

Hydrothermal conversion of biomass into acetic acid

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Hydrothermal process is one of the most promising processes for the conversion of biomass waste into resources among the several biomass conversion processes, because water of high temperature and high pressure has remarkable properties as a reaction medium. This paper described advances in our research involving overall reaction pathways for acetic acid production from biomass, mainly including (1) acetic acid production by controlling pathways of hydrothermal reaction, (2) acid-base behavior of water in the subcritical region and (3) effect of lignin on the acetic acid production in WO of lignocellulosic biomass.

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1. Introduction

Recycling process of the conversion of biomass waste into resources is receiving increased interest due to the perceived need for maintaining the global carbon cycle system to work harmoniously. Any technological process for converting biomass into chemicals involves the breakdown of complex organic structures. Several treatment processes have been under development. Hydrothermal treatment is one of the most effective ways, because water of high temperature and high pressure behaves as a reaction medium with remarkable properties.

Our previous results on supercritical water oxidation (SCWO) of food wastes showed that acetic acid was a stable intermediate product for almost all food wastes [1–3]. This gives us a suggestion that it is possible to obtaining a high yield of acetic acid by SCWO or wet oxidation (WO) of biomass. Further, it is well known that the most common chemicals used as roadway deicer are calcium chloride and sodium chloride and widespread and massive use of these chloride salts have serious corrosion and environment problems. Then, calcium/magnesium acetate (CMA) has been proposed as a substitute for chloride salts, since it has acceptable ice-melting properties, and is much more benign to the environment, non-corrosive and biodegradable [4–6]. The cost, however, of manufacturing CMA, is a major drawback that limits its widespread application as a roadway deicer. CMA's high cost is mostly attributed to the price of acetic acid required to produce CMA. If residual acetic acid in WO of biomass waste can be utilized to produce acetate, more precisely speaking, if acetic acid can be produced in large quantity by WO

of biomass wastes, then it would help not only to reduce the cost of manufacturing CMA, but also to give a new process for organic waste treatment.

Therefore, our research group began research work on the acetic acid production from biomass waste by WO, to produce calcium/magnesium acetate (CMA) [7–11]. Results so far obtained indicate that the direct oxidation of cellulose would produce formic acid but not acetic acid, so that the yield of acetic acid is limited to only 11–13% on the carbon basis by a usual WO. In order to improve the conversion efficiency to acetic acid, a comprehensive research on WO mechanisms, properties of a solution at high temperatures and pressures, etc. has been carried on. In this paper, advances in our research involving overall reaction pathways for acetic acid production by hydrothermal treatment of biomass are described.

2. Experimental methods

2.1. Materials

Rice hulls as a representative of lignocellulosic wastes and potato as a representative of food waste were selected as test materials. Cellulose, starch (potato) and glucose as representatives of the main component of cellulosic waste and food waste were also used as test material. The rice hulls were ground to pass a 100-mesh size screen in a cross-beater mill. Cellulose used in this study is a filter paper powder (under 200-mesh in size). Starch and glucose were of reagent grade. 5-hydroxymethyl-2-furaldehyde (HMF), 2-furadehyde (2-FA), and DL-lactic

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A NOVEL METHOD OF ADVANCED MATERIALS PROCESSING

acid were also used as experimental materials. 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°C over night was made. A HPLC chromatogram assured the purity of the lactic acid after pretreatment. Additionally, following chemicals used for indemnifying intermediate products were used: fructose (99+%), glyceraldehyde (97+%), pyruvaldehyde (40%), dihydroxyacetone (99+%).

Amounts of starting materials were limited to 0.07 g (dry base) to prevent the reaction temperature increase due to WO. Hydrogen peroxide was used as an oxidant. The oxygen supply was defined as the ratio of the amount of oxygen supplied by H₂O₂ to the stoichiometric demand of oxygen for complete oxidation of carbon, calculated from the carbon content of test material, to carbon dioxide. Our previous studies revealed that a 100% oxygen supply was approximately stoichiometric for complete oxidation of carbohydrates [1, 3].

2.2. Experimental procedure

All experiments were conducted in a batch reactor system shown in Fig. 1.

It has been described elsewhere [1, 12], but reactor was horizontally placed into a salt bath during the reaction. A brief summary is given below. The desired amounts of test material and deionized water (for hydrothermal reaction) or a mixture of deionized water and hydrogen peroxide (for WO) were put into a batch reactor. After the loading procedure was completed, the reactor was immersed in a salt bath that had been preheated to the desired temperature. In the salt bath, the reactor was

TABLE I Experimental conditions used for GC/MS and HPLC analyses

GC/MS	
Instrument	GC: Hewlett Packard 5890 Series II MS: Hewlett Packard 5890B Series II
Column	HP-INNOWAX (Cross-Linked PEG 30 m×0.25 m×0.25 μm)
Flow rate	0.7 m/min
Injection temp	230°C
Detection temp	250°C
Oven temp	begin at 40 °C, ramped at 6 or 7°C /min to 250°C, and then held for 20 min.
Injection	splitless
HPLC	
Instrument	Waters
Column	Shodex Ionpak KC-811 × 2 Shodex SUGAR SH1011
Fluent	2 mM HClO ₄
Flow rate	1.0 mL/min
Detector	UV-210 nm for column of Shodex Ionpak KC-811, RI for column of Shodex SUGAR SH1011
Temp	50°C for Shodex Ionpak KC-811 Ambient for Shodex SUGAR SH1011

shaked, keeping it horizontally, to enhance mixing and heat transfer. After the desired reaction time, the reactor was taken out of the salt bath and was immediately put into a cold water bath to quench the reaction. The reaction time was defined as the time that the reactor was kept in the salt bath.

In a two-step process, the two-step procedure was taken: One is a hydrothermal reaction without an oxygen supply (the first step reaction) and the other WO (the second step reaction). That is, at the first step reaction, only the test material and water were added to the reactor for the reaction. After the first step, H₂O₂ was added to the reactor cooled down, and then the second step reaction took place.

2.3. Product analysis

After the reaction, liquid samples were collected and intermediate products were identified and quantified by GC/MS and HPLC. Conditions for GC/MS and HPLC analyses are shown in Table I. All yields reported in this paper are defined as the carbon percent based on that of initial material(s). The residual organic carbon concentration (TOC) in liquid samples was also measured with a TOC analyzer.

3. Phase formation

3.1. A new two-step process for enhancing the acetic acid yield

As described above, the yield of acetic acid is limited to only 11–13% by the conventional WO and the yield

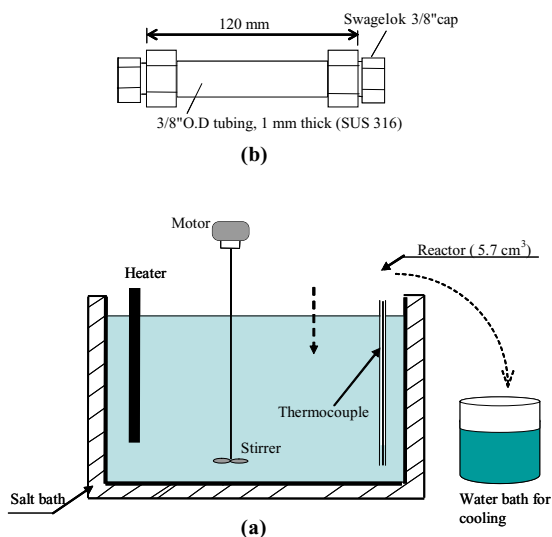


Figure 1 (a) Schematic of batch reactor system; (b) reactor vessel assembly.

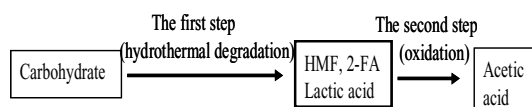


Figure 2 Two-step process for enhancing acetic acid.

of acetic acid from carbohydrate biomass is hardly improved in the direct oxidation (conventional WO). These results mean that the direct oxidation reaction of carbohydrate biomass should be inhibited to improve the acetic acid yield. Therefore, a new two-step process for improving the yield of acetic acid was proposed [13, 14]. As shown in Fig. 2, the two-step process consists of both a hydrothermal reaction process without a supply of oxygen (the first step reaction) and an oxidation reaction process (the second step reaction).

The first step is to convert carbohydrates to 5-hydroxymethyl-2-furaldehyde (HMF), 2-furaldehyde (2-FA) and lactic acid, and the second step is to further convert HMF, 2-FA and lactic acid produced in the first step to acetic acid by oxidation with oxygen newly supplied, because HMF, 2-FA and lactic acid can produce a large amount of acetic acid by their oxidation.

In order to propose the two-step process, experiments were performed to obtain respective favorable conditions for producing HMF, 2-FA and lactic acid by hydrothermal reaction of carbohydrates and acetic acid by oxidation reaction of HMF, 2-FA and lactic acid. Results are summarized in Table II. In the hydrothermal treatment of cellulose and starch, the similar conditions for obtaining the highest yield of HMF, 2-FA and lactic acid were obtained, that is at a temperature of 300°C and for a reaction time of 2 min for cellulose and 1 min for starch. Similar results were also obtained in the oxidation of all of HMF, 2-FA and lactic acid as the conditions for obtaining the highest yield of acetic acid, that is a temperature of 300°C, a reaction time of 1 min and an oxygen supply of 70%. These results indicate that it is easy to control the reaction conditions for obtaining the highest yield of acetic acid in the two-step process.

TABLE III Comparison of acetic acid yields^a and purity^b by a conventional wet oxidation(WO) and a two-step process

	Conventional WO		Two-step process	
	Yield (%)	Purity (%)	Yield (%)	Purity (%)
Rice hulls	11.7	33.4	21.7	75.5
Cellulose	9.0	26.6	16.3	68.5
Starch	9.6	28.2	17.5	70.0
Reaction condition	Temp(°C)	300	300 ^c	300 ^c
	Time (min)	1	2	1
	O ₂ (%)	70	0	70

Under the optimum conditions mentioned above, cellulose and starch as well as rice hulls (at optimum conditions for cellulose) were treated in the two-step process. As shown in Table III, the acetic acid yield obtained in the two-step process became approximately twice as that obtained by the usual WO procedure for all test materials. From Table III, it is also seen that, beside the yield of acetic acid, the purity of acetic acid was also improved greatly. Furthermore, because furans (HMF and 2-FA) and lactic acid are the main intermediate products, which make a great contribution to acetic acid production in the two-step process, the contribution of reaction pathways via furans and lactic acid to form acetic acid was also discussed. It was found that the contribution of furans and lactic acid as detected in a solution after the first-step reaction to form acetic acid were roughly 40 and 20%, respectively. Most of other 40% also mainly come from intermediate products on the reaction pathways via either furans or lactic acid, that is the formation and degradation products of furans and lactic acid, because most of the intermediate products detected were those that appeared on the reaction pathway via either furans or lactic acid. Therefore, the contribution of two pathways via furans and lactic acid in the two-step process to convert carbohydrates into acetic acid was estimated as roughly 90% [14].

TABLE II The highest yields of HMF, 2-FA and lactic acid from hydrothermal treatment of cellulose and starch and the highest yield of acetic acid from the oxidation of HMF, 2-FA and lactic acid and their respective reaction conditions

Material	Hydrothermal reaction					Oxidation reaction			
	Yield ^a (%)			Condition		Yield ^a (%)	Condition		
	HMF	2-FA	Lactic acid	Temp(°C)	Time (min)		Acetic acid	Temp(°C)	Time(min)
Cellulose	18.2	8.7	10.0	300	2.0				
Starch	19.0	8.8	11.5	300	1.0				
HMF						15.5	300	1.0	70
2-FA						20.0	300	1.0	70
Lactic acid						41.6	300	1.0	70

To take advantage of the two-step process further, hydrothermal degradation of HMF, 2-FA and lactic acid were investigated. Results obtained at a temperature between 250 and 300°C and for a reaction time ranging from 10 to 120 s showed that 2-FA and lactic acid were hardly decomposed below 300°C. The highest degradation was only 2–3%. However, the HMF was easily degraded. Even so, as can be seen from Table II, the HMF yield from cellulose and starch was higher than the yields of 2-FA and lactic acid, indicating that the formation reaction of HMF was faster than that of 2-FA and lactic acid. These observations suggest that control of degradation reaction of HMF would lead to the improvement of the acetic acid yield. Experiments of hydrothermal degradation of HMF showed that the degradation products from HMF were mainly 1, 2, 3-benzenetriol with a small amount of levulinic and formic acids. Furthermore, the oxidation experiments with 1, 2, 3-benzenetriol and levulinic acid showed that the acetic acid yield from levulinic acid was much higher than that from 1, 2, 3-benzenetriol. So, if it is possible to control the degradation pathways of HMF to form levulinic acid, rather than forming 1, 2, 3-benzenetriol, then it should further enhance the yield of acetic acid in the two-step process.

3.2. Acid-base catalytic role of water in the subcritical region

3.2.1. The formation mechanisms of lactic acid and base catalytic role of subcritical water

As discussed before, a large amount of lactic acid were formed in hydrothermal reaction of carbohydrates without adding any alkaline catalyst. It is generally known in the sugar chemistry that lactic acid is a product of alkaline degradation of sugar, and the conversion mechanism of sugar to lactic acid in alkaline solution is well established by Nef [15, 16] and Evans [17] with some modifications afterward. However, the conversion mechanism of cellulosic biomass to lactic acid in subcritical water had not been fully understood.

In order to investigate the conversion mechanism of cellulosic biomass to lactic acid in subcritical water without addition of any catalyst [18], intermediate products after hydrothermal treatment of cellulose and glucose were identified in detail by GC/MS, HPLC and NMR. Results showed that fructose, glyceraldehydes, dihydroxyacetone and pyruvaldehyde were found in both cellulose and glucose. More details on the identification of these intermediate products, including lactic acid, are available elsewhere [14, 18]. These intermediate products are also formed in the conversion of sugar in alkaline solution to lactic acid and are considered to be the sources of lactic acid in alkaline solution according to the traditional theory.

On the basis of identified intermediates and the traditional theory of conversion of sugar to lactic acid in an alkaline solution, a mechanism for the formation of lactic acid from glucose in subcritical water was systematically interpreted as shown in Fig. 3.

It was assumed that glucose first undergoes isomerization to fructose by the LBAE transformation. Subsequently, fructose may be converted to glyceraldehyde. An experiment with fructose supported the assumption by showing the formation of glyceraldehyde. At the same time, glyceraldehydes may rearrange into dihydroxyacetone by the LBAE transformation. An experiment with glyceraldehydes also supported the assumption by showing the formation of a considerably high amount of dihydroxyacetone.

In addition, a possible co-product with fructose, if LBAE transformation occurs, would be glucose 1, 2-enediol, because LBAE transformation of glucose would give a series of enediol as well as fructose. Glyceraldehyde would be formed by cleavage of glucose 1, 2-enediol. However, in our study, glucose 1, 2-enediol was not detected. This could probably be due to its instability. Further, both glyceraldehyde and dihydroxyacetone may lose water to form pyruvaldehyde, which subsequently undergoes a benzilic acid rearrangement to lactic acid. According to this mechanism, pyruvaldehyde would be formed in the hydrothermal treatment of glyceraldehyde and dihydroxyacetone, and lactic acid would be the major product in the hydrothermal treatment of pyruvaldehyde. Experiments with glyceraldehydes, dihydroxyacetone and pyruvaldehyde showed that pyruvaldehyde was formed in experiments involving both glyceraldehydes and dihydroxyacetone as reactants, and lactic acid was the major product in the experiment involving pyruvaldehyde as a reactant.

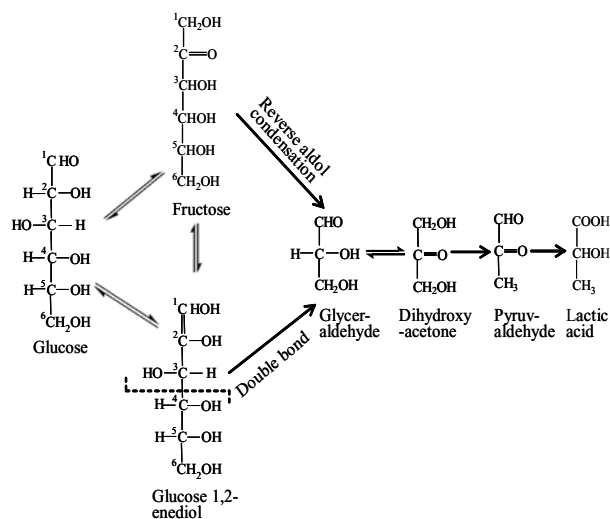


Figure 3 Proposed pathways of conversion of glucose to lactic acid in subcritical water.

The discussion above may imply that the conversion of glucose to lactic acid in subcritical water appears to follow the same pathways elucidated in the conversion of sugar to lactic acid in alkaline solution. This means that subcritical water may act as an effective Bronsted base catalyst.

3.2.2. Acid-catalytic role of water in the subcritical region

Besides lactic acid, HMF and 2-FA were also formed in large quantity in hydrothermal treatment of carbohydrates without addition of any acid catalyst, as discussed before. It suggests that subcritical water may act as an acid catalyst, because it is generally known that HMF and 2-FA is products of the facile, acid-catalyzed dehydration of hexoses and pentoses, respectively. The possibility of the formation of HMF and 2-FA is supposed to be due to autocatalysis (as by acidic initial products). An experiment with formic and acetic acids, to recognize the potential for autocatalysis by formic and acetic acids, showed that an addition of acetic acid and formic acid had no significant effect on the formation of HMF and 2-FA. These results indicate that subcritical water may act not only as Bronsted base catalysts but also as acid catalysts.

The most likely source of hydronium and hydroxide ions is the high temperature water itself because subcritical water has a stronger tendency to ionize than ambient water; the ionization constant reaches a maximum near 300°C at the saturation pressure. As discussed before (see Table II), the highest yields of HMF, 2-FA and lactic acid were obtained in the same temperature range of 280–300°C. This result may be contributed by the fact that the ionization constant at the saturation pressures reaches the maximum in this temperature range.

3.2.3. The action of acid-base catalysts of water in the subcritical region.

To further confirm the action of acid-base catalysts of water in the subcritical region on glucose decomposition, glucose was treated with the addition of either H₂SO₄ or NaOH. As results, lactic acid in the experiment with H₂SO₄, and HMF and 2-FA in the experiment with NaOH were still identified, when the concentration of H₂SO₄ or NaOH was 0.02 mol/L. This indicates that base-catalyzed reactions occurred even with the addition of an acid catalyst, and acid-catalyzed reactions occurred even with the addition of a base catalyst. This means that subcritical water may act as a strong acid-base catalyst as 0.02 mol/L of H₂SO₄ or NaOH.

3.3. Role of lignin in WO of lignocellulosic biomass

Our previous studies on acetic acid production by WO of lignocellulosic biomass found that the acetic acid yields

TABLE IV Acetic acid yield by WO of cellulose, lignin and a mixture of cellulose and lignin

Material	Acetic acid yield ^a (%)
Cellulose	9.0
Lignin	6.3
Mixture of cellulose and lignin (8:2)	11.1
Mixture of cellulose and lignin (5:5)	10.7

from rice hulls and Japan cedar sawdust were higher than those from cellulose [19]. This may imply that lignin most likely affects the reaction of cellulose to produce acetic acid. In other words, lignin may play an important role to increase the acetic acid production in WO of lignocellulosic wastes.

For precise understanding, WO experiments with a mixture of cellulose and lignin were carried out under the condition where the highest acetic acid yield was obtained for all of rice hulls, sawdust and cellulose. As shown in Table IV, in the case of a mixture of cellulose and lignin, the acetic acid yield became higher than that in the case of cellulose and lignin alone, indicating that lignin influences the reaction in WO of cellulose for the production of acetic acid.

Next, the mechanism that lignin increases the yield of acetic acid was discussed. It is generally known that phenols are widely used as oxidation inhibitors in the food chemistry and there were reports that phenols also acted as an oxidation retardant in the oxidation of hydrocarbons in the liquid phase [20, 21]. In addition to this, HMF and 2-FA, which can produce a large amount of acetic acid by their oxidation, was found in the case of mixing cellulose with lignin. On the basis of these facts, the mechanism that lignin enhance the acetic acid yield may be explained as follows, as summarized in Fig. 4.

In general, in the WO reaction of cellulose, there are various competing reaction pathways, each of which is favored by different conditions. When the oxygen supply is sufficient, oxidation reaction takes place over other

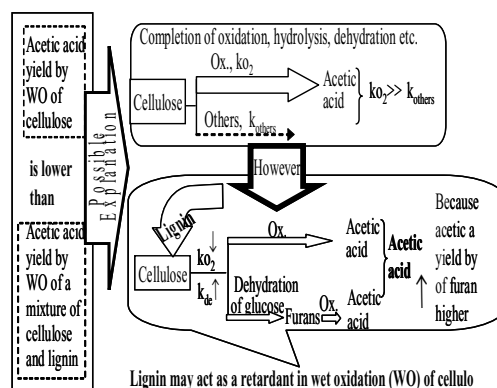


Figure 4 Possible explanations why lignin creases acetic acid yield in WO of lignocellulosic waste.

reactions such as hydration and dehydration, because the rate of oxidation reaction is much more rapid than other reactions. However, if lignin or decomposition intermediates of lignin act as an oxidation retardant like phenols in the oxidation of hydrocarbons in the liquid phase, the existence of lignin will decrease the rate of oxidation reaction of cellulose, while other reactions will proceed. Because cellulose easily forms HMF and 2-FA, which are dehydration products of monosaccharides, by hydrothermal treatment without oxygen supply as discussed before, they would be easily formed when lignin coexists with cellulose. In other words, the formation of HMF and 2-FA in the case of the oxidation of mixture of cellulose and lignin may indicate that lignin would play a retarding role for the oxidation of cellulose in WO at a high temperature and pressure, and the retarding mechanism would be the same as the known-inhibition mechanism in the liquid oxidation of hydrocarbons at a low temperature.

4. Conclusions

In order to gain a high yield of product from hydrothermal conversion of biomass to chemicals, comprehensive researches, such as WO mechanisms and properties of a solution at high temperatures and pressures, are needed. This paper described advances in our research involving overall reaction pathways for acetic acid production from biomass, mainly including (1) The acetic acid production by controlling reaction pathways in the hydrothermal condition, (2) the acid-base behavior of water in the subcritical region and (3) the effect of lignin on acetic acid production in WO of lignocellulosic biomass. Results are summarized as follows.

The acetic acid yield was enhanced about twofold by firstly producing HMF, 2-FA and lactic acid under the condition of non-supply of oxygen (the first-step reaction), and then by oxidizing them to acetic acid (the second-step reaction).

Water in the subcritical region may act as an effective acid-base catalyst. The conversion mechanism of cellulosic biomass to lactic acid in subcritical water without addition of any alkaline catalyst appears to follow the same pathways elucidated in the conversion of sugar to lactic acid in an alkaline solution.

Lignin may indirectly attribute to the increase of acetic acid production in WO of lignocellulosic biomass. A pos-

sible mechanism for this is that lignin would act as a retardant in WO of cellulose, leading to the formation of furans, which can produce a large amount of acetic acid by their oxidation.

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