



Low-molecular-weight carboxylic acids produced from hydrothermal treatment of organic wastes

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Abstract

This article reports production of low-molecular-weight carboxylic acids from the hydrothermal treatment of representative organic wastes and compounds (i.e. domestic sludge, proteinaceous, cellulosic 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 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 polyethylene terephthalate (PET) plastic wastes and glucose, respectively. In addition, production of lactic acid, one of the interesting low-molecular-weight carboxylic acids, was discussed on the viewpoint of resources recovery.

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. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Low-molecular-weight carboxylic acids; Hydrothermal treatment; Organic wastes; Supercritical water oxidation; Lactic acid

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1. Introduction

The use of subcritical and supercritical water for waste destruction and for recovery of useful materials has been gaining interests due to its potential as solvent and catalyst for organic reactions [1]. A lot of research works have been done in this regard, and the technique was found useful especially to wastewater treatment and solid waste resources recovery [2,3]. Although this technology has not been widely utilized in industry, application to destruction of toxic wastes has been tested practical in small scale [4].

To completely decompose organic wastes into volatile carbon (both organic and inorganic) and water, knowledge on the formation of low-molecular-weight carboxylic acids is important. 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 [5]. Devlin and Harris [6] 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 [7–10]. 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 information on low-molecular-weight carboxylic 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). In addition, the production of lactic acid is discussed. Lactic acid is one of the interesting organic acids widely used in pharmaceutical and cosmetic industry, and is considered a possible raw material for the production of biodegradable plastics.

2. Experimental section

2.1. Experimental apparatus and methodology

Experiments were conducted in a reactor made of SUS-316 having an inside volume of about 6 cm^3 . 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 523–623 K at corresponding saturated vapor pressures of 4–16 MPa, respectively. 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, H₂O₂ solution (35 wt.% H₂O₂) was added in equal proportion with the sample. The weight ratio of sample to water was maintained at 1:50.

2.2. 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 (pK_a) of 2–5 and carbon number of five 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. The molecular structures of the acids and organic compounds in this study are shown in Fig. 1.

2.3. Classification of wastes

2.3.1. 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 h using freeze drier (FDU-506), decreasing the water content to 56 wt.%.

The properties of waste fish entrails and sewage sludge are shown in Table 1. Experiment on acid hydrolysis was performed to measure the amino acid content in these wastes and the results are shown in Table 2. Amino acids were analyzed using amino acid analyzer. The analytical procedures are described in details elsewhere [11]. The protein in fish waste (59 wt.%) is more than the amount in sewage sludge (16 wt.%).

Table 1
Properties of waste fish entrails and sewage sludge

	Waste fish entrails	Sewage sludge
Water content (wt.%)	80	56
Elemental analysis (wt.% dry basis)		
C	49	28
N	6	5
H	11	4
Others	34	63
Protein content (wt.% dry basis)	59	16

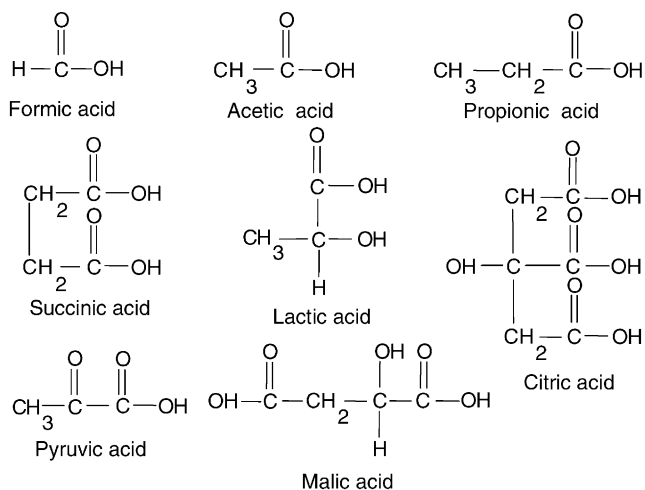
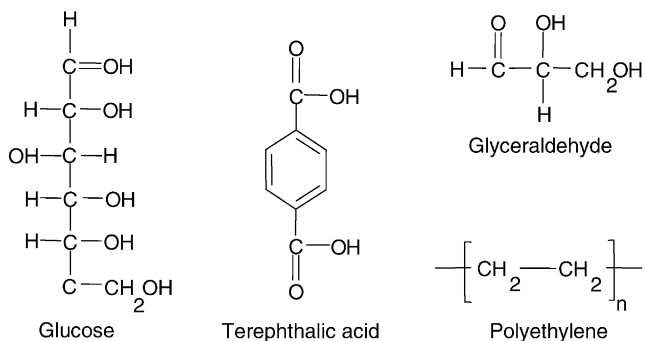
Low-molecular-weight carboxylic acids**Other compounds**

Fig. 1. Molecular structures of organic compounds in this study.

2.3.2. Cellulosic wastes

Glucose was reported to be an appropriate model for cellulosic wastes like paper mill sludges [12]. 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.

2.3.3. Plastic wastes

Terephthalic acid, a monomer obtained by supercritical water hydrolysis of polyethylene terephthalate (PET) [13], was chosen to represent plastic wastes. Next to polyethylene, PET comprises the second largest fraction in plastic wastes stream in the US [14]. The compound has been used as a model in the study of decomposition of plastic wastes under hydrothermal condition.

Table 2
Amino acids obtained from 6N HCl acid hydrolysis of waste fish entrails and sewage sludge (mg/g dry sample)

Amino acids	Waste fish entrails	Sewage sludge
Aspartic acid (Asp)	49.0	15.3
Threonine (Thr)	29.4	5.2
Serine (Ser)	26.9	2.3
Glutamic acid (Glu)	82.8	18.0
Proline (Pro)	33.8	7.8
Glycine (Gly)	77.7	12.6
Alanine (Ala)	32.2	13.8
Cystine (Cys)	3.4	42.9
Valine (Val)	34.1	0.7
Methionine (Met)	13.4	1.1
Isoleucine (Ile)	25.9	6.4
Leucine (Leu)	51.2	12.1
Tyrosine (Tyr)	25.0	3.7
Phenylalanine (Phe)	31.6	7.2
Histidine (His)	16.7	3.9
Lysine (Lys)	37.5	7.4
Arginine (Arg)	27.5	6.9

3. Results and discussion

3.1. Production of low-molecular-weight carboxylic acids

Fig. 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 [15] 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.

Only the carboxylic acids shown in Fig. 1 were considered in this study, but formation of other organic acids is also possible. For example, in addition to formic, acetic, propionic and succinic acid, Goto et al. [16] 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 [10]. Merchant [17] has reported that non-catalytic wet oxidation of acetic acid at 275 °C in 5 h resulted to

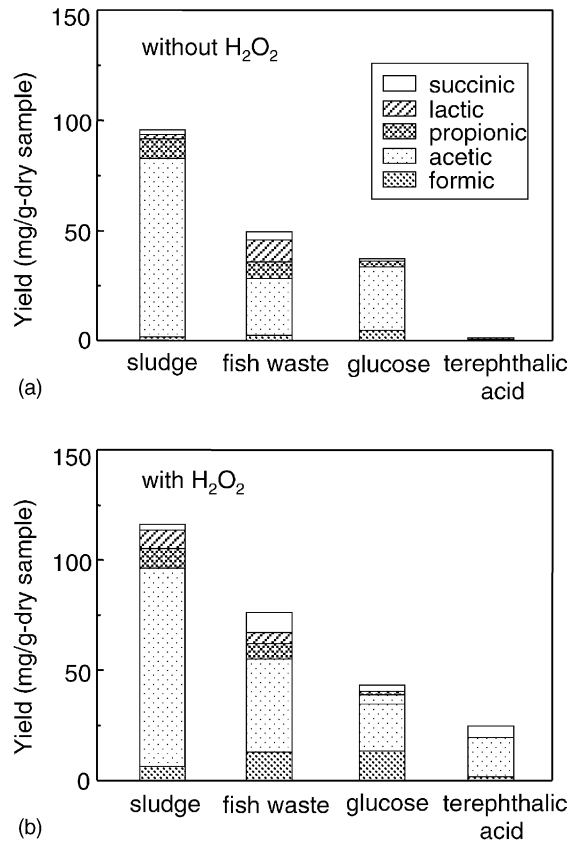


Fig. 2. Low-molecular-weight carboxylic acids obtained from hydrothermal treatment of organic wastes and compounds ($T = 623 \text{ K}$, $P = 16.5 \text{ MPa}$).

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 [Section 4](#).

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.

As shown in [Fig. 3](#), production of acetic acid increases while formic acid decreases with increasing temperature. The same trend was observed with or without the oxidant (H_2O_2), getting a slightly higher yield with H_2O_2 . Formic acid decomposes more readily compare to acetic acid. One possible reason, as previously mentioned, is the relative stability of

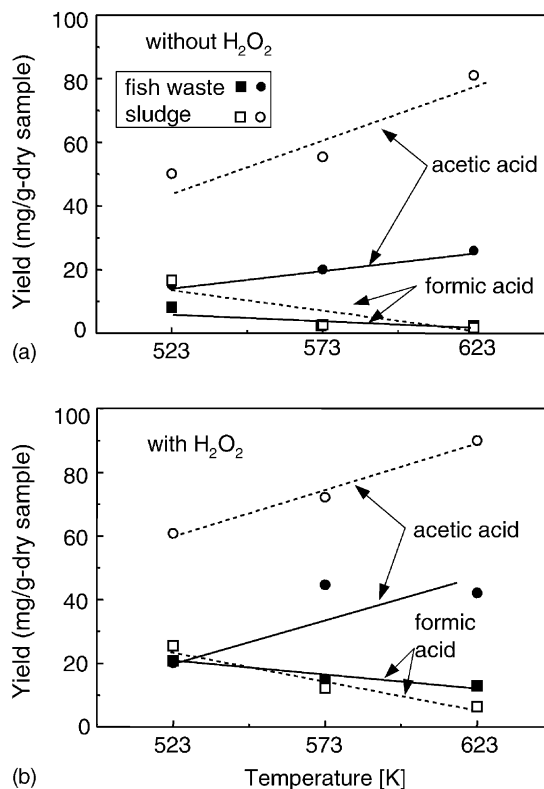


Fig. 3. Effect of temperature on the yield of formic and acetic acid from hydrothermal treatment of fish waste and sludge.

acetic acid compare to other organic acids. It was observed by Merchant [17] that only 7% reduction in COD was achieved during wet oxidation of acetic acid at 548 K in 5 h. Shende and Mahajani [7] 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 our previous studies [11].

For representative compounds such as glucose and glyceraldehyde (a product of glucose hydrolysis), Fig. 4 shows 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 H₂O₂, 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. Taking glyceraldehyde as the starting material, formation of

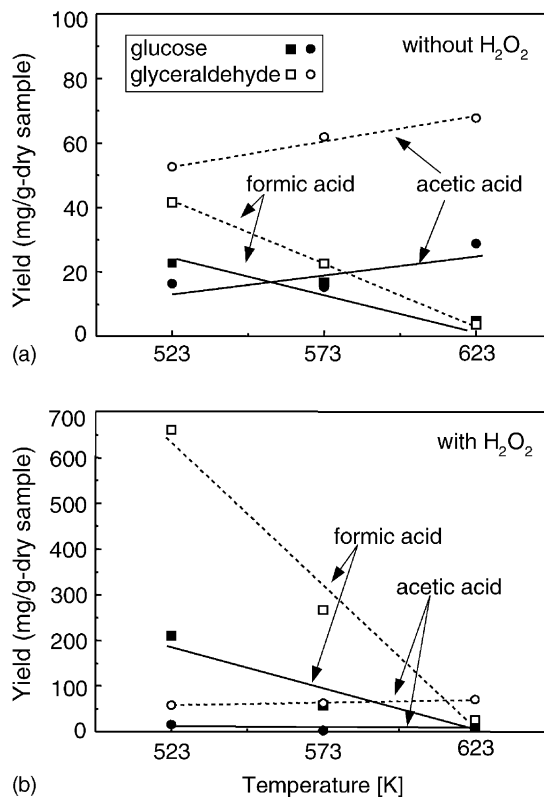


Fig. 4. Effect of temperature on the yield of formic and acetic acid from hydrothermal treatment of glucose and glyceraldehydes.

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 H₂O₂. This indicates that H₂O₂ 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 H₂O₂. 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 H₂O₂, whereas, the presence of H₂O₂ resulted into the yield of about 80 mg of formic acid/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.

3.3. Lactic acid production

Among organic acids previously mentioned, lactic acid is of significant interest. Datta and Tsai [18] reported lactic acid as raw material for manufacture of wide range of useful products including degradable plastics, oxychemicals (propylene glycol, acrylates, propylene oxide) and “green” chemicals/solvents (esters, ester derivatives). In Japan, it is estimated that 20% of annual production of general-purpose plastics (14×10^9 kg) is a potential market of biodegradable plastics [19]. The annual worldwide production of plastics is estimated at 1×10^{11} kg. A wide range of product can also be obtained from lactic acid, the expected US market size is 2.7×10^9 kg per year and the product values could exceed US\$ 4×10^9 per year [18]. The possibility of production of lactic acid from hydrolysis of fish meat in subcritical water was reported by Yoshida et al. [20]. This was confirmed in our previous study using waste fish entrails [11].

Fig. 5 shows the comparison of lactic acid production by hydrothermal treatment of fish waste, sludge and glucose at various temperatures. The yield increases with the increase in temperature from 523 to 573 K, presumably due to maximum ion product of water at 573 K. The dramatic decrease in the yield of lactic acid at 623 K was likely due to its

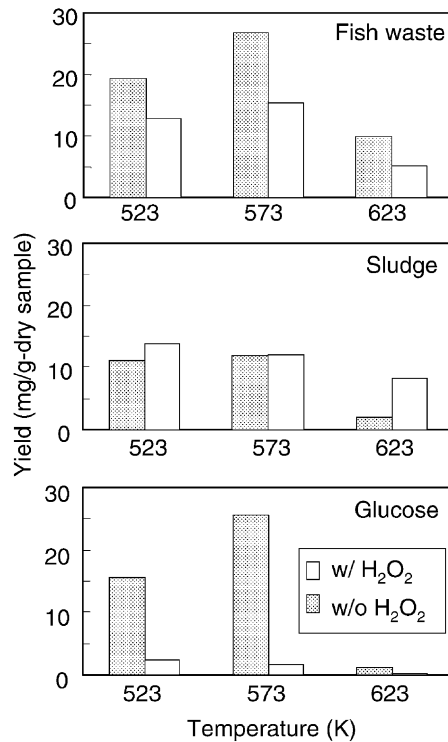


Fig. 5. Comparison of lactic acid production from hydrothermal treatment of fish waste, sludge and glucose at various temperatures.

rapid degradation, thus, producing formic acid, acetic acid, propionic acid, acrylic acid and acetaldehyde [21]. Similar trend was observed for all the wastes and compounds tested in this study, obtaining relatively high yield from fish waste. Formation of lactic acid is favored in the absence of oxidants for almost all wastes tested except in sludge where lactic acid formation is high at 573 K. The presence of oxidants enhances oxidation of lactic acid to volatile compounds, thus, decreasing its yield. However, the dramatic increase in lactic acid formation from sludge at 573 K in the presence of H₂O₂ requires further investigation. The role of H₂O₂ to degradation of organic materials present in sludge is necessary to elucidate the mechanism.

In the case of glucose, further investigation on the production of lactic acid from glyceraldehyde [22] was also performed. It was observed that the yield of lactic acid (150 mg/g dry sample) from hydrolysis of glyceraldehyde is maximum at 573 K and about six times that obtained from glucose hydrolysis. Comparing the molecular structures of lactic acid and glyceraldehyde, it is likely that ionic shift or molecular rearrangement could have taken place to form these isomers. This interesting phenomenon occurring under hydrothermal conditions merits further investigation.

4. General mechanism of formation

Based on the results and related literatures, a proposed general reaction pathway for low-molecular-weight carboxylic acid production from various organic wastes is shown in Fig. 6. From proteinaceous wastes, amino acids are produced from degradation of proteins. Amino acids further degrade to form organic acids. In case of cellulosic wastes, cellulose is mainly converted to glucose by hydrolysis. Glucose further decompose to form

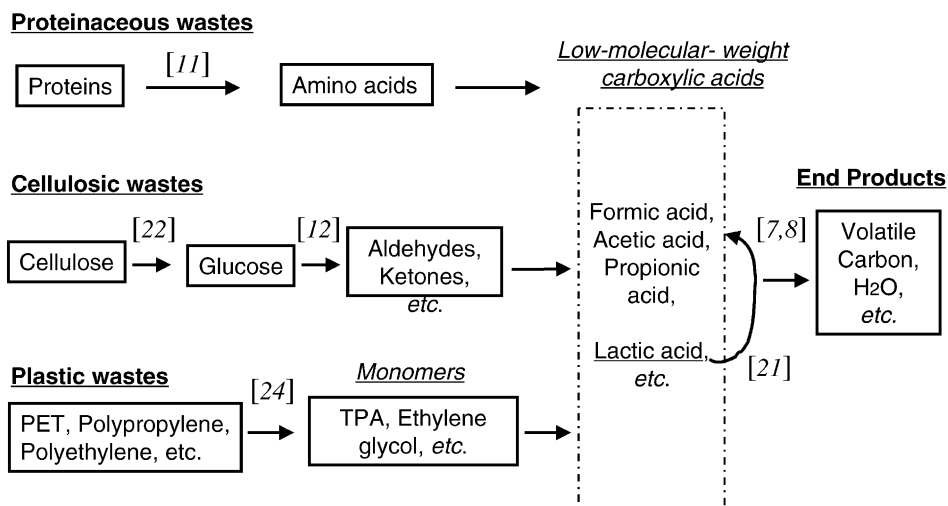


Fig. 6. General reaction pathway for production of low-molecular-weight carboxylic acids from hydrothermal treatment of various organic wastes (number in square bracket denotes literature cited) [24].

other products including aldehydes and ketones, from which organic acids are produced. Organic acids may also be produced from monomers obtained from hydrolysis of plastic wastes.

Lactic acid can be obtained by deamination and hydroxylation of amino acids. Our previous experiments on the degradation rate of various amino acids showed that lactic acid could be produced from amino acids such as alanine and aspartic acid with first-order degradation rate constants of 0.0092 and 1.3 s^{-1} , respectively [23].

For cellulosic wastes, Sasaki et al. [22] have worked on hydrolysis of cellulose in subcritical and supercritical water obtaining glucose and some oligomers as intermediate products. From glucose, they obtained products like erythrose, dihydroxyacetone, fructose, among others. Holgate et al. [12] used glucose as a model compound for cellulosic wastes (i.e. paper mill sludges and human waste), and found traces of lactic acid from hydrolysis and oxidation in supercritical water. The presence of small amount of lactic acid maybe due to high degradation of lactic acid at supercritical condition. Li et al. [21] have reported the degradation rate of lactic acid by hydrolysis and oxidation including reaction pathway and possible products. The pseudo-first-order rate constant for hydrothermal oxidation of lactic acid ($1.52 \times 10^9 \text{ s}^{-1}$) is almost 10^9 times that of acetic acid. The products are diverse from various steps like dehydration, hydrolysis or thermal degradation and oxidation. Oxidation would result into formation of acetic and formic acids. The mechanism of acetic and formic acids formation from lactic acid was also discussed by Li et al. [21].

5. Summary

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. On the viewpoint of resources recovery, lactic acid production was discussed. The information presented here is useful to the design of applicable hydrothermal treatment process of various organic wastes.

From related literatures and results of this study, a general reaction pathway for organic acids production from hydrothermal treatment of various organic wastes was presented. Further investigation is needed to elucidate and clarify the reaction pathway.

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