A NEW HYDROTHERMAL PROCESS FOR IMPROVING ACETIC ACID YIELD FROM CELLULOSIC BIOMASS

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In this paper, a new two-step process to enhance the acetic acid yield from cellulosic biomass is proposed. The first step is to accelerate the formation of lactic acid in a hydrothermal reaction with the addition of alkali, and the second step is further convert the lactic acid produced in the first step to acetic acid by oxidation with newly added oxygen. Results showed that the addition of an alkali promoted the formation of lactic acid in a hydrothermal reaction of glucose. An acetic acid yield of 27% on the carbon base was obtained by the two-step process. The purity of the acetic acid on carbon basis was 90%. Use of $Ca(OH)_2$ as an alkali has the benefit of obtaining calcium acetate as the final product.

1. Introduction

The hydrothermal process is one of the most promising processes for the conversion of biomass to recycled resources among the several biomass conversion processes, because water at high temperature and pressure behaves as a reaction medium with outstanding properties.

We carried out studies on acetic acid production by wet oxidation (WO) of various food wastes and lignocellulosic wastes to produce calcium/magnesium acetate (CMA), known as an environmentally friendly deicer [1-5]. Results showed that the acetic acid yield obtained in the two-step process without adding any catalyst was approximately twice as much as that obtained by the usual WO. The two-step process consists of both a hydrothermal reaction without a supply of oxygen and catalyst (the first step reaction) and an oxidation reaction (the second step reaction). The first step is to accelerate the formation of 5-hydroxymethyl-2-furaldehyde (HMF), 2-furaldehyde (2-FA) and lactic acid that can produce a large amount of acetic acid by their oxidation, and the second step is to further convert the furans and lactic acid produced in the first step to acetic acid by oxidation with newly supplied oxygen.

Although, in the hydrothermal reaction without the addition of a catalyst (the first step), a considerable amount of lactic acid, as well as HMF and 2-FA was formed, the yield of lactic acid could be selectively increased by adding an alkali in the first step, because it is generally known in sugar chemistry that lactic acid is a product of alkaline degradation of sugar and it has been reported that the mechanism of lactic acid formation in a hydrothermal condition is the same [6]. Because the acetic acid yield by the oxidation of lactic acid was much higher than that by the oxidation of furans as reported in a previous report [7], the acetic acid yield can be further improved by adding an alkali in the first step.

The purpose of this study was to construct a new two-step process by modifying the previously developed two-step process using an alkali in the first step reaction.

2. Experimental Methods

Glucose was used as a test material because it is a primary intermediate compound formed during the conversion of cellulosic biomass. DL-lactic acid was also used as a test material. DL-lactic acid is commercially available only in the form of a 85-92 % solution and contains lactic anhydride, lactic acid lactate, and other low molecular oligomers. A pretreatment where a dilute aqueous solution was kept at 85 deg C over night was made [8]. A HPLC chromatogram assured the purity of the lactic acid after pretreatment.

$Ca(OH)_2$ was selected as an alkali, because our purpose in producing acetic acid is to produce calcium/magnesium acetate (CMA) as the final product. The addition of $Ca(OH)_2$ can provide not only an alkaline condition but also a calcium source to produce CMA.

All experiments were carried out with a batch micro-reactor made of SUS 316, with an internal volume of 5.7 cm^3, described earlier [5]. The typical experimental procedure was as follows: The desired amount of test material, alkali, and water were put into the batch reactor, which was then sealed. The reactor was put into a salt bath that had been preheated to a desired temperature. After the desired reaction time, the reactor was removed from the salt bath and put into a cold water bath to quench the reaction. After this step (the first step), H_2O_2 was added into the cooled reactor and the oxidation (the second step reaction) took place in the same procedure as in the first step. The reaction time was defined as the time at which the reactor was maintained in the salt bath. Experimental conditions were as follows; temperature 270-400 ^oC, reaction time 30-180 s, and water fill 30%. The definition of reaction temperature, reaction time and water fill was described earlier [5]. A 0.07 g test material was used in all experiments.

After the reaction was quenched, solution samples were collected and analyzed by HPLC and GC/MS. Details of the conditions for GC/MS and HPLC analyses are available elsewhere [3].

3. Results and Discussion

3.1. Proposal of a new two-step reaction process to enhance the yield of acetic acid. Although it is well-known in sugar chemistry that an alkali can promote the formation of lactic acid, it is unknown how the alkali promotes the formation of lactic acid in a hydrothermal reaction of carbohydrates. To investigate this, experiments with glucose were carried out with and without adding $Ca(OH)_2$ at 300 ^oC for 60 s. Results showed that the yield of lactic acid obtained with the addition of 0.2 M $Ca(OH)_2$ increased to 27.6% from the 11% obtained without alkali. This indicates that an alkali, even $Ca(OH)_2$, can promote the formation of lactic acid in a hydrothermal reaction.

On the basis of these results, a new two-step process is proposed, to enhance the acetic acid yield from cellulosic biomass. As shown in Fig. 1, in the first step, lactic acid is produced in a hydrothermal reaction with alkali, and in the second step, the lactic acid produced in the first step is further converted to acetic acid by oxidation with newly added oxygen. As mentioned before, our purpose in producing acetic acid was to produce calcium acetate. Therefore, the new two-step process requires only changing the timing of the addition of a Ca source from "after reaction" to "before reaction".

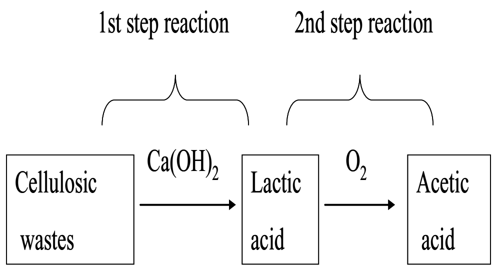

Fig.1. A new two-step process proposed to enhance the yield of acetic acid.

3.2 Lactic acid production in the first step. To obtain a better yield of acetic acid in the two-step process, the yield of lactic acid should be high in the first step. Experiments with glucose, to obtain favorable conditions for the production of lactic acid, were performed. At first, a first series of experiments were carried out at a reaction temperature of 300 ^oC, reaction time 30 s and concentrations of $Ca(OH)_2$ from 0.08 to 0.4 M, to investigate the effect of concentration of $Ca(OH)_2$. As shown in Fig. 2, an increase in the concentration of $Ca(OH)_2$ from 0.08 M to 0.32 M led to a remarkable increase in lactic acid yield while the lactic acid yield was not changed with a further increase of $Ca(OH)_2$ up to 0.4 M. For this reason, the second series of experiments, to study the effects of reaction temperature and time, were conducted at 0.32 M of $Ca(OH)_2$. All yields are reported in carbon percent to the carbon of the initial reactant.

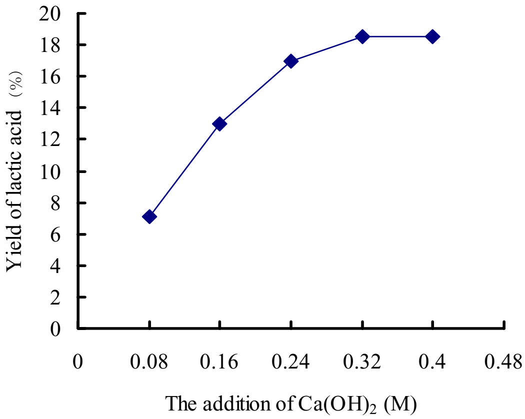

Fig. 2. Influence of $Ca(OH)_2$ concentration on the yield of lactic acid (300℃, 30 s).

The effect of reaction temperature and time is shown in Fig. 3. An increase in lactic acid yield is seen initially then a decrease is seen as the residence time increases. The highest yield occurred at 60 s for all reaction temperatures except 400 °C. The decrease beyond 60 s was not critical at 270 and 300 °C, but the decrease became critical beyond 350 °C. These observations indicate that using a reaction temperature over 350 °C should be avoided to obtain a high yield of lactic acid.

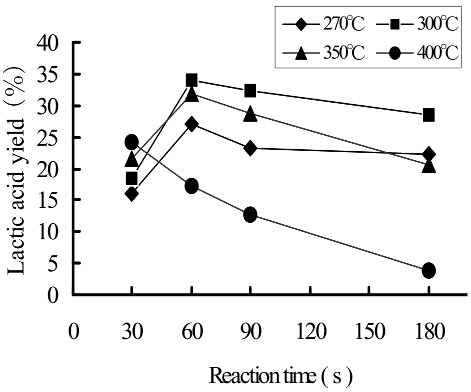

Fig.3. Influence of reaction time and temperature on the yield of lactic acid .

From the discussion above, it can be seen that the highest yield of lactic acid is 34 %, which occurred at a reaction temperature of 300 °C, reaction time of 1 min, and a $Ca(OH)_2$ concentration of 0.32 M.

3.3 Acetic acid production in the two-step process. Having obtained the conditions favorable for the production of lactic acid from glucose, a series of experiments were performed in the two-step process at a reaction temperature of 300 °C for both the first and the second steps, reaction times from 30 to 90 s for the first step and from 60 to 240 s for the second step. The concentration of $Ca(OH)_2$ was 0.32 M in the first step and the oxygen supply was 70 % in the second step. The selection of an oxygen supply of 70 % was based on a previous result that the highest yield of acetic acid was obtained with a 70 % oxygen supply in WO of cellulosic biomass.

The results obtained are shown in Fig. 4. Firstly

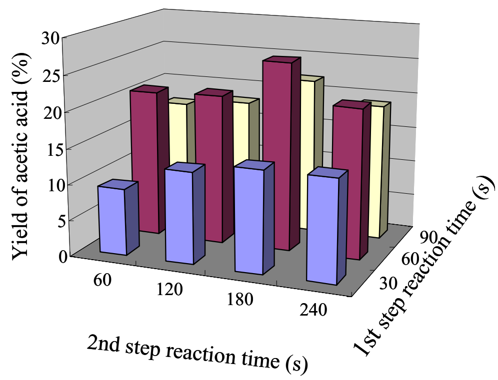

Fig.4. Effect of reaction time on the acetic acid yield in the new two-step reaction (temperature of 300°C, oxygen supply of 70 %).

as to the effect of the reaction time in the first step, it can be seen that the highest yield of acetic acid occurred at 60 s for all reaction times in the second step. This may correspond to the fact that the highest yield of lactic acid occurred at 60 s (see Fig. 3). Consistent times obtained the highest acetic acid yield in the two-step process and the time for the highest lactic acid yield in the first step reaction may suggest that lactic acid, as a main intermediate product, made a great contribution in producing acetic acid among all intermediate products after the first step reaction. In fact, the balance for carbon showed that lactic acid was 62% of the solution after the first step reaction at 300 °C, 90 s. Results of the effect of reaction time in the second step show that the acetic acid yield increased with reaction time of the second step, but the highest yield of acetic acid occurred at 3 min for all reaction times in the first step. Consequently, the highest yield of acetic acid is obtained when the reaction temperature is 300 °C, the reaction time is 1 min, and the concentration of $Ca(OH)_2$ is 0.32 M in the first step, and the reaction temperature is 300 °C, the reaction time is 3 min, and the oxygen supply is 70% in the second step. Under these conditions, a significantly high acetic acid yield of 27% was obtained.

To estimate the purity of acetic acid, intermediate products in samples after the treatment in the two-step process were identified by HPLC and GC/MS. As a result, only small amounts of formic acid, propionic acid and acrylic acid were found, hence the purity of acetic acid is as high as 90%. Here, the purity of acetic acid is defined as the percentage of carbon in a liquid sample of acetic acid against the TOC of the liquid sample after reaction.

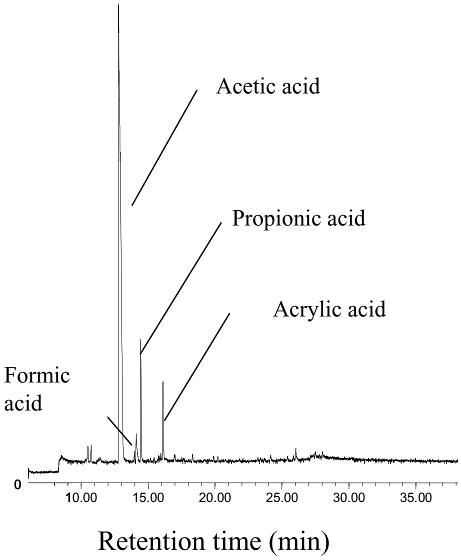

Fig.5. GC/MS chromatogram of intermediate products after the treatment in the two-step process. (300 °C, 60 s and 0.32 M $Ca(OH)_2$ for the first step, 300 °C, 3 min and 70% of oxygen supply for the second step).

3.4 Effect of $Ca(OH)_2$ on the oxidation of lactic acid. As described above, the highest yield of acetic acid occurred at a 3 min reaction time in the second–step for all reaction times in the first step. Our previous study showed that the highest yield of acetic acid by lactic acid oxidation was obtained at 1 min, not at 3 min, at 300 °C, without the addition of an alkali, This may suggest that $Ca(OH)_2$ affects the oxidation of lactic acid. To investigate the effect of $Ca(OH)_2$ on the oxidation of lactic acid, lactic acid was oxidized with an addition of 0.32 M $Ca(OH)_2$, at 300 °C, oxygen supply of 70 % and reaction times between 60 s and 240 s. As shown in Fig. 6, the highest yield of acetic acid occurred at 3-4 min, not at 1 min. Fig.7. displays HPLC chromatograms of samples after reaction with and without $Ca(OH)_2$. In the case of without $Ca(OH)_2$, no residual lactic

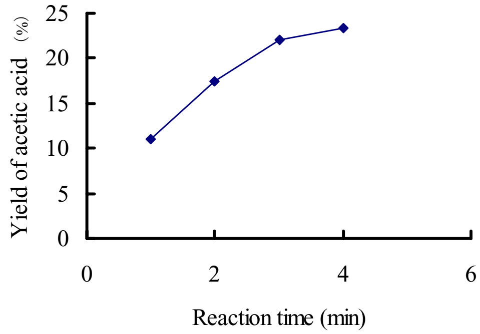

Fig.6. Influence of reaction time on the yield of acetic acid from oxidation of lactic acid with the addition of 0.32 M $Ca(OH)_2$ (temperature 300 °C, oxygen supply of 70%).

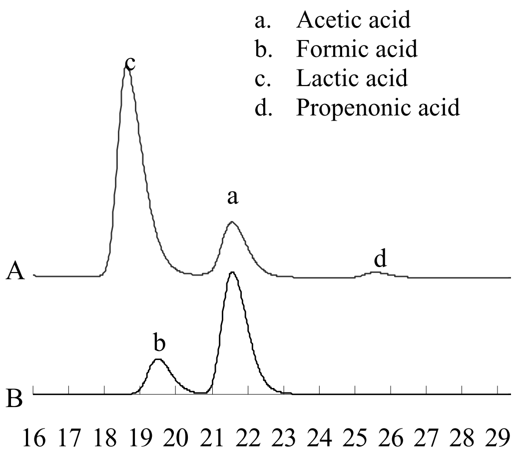

Fig.7. HPLC chromatograms of intermediate products of lactic acid with and without adding of alkaline(temperature 300 °C, oxygen supply 70%, reaction time 60 s). A With the addition of $Ca(OH)_2$ B No addition of $Ca(OH)_2$.

acid was identified, but in the case of addition of $Ca(OH)_2$, considerable amount of lactic acid remained. This indicates that lactic acid is difficult to decompose when $Ca(OH)_2$ is added.

Additionally, Fig.6. shows that an addition of $Ca(OH)_2$ causes a decrease in not only the oxidation rate of lactic acid, but also the formation rate of acetic acid from lactic acid. As reported in our previous paper [7], an excellent yield of about 45% is obtained when lactic acid is oxidized without alkali. However, as shown in Fig. 6, the highest yield of acetic acid was only 25% when oxidation occurred in an alkali solution. This may be the reason why the highest yield of acetic acid obtained by the two-step process with addition of $Ca(OH)_2$ is 27%, that is lower than expected.

4. Conclusions

Previous investigations concerning acetic acid production from cellulosic biomass by hydrothermal treatment have shown that the acetic acid yield can be increased greatly with a two-step process without adding a catalyst in the first step. The purpose of this study was to further enhance the acetic acid yield by improving the two-step process using an alkaline catalyst in the first step of the reaction. Results showed that an alkaline catalyst, even $Ca(OH)_2$, can promote the formation of lactic acid in a hydrothermal reaction of glucose. Acetic acid was obtained with a good yield of 27% on a carbon base in the two-step process. The purity of acetic acid was also considerably high, at about 90%. The acetic acid yield in the two-step process with $Ca(OH)_2$ in the first step can be higher

References and Notes

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