Formic Acid Production from Carbohydrates Biomass by Hydrothermal Reaction

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Abstract. The formation of formic acid or formate salts by hydrothermal oxidation of model biomass materials (glucose, starch and cellulose) was investigated. All experiments were conducted in a batch reactor, made of SUS 316 tubing, providing an internal volume of 5.7 cm³. A 30 wt% hydrogen peroxide aqueous solution was used as an oxidant. The experiments were carried out with temperature of 250°C, reaction time varying from 0.5 min to 5 min, H₂O₂ supply of 240%, and alkaline concentration varying from 0 to 1.25 M. Similar to glucose, in the cases of the oxidation of hydrothermal starch and cellulose, the addition of alkaline can also improve the yield of formic acid. And the yield were glucose>starch> cellulose in cases of with or without of alkaline addition.

1. Introduction
Formic acid, the simplest carboxylic acid, is an important organic chemical and widely used in industries. Recently, it gets more and more attraction to be used as environmental benign storage and transportation medium for hydrogen, the clean energy in future. Extensive studies have shown that hydrogen and CO₂ could be quickly and efficiently generated by the decomposition of formic acid by hydrothermal reaction or catalyst reaction. Also some researchers also have demonstrated that formic acid has the potential to direct power fuel cells for electricity generation and automobiles. Biomass is one of the most important renewable energy sources and expected to be an alternative energy source for the future. Hydrothermal conversion of biomass into more convenient and valuable fuels and value-added products is getting more attentions. Because water under high-temperature and high-pressure is an attractive solvent and reaction medium, and it exhibits very different properties from those of ambient liquid water. Also, it is an environmentally benign solvent. In our past researches, we reported that formic acid is a basic product in the hydrothermal oxidation of glucose, and that 1 mole of glucose can produce 6 mole formic acid. In this paper, the production of formic acid by hydrothermal oxidation of model biomass materials (glucose, starch and cellulose), was investigated. And also, effects of reaction conditions on the formation of formic acid were investigated.

2. Experimental
Reagent-grade glucose (>99%, Nacalai Tesque), Starch (Wako) and Cellulose (100~200 mesh, Toyo Roshi) were used as test materials. \( \text{H}_2\text{O}_2 \) (30% water solution, special class, Wako) was used as an oxidant for experimental convenience in respect to simplified handling. NaOH, KOH and Ca(OH)\(_2\) were used as the alkaline catalysts. All of the other chemicals used in the experiments were reagent grade and obtained from Wako. The stoichiometric oxygen demand for complete oxidation of glucose, starch or cellulose to \( \text{CO}_2 \) and water was defined as 100% oxygen supply ( \( \text{H}_2\text{O}_2/\text{glucose} \) molar ratio of 12:1), and it is 200% \( \text{H}_2\text{O}_2 \) supply assuming 1 mol of \( \text{H}_2\text{O}_2 \) gives 1/2 mol of \( \text{O}_2 \).

The present experiments were performed using a batch reactor consisting of SUS 316 tubing. Experimental procedures and techniques have been described in detail elsewhere \(^7,8\). Briefly, 0.07g of test material and 1.7 cm\(^3\) of \( \text{H}_2\text{O}_2 \)-water mixture were introduced into the reactor to occupy 30% of the total reactor volume. Then, the reactor was closed and immersed into a salt bath for reaction. After the desired reaction time, it was removed from the salt bath and immersed into a cold water bath quickly to quit the reaction.

After the reaction, liquid samples were collected for GC/MS and HPLC analyses. For samples obtained without the addition of alkali, it was filtered through a 0.45 \( \mu \)m filter and analyzed directly. In cases where alkali was added, after filtration, the pH of the solution was adjusted to 3 with HCl solution for analysis. GC/MS analyses were performed with a HP 5890 Series II gas chromatograph equipped with a HP-INNOWAX capillary column (30 m \( \times \) 0.25 mm ID, 0.25 \( \mu \)m film thicknesses) and 5898B mass spectrometer. HPLC analyses were performed on an RSpak KC-811 (SHODEX) column with a UV spectrometric detector (210 nm).

3. Result and Discussion

First, the effect of reaction time on the production of formic acid from the oxidation of model biomass materials (glucose, starch and cellulose) was investigated under the best condition for the produce of formic acid by hydrothermal oxidation of glucose, at 250°C and with 240% \( \text{H}_2\text{O}_2 \) supply. The results are shown in Fig.1. The yield of formic acid from glucose is also shown for comparison. The yield of formic acid is defined as the percentage of formic acid to initial biomass materials on the carbon basis. It can be seen that, although some extent formic acid can be produced from glucose, starch and cellulose, the yield from starch and cellulose was lower than that from glucose, particularly for cellulose. For glucose and starch, the yield of formic acid increased first, and then gradually decreased after 1 min. But for the cellulose, it increased all over the reaction time, through it is the lowest. Fig. 2 shows HPLC chromatograms for liquid samples after the hydrothermal oxidation of glucose, starch and cellulose at 250°C. 1 min and in the case of starch, in addition to formic acid, many other products, for example lactic acid, 5-hydroxymethyl-2-furaldehyde (5-HMF) and 2-Furaldehyde (2-FA) were also formed. In the case of cellulose, formic acid production yield was very low and produced much more kinds of products than glucose or starch. Usually for the reaction of polysaccharides in hydrothermal condition, polysaccharides first hydrolysis to small molecular sugar or partial, then the sugar or particle undergo further reaction to form carboxylic acids or other products. It is know that cellulose molecules bind strongly to each other and is relatively difficult to break down compared to the others. Usually high temperature and pressure or catalyst is needed for breaking down cellulose. But actually in our reaction, the temperature and pressure are not very high, and the reaction time is also very short. So that cellulose hydrolysis is hard to happen and many other side reactions occur. It is the reason that little formic acid and many other by-products were produced. For the starch, it is insoluble to water in room temperature. But it became soluble in water under the hydrothermal condition, undergoes several steps of reaction and transferred to small molecular sugars, which were soluble to water and easy to react with oxidants. So that starch has a similar result with glucose, and the formic acid yield is much bigger than that from cellulose.

As reported in our previous study, the addition of alkaline can improve the yield of formic acid from the oxidation of glucose. The oxidation of starch and cellulose in the presence of NaOH was conducted under 250°C and 240% \( \text{H}_2\text{O}_2 \) supply. Fig.3 showed the HPLC chromatographs from hydrothermal alkaline oxidation of Glucose, Starch and Cellulose. In the case of glucose, the formic
acid peak was very high and with just few other products, which shown great selectivity. But for starch and cellulose, considerable amount of formic acid was produced, but other product like lactic acid, glycolic acid or acrylic acid also increased greatly. Formic acid production from hydrothermal oxidation of starch or cellulose is not as high as we supposed, and also the selectivity is not very well. So we choose glucose as test material for further study.

Fig.1. Variation in yields of formic acid with reaction times from hydrothermal oxidation of Glucose, Starch and Cellulose (Temp.250°C, 240% H$_2$O$_2$ supply).

Fig.2. HPCL chromatographs from hydrothermal oxidation of Glucose, Starch and Cellulose (Temp.250°C, 240% H$_2$O$_2$ supply, 1 min).

Fig.3. HPCL chromatographs from hydrothermal alkaline oxidation of Glucose, Starch and Cellulose (Temp.250°C, 240% H$_2$O$_2$ supply, 1M NaOH, 1 min).
The effect of different kinds of alkaline on the yield of formic acid was examined. As shown in Fig.4, when [OH-] less than 0.2 M, the yield of formic acid decreased; when [OH-] above 0.2 M, the yield of formic acid increased with an increase of alkaline addition. Beside NaOH and KOH, Ca(OH)$_2$ can also catalyze the production of formic acid. Through same amount of [OH$^-$] was added into reactor, the slow dissolution rate and low solubility of Ca(OH)$_2$ cause the week catalyst effect, so that the yield of formic acid using Ca(OH)$_2$ is lower than NaOH or KOH. And the little difference between NaOH and KOH is possible because of the ionic strength effect, which is still being confirming.

![Fig.4. Effect of NaOH, KOH and Ca(OH)$_2$ concentration on yield of formic acid](image)

4. Conclusion
Similar to glucose, in the cases of the oxidation of hydrothermal starch and cellulose, the addition of alkaline can improved the yield of formic acid. The formic acid yields from glucose, starch and cellulose were glucose>starch> cellulose in the cases of with or without alkaline addition. Ca(OH)$_2$ can also improve the yield of formic acid from the oxidation of glucose, however, the yield of formic acid with the presence of Ca(OH)$_2$ was lower than that in NaOH or KOH at the same condition. Further study on improving the yield of formic acid from starch and cellulose is now in progress.

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