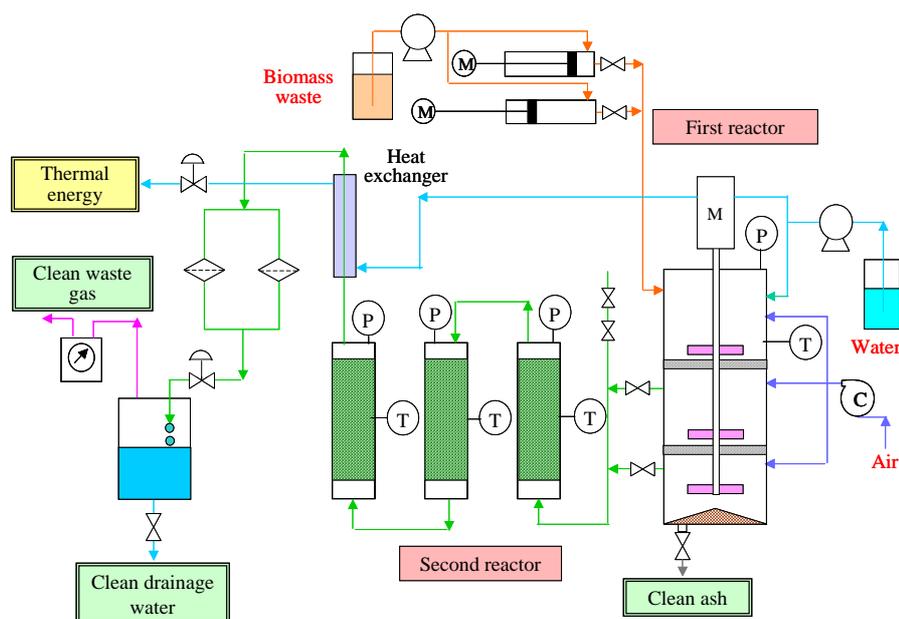
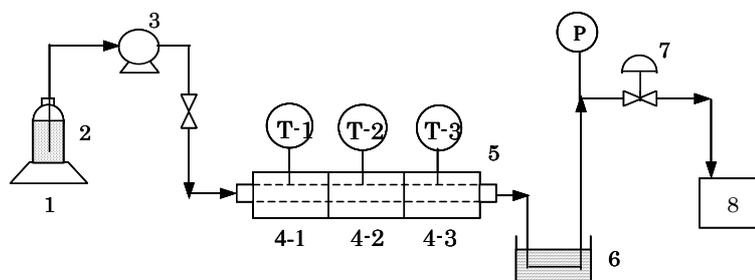


Figure 1 Flow diagram of 2-step subcritical water oxidation process

The compressed air as an oxidant was also introduced into the reactor using compressor and gas buster. In the first reactor, carbon and hydrogen atoms were oxidized to carbon dioxide and water. Nitrogen atoms were converted to ammonia and nitrogen gas. In the second reactor, ammonia and very small amount of TOC component were decomposed to nitrogen gas, carbon dioxide and water on manganese dioxide catalyst. Finally clean drainage water and effluent gas were discharged from the plant.

## 2. Gasification and hydrogen production

Batch-type and flow-type reactors were used in this experiment. Figure 2 shows the flow-type experimental setup. This apparatus used a tubular reactor made of SUS316 having 373 cm<sup>3</sup> in inner volume, 25.4 mm in o.d. and 1000 mm long. The mixed solution of reactant and alkali catalyst was fed into the reactor using a high-pressure pump. The reactor was heated at a given reaction temperature with electric furnaces. After the gasification, the effluent



1. Balance
2. Reactant + alkali solution
3. High-pressure pump
- 4-1-4-3. Electric furnaces
5. Reactor
6. Water bath
7. Back pressure regulator
8. Gas sampling bag
- T-1-T-3. Thermometers
- P. Pressure gauge

Figure 2 Flow-type experimental setup for gasification in subcritical water.

was cooled to room temperature in water bath and depressurized through the back pressure regulator. The gaseous product was collected into a gas sampling bag, and the volume and composition were measured. The liquid and solid products in the reactor were collected with distilled water and filtered. The TOC in the filtrate was analyzed by TOC meter to determine the organic carbon dissolving in water.

### 3. Production of bioethanol from paper sludge

Figure 3 shows the photo of bench-scale plant for hydrolysis of paper sludge using subcritical water. This was a flow-type apparatus and the waste-treatment capacity was 6kg/h. The paper sludge was hydrolyzed in a short time and most cellulose in the paper sludge remained as solid residue. It was saccharified to glucose by cellulase enzyme at 35°C and 120h.

### 4. Production of powder fuel from mixture of garbage and waste plastics

Figure 4 shows the photo and outline of a pilot-plant. This was a batch-type apparatus and the waste-treatment capacity was 100kg/batch. The reactor was made of SUS316 with 0.3m<sup>3</sup> in inner volume and it had a horizontal agitator inside. The target waste was the mixture of garbage and waste plastic. The waste mixture was put in the reactor and the steam was charged into the reactor for heating and supplying subcritical water. The waste mixture was converted to small powder fuel with high calorific value and dried easily.



Figure 3 Bench-scale plant for hydrolysis of paper sludge

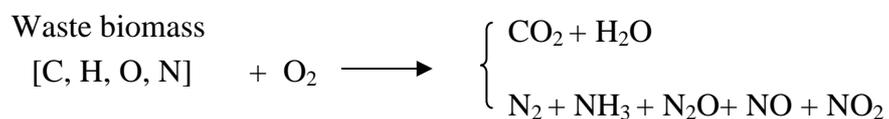


Figure 4 Pilot-scale plant for production of powder fuel

## RESULTS

### 1. Production of thermal energy

We investigated the optimum conditions on clean and complete combustion of sewage sludge, livestock excrement and agricultural waste in subcritical water. When the waste biomass is incinerated in the air, a lot of harmful substances are produced and diffuses into the air. The major products are shown as follows:



On the other hand, when it is incinerated in sub- or supercritical water, there is the possibility to suppress the formation of toxic nitrogen-containing compounds. The reaction condition was that the temperatures of the first and second reactors were 409°C and 384°C, the pressure was 8MPa, the oxygen supply ratio was 1.3, the residence time of the first reactor was 15min, and the space time of the second reactor was 0.5min.

Figure 5 shows the change of the concentration of each nitrogen-containing product and total concentration of nitrogenous products with the elapsed time. The nitrogen atoms in the forms of ammonia and nitrite were less than 5mg/L and those in the form of nitrate were around 25mg/L. The total concentration of nitrogen-containing products defined by ammonia-form nitrogen x 0.4 + nitrite-form nitrogen + nitrate-form nitrogen was around 30mg/L and 1/3 of the emission standards in Japan. Most nitrogen atoms were converted to harmless nitrogen gas.

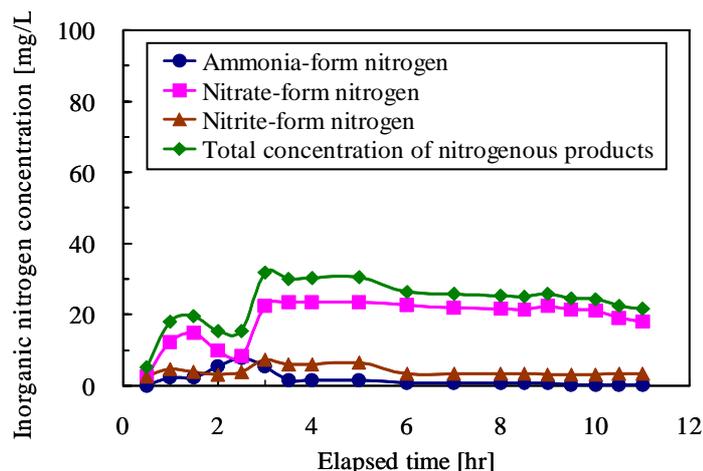
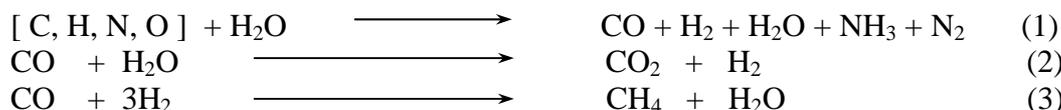


Figure 5 Change of concentration of each nitrogen-containing product and total concentration of nitrogenous products with elapsed time

(First reactor 409°C, 8MPa, Second reactor 384°C, 8MPa, Oxygen supply ratio 1.3)

## 2. Gasification and hydrogen production

The main reactions of the gasification of waste biomass in subcritical water are given by



where [C, H, N, O] is waste biomass consisting of carbon, hydrogen, nitrogen, oxygen atoms.

Figure 6 shows the effect of the catalysts on the gas productivity from pig's excrement at 700°C, 10MPa, 20min and 20 of molar ratio of water to carbon in sample. The amount of the catalyst was 20wt% to the organic component in the sample. The y-axis represents the volume of the gaseous products at 25°C and 101.3kPa for 1 gram of the

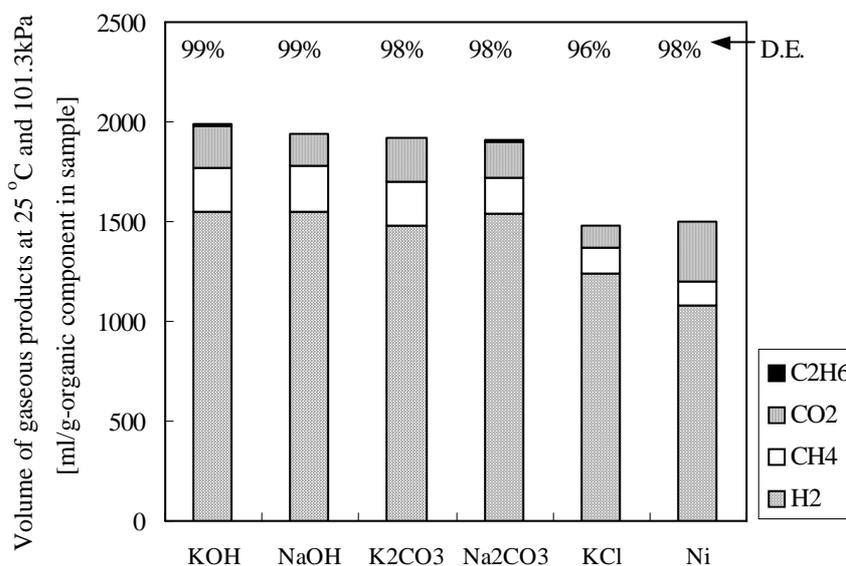


Figure 6. Effect of catalysts on gas productivity from pig's excrement in gasification with subcritical water. (700°C, 10MPa, 20min, 20wt% catalyst)

organic component in sample. Using alkali catalyst of KOH or NaOH, the pig's excrement was decomposed completely and 1550 cm<sup>3</sup> of hydrogen gas was produced. In the case of salt catalyst of K<sub>2</sub>CO<sub>3</sub> or Na<sub>2</sub>CO<sub>3</sub>, the decomposition efficiency and the volume of hydrogen gas were almost the same as those using alkali catalyst. On the other hand, the conventional nickel catalyst formed 1080 cm<sup>3</sup> of hydrogen gas from the pig's excrement and lowest among six kinds of catalysts. This was because a small amount of chlorine and sulfur atoms in the pig's excrement deactivated nickel catalyst.

The origin of hydrogen gas was investigated for the gasification of the pig's excrement using subcritical water with KOH catalyst. About 40% of hydrogen gas was released from the hydrogen atom in the pig's excrement. Other 60% generated from water, judging from the gasification reactions in (1)–(3). In this case, active subcritical water reacted with carbon monoxide to produce hydrogen gas.

### 3. Production of bioethanol from paper sludge

The target raw material is paper sludge discharged from Japanese-manufacturing companies by 5.5million tons for a year. In this study, cellulose was chosen as the paper sludge alternative because cellulose is main component in the paper sludge. Figure 7 shows the reaction time dependence of the cellulose decomposition efficiency and product yields for the hydrolysis with subcritical water at 260°C and 5MPa. The important point of this hydrolysis was that cellulose with low reactivity has to convert to easy-saccharifying type and the formation of ethanol-fermentation inhibitor has to be avoided. From these criteria, less than 5min was selected as the reaction time. Figure 8 shows the change of glucose yield with elapsed time for the cellulase saccharification of cellulose pretreated by subcritical water at 1-5min. The glucose yield increased by the pretreatment of subcritical water. Especially a minute pretreatment enhanced the

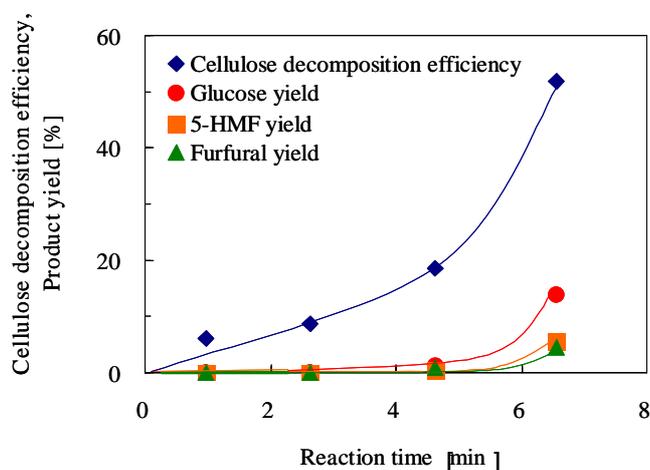


Figure 7 Reaction time dependence of cellulose decomposition efficiency and product yields in subcritical water at 260°C and 5MPa

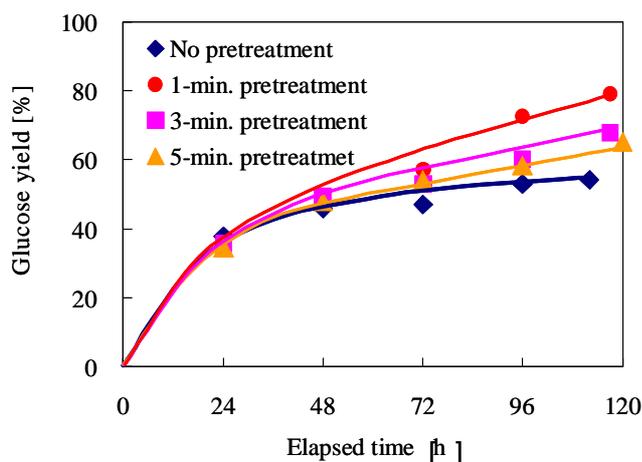


Figure 8 Change of glucose yield with elapsed time for cellulase saccharification of cellulose pretreated by subcritical water at 260°C and 5MPa

glucose yield by 25%, comparing with the result without pretreatment.

#### 4. Production of powder fuel from mixture of garbage and waste plastics

Figure 9 shows the photos of waste mixture treated by subcritical water at various temperatures. The sample was the mixture of garbage and waste plastic from a supermarket. At 150°C, both garbage and plastic did not decompose much.

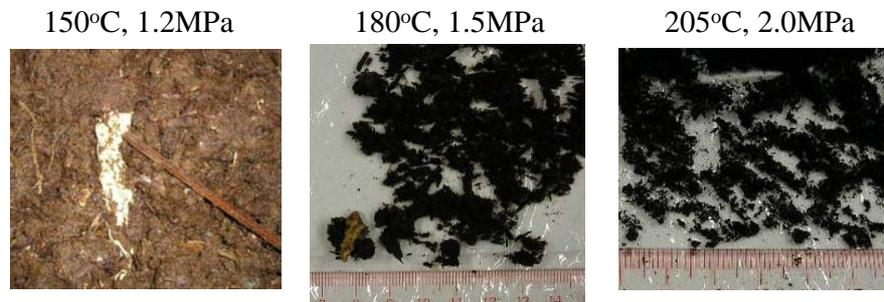


Figure 9 Appearance of waste mixtures treated by subcritical water at various temperatures

However, at 250°C, the waste mixture changed to the powder fuel with 1-2mm in diameter. The calorific value of the powder portion was measured. The result is shown in Figure 10, where the calorific values of typical solid fuels are also given. The calorific value of the powder fuel increased with reaction temperature. The value was almost the same as that of coal when the reaction temperature was more than 200°C. This was because the waste plastic was dispersed well at the reaction temperature above the melting temperature of the plastics. The powder fuel was a composite fuel with 2-layer structure: the center was plastic particle and the surrounding was biomass powder.

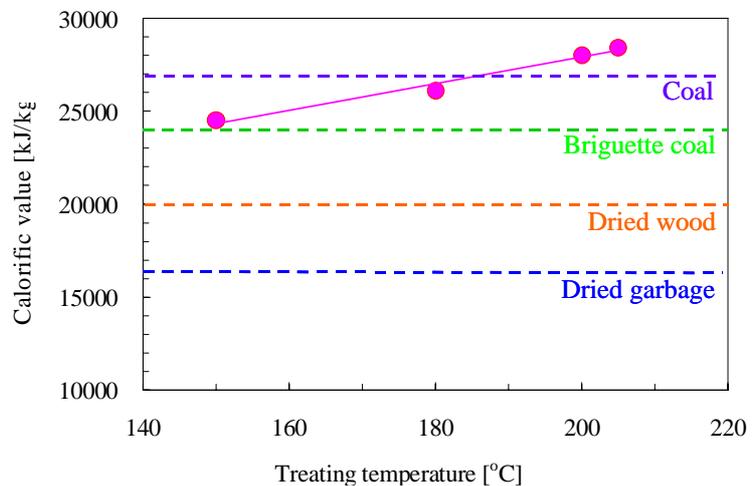


Figure 10 Dependence of calorific value of powder fuel on treating temperature (1.2-2MPa, 30min)

#### CONCLUSION

Sub- and supercritical water was powerful and environmentally friendly solvent for biomass conversion. Many kinds of applications and commercialization will be developed in new future.

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