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The Thermochemical Conversion of Lactic Acid in Subcritical and Supercritical Water

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Abstract**—**One way to utilize biomass is to thermochemically convert it into gases and chemicals. For conversion of biomass, glucose is a particularly popular model compound for cellulose, or more generally for biomass. The present study takes a different approach by employing lactic acid as the model compound for cellulose. Since lactic acid and glucose have identical elemental composition, they are expected to produce similar results as they go through the conversion process. In the current study, lactic acid was thermochemically converted to assess its reactivity and reaction mechanism in subcritical and supercritical water, by using a 16-ml autoclave reactor. The major operating parameters investigated include: The reaction temperature, from 673 to 873 K, the reaction pressure, 10 and 25 MPa, the dosage of oxidizing agent, 0 and 0.5 chemical oxygen demand, and the concentration of lactic acid in the feed, 0.5 and 1.0 M. Gaseous products from the conversion were generally found to be comparable to those derived from the conversion of glucose.

Keywords**—**Lactic acid, subcritical water, supercritical water, thermochemical conversion.

I. INTRODUCTION

LACTIC acid is one of the major intermediates from the reaction of glucose in subcritical water (SubCW) and supercritical water (SCW) [1], [2]. It can be produced by transforming fructose in SCW [3] or by catalytic converting carbohydrates in SubCW [4]. For thermochemical conversion of biomass, a number of Aldoses, including glucose and fructose, have been employed as the model compound [5]-[8]. Among them, glucose is a particularly popular model compound for cellulose. The current work attempts a different approach by adopting lactic acid as the model compound for cellulose, or even for biomass. Lactic acid has a chemical formula, $C_3H_6O_3$, just half that of glucose, $C_6H_{12}O_6$. It will be interesting to study and compare its reaction with that of glucose or cellulose in SubCW, as well as in SCW. High temperature processes usually approach equilibrium, such as combustion, gasification, SCW and SubCW, for which thermodynamic equilibrium model is a useful tool for predicting the outcomes of these processes. Since lactic acid and glucose have the same elemental proportion of carbon, hydrogen and oxygen, thermodynamic equilibrium models [9], [10] predict that SubCW and SCW thermochemical conversion of lactic acid and glucose shall produce the same products if identical reaction conditions are employed and equilibrium is reached. SubCW and SCW are non-hazardous, environmentally benign and promising reaction media. They have served as the reaction media for numerous chemical compounds and biomass materials, including methane [11], hexadecane [12], polyethylene [13], phenol [14], cellulose, hemicellulose, lignin, and real biomass [15].

II. EXPERIMENTS

A. Materials

Reagent-grade lactic acid (LA) was adopted as the organic reactant. Hydrogen peroxide solution, 30 wt. % H_2O_2(aq), was used as the oxidizing agent. DI water was the water source for SubCW and SCW.

B. Apparatus and Procedures

Experimental runs were conducted with a 16-ml isochoric autoclave reactor. The autoclave, tubing and valves were all made of cold-worked 316L stainless steel rated 140 MPa at room temperature. An experimental routine proceeds as follows. Depending on the intended reaction conditions, pre-determined amounts of DI water, lactic acid and H_2O_2(aq) are first loaded into the batch reactor, which is then moved into a furnace. The furnace launches heating, after its target temperature and ramping speed are set. The temperature inside the furnace will reach the target temperature in about 25 minutes, and the reaction is initiated and allowed to continue for about 35 minutes at the preset temperature to ensure the completion of the reaction. Then, the heating is terminated, and the reactor assembly is removed from the furnace and cooled by forced air to room temperature. The main valve of the reactor is then carefully opened and the gaseous product is collected and weighed with its volume measured by way of water displacement. The reactor is opened afterwards to collect liquid products, and the existence of solids is only qualitatively observed. Gaseous product is analyzed with a gas chromatogram/thermal conductivity detector (GC-TCD, ThermoQuest TRACE 2000) for its H_2, N_2, O_2, CO, CO_2 as well as light hydrocarbons.

The main operating parameters are reaction temperature, dosage of the oxidizing agent and the concentration of lactic acid in the feed (FC). Relatively high operating temperatures were employed, from 773 to 873 K at 25 K intervals, to enhance the reactivity of the reaction. As a result, a low operating pressure at 10 MPa was adopted to ensure safety. For the purpose of comparison, reactions at 25 MPa were also performed, only for lower temperatures, from 698 to 773 K at 25 K intervals, again to ensure safety. Therefore, reaction pressure serves as a minor parameter. Two levels of lactic acid

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concentration were employed, 0.5 and 1.0 M, to examine the effect of reactant concentration on the thermochemical conversion of lactic acid. Addition of oxidizing agent will promote the partial oxidation of lactic acid, thereby reducing the amount of external energy input needed to drive the process, or even completely eliminating the need of external energy input. The level of oxidizing agent used corresponds to 0.5 chemical oxygen demand (COD), defined here as the amount of oxidant needed to completely oxidize the organic reactant. A 0.0 COD indicates that no oxidizing agent was used.

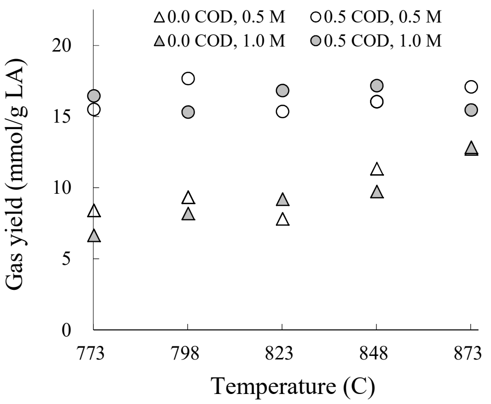

Fig. 1 Dry gas yield versus temperature with FC and amount of oxidizing agent as the parameters under 10 MPa

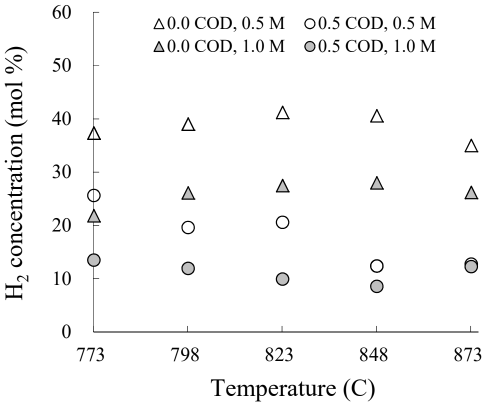

Fig. 2 H_2 concentration in dry gas versus temperature with FC and amount of oxidizing agent as the parameters under 10 MPa

III. RESULTS AND DISCUSSIONS

A total of 56 experimental runs were successfully completed from 24 different set of experimental conditions. Each data point in the figures to follow represents an average of 2-4 data values from runs of identical experimental conditions. The gaseous product was determined to consist mainly of H_2, CO, CH_4 and CO_2, as well as minute amount of C_2H_6. The gaseous species with three to five carbon atoms were determined to be insignificant in the product gas. Oxygen is not expected to be present in the product gas, since this conversion process is highly oxidant deficient and oxygen should be depleted during the conversion. Thus, it is assumed that any oxygen detected by the GC-TCD is due to leakage from the environment in the sampling procedure. The liquid product was collected, weighed, and visually inspected. Solids were generally not observed in the product.

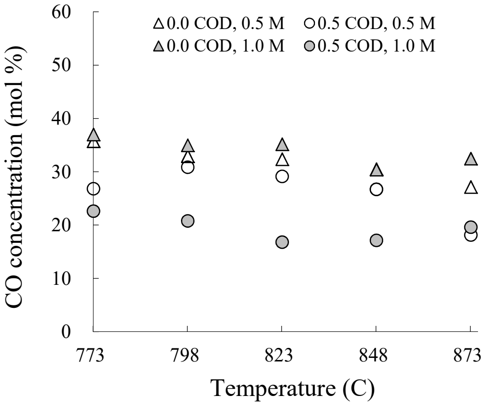

Fig. 3 CO concentration in dry gas versus temperature with FC and amount of oxidizing agent as the parameters under 10 MPa

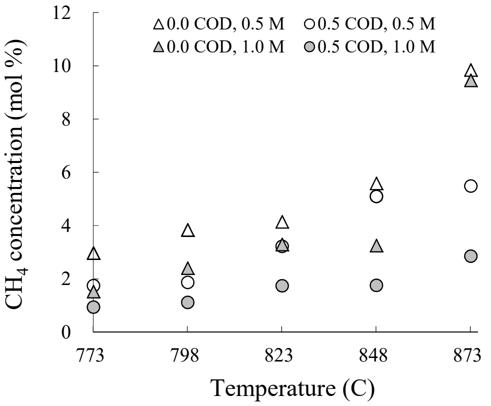

Fig. 4 CH_4 concentration in dry gas versus temperature with FC and amount of oxidizing agent as the parameters under 10 MPa

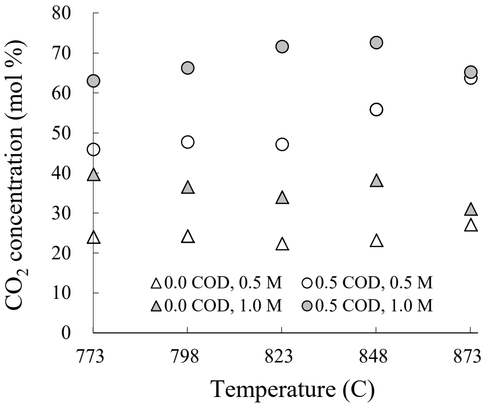

Fig. 5 CO_2 concentration in dry gas versus temperature with FC and amount of oxidizing agent as the parameters under 10 MPa

The effects of reaction temperature, addition of oxidizing agent, and feed concentration on the dry gas yield are shown in Fig. 1. The dry gas yield is defined as mmols of dry gas produced per gram of lactic acid reacted. The dry gas yield is seen to have an increasing trend with rising temperature for the case without oxidizing agent, and remains roughly constant with the variation of temperature with oxidizing agent. It seems increasing the feed concentration from 0.5 to 1.0 M does not significantly affect the dry gas yield, meaning that more lactic acid can be converted in the same reactor without suffering the drop of the dry gas yield. The use of oxidizing agent, on the other hand, dramatically increases the dry gas yield. Gas yields with the use of oxidizing agent are consistently and substantially higher than those without oxidizing agent. It is evident that the use of oxidizing agent helps to convert LA into gas products, especially when the reaction temperature is relatively low, e.g. 773 K. The use of oxidizing agent can also reduce or even eliminate the need of external heating through increased oxidation.

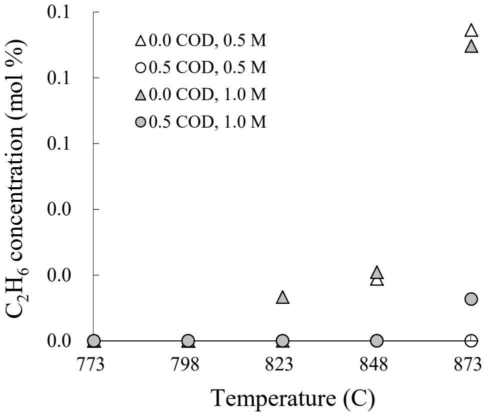

Fig. 6 C_2H_6 concentration in dry gas versus temperature with FC and amount of oxidizing agent as the parameters under 10 MPa

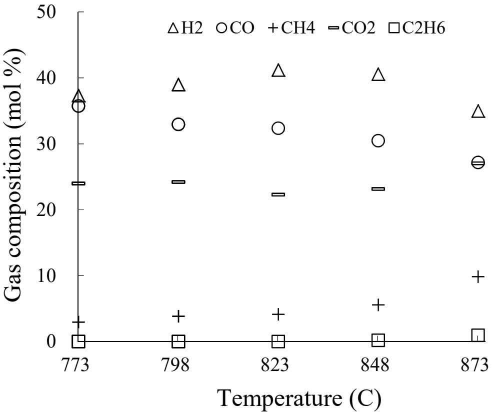

Fig. 7 Dry gas composition versus temperature for FC = 0.5 M and oxidizing agent = 0.0 COD under 10 MPa

Figs. 2-6 show the variation of individual gas species concentration with reaction temperature in the dry gas for H_2, CO, CH_4, CO_2 and C_2H_6, respectively. The hydrogen content of the gas is seen from Fig. 2 to increase mildly from 773 to 823 K and then to decrease when the temperature is higher than 823 K for the case without oxidizing agent. It exhibits a slightly decreasing trend with temperature for the case of using oxidizing agent. While the use of oxidizing agent dramatically lowers the hydrogen content in the product gas, raising the feed concentration also significantly reduces it. The former may be realized by the increased extent of oxidation of hydrogen with the addition of oxidant, and the latter is harder to explain.

The CO content of the gas seems to decrease slowly and steadily over the temperature range investigated, as depicted in Fig. 3. The addition of oxidizing agent tends to lower the CO concentration appreciably due to an extra oxidation of CO to produce CO_2, while raising lactic acid concentration slightly increases the CO concentration without using oxidizing agent and suppresses the CO concentration for the temperature range from 798 to 848 K with oxidizing agent.

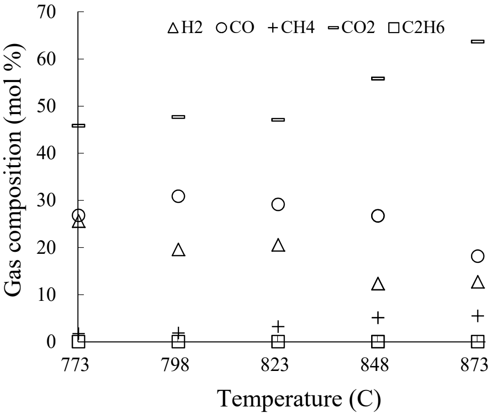

Fig. 8 Dry gas composition versus temperature for FC = 0.5 M and oxidizing agent = 0.5 COD under 10 MPa

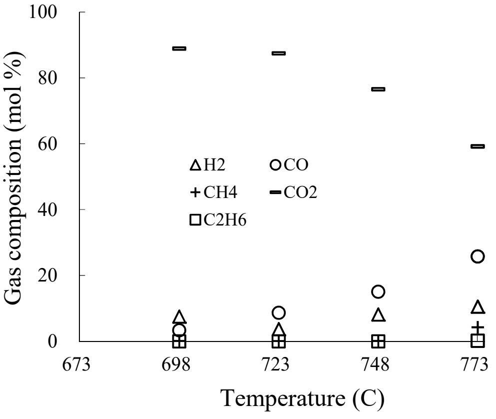

Fig. 9 Dry gas composition versus temperature for FC = 0.5 M and oxidizing agent = 0.0 COD under 25 MPa

The CH_4 concentration appears to increase exponentially from 773 to 873 K, and to be suppressed appreciably both by raising the lactic concentration and by the use of oxidizing agent, as seen in Fig. 4.

The CO_2 content of the gas remains roughly constant with the variation of temperature without oxidizing agent, and increases moderately with oxidizing agent, as illustrated in Fig. 5. It approximately doubles when oxidizing agent is employed, and increases by about 50% when raising the lactic acid from 0.5 to 1.0 M. When oxidizing agent is used, the increase in CO_2 content and the decrease in CO content is related, since oxidation of CO produces CO_2. However, the dramatic increase of CO_2 content may not be all attributed to the increased oxidation of CO.

The concentration of C_2H_6, a minor component, is shown in Fig. 6 to rise exponentially with temperature without oxidizing agent, and virtually nil with oxidizing agent. It is minimally affected by the change of lactic acid concentration.

The dry product gas composition for FC = 0.5 M and 0.0 COD is illustrated in Fig. 7. The dominant species are H_2, ranging from 35 to 41 mol. %, CO, ranging from 27 to 36 mol. %, and CO_2, ranging from 22 to 27 mol. %. Two minor species are CH_4, ranging from 3 to 10 mol. %, and C_2H_6, ranging from 0 to 1 mol. %. For comparison, the dry product gas composition for FC = 0.5 M and 0.5 COD is illustrated in Fig. 8. Evidently, when oxidizing agent is applied, CO_2 content in the product gas shoots up substantially and both H_2 and CO contents in the product gas go down significantly, especially where temperature is high. For another comparison, Fig. 9 displays the dry product gas composition for FC = 0.5 M and 0.5 COD from experiments conducted at 25 MPa, as opposed to all other data, presented in Figs. 1-8 and to be shown in Figs. 10 and 11, conducted at 10 MPa. Experiments at 25 MPa were only conducted for temperatures less or equal to 773 K for safety reason, as mentioned in the previous section. As shown in Fig. 9, CO_2 is the only dominant component in the product gas when the temperature is relatively low.

The high heating value (HHV) of the dry product gas is shown in Fig. 10 against reaction temperature with dosage of oxidizing agent and FC as the parameters. It displays a slightly upward trend with temperature for the case without oxidizing agent, and no specific trend with temperature for the case with oxidizing agent. It is obviously severely decreased by the addition of oxidizing agent. Raising the lactic acid level in the feed also drives down the HHV of gas except where temperature is high at 873 K.

Fig. 11 presents the energy yield, the energy stored in the product gas from one mole of lactic acid reacted, for the process against reaction temperature with dosage of oxidizing agent and FC as the parameters. The energy yield is derived by multiplying gas yield presented in Fig. 1 with gas HHV presented in Fig. 10. It shows an increasing trend with rising temperature without oxidizing agent, and stays roughly constant with rising temperature when oxidizing agent is added. A crossover occurs at around 823 K, where the energy yield without oxidizing agent surpasses that with oxidizing agent. It means at temperatures lower than 823 K addition of oxidizing agent helps to convert the energy originally stored in lactic acid into the energy stored in the product gas, whereas at temperature higher than 823 K, the addition of oxidizing agent does not. Raising the lactic concentration in the feed generally does not favor the energy conversion.

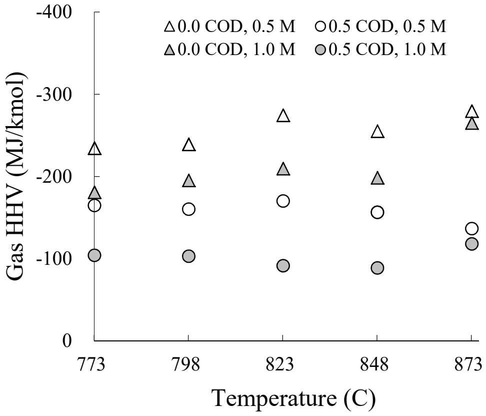

Fig. 10 HHV of the dry gas versus temperature with FC and amount of oxidizing agent as the parameters under 10 MPa

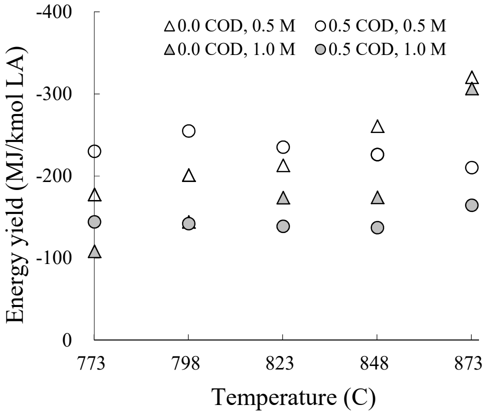

Fig. 11 Energy yield versus temperature with FC and amount of oxidizing agent as the parameters under 10 MPa

IV. CONCLUSIONS

Lactic acid, with a chemical formula, $C_3H_6O_3$, just half that of glucose, has been thermochemically converted in near-critical water from 673 to 873 K, mostly under a pressure of 10 MPa. The product gas was determined to consist mainly of H_2 (10-40 mol. %), CO (15-35 mol. %), CH_4 (1-10 mol. %) and CO_2 (20-70 mol. %), as well as minute amount of C_2H_6 (0-1 mol. %). Raising the reaction temperature from 773 to 873 K enhances the gas yield by about 70% without the use of oxidizing agent, and has virtually no effect on the gas yield with the use of oxidizing agent. The energy yield ranges from -100 to -300 MJ/kmol of lactic acid reacted, representing only about 25% of the energy originally contained in lactic acid. Increasing lactic acid concentration in the feed generally suppresses the energy yield, while addition of oxidizing agent benefits the energy yield only for temperature below 823 K. In terms of energy yield, the best result occurs where temperature is at its highest, 873 K, FC is moderate at 0.5 M, and no oxidizing agent is added.

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