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A continuous flow reaction system for producing acetic acid by wet oxidation of biomass waste

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A continuous flow reaction system designed for producing acetic acid by wet oxidation (WO) of biomass with the maximum treatment capacity of 1 kg/h of dry biomass was developed. Experimental runs with rice hulls and starch were conducted at reaction temperatures between 300–320°C, for time of 2 and 3 min, with oxygen supplies between 70 and 100%, and at pressures between 10 and 30 MPa. The influence of each of these parameters was evaluated.

1. Introduction

The hydrothermal process is one of the most promising for the conversion of biomass, one of the most important renewable resources into chemicals, at high temperature and high pressure water has outstanding properties as a reaction medium. There is therefore extensive research into the conversion of biomass into chemicals by hydrothermal treatment. Our past studies on acetic acid production by wet oxidation (WO) of various food wastes and lignocellulosic wastes showed that acetic acid is a stable and highly recoverable intermediate product in wet oxidation for almost all organic wastes [1–4], and acetic acid is a useful chemical for production of calcium acetate, which is known as an environmentally friendly deicer. Because hydrothermal conversion of biomass into chemicals is a new technology, many previous studies including have been basic, using a batch reactor or a small laborlatory-scale continuous flow reactor. For the hydrothermal conversion process to become a practical technology as soon as possible, experiments using a larger-scale continuous flow reaction system are needed. The purpose of this study is to develop a hydrothermal reaction process selectively to convert carbohydrate biomass into acetic acid, as a practical technology in the near future.

2. Experimental

2.1. Apparatus

The test apparatus used in this study is a rather large-scale continuous-flow reaction system for university laboratories, with a treatment capacity of 1 kg/h of organic material. This apparatus mainly consists of a slurry pump, plunger pump for H_2O_2 supply, preheater, WO reactor, cooler, solid-liquid separator, filter, back-pressure regulator and gas-liquid separator (Fig. 1). The developed two-unit type stroke pump made of SUS316 was used to feed the slurry. This pump can change the flow rate between 8 and 20 L/h, was a maximum operating pressure of 40 MPa, and operates at a maximum slurry concentration of 10 wt%.

The pressurized feed slurry was preheated during the flow at the preheater. The preheater is composed of a 15-m-long, 6-mm-id, and 2-mm thick SUS316L tubing and has a coil heater and can heat the slurry from room temperature to 250°C. Hydrogen peroxide solution was supplied with a plunger pump with maximum feed rate of 7 L/h, so that the total flow rate would be between 14 and 27 L/h. The feed slurry and hydrogen peroxide solution were mixed at the preheater inlet. The reactor is a vertical cylinder made of Hastelloy C276 (HC-276)

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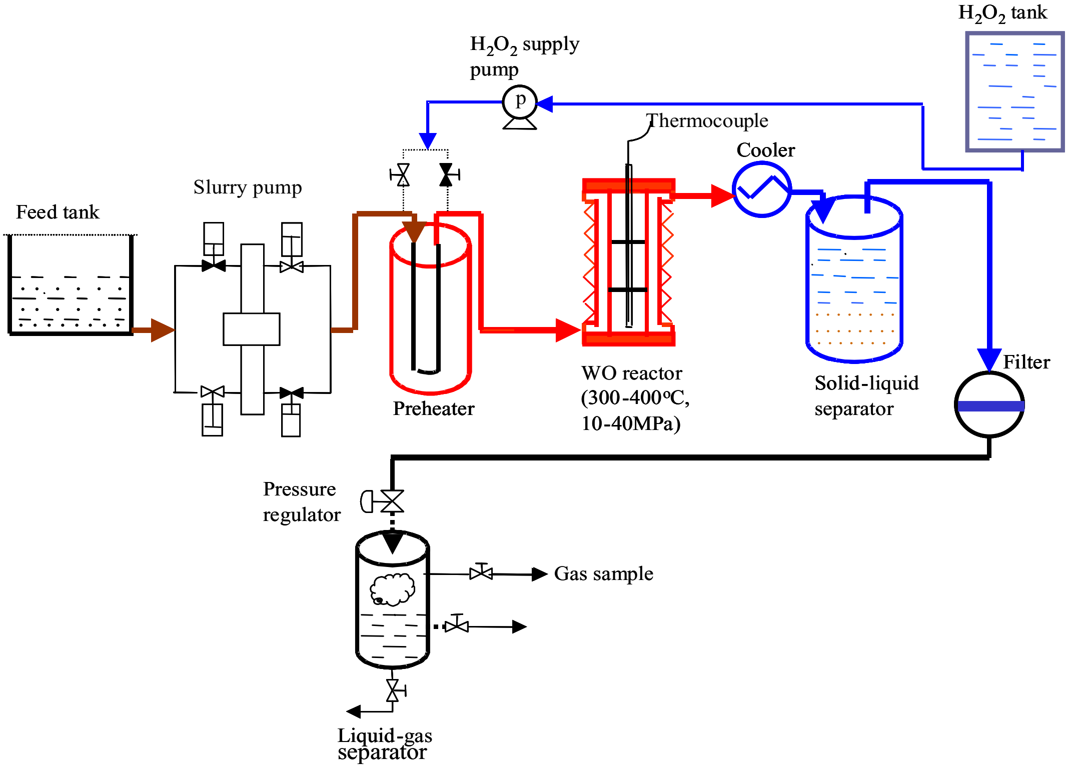

Figure 1 Flow diagram of continuous flow reaction system.

and is 660 mm high, 50 mm id, and 10 mm wall thickness. The temperature at the top, middle and the lower parts can be controlled and measured individually by three sets of ceramic heater and three sets of thermocouple. The maximum operating temperature and pressure of the reactor was 430°C and 40 MPa, respectively. The inlet and outlet of the reactor were at the bottom and the top, respectively. In order to promote mixing of hydrogen peroxide with slurry and prevent backward flow, two pieces of baffle plate were placed horizontally at the middle and the lower part of the reactor about 50 mm above the bottom of the reactor. In some cases, the reactor was filled with ceramic beads of 5 mm in diameter to further increase mixing of oxygen with organics in the reactor.

After WO reaction, the reactor effluent was cooled during flowing through the cooler. The cooler is composed of a double vertical pipe, where the inside pipe (HC-276) is for the flow of the reactor effluent, and an outside pipe (SUS316L) is for cooling water. The cooled effluent passed the solid-liquid separator consisting of a 900 mm high and 150 mm id cylinder made of SUS316L, then passed through a sintered stainless steel filter with a pore size of 10 μm, and finally passed to the back-pressure regulator. At a low pressure this cooled effluent then flowed into the gas-liquid separator consisting of a 900 mm high and 150 mm id cylinder made of SUS316L. The separated liquid and gaseous effluent was removed from the top and bottom of the separator, respectively.

2.2. Experimental procedure

Each experimental run was started by preparing the feed slurry, which consisted of tap water and rich hulls or starch. 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, meanwhile, the pressure of 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 hydrogen peroxide was allowed to flow for about 30 min, the feed slurry pump was switched on. Hydrogen peroxide solution was mixed with the feed slurry at the inlet of the preheater. One hour after the feed slurry pump was switched on, liquid sample and gas sample were collected at the bottom and the top of the gas-liquid separator. The effluent gas flow rate was also measured.

2.3. Materials

Rice hulls and starch were used as test materials (Table I). Rice hulls were ground to pass a screen of 150 μm (100 mesh) in size with a cross-beater mill (SK-100 type made by Retsch, Germany). The starch is an industrial potato starch (Nishida starch plant, Hokkaido, Japan), and its carbon content (dry base) is 43.9 wt%.

The oxygen supply was defined as the ratio of oxygen supplied by a H_2O_2 solution to the stoichiometric demand

TABLE I C, H, Si composition of rice hulls

C[a]	H[b]	Si[c]
34.9	6.5	11.2

C, H, Si: dry base (wt%).
[a] Measured with CNS2000 (Leco, US).
[b] Measured with MT-6 (Yanako Analysis Industry, Japan).
[c] Measured with ICP P-4000 (Hitachi, Japan) after dissolved with HF.

of oxygen calculated from carbon content of the test material for complete oxidation of carbon to carbon dioxide. Our previous study revealed that a 100% oxygen supply was approximately stoichiometric for complete oxidation of carbohydrates [1].

2.4. Analyses of liquid sample and off-gas

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 (Cross-Linked Polyethylene Glycol) 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 times of products 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, we used an RSpak KC-811 (Shodex) for organic acids analysis with a UV detector. To identify sugars, we used a SUGAR SH1011 (Shodex) for saccharide analysis with a RI detector. When RSpak KC-811 was used, samples were separated through a series of two identical columns to obtain a better separation. Peak identification was accomplished by comparison of sample peak retention times with those of standard solutions of pure compounds. Details on the conditions for GC/MS and HPLC analyses are available elsewhere [5, 6]. Acetic acid was obtained quantitatively with a GC/MS. Gas chromatograph (Hewlett Packard 5890 series plus) was also used to analyze the off-gas samples.

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

2.5. Experimental conditions

Experimental conditions are summarized in Table II. In all runs, the concentration of slurry was fixed at 2 wt%. The reactor was separated into three chambers with two baffle plates. The lowest chamber was used for mixing the slurry and H_2O_2 solution, and temperature was 270°C. The upper two chambers were used for reaction. In the reaction chamber, the baffle plate works to prevent the direct breakthrough to the exit of the reaction chamber. Reaction time was defined as follows:

TABLE II Experimental conditions

Preheator temperature (°C)	250
Reaction temperature (°C)	300, 320
Slurry flow rate (L/h)	10–15
Slurry concentration[a] (wt%)	2
System pressure (MPa)	10, 20, 30
Oxygen supply[b] (%)	70–100
Reaction time[c] (min)	2, 3

[a] Percentage of dry material in slurry.
[b] The ratio of oxygen supplied as H_2O_2 to the stoichiometric demand of oxygen calculated from carbon content of the test material for complete oxidation of carbon to carbon dioxide.
[c] Average residence time to the volume of reaction room.

$$T = V/V_p'$$

$$V_{p\prime} = V_a'\rho_a/\rho_p$$

V: Real volume of reaction chamber;
V_a': Flow rate of feed slurry at ambient temperature;
ρ_a: Density of slurry at ambient temperature;
ρ_p: Density of slurry under experimental conditions.

Here, water density was taken as ρ_a and ρ_p, although there were about 2 wt% solids in the feed slurry.

3. Results and discussion

3.1. Confirmation of fundamental performance of the system in producing acetic acid from biomass by WO

In order to confirm fundamental performance of the continuous flow reaction system in producing acetic acid from biomass by WO, a run with starch was performed at a temperature of 300°C, with a reaction time of 2 min, an oxygen supply of 80%, and a system pressure of 20 MPa. The results showed the acetic acid yield was about 9%, which was almost the same as those in batch experiments. This may indicate that the continuous flow reaction system has a performance for producing acetic acid by WO of biomass.

3.2. Evaluation of the performance in producing acetic acid

3.2.1. Acetic acid production

3.2.1.1. Effect of pressure. The influence of pressure on the acetic acid yield was investigated at 300°C, for 2 min and with 80% oxygen supply used rice hulls as test material. The acetic acid yield was about 11% at a pressure of 10 MPa, and then the acetic acid yield increased to about 12% when the pressure increased to 20 MPa (Fig. 2A).

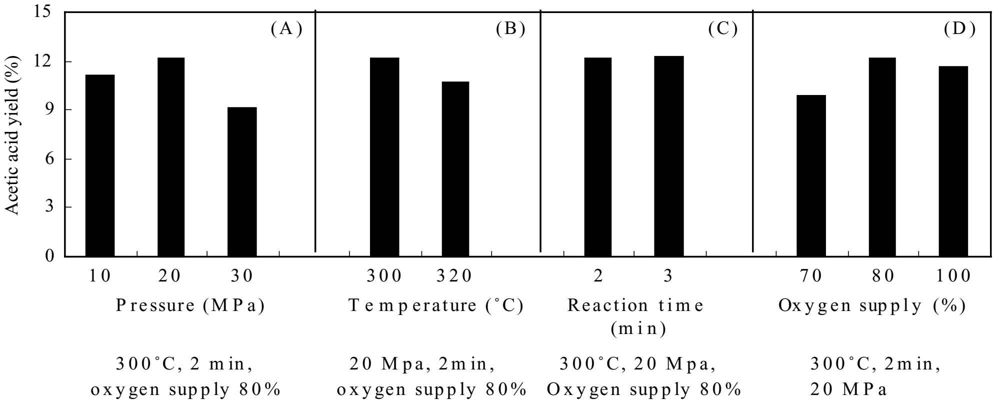

Figure 2 Effects of pressure (A), temperature (B), reaction time (C), and oxygen supply (D) on the acetic acid yield in the case of rice hulls oxidation reaction.

However, the acetic acid yield decreased when the pressure further increased to 30 MPa. Although there are a few reports on the effect of pressure on supercritical water oxidation (SCWO) of organics, few studies report the effect of pressure on WO of organics. Some papers report that the decomposition of organics was promoted with an increase in pressure [7, 8]. There are two possible explanations for a decrease in the acetic acid yield upon pressure increase to 30 MPa. The first is that the acetic acid produced decomposed, and the other is that many organics were not yet oxidized into acetic acid. In order to investigate the reason lead to the decrease in the acetic acid yield, intermediate products in liquid samples were identified and quantified by GC/MS and HPLC. Results show that the carbon concentrations of all intermediate products and residual total organic carbon (TOC) in liquid samples at 30 MPa were lower than those at a pressure of 20 MPa (Fig. 3). These observations may suggest that the decrease in the acetic acid yield at a pressure of 30 MPa is due to an increase in pressure promoting the oxidization decomposition of produced acetic acid. An increase in pressure promoting the oxidization decomposition of organics is most likely because an increase in pressure leads to good mixing of oxygen with organics and hence the reaction time becomes too long to obtain the maximum yield of acetic acid. In order to examine this, the residual oxygen in discharged gas was analyzed. The result showed that the residual oxygen ratio (the ratio of the amount of residual oxygen and the amount of supplied oxygen) decreased from 5% at 20 MPa to 1.4% at 30 MPa.

3.2.1.2. Effect of reaction temperature and reaction time. In order to investigate the effect of reaction temperature, two runs at reaction temperatures of 300 and 320°C were performed at a pressure of 20 MPa, a reaction time of 2 min, and an oxygen supply of 80%. The acetic acid

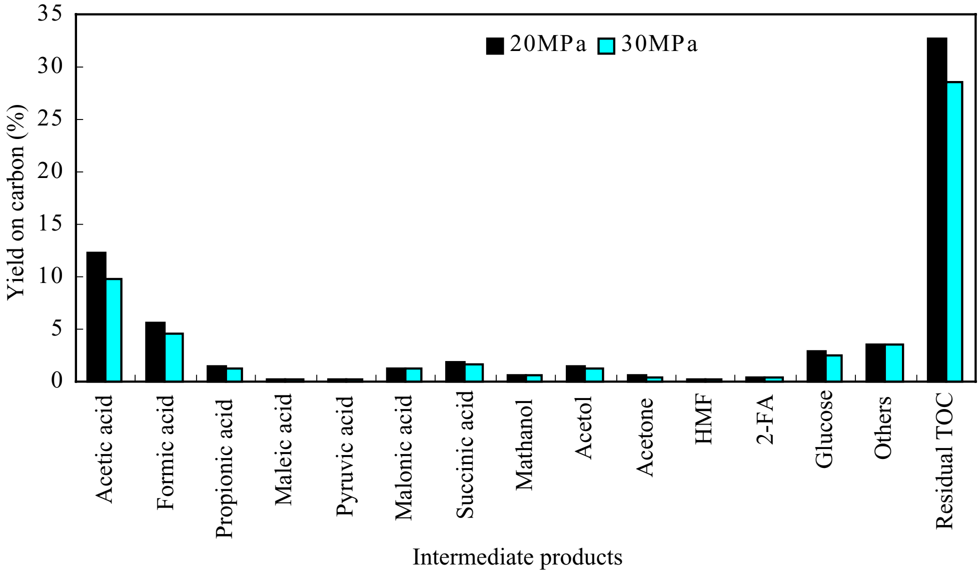

Figure 3 Effect of pressure on products in liquid samples after reaction at 300°C, 2 min, and oxygen supply 80%.

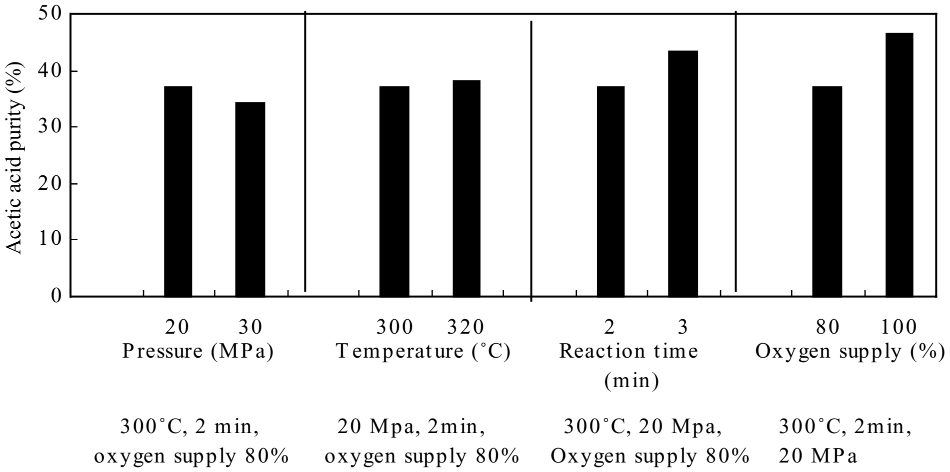

Figure 4 Effect of changing reaction conditions on the acetic acid purity in the case of rice hulls oxidation reaction.

yield obtained at a temperature of 300°C was 12%, which was slightly higher than that obtained at 320°C (Fig. 2B). This result is similar to that obtained with the batch reactor [4]. Subsequently, other two runs for reaction times of 2 and 3 min were performed with a reaction temperature of 300°C, pressure of 20 MPa, and oxygen supply of 80%, to investigate the effect of the reaction time. The acetic acid yield for reaction times of 2 and 3 min were almost the same about 12% (Fig. 2C), possibly indicating that a reaction time of 2 min is sufficiently long and extension of reaction time does not have much influence much on the oxidative decomposition of acetic acid because less oxygen remains and acetic acid is stable.

3.2.1.3. Influence of oxygen supply. Oxygen supply was varied from 70 to 100%. The acetic acid yield increased and then decreased as an oxygen supply increased (Fig. 2D). The highest acetic acid yield was obtained at an oxygen supply of 80%. As reported in our previous study [9], the highest acetic acid yield was obtained at an oxygen supply of 70% in the batch experiments. This difference may be caused by the difference of oxygen consumption resulting from the degree of mixing of oxygen and organics.

In summary, the highest acetic acid yield obtained by the continuous flow reaction system was 12%, which occurred at temperature of 300°C, reaction time of 2 min, oxygen supply of 70–80%, and system pressure of 20 MPa. These results were similar to those obtained using a batch reactor.

3.2.2. Purity of acetic acid

For utilization of acetic acid, both a high yield of acetic acid and a high purity of acetic acid are desired. The influence of system pressure, reaction temperature, reaction time, and oxygen supply on the purity of acetic acid was also investigated. The results are summarized in Fig. 7. The purity of acetic acid is defined here as the percentage of organic carbon of acetic acid in liquid sample against the TOC of the liquid sample. Although the purity of acetic acid can be increased by increasing a reaction temperature, reaction time, oxygen supply and system pressure as discussed before (see Fig. 2), the acetic acid yield under these conditions would simultaneously decreases (Fig. 4). Therefore, the conditions for obtaining the highest yield of acetic acid differ from those for obtaining the highest purity of acetic acid.

3.2.3. Intermediate products other than acetic acid

Residual products other than acetic acid were identified and quantified by GC/MS and HPLC analyses. The results obtained are summarized in Fig. 3. A variety of low molecular weight carboxylic acids, acetol, acetone, HMF, 2-FA, etc. were detected. These intermediate products were also detected in the experiments using a batch reactor. However, the concentrations of all these intermediate, especially HMF and 2-FA, were higher than those in batch experiments. As reported in our previous study [9], HMF and 2-FA are not oxidation products but dehydration products of monosaccharides. These results also suggest that the mixing of oxygen with organics may be insufficient. Moreover, in low molecular weight carboxylic acids, succinic acid and propionic acid may mainly come from the oxidation of lignin in rice hulls, because our study on oxidation mechanism of model compounds of lignin found that the oxidation of phenols can form succinic acid and propionic acid. For methanol and acetone, many studies also showed that methanol and acetone were formed in hydrothermal treatment of carbohydrates with and/or without oxygen [10–12].

TABLE III Comparison of results obtained in the case of filling and non-filling with ceramic beads

	Liquid sample					Off-gas sample				
						Carbon distribution[a] (%)		Oxygen distribution[b] (%)		
	Acetic acid yield (%)	Acetic acid purity (%)	Formic acid yield (%)	Formic acid purity (%)	Residual TOC (%)	CO_2	CO	CO_2	CO	O_2
With ceramic beads	7.0	19.4	21.1	58.6	36.0	63.0	6.6	90.1	4.8	2.5
Without ceramic beads	7.6	21.6	18.2	51.7	35.2	62.8	5.6	89.6	4.0	4.3

Conditions: Potato starch as experimental material, reaction temperature 300°C, reaction time 2 min, system pressure 20 MPa, oxygen supply 70%.

[a] Ratio of carbon amount in each ingredient to carbon amount in experimental material.

[b] Ratio of oxygen amount in each ingredient to oxygen amount in supplied oxidant.

3.2.4. Composition of the off-gas

Fig. 5 shows the composition of an off-gas at the conditions where the highest acetic acid yield was obtained. Although most of the produced gas was carbon dioxide, a little carbon monoxide, methane, hydrogen, and oxygen were also detected. This indicates that the oxidation of organics was almost complete. But, remaining of oxygen even under the condition of insufficient oxygen supply of 80% may show that mixing of oxygen with organics was incomplete.

3.3. Evaluation of critical engineering issues

After successfully producing acetic acid from WO of biomass using the continuous flow reaction system, critical engineering issues were further assessed. As discussed above, although the continuous flow reaction system can work to obtain almost the same acetic acid yield as that in batch experiments, these are still some critical engineering issues such as mixing of oxygen with organics. In order to improve mixing of oxygen with organics, further tests with starch were conducted with and without ceramic beads in the reactor chamber. The results are summarized in Table III. Table III shows that for the yields of acetic acid and formic acid, and the residual TOC, there was no significant difference between these two cases. However, when ceramic beads were used, residual oxygen in the off-gas decreased to 2.5 from 4.3% in the case of without ceramic beads. These observations may indicate that a baffle plate in the reaction chamber is not sufficient to enhance the mixing of oxygen with reactants and ceramic beads in the reaction chamber improve mixing.

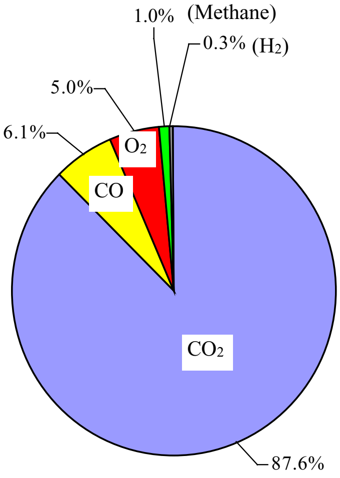

Figure 5 Composition of off-gas at 300°C, 20 MPa, 2 min, and oxygen supply 80%.

4. Summary

A continuous flow reaction system for producing acetic acid by WO of biomass with treatment capacity of 1 kg/h was developed. Experimental runs with rice hulls and potato starch were conducted at temperatures between 300–320°C, for reaction times of 2 and 3 min, with oxygen supplies between 70 and 100%, and at pressures between 10 and 30 MPa. The highest yield of acetic acid and the conditions for obtaining the highest yield of acetic acid in this continuous flow reaction system were almost the same as those obtained in batch experiments, indicating that the developed continuous flow reaction system has the fundamental performance for producing acetic acid by WO of biomass.

These results obtained in this study are important for accomplishing acetic acid production by WO of biomass.

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