

# Reaction of Bio-Related Compounds in Hydrothermal Electrolysis

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## Abstract

We carried out electrolysis experiments of bio-related compounds such as 1-butanol, 2-furfural, glucose, and lignin as a starting material in subcritical water to clarify the reaction mechanism and pathway. Experiments were conducted using a specially-designed hydrothermal electrolysis autoclave (internal volume: 500 mL) under the experimental conditions: Temperature = 200-250 °C, pressure = 7-9 MPa, time for electrolysis = 10-100 min, and DC current loaded = 0-3 A. As a result, it was found that reactants were effectively converted even at 250 °C and 30min by this treatment. After every electrolysis reaction, the formation of hydrogen and carbon dioxide was confirmed by GC analysis and the yields of hydrogen and carbon dioxide gradually increased with electrolytic time. On the contrary, it was hardly decomposed in the case of hydrothermal degradation without electric current at the same condition. These experimental results clearly indicated that the hydrothermal electrolysis was one of useful techniques for rapid degradation of thermally stable organic materials which was recovered during biomass decomposition to gaseous and/or liquid fuels.

## Introduction

Electrochemical reaction usually operated at atmospheric condition of water and the reaction is generally slow, although it has advantages over chemical reaction such as suppression of side reaction by tuning operating condition. Since subcritical water has high ion product and low dielectric constant, it could be a good media for electrochemical reaction. Hydrothermal electrolysis has therefore a potential as a new reaction media<sup>1-3</sup>.

In this study we studied hydrothermal electrolysis of bio-related compounds such as 1-butanol, 2-furfural, glucose, and lignin, in an autoclave and analyzed the decomposition products to reveal the reaction mechanism.

## Experimental Section

A schematic representation of experimental apparatus is shown in Fig. 1. The experiment was carried out as follows. Aqueous solution of raw material of 200mL (0.02mol/L 2-furfural or glucose + 20g/L KCl) was charged in titanium beaker of the autoclave. After its lid was closed, argon gas was charged at 2 - 7MPa. The autoclave heated up at 523K with stirring. When the temperature reached 523K, the reaction was started at constant current of 0 - 3A or no current. After 10-60min, the autoclave was cooled down until 313K with stirring. Then, gas and aqueous products in the autoclave were retrieved. The residue contained in the solution were separated by suction filtration. Analysis of the gas and aqueous products was conducted with GC and HPLC, and TOC analyzer.

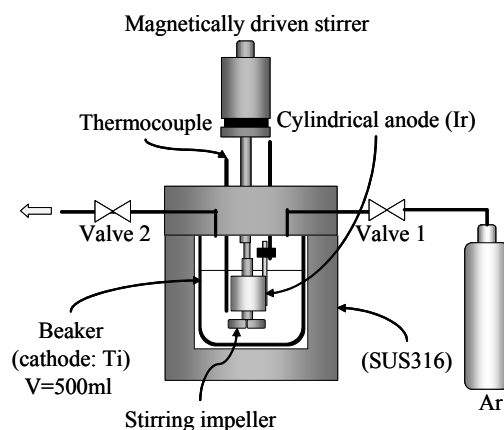


Fig. 1 Schematic diagram of experimental apparatus.

## Results and Discussion

### *1-Butanol*

The effect of electric current on the conversion of 1-butanol is shown in Fig. 2. The conversion increased with increase in the electric current and the highest conversion of 62.1 % was obtained at current of 3 A and reaction time of 90 min. The productions of hydrogen and carbon dioxide are shown in Figs. 3 and 4. Both the amount of hydrogen and carbon dioxide increased with increase in the electric current. However, hydrogen and carbon dioxide were not produced without the electric current.

The initial pressure in the reactor was changed from 2 to 7 MPa. The conversion was slightly increased with pressure.

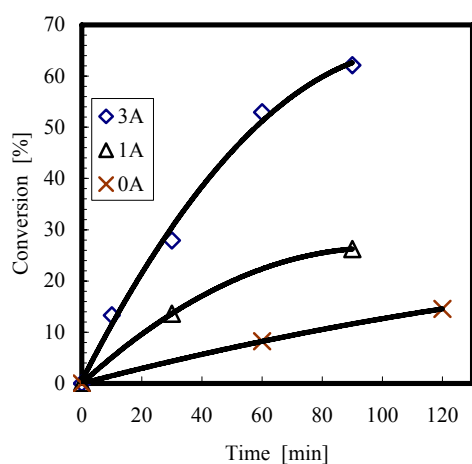


Fig. 2 Effect of electrolytic current on the conversion of 1-butanol.

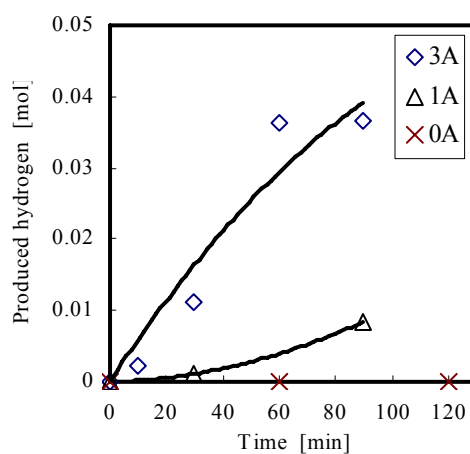


Fig. 3 Effect of electric current on the amount of produced hydrogen.

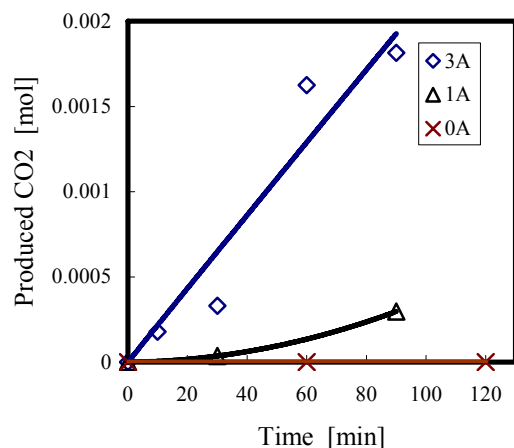


Fig. 4 Effect of electric current on the amount of produced carbon dioxide.

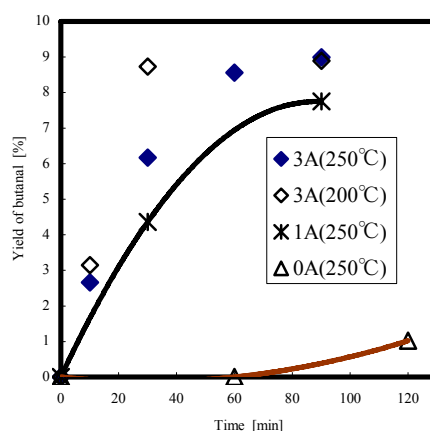


Fig. 5 Effect of electric current on the yield of butanal

Figures 5 and 6 show the yield of butanal and butyric acid at various electric current and temperature. The yield of butanal was higher at larger electric current at 250 °C. At the electric current of 3A, the production rate of butanal was higher at higher temperature. The butyric acid was produced at higher rate for larger electric current. At the current of 3A, the yield of butyric acid increased significantly at 90 min. From these figures, the decomposition of butanol proceeded consecutively to butanal and then butyric acid.

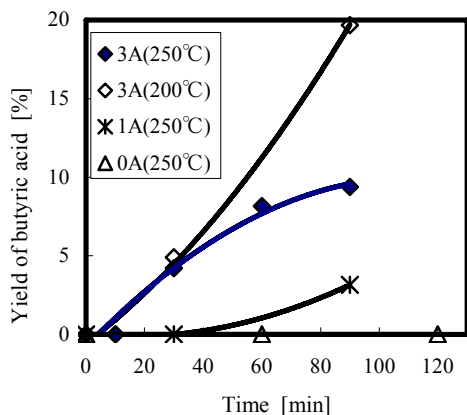


Fig. 6 Effect of electrolysis current on the yield of butyric acid.

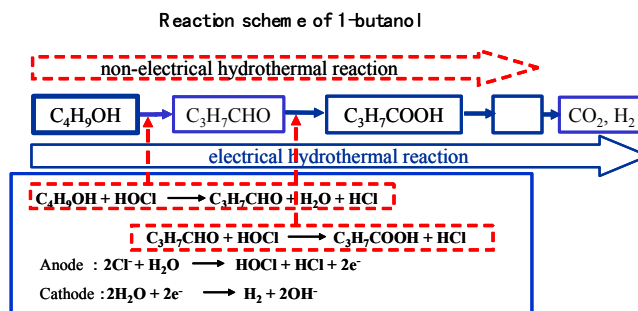


Fig. 7 Reaction scheme for 1-butanol decomposition by hydrothermal reaction with/without electrolysis.

From these results combined with reaction started from butanal as a reactant, the following reaction scheme is proposed for both hydrothermal reaction and electric hydrothermal reaction.

### 2-Furfural

In case of hydrothermal reaction and electrolysis by applying current to the system, the solution became yellow, and then it became transparent and colorless. However, for hydrothermal reaction without electrolysis, the solution was still yellow. Figure 8 shows the influence of

electrolysis on the conversion of 2-furfural. 2-Furfural was completely decomposed in about 30min regardless of electric current. However, the total organic carbon (TOC) yield in the solution kept high value throughout the reaction time in case of hydrothermal reaction (0A) as shown in Fig. 9.

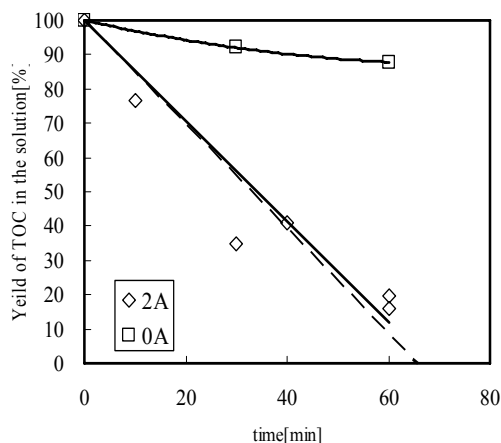
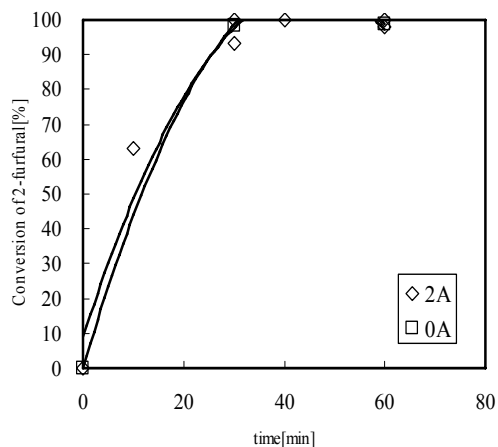


Fig. 8 Variation of conversion of 2-furfural. (T=523K, P=7-9MPa, Initially charged gas=3MPa). Fig. 9 Variation of yield of total organic carbon (TOC) in the solution.

The yields of hydrogen and carbon dioxide generated during the reaction are shown in Figs 10 and 11. For electrolysis, both hydrogen and carbon dioxide increased with time, whereas hydrogen was not generated and carbon dioxide was slightly generated for the case without electric current.

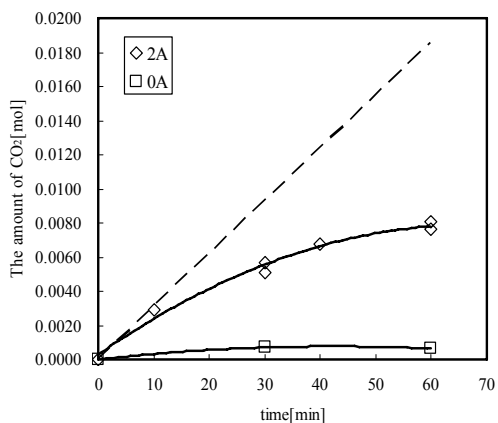
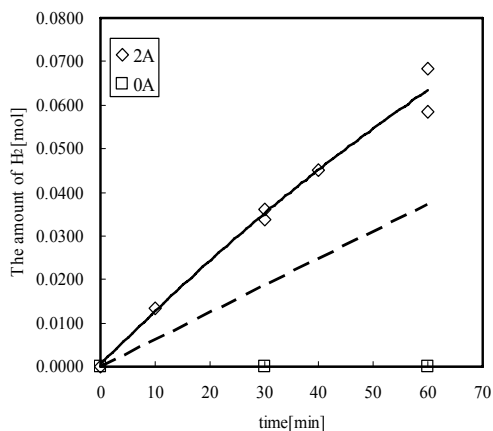
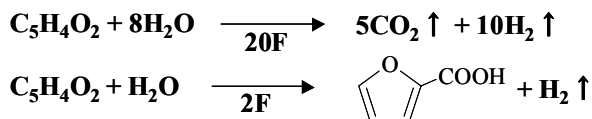


Fig. 10 Amount of hydrogen produced for hydrothermal electrolysis of 2-furfural. Fig. 11 Amount of carbon dioxide produced.

The combustion reaction formula and oxidation one to furancarboxylic acid of 2-furfural are shown as follows.



Theoretical value for the production of hydrogen was calculated according to the first equation.

The pH value was slightly decreased during 0 to 30min and increased up to the initial pH value after 60min due to the generation of acidic compounds as shown in Fig. 12. These results indicate that hydrothermal electrolysis can promote the conversion of water-soluble intermediates to gaseous products, hydrogen and carbon dioxide.

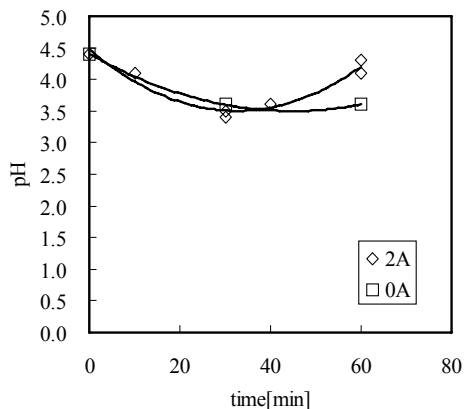


Fig. 12 Variation of pH in the solution.

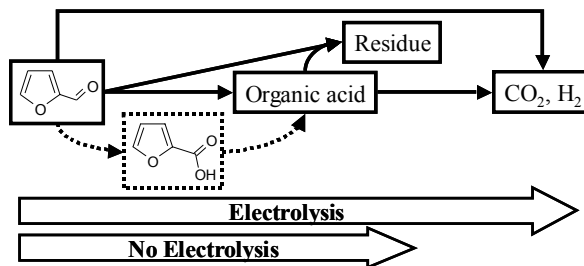


Fig. 13 Reaction pathway for hydrothermal electrolysis of 2-furfural.

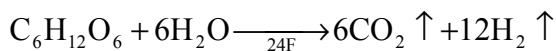
2-Furfural was rapidly converted to organic acids and gaseous products by hydrothermal electrolysis at 523K in 30min. In case of 2-furfural, the yield of H<sub>2</sub> and CO<sub>2</sub> formed by the decomposition of intermediates greatly increased with the reaction time. The reaction pathway for 2-furfural decomposition could be proposed as shown in Fig. 13.

### Glucose

The observed phenomena were similar to those for furfural. The TOC yield for hydrothermal electrolysis at 2 A and 0.2 A in comparison with hydrothermal reaction (0A) is shown in Fig. 14. For electrolysis at 2 A, remaining organic carbon is about 9 % in 100 min. On the other hand, about 75 % of organic carbon remained in 100 min in case of no electrolysis.

In hydrothermal electrolysis of glucose, hydrogen and carbon dioxide were produced as shown in Figs 15 and 16. Without electrolysis, there is no hydrogen produced. Char was observed around the electrode.

Oxidation of glucose is expressed as:



Amount of hydrogen produced is larger than calculated value according to the above equation, which is indicated as broken line in figure. Since the amount of hydrogen obtained for the experiment was larger than calculated one, the electrochemical reaction does not proceed according to the above equation.

As organic acids, small amount of glycolic acid, formic acid, and lactic acid were produced for both hydrothermal electrolysis and hydrothermal reaction. The pH of the liquid phase decreased from 5.5 in feed solution to around 2.9 due to the generation of organic acids. For hydrothermal electrolysis, pH increased later up to 3.9 in 100 min. due to the decomposition of organic acids.

However, pH did not increase for hydrothermal reaction, because organic acids were stable there.

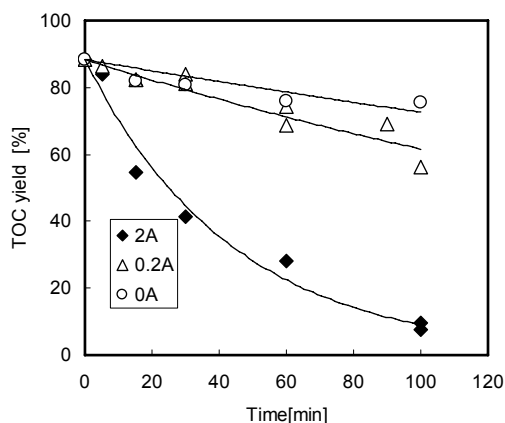


Fig. 14 TOC yield for hydrothermal electrolysis of glucose (Temperature 250 C, Pressure 8.8-9.0 MPa, Initial pressure 3 MPa) .

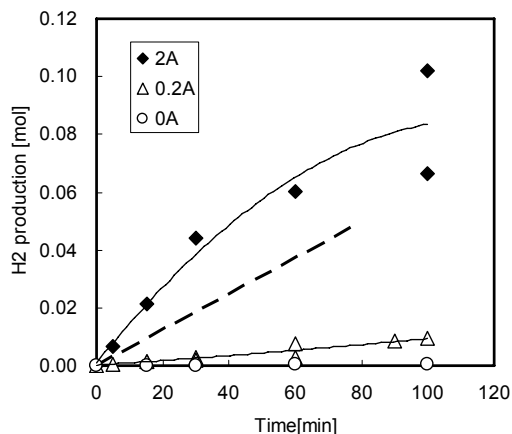


Fig. 15 Amount of hydrogen produced for hydrothermal electrolysis of glucose.

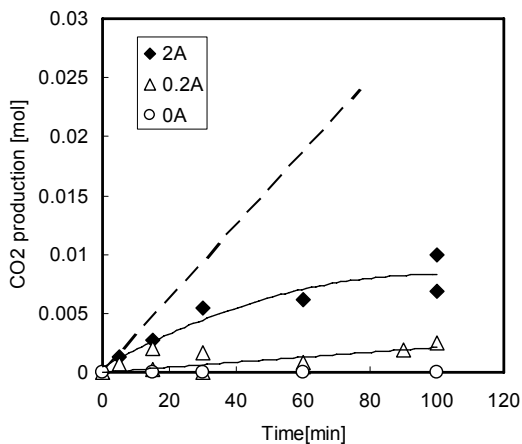


Fig. 16 Amount of carbon dioxide produced for hydrothermal electrolysis of glucose.

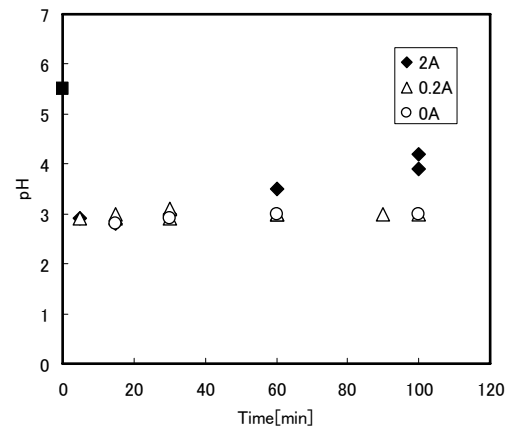


Fig. 17 pH variation for hydrothermal electrolysis of glucose.

### Lignin

Lignin was also decomposed by the hydrothermal electrolysis. The results were similar to 2-furfural and the yield of gaseous products gradually increased with time.

### Conclusions

Bio-related compounds such as 1-butanol, 2-furfural, glucose, and lignin were rapidly converted to organic acids and gaseous products by hydrothermal electrolysis. As a gaseous product, hydrogen and carbon dioxide were produced. The pH of the solution decreased initially due to the generation of organic acids, and then increased. From the experimental results, the reaction pathway

for hydrothermal electrolysis were proposed.

### ***Acknowledgements***

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