



## Production of Valuable Organic Acids from Organic Wastes with Hydrothermal Treatment Process

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### Abstract

This article reports production of valuable organic acids from the hydrothermal treatment of representative organic wastes and compounds (*i. e.* domestic sludge, proteinaceous, cellulose and plastic wastes) with or without oxidant ( $H_2O_2$ ). Organic acids such as acetic, formic, propionic, succinic and lactic acids were obtained in significant amounts. At 623 K (16.5 MPa), acetic acid of about 26 mg/g-dry waste fish entrails was obtained. This increased to 42 mg/g-dry waste fish entrails in the presence of  $H_2O_2$ . Experiments on glucose to represent cellulose wastes were also carried out, getting acetic acid of about 29 mg/g-glucose. The study was extended to terephthalic acid and glyceraldehyde, reaction intermediates of hydrothermal treatment of PET plastic wastes and glucose, respectively. Studies on temperature dependence of formation of organic acids showed thermal stability of acetic acid, whereas, formic acid decomposed readily under hydrothermal conditions. In general, results demonstrated that the presence of oxidants favored formation of organic acids with acetic acid being the major product.

**Keywords:** hydrothermal treatment, organic acids, organic wastes, oxidant, supercritical water oxidation

### 1. Introduction

Industrial processes always accompany wastes that are of great risk to environment. Technologies that would treat these wastes or much better recover some useful organic materials before disposal are necessary to prevent pollution. One of the possible techniques is the use of hydrothermal treatment process. Reactions under hydrothermal conditions have been gaining interests recently because of the fascinating properties of water as a reaction media at elevated temperatures and pressures (Faisal *et al.*, 2007a; Faisal *et al.*, 2005; Savage *et al.*, 1995). At room temperature and atmospheric pressure, water has a dielectric constant of 80 and ion product ( $K_w$ ) of  $10^{-14}$ . These values can be controlled by manipulating temperature and pressure, and could greatly affect the reactivity of various compounds in water. The dielectric constant expresses the affinity of water as a solvent to reaction substances especially for non-polar materials. In addition, ion product of water can also be adjusted to control the ability of hydrolysis. High ion product is good for hydrolysis. Under saturated vapor pressure, water has a maximum ion product at around 250°C.

Hydrothermal treatment has been widely applied to various reactions such as

reduction, pyrolytic, decomposition and dehydration (Faisal *et al.*, 2007b). Examples are oxidation of phenols (Martino and Savage 1999), pyridine (Aki *et al.*, 1999) and methanol (Anitescu *et al.*, 1999); and hydrolysis of esters (Krammer and Vogel, 2000) and thiodiglycol (Lachance *et al.*, 1999), among others. The technique was also applied to chemical recycling processes such as hydrolysis of polyethylene terephthalate (PET) into ethylene glycol and terephthalic acid (Arai and Adschiri, 1999).

The most significant applications are those in environmental processes such as decomposition of municipal sewage sludge and alcohol distillery wastewater and oxidation and decomposition of toxic organic compounds such as PCB and dioxins. However, there were only few studies reported on the application from the viewpoint of resources recovery. Although this technology has not been widely utilized in industry, application to destruction of toxic wastes has been tested practical in small scale (Shaw *et al.*, 1991)

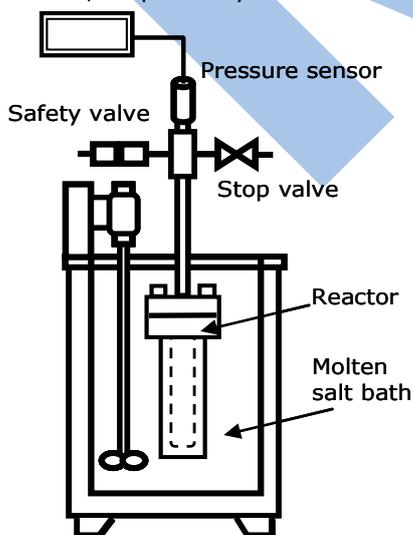
To completely decompose organic wastes into volatile carbon (both organic and inorganic) and water, knowledge on the formation of organic acids (*i.e.* low-molecular-weight carboxylic acids) is important. The low-molecular-weight carboxylic acids are usually the refractory materials in wet oxidation of

organic wastes, which has been reported to control the oxidation rate (Mishra *et al.*, 1995). It was found that wet oxidation of phenol gives formic, acetic, glyoxalic and oxalic acids as products. Oxidation of these low-molecular-weight carboxylic acids serves as model for supercritical water oxidation of organic compounds (Shende and Levec, 1999). Information on the amount and which carboxylic acids can be obtained from the hydrothermal treatment of various organic wastes is also important and useful in designing applicable processes. However, to our knowledge, there is no written account on the formation of these carboxylic acids from various organic wastes.

This article consolidates the information on some organic acids obtained from the hydrothermal treatment of various representative organic wastes and compounds. This includes experimental results on the effect of reaction temperature on organic acid production with or without oxidant ( $H_2O_2$ ).

## 2. Methodology

Experiments were conducted in a reactor made of SUS-316 having an inside volume of about  $6\text{ cm}^3$ . The schematic diagram of batch reactor apparatus is shown in Figure 1. The allowable pressure depends on the operating temperature. At 373 K, the pressure can be up to 45 MPa. At higher temperature of 700 K, the operating pressure should not exceed 35 MPa. Experiments were conducted over a temperature range of 523 to 623 K at corresponding saturated vapor pressures of 4 to 16 MPa, respectively.



**Figure 1.** Schematic diagram of batch reactor apparatus.

The reaction time was held constant at 30 min in all experiments. In each experimental run, about 0.1 g sample and 5 g of deionized water (weight ratio = 1:50) were charged into the reactor. The reactor was sealed with Swagelok caps, and then the air inside was purged using Argon gas. The reactor was immersed into the preheated molten salt bath (containing a mixture of potassium nitrate and sodium nitrate) set at the desired reaction temperature.

After the desired reaction time had elapsed, the reactor was plunged into a water bath to bring them quickly to room temperature, thus, effectively ceasing any occurring reactions. In the study of the effect of oxidants,  $H_2O_2$  solution (35 % wt  $H_2O_2$ ) was added in equal proportion with the sample. The weight ratio of sample to water was maintained at 1:50.

### 2.1 Analysis

Low-molecular-weight carboxylic acids were analyzed using an organic acid analyzer (LC-10A, Shimadzu Corp.) consisting of ion exclusion column (Shim-Pack SCR-102H) and electroconductivity detector (CDD-6A, Shimadzu Corp.). The compounds that can be analyzed are aliphatic carboxylic acids, hydroxycarboxylic acids, ketocarboxylic acids, and other organic acids having dissociation constant (pKa) of 2 to 5 and carbon number of 5 or less.

In this study, the resulting products were analyzed for the presence of the following low-molecular-weight carboxylic acids; formic, acetic, propionic, pyruvic, lactic, succinic, malic and citric acid.

### 2.2 Classification of Wastes

**Proteinaceous Wastes.** Waste fish entrails and sewage sludge represent proteinaceous wastes. In this paper, entrails of "white croaker" obtained from local seafood processing company are studied. Prior to the experiments, the entrails were homogenized for 5 min using a mixer (CQM-N1, Toshiba Corp.) at maximum speed setting. The resulting homogeneous entrails were kept in a freezer at 252 K.

The sludge was obtained from the university sewage plant. The samples were centrifuged for 10 min at 7000 rpm (High Speed Refrigerated Centrifuge, RS206). The solids were freeze-dried for about 8 hours using Freeze Drier (FDU-506), decreasing the water content to 56 wt %. The properties of waste

fish entrails and sewage sludge are described in details by Kang *et al.* (2001). The protein in fish waste (59 wt %) is more than the amount in sewage sludge (16 wt %).

**Cellulosic Wastes.** Glucose was used as a model for cellulosic wastes. In this study, experiments on glucose (Nacalai Tesque) as a model for cellulosic wastes were conducted. No pretreatment was done prior to each experiment. Experiments on glyceraldehyde (DL-glyceraldehyde, Nacalai Tesque), one of the products of glucose hydrolysis, were also carried out.

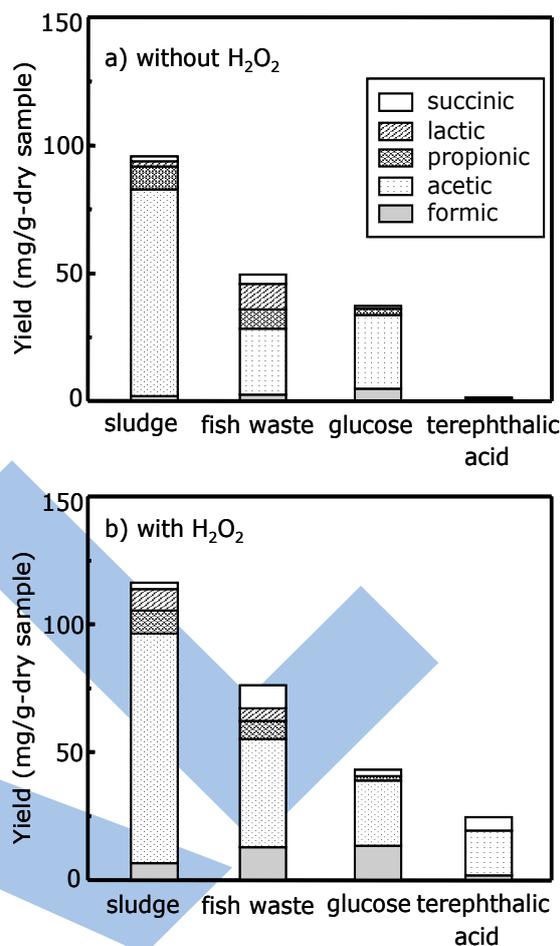
**Plastic Wastes.** Terephthalic acid, a monomer obtained by supercritical water hydrolysis of polyethylene terephthalate (PET), was chosen to represent plastic wastes. Next to polyethylene, PET comprises the second largest fraction in plastic wastes stream in the US (Subramanian, 2000). The compound has been used as a model in the study of decomposition of plastic wastes under hydrothermal condition.

### 3. Results and Discussion

#### 3.1 Production of Low-Molecular-Weight Carboxylic Acids

Figure 2 shows low-molecular-weight carboxylic acids obtained from hydrothermal treatment of representative organic compounds and wastes at 623 K ( $P = 16.5$  MPa) and reaction time of 30 min. Organic acids such as acetic, formic, propionic, succinic and lactic acids were obtained in significant amounts. Acetic acid of about 26 mg/g-dry waste fish entrails was obtained, relatively lower than that of sludge at about 81 mg/g-sludge. In the presence of  $H_2O_2$ , the amount increased to 42 mg/g-dry waste fish entrails and 90 mg/g-sludge.

In the case of glucose, acetic acid of about 29 mg/g-glucose was obtained. As seen from the slight difference in the yield, addition of oxidant ( $H_2O_2$ ) favors formation of organic acids. This is probably due to the easy formation of OH radicals from  $H_2O_2$  that could aid in the production of low-molecular-weight carboxylic acids. The difference is not significant, presumably due to the insufficient amount of  $H_2O_2$  added. Higher amount of  $H_2O_2$  may lead to complete oxidation of organic wastes.



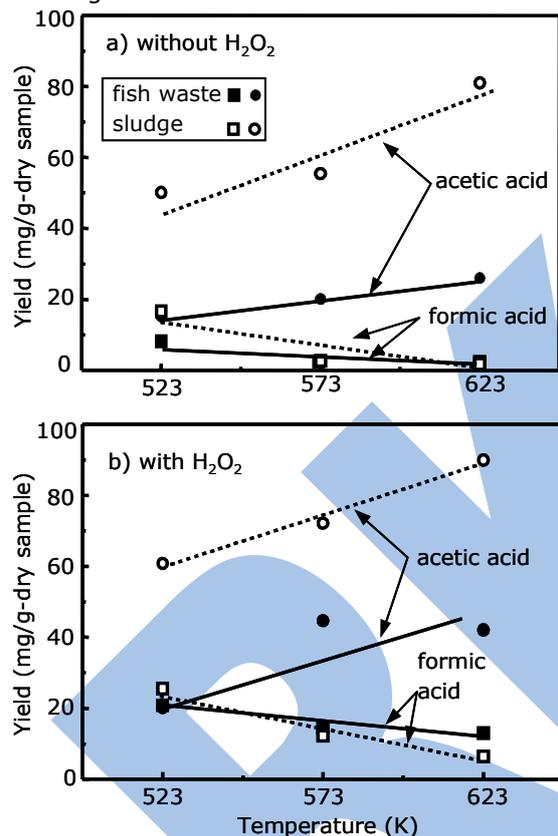
**Figure 2.** Low-molecular weight carboxylic acids obtained from hydrothermal treatment of organic wastes and compounds ( $T = 623$  K,  $P = 16.5$  MPa).

Only a few carboxylic acids were considered in this study. Formation of other organic acids is also possible. For example, in addition to formic, acetic, propionic and succinic acid, Goto *et al.* (1998) obtained iso-valerianic acid from destruction of municipal excess sludge using supercritical water. Butyric acid was also found from destruction of alcohol distillery wastewater.

Among the low-molecular-weight carboxylic acids obtained from various wastes, acetic acid is the major product due to its relative stability or refractory behavior. Merchant (1992) has reported that non-catalytic wet oxidation of acetic acid at  $275^\circ\text{C}$  in 5 h resulted to only 7% reduction in COD. To further study the behavior of formation of acetic and formic acid from various organic wastes under hydrothermal condition, temperature dependence is discussed in subsequent section.

### 3.2 Temperature Dependence of Yield of Formic and Acetic Acids

Formic and acetic acids are usually the major intermediate products prior to complete degradation to volatile carbon and water. In this regard, and as a basic consideration for the design of applicable hydrothermal treatment process, the temperature dependence of the yield of these compounds was investigated.

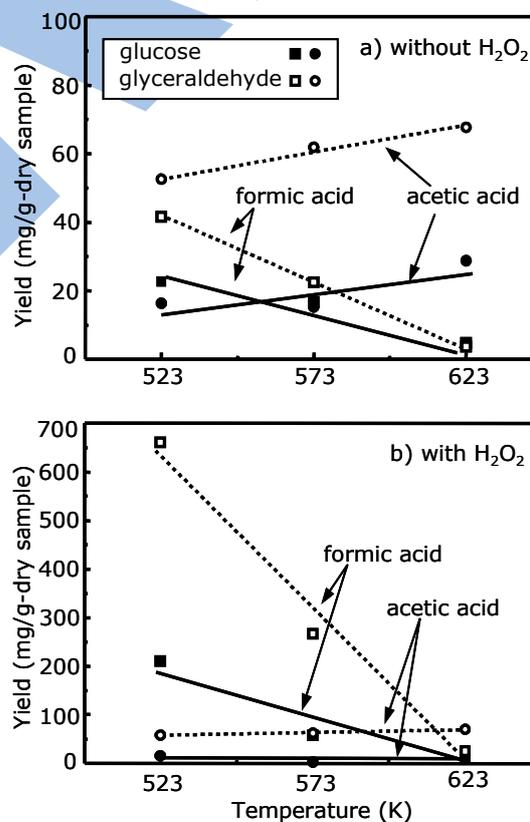


**Figure 3.** Effect of temperature on the yield of formic and acetic acid from hydrothermal treatment of fish waste and sludge.

As shown in Figure 3, production of acetic acid increases while formic acid decreases with increasing temperature. The same trend was observed with or without the oxidant (H<sub>2</sub>O<sub>2</sub>), getting a slightly higher yield with H<sub>2</sub>O<sub>2</sub>. Formic acid decomposes more readily compare to acetic acid. One possible reason, as previously mentioned, is the relative stability of acetic acid compare to other organic acids. It was observed by Merchant (1992) that only 7 % reduction in COD was achieved during wet oxidation of acetic acid at 548 K in 5 h. Shende and Levec (1999) reported that in the presence of copper sulfate as catalyst, about 80 % COD reduction was obtained after 5 h at 508 K. In

addition, it is likely that easily decomposable organic compounds, other than proteins, may have contributed to the relatively high amount of organic acids produced from sewage sludge as compare to waste fish entrails. It was observed that waste fish entrails contain higher amount of proteins (59%, dry basis) compared to sludge (16%, dry basis). The proteins in fish wastes could not be easily decomposed to low-molecular-weight carboxylic acids as confirmed from the results of previous studies (Kang *et al.*, 2001).

Figure 4 shows the effect of temperature on the yield of formic and acetic acids for representative compounds of glucose and glyceraldehyde (a product of glucose hydrolysis). It can be seen that formic acid was readily obtained even at low temperature, but decomposed easily with the increase in temperature. Using glucose as starting material and in the absence of H<sub>2</sub>O<sub>2</sub>, at 523 K, the yields of formic and acetic acids were low at 41 and 10 mg/g-glucose, respectively. This was presumably due to difficulty decomposing glucose at the tested conditions.



**Figure 4.** Effect of temperature on the yield of formic and acetic acid from hydrothermal treatment of glucose and glyceraldehyde.

Taking glyceraldehyde as the starting material, formation of formic and acetic acids was much favored, getting yields of 42 and 53 mg/g-glyceraldehyde, respectively. At 523 K, the yield of formic acid increased by about three times that of glucose in the presence of  $H_2O_2$ . This indicates that  $H_2O_2$  significantly affects the degradation of glyceraldehyde compared to glucose. Being a more complex and high-molecular compound, glucose takes a more complicated degradation path to low-molecular weight carboxylic acids. No significant change on the trend of formic acid decomposition and acetic acid formation was observed for both compounds with or without  $H_2O_2$ . Almost all formic acid decomposed at 623 K.

Furthermore, experiments on terephthalic acid to represent plastic wastes were conducted under the same conditions. Only traces of acetic and formic acids were obtained in the absence of  $H_2O_2$ , whereas, the presence of  $H_2O_2$  resulted into the yield of about 80 mg of formic acid per g-dry sample at 523 K. The yield decreased with increasing temperature. No significant changes in the yield of acetic acid (about 20 mg/g-dry sample) were observed even with the increase in temperature from 523 to 623 K. This low yield of organic acids was due to incomplete decomposition of terephthalic acid at the tested conditions, evident from unconverted solid particles even after reaction time of 30 min has elapsed.

#### 4. Conclusion

The application of sub and supercritical water to destruction of toxic and organic wastes has been attracting attention in recent years. Several related works deal with the oxidation of low-molecular-weight carboxylic acids under supercritical conditions as model for destruction of organic wastes. It is also necessary to investigate the formation of these compounds from various organic wastes.

This work has shown that several low-molecular-weight carboxylic acids can be produced from hydrothermal treatment of various wastes including proteinaceous, cellulosic and plastic wastes. Acetic acids was dominant among the several carboxylic acids obtained which include formic, propionic, succinic and lactic acids. At 623 K (16.5 MPa), acetic acid of about 26 mg/g-dry waste fish entrails was obtained. This increased to 42 mg/g-dry waste fish entrails in the presence of  $H_2O_2$ . Experiments on glucose to

represent cellulosic wastes were also carried out, getting acetic acid of about 29 mg/g-glucose. The study was extended to terephthalic acid and glyceraldehyde, reaction intermediates of hydrothermal treatment of PET plastic wastes and glucose, respectively.

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