

Short communication

## Change of monochloroacetic acid to biodegradable organic acids by hydrothermal reaction

Kyoungrean Kim, Masafumi Fujita<sup>1</sup>, Hiroyuki Daimon, Koichi Fujie\*

*Department of Ecological Engineering, Toyohashi University of Technology, Hibarigaoka 1-1, Tempaku-cho, Toyohashi, Aichi 441-8580, Japan*

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### Abstract

The feasibility of biodegradability improvement induced from the structural conversion of refractory pollutants by hydrothermal reaction was investigated. Monochloroacetic acid (MCAA) was selected as a preliminary material represented for linear hydrocarbon structured refractory pollutants. Under the tested conditions, MCAA was partially destructed and then converted to biodegradable reaction products by hydrolysis, dehydration and thermal decomposition. The identified products were glycolic acid, citric acid and formic acid. Total organic carbon (TOC) reduction during the structural conversion did not exceed 24%, except the results at the reaction conditions of 350 °C and 17 MPa. However, Produced biodegradable organic acids were reduced by thermal decomposition with increasing reaction temperature and time. At the reaction temperature of 250 and 300 °C, biodegradability (BOD/COD<sub>Cr</sub>) was reached at 0.51 in 6.9 min and 0.52 in 7.4 min despite the presence of dissociated chlorine ions. The detachment of recalcitrant chlorine ion from MCAA and the production of biodegradable organic acids by hydrothermal reaction were directly related to the biodegradability improvement of reaction products.

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### 1. Introduction

The awareness of refractory pollutants regarding their treatment and biodegradability improvement has been increased. Conventional biological treatment methods such as activated sludge process are retarded by stable chemical structures, high-molecular-weight structures and attached recalcitrant radicals. Structural conversion from refractory pollutants to easily degradable substances is inevitably required to improve biodegradability of refractory pollutants. It could not be easily achieved by advanced treatment methods as well as conventional biological treatment methods. However, biodegradation of refractory pollutants has been continuously researched, because it is the basic and ultimate fate in aquatic and terrestrial ecosystems [1]. Therefore, the introduction of a new pretreatment method is essen-

tially required to attain structural conversion of refractory pollutants enough to improve their biodegradability.

Monochloroacetic acid (MCAA) is detected at widespread area in our environment from synthetic and natural sources [2–5]. Because of its low acute toxicity, high solubility in water and low volatility, MCAA could give toxic effect to plant, algae and animal [6,7] and resist to biodegradation [8]. For these reasons, MCAA was selected as a preliminary material represented for linear hydrocarbon structured refractory pollutants having recalcitrant radicals.

Hydrothermal reaction has been attracting many researchers, because of the fascinating characteristics of water as reaction medium at elevated temperatures and pressures [9]. Under sub- and supercritical water conditions ( $T_C = 374\text{ °C}$ ,  $P_C = 22.1\text{ MPa}$ ), various reactions such as oxidation, hydrolysis, dehydration, reduction and thermal decomposition can be produced energetically [10]. This technology is used for degradation of refractory pollutants [11], toxic chemicals [12], waste sludge [13] and garbage [14]. Catalyst and oxidant are usually used to increase decomposition efficiency [11]. At sub-critical water conditions, reaction is particularly suitable for hydrolysis of organic compounds [15]. In case of resource recov-

\* Corresponding author. Tel.: +81-532-44-6905; fax: +81-532-44-6349.

*E-mail addresses:* kim@fujielab.eco.tut.ac.jp (K. Kim), fujie@eco.tut.ac.jp (K. Fujie).

<sup>1</sup> Department of Civil and Environmental Engineering, University of Yamanashi, 4-3-11 Takeda, Kofu, Yamanashi 400-8511, Japan.

ery, reactions must be conducted under sub-critical water conditions to prevent complete decomposition of desired products [16,17]. However, hydrothermal reaction has not been applied as a method for partial destruction of refractory pollutants enough to improve their biodegradability, except our previous results related to biodegradability improvement and structural conversion of polyvinyl alcohol [18].

In this research, the structural conversion of refractory pollutants under sub-critical water conditions is focused. Under the conditions, hydrolysis, thermal decomposition and catalytic effect of water could derive the fracture of attached recalcitrant radicals, stable chemical structures and high-molecular-weight structures of refractory pollutants within short reaction time. This process may allow biodegradability improvement of refractory pollutants. Thus, the objective of this research is to investigate the feasibility of biodegradability improvement induced from the structural conversion of MCAA by hydrothermal reaction. Besides, the application of hydrothermal reaction as a new pretreatment method for refractory pollutants is also studied.

## 2. Materials and methods

### 2.1. Reagent

MCAA and other organic acids (glycolic, citric and formic acid) were obtained from Tokyo Chemical Industry Co. (Tokyo, Japan). All reagents were guaranteed grade. Glycolic, citric and formic acid were used as standard materials for qualitative and quantitative analysis of reaction products obtained from MCAA.

### 2.2. Batch reactor apparatus

Experiments were carried out using a batch reactor apparatus (TSC-006, Taiatsu Glass Corporation). It mainly con-

sists of a stirrer, a pressure gauge, a reactor and a molten salt bath containing mixture of potassium nitrate and sodium nitrate [19]. Two batch reactors were used during the experimental periods. One batch reactor (reactor 1) made up of hastelloy C22 (Ni, Cr, Mo alloy) has a total inner volume of 65.9 cm<sup>3</sup>. The other reactor (reactor 2) made by stainless steel (sus 316) has a effective inner volume of 5.9 cm<sup>3</sup>. The maximum operational conditions of both reactors are 450 °C and 45 MPa. Reactor 1 takes 7.5 min to reach heat-up at 350 °C. In case of reactor 2, the required time is 1.5 min at the same temperature. The heat-up time is depending on the desired reaction temperatures [17]. Reactor 2 was only used to investigate reaction rates within 7.4 min, for its fast heat-up time.

### 2.3. Experimental methodologies

Prior to experiments, MCAA was adjusted to the concentration of 4.23 mM using distilled water. In order to test the feasibility of short time treatment of high concentration refractory pollutants by hydrothermal reaction, higher concentration range than that of real wastewater stream was selected. Experiments were conducted at various temperatures (250, 300 and 350 °C) and specific pressures (4, 9 and 17 MPa). The reaction times were set as shown in Table 1. They were defined as the elapsed time from the heat-up time to reach 90% of each reaction temperature [18]. Saturated vapor pressures at the specific temperature were selected for liquid phase reaction. The desired pressure was obtained by adjusting the initial sample volume using the data on steam table. During the experiments, reaction pressures were verified from the pressure gauge of a batch reactor apparatus. In each experiment, sample was placed into a reactor. The reactor was sealed, and then the air inside was purged using pure nitrogen gas. The reactor was put into the preheated molten salt bath during the desired reaction time. Then the reactor was immediately quenched in water bath, effectively ceasing any occurring reactions.

Table 1  
Change of water quality indexes under sub-critical water conditions

Specification	Reaction time (min)	TOC (mg l <sup>-1</sup> )	DOC (mg l <sup>-1</sup> )	COD <sub>Cr</sub> (mg l <sup>-1</sup> )	BOD (mg l <sup>-1</sup> )	pH (-)
MCAA	–	1020	1020	2600	0	2.3
250 °C, 4 MPa	6.9	1010	1010	2600	1330	1.5
	16.9	1010	1000	2600	1330	1.5
	26.9	1000	990	2500	1300	1.5
	56.9	990	990	2500	1300	1.5
300 °C, 9 MPa	7.4	1010	1010	2400	1250	1.7
	17.4	1000	1000	2100	1340	1.6
	27.4	980	970	2000	910	1.6
	57.4	780	770	1800	620	1.6
350 °C, 17 MPa	7.4	660	640	1900	330	1.7
	17.4	390	380	1500	270	1.6
	27.4	330	330	1100	250	1.6
	57.4	220	210	600	160	1.7

## 2.4. Analytical methods

For the evaluation of products and reaction mechanism, MCAA and reaction products were analyzed using an organic acid analyzer (LC-10A, Shimadzu Corporation) with two ion-exclusion columns (Shim-park SCR-102H, Shimadzu Corporation) connected in series and an electro-conductivity detector (CDD-6A, Shimadzu Corporation). The chlorine ions of reaction products were determined using an ion chromatography analyzer (DX-120, DIONEX Corporation). It consists of an analytical column (Ionpac AS14 P/N 46124, DIONEX Corporation), a guard column (Ionpac AS14 P/N 46134, DIONEX Corporation) and a conductivity detector (DS4, DIONEX Corporation) supported by self-regenerating suppressor (ASAR P/N 53946, DIONEX Corporation). In order to evaluate the change of water quality indexes, following items were analyzed before and after reactions. Total organic carbon (TOC) and dissolved organic carbon (DOC) were measured with a TOC analyzer (TOC-5000A, Shimadzu Corporation). Chemical oxygen demand ( $\text{COD}_{\text{Cr}}$ ) was analyzed with a COD analyzer consisting of a COD reactor (P/N 45600-00, HACH Corporation) and a spectrophotometer (DR/3000, HACH Corporation). Biological oxygen demand (BOD) was done with a BOD tester (BOD Tester 200F, Taitec Corporation). In the beginning of BOD analysis, all samples were adjusted to the pH value of 7. pH was measured by pH meter (F-23, HORIBA). Before analysis of organic acid, ion chromatography and DOC, all samples were filtered to separate solid parts using micro-syringes and filters with pore size of 0.45  $\mu\text{m}$ .

## 3. Results and discussion

### 3.1. Change of water quality indexes under sub-critical water conditions

Table 1 shows the change of water quality indexes before and after reaction under sub-critical water conditions. Under these experimental conditions, water has unique characteristics comparing to water under normal conditions as shown by Savage [9] and Shaw et al. [10]. Thus, hydrothermal reaction is mainly affected by various characteristics of water at the specific temperatures and pressures. Water quality indexes of MCAA represent the state of MCAA in ambient water before hydrothermal reaction. In that case, water quality indexes of MCAA not changed. In order to check reproducibility of data, every experiments were conducted at three times under same reaction conditions. Then average values were achieved and used. Deviation of water quality indexes was less than 3% of each average value. In the results of TOC and DOC, the difference between total and soluble contents was not much under all the reaction conditions. At the reaction temperature of 350 °C, the reduction of TOC, DOC and  $\text{COD}_{\text{Cr}}$  was more increased by thermal de-

composition than that of lower temperature conditions. The initial BOD value of MCAA was lower than detection limits in the laboratory experiments. Although slow biodegradation of MCAA was possible, this result was corresponding to the results of Ellis et al. [8] including the long induction time and half-life time of MCAA in the field and laboratory study. At the reaction temperature of 250 °C, the BOD value of 1330  $\text{mg l}^{-1}$  was attained within 6.9 min then not varied much. However, BOD decreased with increasing reaction temperature and time after the reaction time of 17.4 min at 300 °C. During experiments, pH slightly decreased from the initial value of 2.3 then did not change much under all the reaction conditions. Besides, attached chlorine ion of MCAA was separated within 7.4 min under all the tested conditions. Thus, the results of pH and ion chromatography imply that the production of hydrochloric acid originated from separated chlorine ions by hydrolysis reaction under sub-critical water conditions.

### 3.2. Products evaluation

Fig. 1 shows the effect of reaction time on the change of composition of products at each reaction temperature. These data are average values of three times experiments. Deviation of data is from 0.6 to 3.5% of each average value. After hydrothermal reaction, MCAA was not detected under all the reaction conditions. In the total carbon contents, 93% of glycolic acid and 6% of unknown materials were detected in 6.9 min at the reaction conditions of 250 °C and 4 MPa, respectively. When the reaction time increased, the amount of products was not changed much. Under saturated vapor pressure, water has a maximum ion product at around 250 °C [10]. Therefore, MCAA was converted to glycolic acid by hydrolysis reaction derived from high ion product under the reaction conditions of 250 °C and 4 MPa. And mineralization did not exceed 3%. The reason was that further decomposition of glycolic acid did not occur at the reaction conditions. Under the reaction conditions of 300 °C and 9 MPa, the tendency of production of glycolic acid within 7.4 min was not different from the reaction occurred at 250 °C and 4 MPa. However, citric acid was produced in the reaction time of 17.4 min. Besides, complete structural conversion from MCAA to organic acids was attained at the reaction time of 17.4 min. The reduction of total carbon contents increased from 1% in 7.4 min to 24% in 57.4 min at the reaction temperature of 300 °C. Moreover, 78% of carbon contents were reduced within 57.4 min at the reaction temperature of 350 °C. It implies that reaction products were decomposed by thermal decomposition with increasing reaction temperature and time. Thus, formic acid was produced from the decomposition of citric acid and glycolic acid in 27.4 min at the reaction temperature of 300 °C. Because of much reduction of total carbon contents by thermal decomposition, the amounts of identified products at the reaction conditions of 350 °C and 17 MPa were lower than that of lower temperature

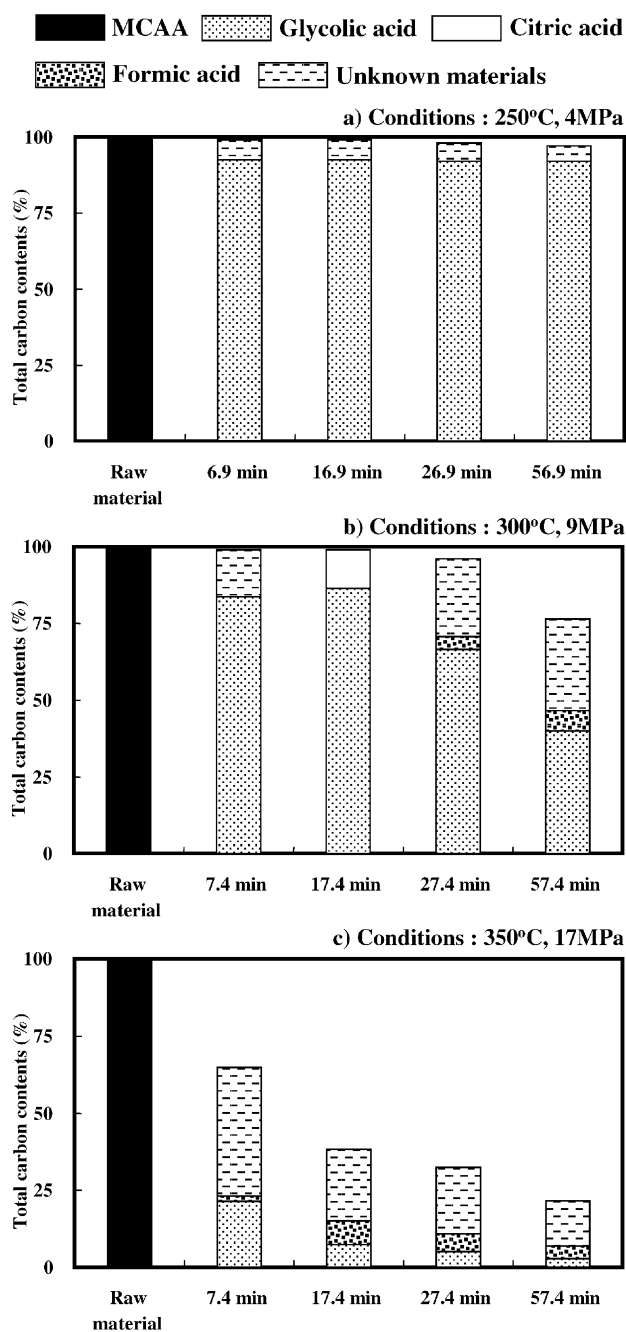


Fig. 1. Effect of reaction time on the change of composition of products at each reaction temperature (conditions: (a) 250 °C, 4 MPa; (b) 300 °C, 9 MPa; (c) 350 °C, 17 MPa).

conditions. From the results of Fig. 1, glycolic acid was the main identified product under all the reaction conditions.

### 3.3. Reaction pathway of MCAA under sub-critical water conditions

The reaction pathway of MCAA under sub-critical water conditions is represented in Fig. 2. MCAA was con-

Table 2

Reaction rate constants at each reaction temperature and activation energy for the reduction of MCAA

Temperature (°C)	250	300	350
Reaction rate constant ( $k$ , $\times 10^{-3} \text{ s}^{-1}$ )	6.4	8.3	10.7
Activation energy ( $E_a$ , $\text{kJ mol}^{-1}$ )	13.9		
Frequency factor ( $A$ , $\text{s}^{-1}$ )	0.16		
Correlation coefficient ( $R^2$ )	0.99		

verted to glycolic acid by hydrolysis reaction in the beginning of hydrothermal reaction. Besides, hydrochloric acid was produced from separated chlorine ions at the same time. Reaction pathway from MCAA to glycolic acid was not varied under all the tested conditions. After the structural conversion, citric acid was produced from the dehydration reaction of glycolic acid under the reaction temperatures higher than 300 °C. Formic acid was yielded from the thermal decomposition of glycolic acid and citric acid. Then, glycolic acid and formic acid were reduced and mineralized by thermal decomposition depending on reaction conditions.

From the results of reaction pathway, the structural conversion from MCAA to glycolic acid was the most important step on the viewpoint of the pretreatment of refractory pollutants by hydrothermal reaction. The reason was that the disappearance of attached recalcitrant chlorine ion of MCAA was attained from the process. Therefore, obtained activation energy and reaction rate constants at each reaction temperature for the reaction of MCAA reduction are summarized in Table 2.

### 3.4. Relationship between BOD improvement and the yield of glycolic acid

Glycolic acid was the main identified product under all the reaction conditions, as shown by Fig. 1. Thus, the relationship between the production of glycolic acid and the change of BOD of reaction products is discussed here. Fig. 3 shows the effect of yield of glycolic acid on the BOD improvement of reaction products. At the reaction temperature of 250 °C, the yield of glycolic acid was reached around 3000  $\text{mg l}^{-1}$  and attained BOD values were higher than 1300  $\text{mg l}^{-1}$ . The ultimate BOD value of reaction products was 1340  $\text{mg l}^{-1}$  at the reaction temperature of 300 °C. In that case, the yield of glycolic acid was reached at 2790  $\text{mg l}^{-1}$ . The yield of glycolic acid gradually decreased with increasing reaction temperature, because of the thermal decomposition of reaction products as discussed in Section 3.2. There is a linear relationship between the yield of glycolic acid and BOD of reaction products. It means that the BOD improvement of reaction products is proportional to the increasing of the yield of glycolic acid under all the reaction conditions. Additionally, the results of Figs. 1 and 3 imply that most of reaction products are degradable substances by microorganism.

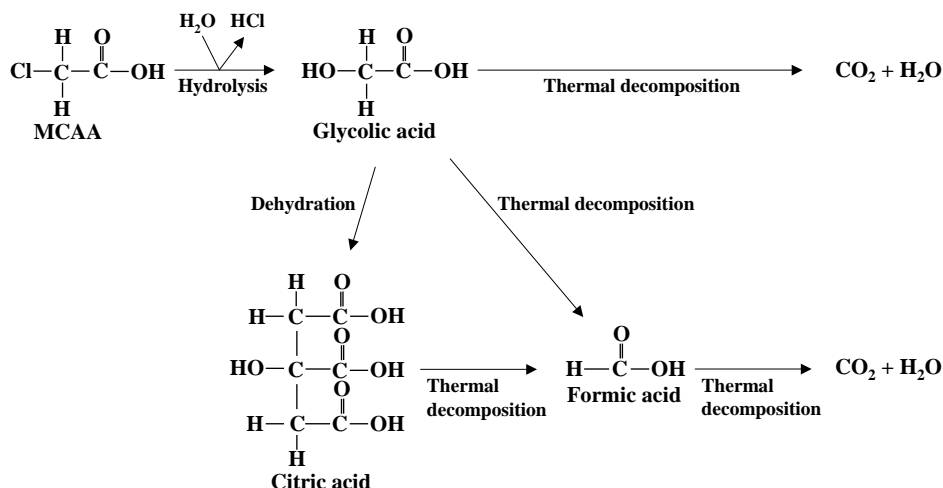


Fig. 2. Reaction pathway of MCAA under sub-critical water conditions.

3.5. Biodegradability improvement depending on reaction conditions

Both the ratio of BOD/TOC and BOD/COD<sub>Cr</sub> represent the biodegradable portion of all organic carbon contents in a substance. Thus, the ratios are commonly used to evaluate biodegradability of substances [18]. In this research, the ratio of BOD/COD<sub>Cr</sub> was selected as the index of biodegradability. Fig. 4 represents the effect of reaction time on the biodegradability improvement of reaction products at each reaction temperature. During the transition state, the temperature of reactant in a reactor was reached at 90% of each reaction temperature. The initial biodegradability of MCAA was extremely low enough to reach zero. Under the reaction conditions of 250 °C and 4 MPa, biodegradability suddenly jumped to 0.51 within 6.9 min then was not much varied until the reaction time of 56.9 min. At the reaction conditions of 300 °C and 9 MPa, the initial trend of biodegradability improvement of reaction products was nearly same until the reaction time of 7.4 min. However, biodegradability

was continuously improved and then reached at 0.64 within 17.4 min. It can be explained by the fact that the complete structural conversion from MCAA to organic acids as shown by Fig. 1. After the reaction time, biodegradability was gradually reduced until 0.34 at the reaction time of 57.4 min. Although biodegradability gradually increased with increasing reaction time, attained biodegradability was lower than 0.3 under the reaction conditions of 350 °C and 17 MPa. The reason was that much reduction of biodegradable reaction products by thermal decomposition as represented by Figs. 1 and 3.

Generally, some substances having the ratio of BOD/COD<sub>Cr</sub> higher than 0.4, are usually considered as thoroughly biodegradable materials [20]. Thus attained biodegradability at the reaction temperature of 250 °C and the results within 27.4 min at the reaction temperature of 300 °C were suitable values for conventional biological treatment methods. Comparing to the results of Fig. 1, the biodegradability improvement of reaction products was closely related to the amount

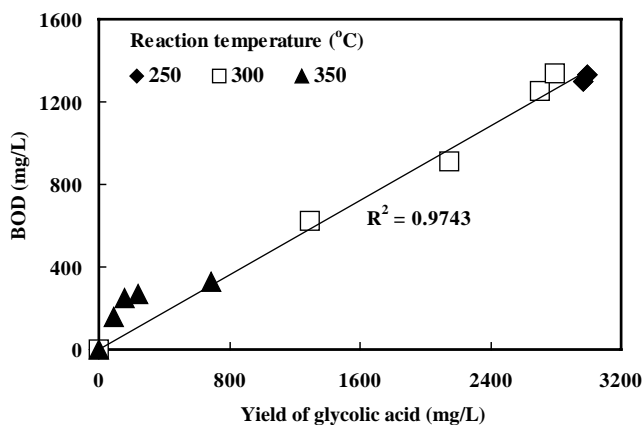


Fig. 3. Relationship between the yield of glycolic acid and the BOD improvement of reaction products.

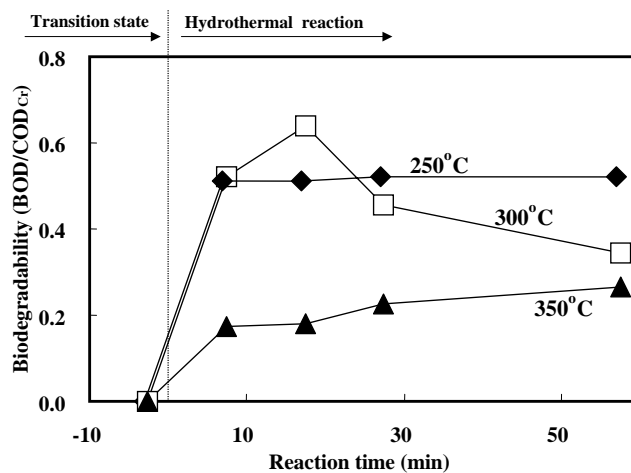


Fig. 4. Effect of reaction time on the biodegradability improvement of reaction products at each reaction temperature.

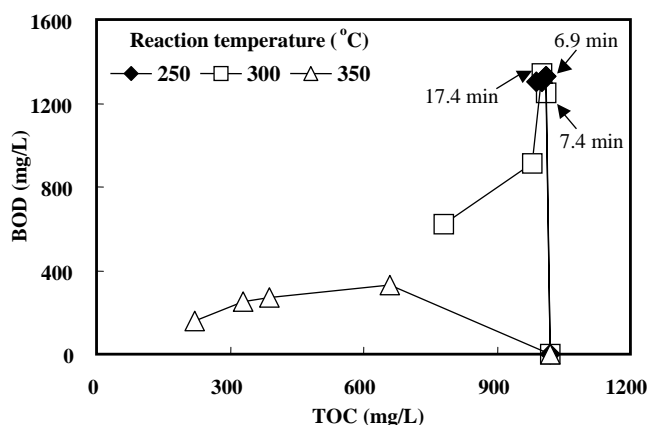


Fig. 5. Relationship between TOC reduction and BOD improvement of reaction products at each reaction temperature.

and the composition of each product at the same reaction conditions. Besides, chlorine ions were present in the reaction products because of the dissociation of converted hydrochloric acid from MCAA as discussed in Section 3.1. From the results of ion chromatography, the concentration of chlorine ions was  $1500 \text{ mg l}^{-1}$ . The presence of chlorine ion may retard biodegradability improvement. However, biodegradability higher than 0.4 was successfully achieved under tested conditions. Therefore, it was inferred that the biodegradability improvement of reaction products was not mortally retarded at the concentration range of chlorine ions tested in this research.

### 3.6. Suitable TOC reduction range based on BOD improvement

Fig. 5 shows the relationship between TOC reduction and BOD improvement of reaction products at each reaction temperature. In order to know the minimum TOC reduction range to attain the maximum BOD improvement, the BOD improvement per unit TOC reduction of reaction products at each reaction temperature is discussed here. Under the reaction temperature of  $250^\circ\text{C}$ , BOD value was improved until  $1330 \text{ mg l}^{-1}$  in 6.9 min then, remained despite increasing reaction time. Under all the cases, TOC reduction did not exceed 4%. At the reaction temperature of  $300^\circ\text{C}$ , the initial trend of BOD improvement per unit TOC reduction at 7.4 and 17.4 min was not much different from the results at the reaction temperature of  $250^\circ\text{C}$ . After the reaction conditions, BOD gradually decreased and TOC reduction simultaneously increased with increasing reaction temperature and time. Thus, attained BOD values were lower than  $400 \text{ mg l}^{-1}$  and TOC reduction was extended to 78% under the reaction temperature of  $350^\circ\text{C}$ .

From the results of Figs. 1, 3 and 5, the thermal decomposition of biodegradable reaction products such as glycolic acid induced the reduction of BOD and TOC with increasing reaction temperature and time. On the contrary, mineraliza-

tion increased depending on reaction temperature. Moreover, MCAA was successfully converted to biodegradable reaction products in the beginning of hydrothermal reaction. Therefore, reactions must avoid much TOC reduction after achieving the structural conversion enough to improve BOD. For the reason, the suitable TOC reduction range was within 4%. The optimal BOD improvement was attained in 6.9 min at the reaction conditions of  $250^\circ\text{C}$  and 4 MPa. In that case, TOC reduction was within 1%. Considering the heat-up time of reactor 1, the required time to attain BOD values higher than  $1200 \text{ mg l}^{-1}$  was within 3 min after reaching the desired conditions at the reaction temperature of 250 and  $300^\circ\text{C}$ . It implies that the significant feasibility of hydrothermal reaction in case of the application of a continuous reactor for pretreatment of refractory pollutants.

## 4. Conclusions

The feasibility of biodegradability improvement induced from the structural conversion of MCAA by hydrothermal reaction was investigated in this research. The structural conversion from MCAA to biodegradable reaction products was successfully achieved by hydrolysis, dehydration and thermal decomposition under tested sub-critical water conditions. The identified reaction products were glycolic acid, citric acid and formic acid. TOC reduction for the structural conversion did not exceed 24%, except the results at the reaction conditions of  $350^\circ\text{C}$  and 17 MPa. The separation of recalcitrant chlorine ion from MCAA by hydrolysis brought the production of hydrochloric acid and biodegradable glycolic acid. It was the key reaction to attain biodegradable reaction products on the viewpoint of the pretreatment of refractory pollutants. The concentration of dissociated chlorine ions from hydrochloric acid was  $1500 \text{ mg l}^{-1}$ . The presence of chlorine ions in reaction products may retard biodegradability. However, the biodegradability improvement of reaction products was not fatally retarded under all the tested sub-critical conditions. To avoid the thermal decomposition of biodegradable reaction products, reactions must be conducted under the minimum TOC reduction range to attain structural conversion enough to improve BOD. The optimal biodegradability ( $\text{BOD}/\text{COD}_{\text{Cr}}$ ) was 0.51 in 6.9 min under the reaction conditions of  $250^\circ\text{C}$  and 4 MPa. In that case, TOC reduction was within 1%. The amount of biodegradable organic acids and the composition of products were closely related to the biodegradability improvement of reaction products. Besides, the application feasibility of hydrothermal reaction was found in case of the use of a continuous reactor for pretreatment of refractory pollutants. Therefore, hydrothermal reaction could be accepted as the most suitable alternative pretreatment method for biodegradability improvement of refractory pollutants like MCAA. Further, investigation is needed to apply hydrothermal reaction in real wastewater and to clarify reaction mechanism for other refractory pollutants.

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## References

- [1] J.W. Raymond, T.N. Rogers, D.R. Shonnard, A.A. Kline, *J. Hazard. Mater.* B84 (2001) 189.
- [2] A. McCulloch, *Chemosphere* 47 (2002) 667.
- [3] L. Von Sydow, H. Borén, A. Grimvall, *Chemosphere* 39 (1999) 2479.
- [4] V. Camel, A. Bermond, *Water Res.* 32 (1998) 3208.
- [5] H. Frank, A. Vincon, J. Reiss, H. Scholl, *J. High Resolut. Chromatogr.* 13 (1990) 733.
- [6] R. Kühn, M. Pattard, *Water Res.* 24 (1990) 31.
- [7] L. Tao, P.M. Kramer, R. Ge, M.A. Pereira, *Toxicol. Sci.* 43 (1998) 139.
- [8] A.D. Ellis, L.M. Hanson, K.P. Sibley, T. Shahid, A.N. Fineberg, R.K. Solomon, C.G.D. Muir, A.S. Mabery, *Chemosphere* 42 (2001) 309.
- [9] P.E. Savage, *Chem. Res.* 99 (1999) 603.
- [10] R.W. Shaw, T.B. Bill, A.A. Clifford, C.A. Eckert, U.E. Frank, *Chem. Eng. News* 12 (1991) 26.
- [11] C. Aymonier, P. Beslin, C. Jolival, F. Cansell, *J. Supercrit. Fluids* 17 (2000) 45.
- [12] C.N. Staszak, K.C. Malinkowski, W.R. Killilea, *Environ. Prog.* 6 (1987) 39.
- [13] A. Shanableh, *Water Res.* 34 (2000) 945.
- [14] F.-M. Jin, A. Kishita, T. Moriya, H. Enomoto, *J. Supercrit. Fluids* 19 (2001) 251.
- [15] P. Krammer, H. Vogel, *J. Supercrit. Fluids* 16 (2000) 189.
- [16] H. Daimon, K. Kang, N. Sato, K. Fujie, *J. Chem. Eng. Jpn.* 34 (2001) 1091.
- [17] K. Kang, A.T. Quitain, H. Daimon, R. Noda, N. Goto, K. Fujie, *Can. J. Chem. Eng.* 79 (2001) 65.
- [18] K. Kim, M. Fujita, H. Daimon, K. Fujie, *J. Chem. Eng. Jpn.* (2004) in press.
- [19] A.T. Quitain, N. Sato, H. Daimon, K. Fujie, *Ind. Eng. Chem. Res.* 40 (2001) 5885.
- [20] E. Chamapro, A. Marco, S. Esplugas, *Water Res.* 35 (2001) 1047.