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Production of Acetic Acid by Hydrothermal Two-step Process of Vegetable Wastes for Use as a Road Deicer

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Abstract. This study aimed to produce acetic acid from vegetable wastes by a new hydrothermal two-step process. A continuous flow reaction system with a maximum treatment capacity of 2 kg/h of dry biomass developed by us was used. Five kinds of vegetables of carrots, white radish, chinese cabbage, cabbage and potato were selected as the representation of vegetable wastes. First, batch experiments with the selected vegetables were performed under the condition of 300°C, 1 min for the first step, and 300°C, 1 min and 70% oxygen supply for the second step, which is the optimum condition for producing acetic acid in the case of using starch as test material. The highest yields of acetic acid from five vegetables were almost the same as those obtained from starch. Subsequently, similar the highest yield of acetic acid and experimental conditions from vegetables were also obtained successfully using the continuous flow reaction system. These results should be useful for developing an industrial scale process.

1. Introduction
With increasing environmental awareness and crude oil price, the conversion of biomass into chemicals is receiving an increased interest. Among several biomass conversion processes, the hydrothermal process is one of the most promising processes, because water at a high temperature and high pressure behaves as a reaction medium having outstanding properties. There have been extensive researches on the conversion of biomass into chemicals by hydrothermal treatment [1-4]. Our past studies on the oxidation of various food wastes in supercritical water showed that acetic acid was a stable intermediate product for almost all organic wastes selected [5-6]. This result gave us a hint, that is a large amount of acetic acid can be obtained by controlling reaction condition. So, we carried our a study on acetic acid production by wet oxidation (WO) of various carbohydrate biomasses for producing calcium/magnesium acetate (CMA) known as an environmentally friendly deicer [7-8].
These results indicated that acetic acid can be obtained as a product and can be increased by optimizing the reaction condition of WO of organic waste, but there is a limit to the yield of acetic acid, i.e. only 11-13 % at most on a carbon basis. To enhance the production of acetic acid from carbohydrate biomass, a new two-step process was proposed [9-10]. The two-step process consists of both a hydrothermal reaction without a supply of oxygen (the first reaction step) and an oxidation reaction (the second reaction step). The first step is to accelerate the formation of 5-hydroxymethyl-2-furaldehyde (HMF), 2-furaldehyde (2-FA) and lactic acid because they can produce a large amount of acetic acid by their oxidation, and the second step is to further convert these products formed in the first step to acetic acid by oxidation with newly supplied oxygen. It was shown that the acetic acid yield was greatly increased by the two step process.

Further, according to results obtained with batch reactor, we developed a continuous flow reactor system to produce acetic acid, then convert the produced acetic acid into CMA [11], and examined the fundamental performance with starch as test material. Results indicated that the continuous-flow reactor system has the expected fundamental performance to produce acetic acid by the two-step reaction.

The purpose of this study was to produce acetic acid from vegetable wastes by the two-step process with the continuous-flow reactor system. The selection of vegetable waste as treatment target is because component of vegetable waste is singleness and the amount of vegetable wastes generated from vegetable market in the big city is considerably large very day. Particularly, a single component of wastes is important for easily controlling a continuous-flow process.

2. Experimental

2.1. Experiments with a batch reactor
All batch experiments were conducted in a batch reactor system described previously [5, 10]. A brief summary is as follows. First, the desired amounts of test material and deionized water were loaded into a batch reactor. After the loading procedure was completed, the reactor was immersed in a salt bath preheated to the desired temperature. After the desired reaction time, the reactor was taken out of the salt bath and immediately put into a cold water bath to quench the reaction. This procedure is called the first step reaction. After the first step reaction was completed, \( \text{H}_2\text{O}_2 \) was added to the cooled reactor and then the oxidation reaction took place in the salt bath as the second step. In the salt bath, the reactor was shaken, keeping it horizontal, to enhance mixing and heat transfer. Loading of a mixture of deionized water and hydrogen peroxide was set at 50% of the inner volume of the batch reactor in all experiments. The reaction time was defined as the time that the reactor was kept in the salt bath. Since the time required to raise the temperature of the reaction medium from 20 to 300°C is about 15 s, the real reaction time is shorter than the defined reaction time. Reaction pressures with and without a \( \text{H}_2\text{O}_2 \) supply were about 17 MPa and 9 MPa, respectively. All batch experiments were performed with degassed water and the reactor was purged with nitrogen in the first-step reaction.

2.2. Experiments with continuous flow reactor system

2.2.1. Apparatus
A continuous flow reactor for producing acetic acid from hydrothermal treatment of biomass developed by us was used in this study. Fig 1 shows flow diagram of the continuous flow reaction system. The system mainly consists of a slurry pump, plunger pump for the \( \text{H}_2\text{O}_2 \) supply, preheater and cooler for the reaction media, reactor, solid-liquid separator, filter, back-pressure regulator and a gas-liquid separator.

The reactor chamber is divided into two parts, bottom and top chambers, by placing two horizontal pieces of baffle plate near the mid-height (see Fig 2) for taking place the two-step reaction. The bottom chamber of the reactor is used for the hydrothermal reaction without \( \text{H}_2\text{O}_2 \) (the first reaction step), the top is for the oxidation reaction (the second reaction step), and the mixing chamber is set
between the top and bottom chambers to mix the $\text{H}_2\text{O}_2$ and reactants. The $\text{H}_2\text{O}_2$ solution is fed into the mixing chamber from the top of the reactor through a pipe. The inlet of the feed slurry is at the bottom of the reactor and the outlet for the effluent is at the top of the reactor.

This continuous flow reactor has a maximum treatment capacity of 2kg/h of dry biomass. The treatment capacity and specification of the main compositions of the continuous flow reaction system is summarized in Table 1. Details on the description of the continuous flow reactor are available elsewhere [11].

![Flow diagram of hydrothermal conversion of biomass into acetic acid.](image1)

**Figure 1.** Flow diagram of hydrothermal conversion of biomass into acetic acid.

![Schematic diagram of the two-step reactor.](image2)

**Figure 2.** Schematic diagram of the two-step reactor.

2.2.2. Experimental procedure

Each experimental run was started by preparing the feed slurry, which was a mixture of water and vegetables. The feed slurry tank was agitated using a stirrer throughout the experiment. After preparation of the feed slurry, the system was heated while only water flowed. The pressure of the
Table 1 Treatment capacity and specification of the main compositions of the continuous flow reaction system.

| Specification                  |          |
|-------------------------------|----------|
| Treatment capacity            | 2 kg/h (dry base) |
| Feed pump                     |           |
| Flow rate:                    | 7.5-20 L/h|
| Pressure:                     | 40 MPa max.|
| Slurry Concentration:         | 10 wt% max.|
| Preheater                     |           |
| Temperature:                  | 200-250°C |
| Pressure:                     | 40 MPa, max.|
| Reactor                       |           |
| Temperature:                  | 430°C max.|
| Pressure:                     | 40 MPa, max.|
| Size:                         | φ50×660 mm |
| Volume:                       | 1.3 L (HC-276) |
| Pressure valve                |           |
| Temperature:                  | 40°C, max. |
| Pressure:                     | 40 MPa, max.|

system was adjusted with the back-pressure regulator. After both the preheater and the reactor reached the desired temperature and pressure, the pump of hydrogen peroxide-water solution was switched on. After the hydrogen peroxide solution was allowed to flow for about 30 min, the feed slurry pump was turned on. One hour after the feed slurry pump was switched on, liquid and gas samples were collected at the bottom and top of the gas-liquid separator. The effluent gas flow rate was also measured.

2.3. Materials and oxygen supply
Five kinds of vegetables of carrots, white radish, chinese cabbage, cabbage and potato, as well as starch, were used as test materials. Vegetables were obtained from local vegetable market. Carrots, white radish are without leafage. In preparing vegetable slurry, the raw vegetable without dry was smashed into slurry by a mixer. The starch was an industrial potato starch (Nishida starch plant, Hokkaido, Japan) for continuous-flow experiments, and reagent grade potato starch for batch experiments. H₂O₂ was used as an oxidant for experimental convenience. The oxygen supply was defined as the ratio of the amount of H₂O₂ supplied to the stoichiometric demand for complete oxidation of a test material to carbon dioxide and water.

2.4. Analyses of samples
The solution and off-gas samples after reaction were analyzed by GC/MS, GC and HPLC. For batch experiments, only solution samples were analyzed. For GC/MS analyses, a Hewlett-Packard model 5890 Series II Gas Chromatograph equipped with a model 5989B Mass Selective Detector was used, with a HP-INNOWAX capillary column for water-soluble compounds using helium as the carrier. Intermediate products were identified with total and selected ion chromatograms with the aid of a computer library, as well as a comparison of GC retention time of the product and authentic compounds. HPLC analysis was performed with a Waters HPLC system equipped with a tunable absorbance detector (UV/VIS detector) (Waters 486) and a differential refractometer (RI detector) (Waters 410), controlled with a Millenium 600 workstation. Two kinds of column were used to separate intermediate products. To identify polar compounds, such as carboxylic acids, alcohols and ketones, RSpak KC-811 (Shodex) was used with a UV detector. To identify sugars, SUGAR SH1011 (Shodex) was used with a RI detector. Peak identification was accomplished by comparison of a sample peak retention time with that of standard solution of pure compound. Details on the conditions for GC/MS and HPLC analyses are described elsewhere [5,10]. Acetic acid was obtained quantitatively with a GC/FID/TCD (Hewlett Packard 5890II series plus). It was also used to analyze the off-gas samples.

The residual total organic carbon (TOC) in a liquid sample was measured with a TOC analyzer (Shimadzu TC 5000A, Japan).

3. Results and Discussion

3.1. Batch experiments
As reported in our previous study using starch as test material [10], the optimum conditions for producing acetic acid in two-step process were at temperature and reaction time of 300°C, 1 min for the first reaction step, and at temperature, reaction time and oxygen supply of 300°C, 1 min and 70% in the second reaction step, respectively. Thus, experiments with five kinds vegetables were conducted under the same conditions. As shown in Table 2, the yields of acetic acid obtained from five vegetables were almost the same each other. Comparing to starch, the acetic acid yield from vegetables seem to be a little lower than that from starch, but no significant difference was observed. These observations indicate that a little of composition in vegetable, for example protein, fatty acids, may have no significant effect on the production of acetic acid in the two-step reaction, although a significant difference between starch and vegetable in the yield of acetic acid, which the acetic acid yield from vegetable was lower than starch, was observed in general wet oxidation or directive oxidation. The study for reason why the acetic acid yield from vegetable was lower than one from starch is currently in progress.

Further, considering that real vegetable waste is a mixture, an experiment with a mixture of five kinds of vegetable was also performed at the same condition mentioned above. The mixture was prepared in the same weight percentage in dry base for each vegetable. As shown in Table 2, the acetic acid yield is also the almost same as those from each individual vegetable, indicating that each vegetable has no significant interaction in the production of acetic acid in the two-step reaction.

### Table 2 Acetic acid yield obtained with batch experiments

| Vegetable       | Chinese cabbage | Cabbage | Potato | Carrots | White radish | Mixture | Starch |
|-----------------|----------------|---------|--------|---------|--------------|---------|--------|
| Yields (wt%)    | 16.5           | 17.0    | 17.3   | 16.8    | 17.1         | 17.0    | 17.5   |

*300°C, 1 min for the first step, and 300°C, 1 min, 70% oxygen supply for the second step.*

*a The percentage of TOC of acetic acid and initial material.

*b Mixture of five kinds in the same weight proportion for each vegetable.

### 3.2. Continuous flow experiments

According to the results with the batch reactor, continuous flow experiments with vegetables were performed. In continuous flow experiments, only the mixture was used as test material. Two runs were carried out. The detail conditions for two run are shown in Table 3. Although results with batch experiments showed that there are no significant difference in the yield of acetic acid between starch and vegetables, considering that vegetables contains a little of cellulose being more difficult hydrolysis than starch, and the protein being more oxidation decomposition than starch, a longer reaction time of 2.0 min in the first-step reaction and 1.4 min in the second reaction step, as well as a higher H\(_2\)O\(_2\) supply of 85% in

| Condition            | Vegetable mixture |
|----------------------|--------------------|
| Temp. in Preheater/°C| Run 1 | Run 2 | Starch |
| Slurry               | 270   | 270   | 260    |
| Flow/L/h             | 10    | 10    | 10     |
| Concentration/ wt%   | 3.5   | 3.5   | 3.5    |
| The first-step       |        |       |        |
| Reaction Temp./°C    | 300   | 300   | 300    |
| Residual time/ min   | 2.0   | 2.0   | 1.0    |
| The two-step         |        |       |        |
| Reaction Temp./°C    | 300   | 300   | 300    |
| Residual time/ min   | 1.4   | 1.4   | 1.0    |
| H\(_2\)O\(_2\) solution |       |       |        |
| Flow/L/h             | 5.5   | 6.0   | 6.5    |
| Oxygen supply/%      | 66    | 85    | 75     |
| Pressure/ MPa        | 15    | 15    | 20     |
the second reaction step were chosen. But, for comparison, a run with 65% oxygen supply was also carried out. In order to attain economically viable acetic acid production, a higher concentration of initial material is desired, so, 3.5wt% slurry concentration was used. Moreover, system pressure decreased to 15MPa because our past research showed that the increase in pressure improved the oxidation of intermediate products, thus leading to the decrease in the acetic acid [11]. Table 4 shows the yield and purity of acetic acid, and gas composition. It can be seen that, from Table 4, the acetic acid yields are almost the same to the result obtained with starch for both two runs. However, the purity is lower for run 1 with 65% oxygen supply. So, the condition of run 2 should be a better condition for producing acetic acid from vegetables.

As mentioned before, our purpose in producing acetic acid is to produce calcium magnesium acetate (CMA), as a noncorrosive road deicer. So, products other than acetic acid are important. We made detailer identification for products in solution samples for the case of run 2 by GC/MS, HPLC. The identified products and their yield and purity are shown in Fig 3. Addition to acetic acid, many low molecular weight carboxylic acids were detected. Calcium compounds of these lower molecular weight carboxylic acids can also be used as a noncorrosive deicer. So, these low molecular weight carboxylic acids are useful products. In this case, the total purity of all carboxylic acids arrived to 70%. Moreover, a little of amides, may come from the oxidation protein, are also formed. Amides can also be used a noncorrosive deicer. So, most of the identified products other than acetic acid are useful products in the case of manufacturing CMA.

4. Conclusions
Batch experiments with the selected five kinds of vegetables were performed at the optimization condition for the case of using starch, the main component of vegetable, as a test material. The highest yield of acetic acid and the conditions for obtaining the highest acetic acid yield from vegetables were

| Table 4 Results obtained by continuous-flow reactor system for run 2 |
|---------------------------------------------------------------|
| Vegetable mixture | Run 1 | Run 2 | Starch |
| Acetic acid yield /%a | 15.5 | 16.0 | 17.5 |
| Acetic acid purity/%b | 40 | 60 | 65 |
| **Off-gas composition** | | | |
| CO₂ | 90 | 81 | 91 |
| CO | 5 | 4 | 6 |
| O₂ | 3 | 14 | 3 |

a The percentage of TOC of acetic acid and initial material.  
b The percentage of TOC of acetic acid and other residuals remaining in the liquid.
almost the same as those obtained from starch. Similar the highest yield of acetic acid and experimental conditions from vegetables were also obtained successfully using the continuous flow reaction system. These results should be useful for developing an industrial scale process.

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