

## HYDROTHERMAL CONVERSION OF BIOMASS INTO VALUE-ADDED PRODUCTS: TECHNOLOGY THAT MIMICS NATURE

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The term “hydrothermal” comes originally from the field of geology. Hydrothermal reactions generally can be defined as reactions in the presence of aqueous solvents under high temperature and pressure. Such reactions played a very important role during formation of fossil fuels. On the basis of the natural phenomena, we have conducted a series of studies concerning hydrothermal conversion of biomass into value-added products. This article gives an overview of some recent advances in our research on hydrothermal conversion of biomasses, mainly including the production of low molecular weight carboxylic acids, such as acetic acid, lactic acid, and formic acid, from carbohydrate and lignocellulosic biomasses, as well as glycerin, which is a by-product of the bio-diesel fuel manufacturing process.

*Keywords: Hydrothermal reaction; Biomass; Fuels; Lignocelluloses; Cellulose, Low molecular weight carboxylic acids*

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### INTRODUCTION

A serious global energy crisis is the result of imbalance of rapid consumption of fossil fuels and slow formation of fossil fuels. The most essential route for diminishing the imbalance should involve rapid conversion of organic wastes and biomass into fuels and/or chemicals. One of the promising methods is to simulate the natural phenomena of the formation of fossil fuels. It is very well known that over millions of years, plant and animal remains were buried deeper and deeper under sediments. The enormous heat and pressure deep within the strata turned these fossils into oil and natural gas. Two factors appear to be key points in the natural process of turning plant and animal remains into fossil fuels. One is high temperature and pressure with the help of water, and the other one is the duration of hundreds of millions of years. For the latter, the length requirement of time is because of the need for sedimentation of plant and the animal remains deep into the underground, where the reaction to turn fossils into fuels can occur; however, we do not believe that the reaction rate to turn plant and animal remains into fossil fuels is that slow. In fact, we propose that the reaction rate to turn plant and animal remains into fossil fuels is very fast. Thus, if humans could simulate the conditions of high temperature and pressure underground, then, the process should quickly turn organic waste and biomass into fuel and chemicals. Such a process has the potential to efficiently and harmoniously circulate the earth's energy and resources, thus helping to maintain the needed balance of

energy and resources. Bearing this in mind, our research group has carried out a series of studies related to application of hydrothermal reaction to the conversion of biomass into chemicals (Jin et al. 2000 b; 2001; 2002 a, b; 2005; 2007; Kishita et al. 2005; Zhou et al. 2006). Also, many researchers have reported that hydrothermal conversion of biomass, particular for cellulose biomass, into chemicals is a very effect method (Sasaki et al. 2000; Fukuoka et al. 2006; Matsumura et al. 2006; Fang et al. 2008), most likely because high temperature water exhibits properties that are very different from those of ambient liquid water (Akiya et al. 2002; Smith et al. 2009). This article gives an overview of some recent advances in our research on hydrothermal conversion of biomass. It mainly focuses on the production of acetic acid, formic acid, and lactic acid from the carbohydrate portion of biomasses, which constitutes approximately 75% of the dry weight in herbaceous and woody biomasses.

## **EXPERIMENTAL**

Glucose, as a model compound of carbohydrate, and cellulose and potato starch, as the main components of carbohydrate biomass, were used as test materials. Rice hulls and sawdust as representatives of lignocellulosic biomass and potato as a representative of carbohydrate biomass were also selected as test materials. Starch and glucose were of reagent grade. Cellulose used in this study was a filter paper powder. The rice hulls and sawdust were ground to pass a 100-mesh size screen in a cross-beater mill.

Amounts of starting materials were limited to 0.07 g (dry base) in all batch experiments. In the case of hydrothermal oxidation, hydrogen peroxide was used as an oxidant for experimental convenience. The oxygen supply was defined as the ratio of the amount of oxygen supplied by H<sub>2</sub>O<sub>2</sub> to the stoichiometric demand of oxygen for complete oxidation of carbon, calculated from the carbon content of test material, to carbon dioxide.

All batch experiments were conducted with a reactor constructed of SUS 316 tubing (Jin et al. 2000 a; 2003). The experimental procedure is available elsewhere (Jin et al. 2000a, 2003). After the reaction, liquid samples were collected and intermediate products were identified and quantified by GC/MS and/or HPLC. Details of the conditions for GC/MS and HPLC are available elsewhere (Jin et al. 2000 a; 2003). The product yields reported in this paper are defined as the percentage of products to initial material (s), on a carbon basis. The products purity reported in this paper is defined as the percentage of carbon in a liquid sample of products against the TOC of the liquid sample after the reaction.

## **RESULTS AND DISCUSSION**

### **Conversion of Cellulose and Lignocellulosic Biomasses into Acetic acid**

Our previous studies have indicated that hydrothermal oxidation is effective for treatment of organic waste, and that acetic acid is a stable intermediate product, whilst a high reaction temperature or catalyst is required for its complete decomposition. Acetic

acid is an important petrochemical that is currently produced from methane (or coal). One important industrial use of acetic acid is to produce calcium magnesium acetate (CMA) as a non-corrosive road deicer. CMA has been proposed as a substitute for chloride salt deicers, since it has acceptable ice-melting properties and is also relatively benign to the environment, non-corrosive to automobiles, and is biodegradable (Chollar et al. 1984; Fritzsche et al. 1992; Mathews et al. 1996). The cost, however, of manufacturing CMA is a major drawback that limits its widespread application as a roadway deicer. For example, in the USA, the cost of CMA is approximately \$600/ton, and it is about 15 times greater compared to approximately \$40/ton for sodium chloride (New Hampshire 1996). If the residual acetic acid in hydrothermal oxidation of organic wastes can be utilized to produce acetate rather than being decomposed, then it should reduce the cost of manufacturing CMA.

We have developed a new method using organic waste to produce acetic acid. These results showed that the yield of acetic acid from carbohydrate biomass was limited to only 11-13% by usual hydrothermal oxidation or the direct oxidation (see Table 1). More precisely, the acetic acid yield from carbohydrate biomass by usual direct oxidation was hardly further improved. These results suggested 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 (Jin et al. 2005). Scheme a in Fig. 1 shows the two-step process, which consists of both a hydrothermal reaction process without the supply of oxygen (the first step reaction) and a subsequent oxidation reaction process (the second step reaction). The first step is to convert carbohydrates mainly to 5-hydroxymethyl-2-furaldehyde (HMF) and 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 the oxidation with newly supplied oxygen. HMF, 2-FA, and lactic acid can produce a large amount of acetic acid by their oxidation.

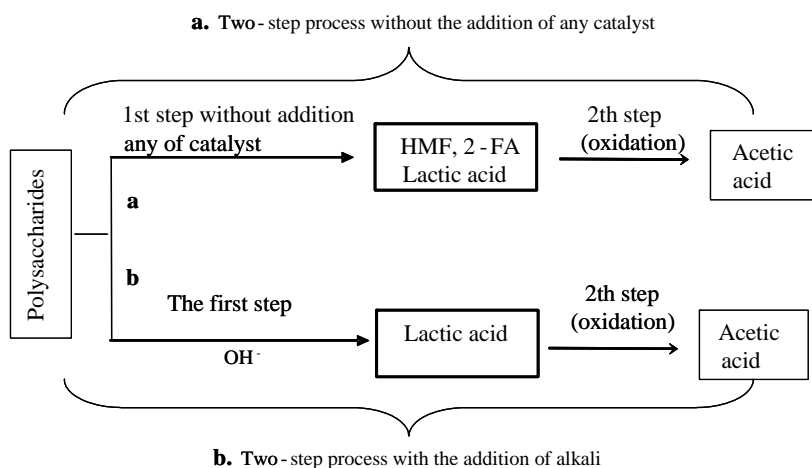
**Table 1.** Acetic Acid Yields by the Oxidation of Various Biomass Wastes

Materials	Yield <sup>a</sup> (%)	Conditions		
		Temp. (°C)	Time (s)	H <sub>2</sub> O <sub>2</sub> (%)
Carrots	13.0	400	30	50
Welsh onion	12.9	400	30	50
Mixture <sup>b</sup>	13.2	400	30	50
Beef suet	9.2	400	30	50
Potato	11.1	300	60	70
Rice hulls	11.7	300	120	70
Sawdust	9.7	300	120	80
Cellulose	9.0	300	120	70
Starch	9.6	300	60	70
Carrots	13.0	400	30	50

<sup>a</sup> TOC/TOC from initial material; <sup>b</sup> The mixture of six kinds of vegetables (carrots, white radish, potato, burdock, cabbage, and eggplant)

Cellulose and starch, as well as rice hulls, were treated using the two-step process. As shown in Table 2, the acetic acid yield obtained in the two-step process became

approximately twice as much as those obtained by the usual hydrothermal oxidation procedure for all test materials. From Table 2, it is also seen that, besides the yield of acetic acid, the purity of acetic acid was also greatly improved. It should be noted that most of the content in the liquid phase other than acetic acid was formic acid. Since our purpose for generating acetic acid is to produce calcium/magnesium acetate as a noncorrosive road deicer, and calcium formate ( $\text{Ca}(\text{HCOO})_2$ ) as well as other carbonic acids of lower molecular weight than oxalic acid can also have the deicing effect: formic acid and other carboxylic acids could be also useful products. In this case, total purity of all carboxylic acids was over 99 %, indicating that a separation of acetic acid from other residual products in the solution after the two-step reaction process would not be necessary.



**Fig. 1.** Proposed two-step process for enhancing acetic acid yield

**Table 2.** The Acetic Acid Yields <sup>a</sup> and Purity <sup>b</sup> by Two-step Process

Materials	Yield (%)		Purity (%)		Conditions			
					1st step		2nd step	
	Temp.(°C)	Time (min)	Temp.(°C)	Time (min)				
Rice hulls	21.7 (11.7)	75.5 (33.4)	300	2	300	1	70	
Cellulose	16.3 (9.0)	68.5 (26.0)	300	2	300	1	70	
Starch	17.5 (9.6)	70.0 (28.2)	300	1	300	1	70	
Glucose <sup>c</sup>	27.0(5.4)	90.0(25.0)	300	1	300	1	70	

<sup>a</sup> The percentage of TOC of acetic acid and starting material; <sup>b</sup> The percentage of TOC of acetic acid and the all residual remaining in the liquid after reaction; The yield and purity in parentheses correspond to those obtained by usual hydrothermal oxidation. <sup>c</sup> Alkaline two-step process.

Although, in the first step, a considerable amount of lactic acid was formed without the addition of any catalyst, it could be expected that the yield of lactic acid would 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. Since the acetic acid yield obtained by the oxidation of lactic acid was much higher than

that obtained by the oxidation of furans in a previous report (Jin et al. 2005), it could be expected that the acetic acid yield would be further improved by adding an alkali in the first step. Therefore, a new alkali two-step process was proposed using an alkali in the first step reaction (see Fig. 1b). In this study,  $\text{Ca}(\text{OH})_2$  was used as an alkali catalyst, because  $\text{Ca}(\text{OH})_2$  has the benefit of obtaining calcium acetate as the final product of CMA. Results showed that addition of an alkali promoted the formation of lactic acid in a hydrothermal reaction of glucose, and a good acetic acid yield of 27 % on the carbon base was obtained by alkali two-step process (see Table 2 line 4). The purity of the acetic acid on carbon basis was about 90 %.

### Development of a Continuous-flow Reaction System for Producing Acetate Deicer from Carbohydrate Biomass

Based on the results with the batch reactor, a continuous flow reaction system to produce acetic acid and then convert it to CMA was developed. As shown in Fig. 2, the major components of the system comprised of tanks for slurry and  $\text{H}_2\text{O}_2$ -water solution, feed pump for slurry,  $\text{H}_2\text{O}_2$  supply pump, preheater, hydrothermal reactor, cooler, solid-liquid separator, pressure regulator, gas-liquid separator, and reactor for producing CMA. The section before the pressure regulator along the flow line is maintained at a high temperature (250-300°C) and a high pressure (12-20 MPa) for producing acetic acid. The section after the pressure regulator is for converting the acetic acid into CMA by reacting with oyster shells at normal temperature and pressure. The treatment capacity of this continuous-flow reaction system is 2 kg/h.

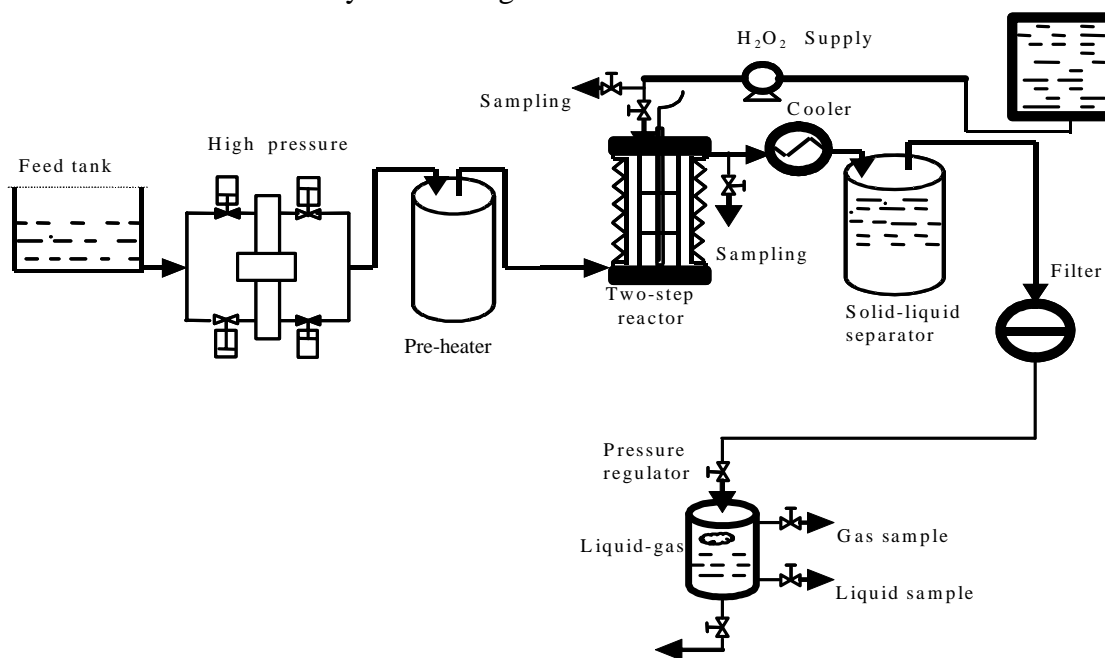


Fig. 2. Flow diagram of continuous flow reactor system

Experiments with rice hulls and starch were conducted using this continuous-flow system with a temperature varying from 280 to 320 °C, an oxygen supply varying from 70 to 120 %, and a reaction time varying from 1 to 3 min. As shown in Table. 3, the highest acetic acid yields obtained in the continuous-flow system and their operation

conditions were almost the same as those obtained in the batch study for both usual hydrothermal oxidation and the two-step reaction process. These results indicate that the developed continuous flow reaction system has the expected fundamental performance to produce acetic acid for both usual hydrothermal oxidation and a new two-step process.

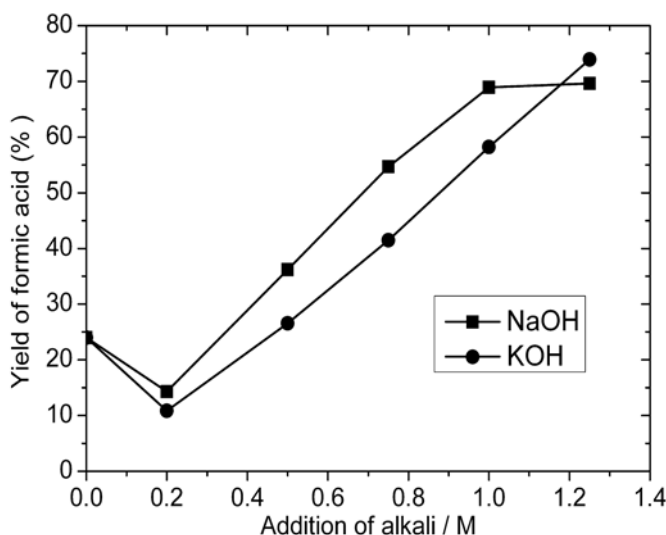
**Table 3.** Comparison of the Highest Acetic Acid Yields and Their Respective Experimental Conditions Between Batch and Continuous Flow Experiments

Materials	Batch Experiment				Continuous Flow Experiments			
	Conditions							
	Yield (%)	Temp. (°C)	Time (s)	O <sub>2</sub> (%)	Yield (%)	Temp. (°C)	Time (s)	O <sub>2</sub> (%)
Starch	17.5	300 (300)	1 (1)	0 (70)	17.5	300 (300)	1 (1)	0 (70)
Rice hulls	21.7	300 (300)	2 (1)	0 (70)	-	-	-	-

\* The carbon percent based on that of initial material(s); The values in parentheses correspond to the second step reaction; For continuous flow experiments: slurry concentration of 2 wt% (dry base), system pressure of 20 MPa, the flow rate of 10-15 L/h.

### Formic Acid Production from Hydrothermal Oxidation of Carbohydrates

Although many studies (Akiya et al. 2002; An et al 1997; Ikushima, et al. 2000), including our own research, have investigated the hydrothermal conversion of biomass into added-value products, few of them have had a goal of obtaining a high yield of formic acid, to the best of our knowledge. The present study investigated the production of formic acid by hydrothermal oxidation of glucose. Experiments were performed at temperatures from 200 to 350 °C, reaction times from 10 s to 180 s, and with and without the addition of alkali. It was found that in the hydrothermal oxidation of glucose without the addition of alkali, the highest yield of formic acid was about 24 %, which occurred at a temperature of 250 °C for the reaction time of 60 s with a 60 % H<sub>2</sub>O<sub>2</sub> supply. However, when an alkali was added, an excellent formic acid yield of about 75 % with purity higher than 95 % was obtained at 250 °C for 60 s of reaction time (see Fig. 3).



**Fig. 3.** Effect of NaOH and KOH concentration on the yield of formic acid. (temp.: 250 °C; reaction time: 60 s; H<sub>2</sub>O<sub>2</sub> supply 120 %)

The results shown in Fig. 3 should help to facilitate studies for developing a process for converting of carbohydrate biomass into formic acid for use as a potential intermediate for hydrogen production from carbohydrate biomass and for direct use as formic acid in fuel cells. Recent research has demonstrated that formic acid has the potential to power fuel cells for electricity generation and automobiles (Rice et al. 2002; Uhm et al. 2008), as well as for many other applications as a chemical.

### Lactic Acid Production from Carbohydrate Biomass

Recently, lactic acid has been receiving increased attention as a material for producing biodegradable lactic acid-based polymers. The major method for producing lactic acid is starch fermentation. Bioconversion (bacterial fermentation), however, has not been directly available to produce lactic acid from cellulose and lignocelluloses. As shown, the addition of alkali can improve the production of lactic acid. Therefore, it is quite possible that lactic acid can be formed in large quantity under hydrothermal conditions with the addition of alkali. In this study, the production of lactic acid by alkaline hydrothermal reaction of carbohydrate biomass was investigated.

Figures 4 and 5 show the influence of NaOH concentration, reaction temperature, and time on the production of lactic acid. All yields are reported in carbon percent relative to the carbon in the initial reactant. A considerably high lactic acid yield of 20% by the use of  $\text{Ca}(\text{OH})_2$  and 27% by the use of NaOH was obtained at 300 °C for 1 min.

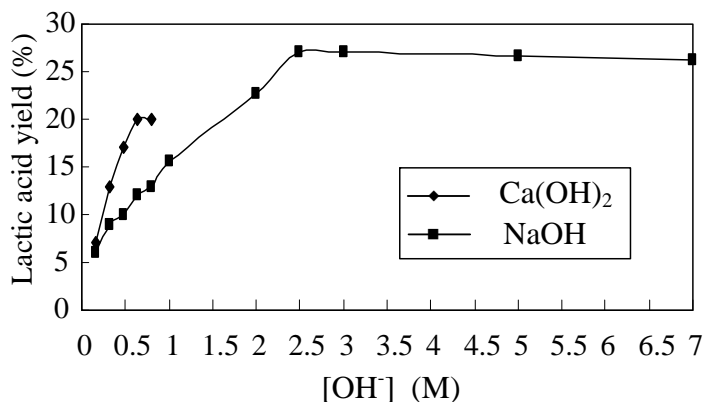


Fig. 4. Influence of the initial [OH] on the yield of lactic acid at 300 °C for 60 s

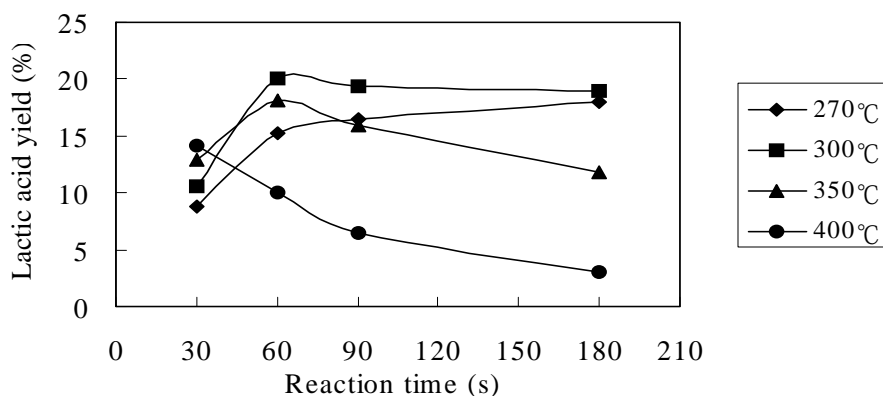
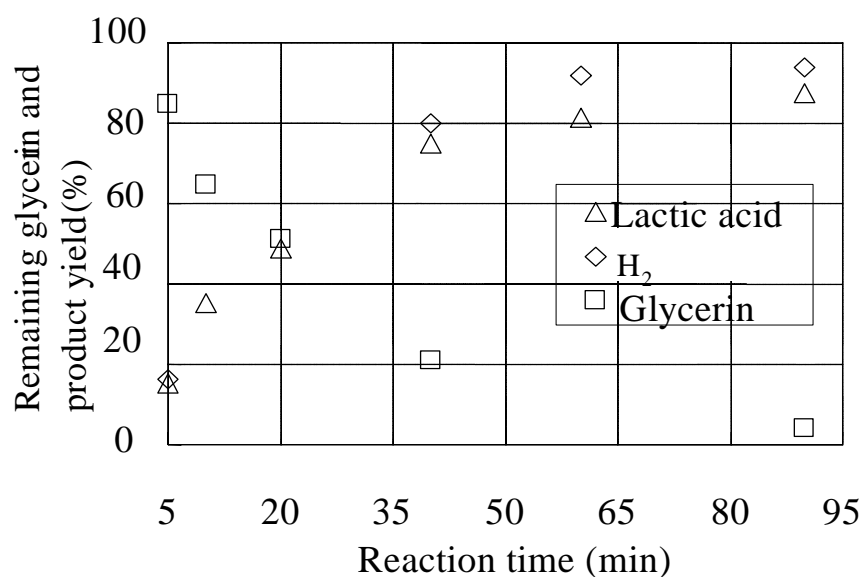


Fig. 5. Influence of temperature and time on the yield of lactic acid at 0.34 M  $\text{Ca}(\text{OH})_2$

### Lactic Acid Production by Alkaline Hydrothermal Reaction of Glycerin

In recent years, bio-diesel fuel (BDF) derived from the transesterification of vegetable oil and fat has been gathering attention. As the production of BDF increases, it becomes increasingly important to find an effective and acceptable conversion of glycerin, which is a by-product of the BDF manufacturing process, into value-added products. The most common way to produce BDF is to transesterify triglycerides in vegetable oils and animal fats with an alcohol in the presence of an alkali catalyst. Thus, glycerin after transesterification of vegetable oils and/or animal fats contains a large amount of alkali. A study on hydrothermal conversion of glycerin in presence of an alkali was performed. As shown in Fig. 6, glycerin was converted into lactic acid with an excellent yield of about 90 mol% based on the glycerin used (Kishita et al. 2005).



**Fig. 6.** Variation of lactic acid yield, remaining glycerin and H<sub>2</sub> yield with reaction time. (temp.; 300 °C, NaOH; 1.25 M)

### CONCLUSIONS

Recent advances have been achieved in our research regarding the application of hydrothermal reaction to conversion of biomass into chemicals, which mainly include (1) acetic and formic acid acids production from the oxidation of carbohydrate biomasses; (2) lactic acid production from carbohydrate biomasses by alkali hydrothermal reaction; and (3) lactic acid production from glycerin by alkali hydrothermal reaction. Results indicate that hydrothermal reactions can easily and directly convert selected biomass into acetic acid, formic acid, and lactic acid, indicating that the hydrothermal process possesses a high potential for converting a wide range of biomass into useful bulk products.



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