Effects of operational conditions on sludge degradation and organic acids formation in low-critical wet air oxidation

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ABSTRACT

Wet air oxidation processes are to treat highly concentrated organic compounds including refractory materials, sludge, and night soil, and usually operated at supercritical water conditions of high temperature and pressure. In this study, the effects of operational conditions including temperature, pressure, and oxidant dose on sludge degradation and conversion into subsequent intermediates such as organic acids were investigated at low critical wet oxidation conditions. The reaction time and temperature in the wet air oxidation process was shown an important factor affecting the liquefaction of volatile solids, with more significant effect on the thermal hydrolysis reaction rather than the oxidation reaction. The degradation efficiency of sludge and the formation of organic acids were improved with longer reaction time and higher reaction temperature. For the sludge reduction and the organic acids formation under the wet air oxidation, the optimal conditions for reaction temperature, time, pressure, and oxidant dose were shown approximately 240 °C, 30 min, 60 atm, and 2.0 L/min, respectively.

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1. Introduction

The subject in sludge treatment recently is the organic sludge containing more than 40% of organic matter and typically formed in sewer and wastewater discharge facility systems. This sludge possesses high moisture content, in addition to high organic content, due to the difficulty of excluding moisture efficiently at dewatering stage, and may cause secondary environmental pollution. Therefore, it should be treated by an appropriate method as soon as it is formed. Considering the wastewater treatment systems increasing every year, the amount of wasting sludge will continuously increase, and the countermeasures to handle it should be prepared quickly. By the year 2000, about 1.5 million tons of sewage sludge was being generated annually in Korea and the amount to be generated in 2005 was expected to exceed 3.5 million tons. Then, it would cost approximately 46 million U.S. dollars for the sludge disposal. Despite the increasing trend of sludge generation, it still shows no sign of less reliance on landfill and ocean dumping for the disposal. Ocean dumping still accounts for 74% whereas landfill has been decreased to as low as 12% by stricter regula-

tions in Korea. As the law regulating the waste management gets more stringent, landfill is banned if the water content of sludge is >75%, and ocean dumping is being restricted by the international treaties. Subsequently, a technology to replace the current sludge treating process is a prerequisite, and the thermal oxidation (TO) was applied in this study to develop an alternative sludge reduction technology. Wet air oxidation (WAO) among TO methods is considered suitable for highly concentrated organic matters including difficult-to-decompose ones, excretions, or sludge containing small amount of organic matters when incinerated and biologically processed [1–6]. The WAO accomplishes oxidation at elevated temperatures (150–325 °C) and oxygen pressures (10–200 atm). High temperature accelerates the dissolution of sludge, and high pressure, higher than the vapor pressure, increases the solubility of oxidant and represses pollutants that are transferred to the air [7]. The oxidation products may be inorganic salts, simpler forms of biodegradable compounds, or carbon dioxide and water through the complete oxidation. Water which makes up the bulk aqueous phase serves to modify the oxidation reactions to proceed at relatively low temperatures as well as to moderate them to remove excess heat by evaporation. In addition, water is an excellent heat transfer medium which enables the efficient heat transfer. The oxygen required by the WAO reactions is provided by air bubbles through the liquid phase in a reactor used to contain the
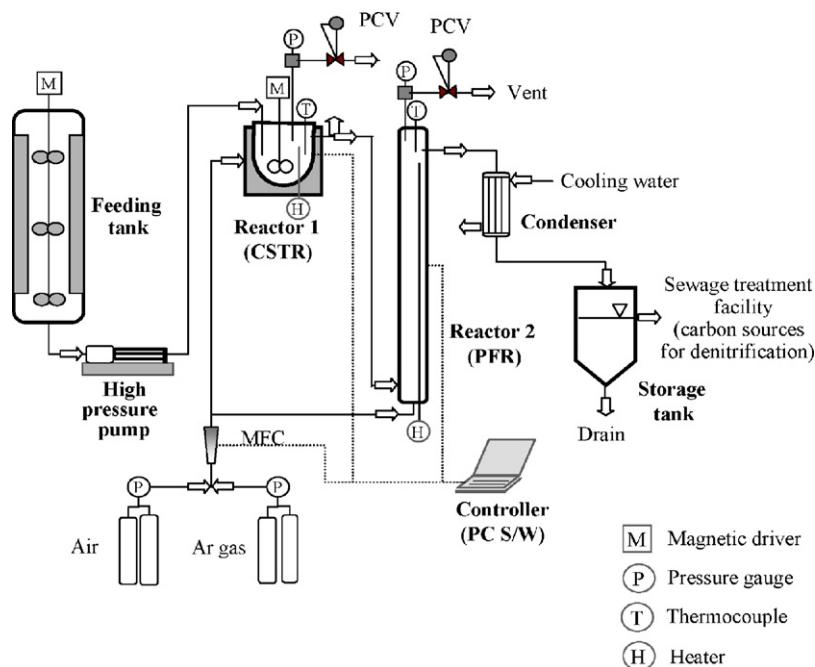
Fig. 1. Schematic of the lab-scale wet air oxidation process.

process [2,8,9]. One advantage of WAO is that it causes no secondary environmental pollution as the reaction proceeds under the liquid condition, capable of minimizing the discharge of air pollutants [10–12]. The other is that organic acids can be obtained as byproducts through the WAO process, at relatively low temperature and pressure, subsequently capable of reducing high initial investment and energy cost needed for maintaining high temperature and pressure. The aim of this study was to investigate whether the wasting sludge generated from the wastewater treatment system could be reduced and simultaneously produce such useful matters as organic acids under the sub-critical WAO condition of <250 °C and 20–60 atm, a more relaxed condition than the general operational condition of WAO.

2. Materials and methods

2.1. Lab-scale WAO system

The laboratory-scale experimental setup is shown in Fig. 1. The WAO system was composed of sludge inflow pump, TO reactor, and oxidizer supplying device, and the whole process was designed automatically controlled and operated by the computer program. The thermal reactors were made up of completely stirred tank reactor (CSTR; 1 L capacity) and plug-flow reactor (PFR; 1 L capacity). A feeding tank (50 L capacity) was located before CSTR (Reactor 1) with impeller to keep the sludge concentration constant and the cooling system placed after PFR (Reactor 2). A device automatically adjusting the pressure control valve (PCR) (ER3000, Tescom) was attached at the rear end of the cooling device to keep the constant pressure for each reactor, together with the pressure transducer to adjust the pressure up to 70 atm. The pump for supplying sludge was mounted with a screw type pump (NM005SY36S72B, NETZSCH) to make it possible to transfer the high pressure to ensure the regular amount by adjusting the flux at 50–150 L/min. The air as the oxidizing matter was supplied to change the flux to 30 L/min by adjusting a mass flow controller (MFC) (F-202AC, BRONKHORST, The Netherlands). The temperature of thermal reactor was heated up to the desired reaction temperature and the oxidizing matter

was introduced. This injection was considered as the starting point of the experiment. Since the temperature of liquefied compound discharged after the final reaction was same as that of reactor, the temperature of effluent from the condenser was decreased below 50 °C with cooling water. Finally, the discharges from condenser were stored at the storage tank and most organic solids were converted to organic acids after liquefaction or decomposed into CO_2 and water, but inorganic solids were remained as by-product, ashes. Therefore, the corn-typed storage helped the by-product be removed by the gravitational sedimentation.

Properties of the sewage sludge used in the lab-scale experiment are shown in Table 1. The operational parameters known to affect the decomposition of sludge and the formation of organic acids include temperature, pressure, reaction time, and oxidant dose. Therefore, in order to see the reduction of sludge and the formation of organic acids according to the reaction temperature, batch test was performed by changing reaction temperatures from 180 °C to 240 °C with 20 °C intervals. Pressure was kept at 50 atm, bigger than the vapor pressure, to make sludge react in the liquid condition within the test temperature. The air flow rate was fixed at 1.0 L/min, considering the stoichiometric oxygen requirement (SOR) required for the reaction. For the effect of reaction pressure, it was varied to 40, 50, and 60 atm, while reaction temperature and air flow rate were fixed at 240 °C and 1.0 L/min, respectively. For the effect of oxidant dose on the suspended solids (SS) reduction, the following operational condition was employed: temperature at 240 °C, pressure at 50 atm, and air flow rate was varied to 0, 0.5, 1.0, 2.0, and

Table 1
Properties of sludge used in the experiment

Constituent	Values
COD (mg/L)	7500 ± 200
SS (mg/L)	6500 ± 210
pH	6.9–7.3
VSS (%)	1.1
T–N (mg/L)	450 ± 40
NH_4^+ (mg-N/L)	28 ± 4
T–P (mg/L)	215 ± 35

3.0 L/min. The SS concentration of sludge used in all the experiments was 3%. Further details on this system and its operation are described elsewhere [13].

2.2. Sampling and analysis

Throughout the operating period, routine samplings and analyses were carried out on a daily basis, according to the operation and treatment involved. The chemical oxygen demand (COD) test measures the amount of oxygen required for the chemical oxidation of organic matter to carbon dioxide and water. Since the COD indicates only a part of the organic matter, with the proportion varying depending on the chemical oxidant used and the structure of organic compound, the dichromate reflux method was selected for the COD determination because it has many advantages over others especially in terms of oxidizability, reproducibility, and applicability to a wide variety of samples [14]. For the soluble COD (SCOD), the sample was centrifuged at $16,000 \times g$ for 10 min to remove biomass and then the supernatant was used for the COD measurement as stated above. The concentrations of volatile fatty acids (VFAs) were determined by gas chromatography (Shimadzu, model GC-14B, Japan) equipped with a capillary column (HP-INNOWax, $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ μm}$) and a flame ionization detector (FID). The oven and detector temperature was 120 °C and 250 °C, respectively. The split–splitless ratio was 10 and helium was used as a carrier gas at the flow rate of 1.8 mL/min, and the air flow rate was set at 300 mL/min. The determination of total nitrogen (TN), total phosphorus (TP), total solids (TS), suspended solids (SS), and

volatile suspended solids (VSS) was carried out according to the standard methods for water and wastewater [14]. The results represent averages of duplicates.

3. Results and discussion

3.1. Effects of reaction temperature on degradation of organic compounds

In order to investigate the effects of reaction temperature and time on the biodegradation of organic matter as total chemical oxygen demand (TCOD), the initial COD concentration used for RT1 (180 °C), RT2 (200 °C), RT3 (220 °C), and RT4 (240 °C) under the corresponding reaction temperature (RT) was 7610, 7230, 7740, and 7530 mg/L, respectively. As shown in Fig. 2(a), the higher the reaction temperature was, the faster the TCOD concentration decreased. During the reaction time of 10 min, the concentrations of TCOD, as the reaction temperature increased, were gradually shown relatively lower concentration, indicating the removal efficiency of 7.5, 15.3, 24.7, and 34.5%, respectively, for the RTs of 180 °C, 200 °C, 220 °C, and 240 °C. For the reaction time of 80 min, the TCOD removal efficiencies for RT1 and RT2 were 29.4% and 43.2%, respectively, whereas at RT3 and RT4 57.7% and 66.9%, respectively, for the same reaction time. This implies that the higher the reaction temperature was, the higher the removal efficiency for TCOD during a short reaction time. On the other hand, the SCOD concentrations for all RTs were dramatically increased at 10 min reaction time [Fig. 2(b)]. After 20 min, the SCOD concentration was decreased
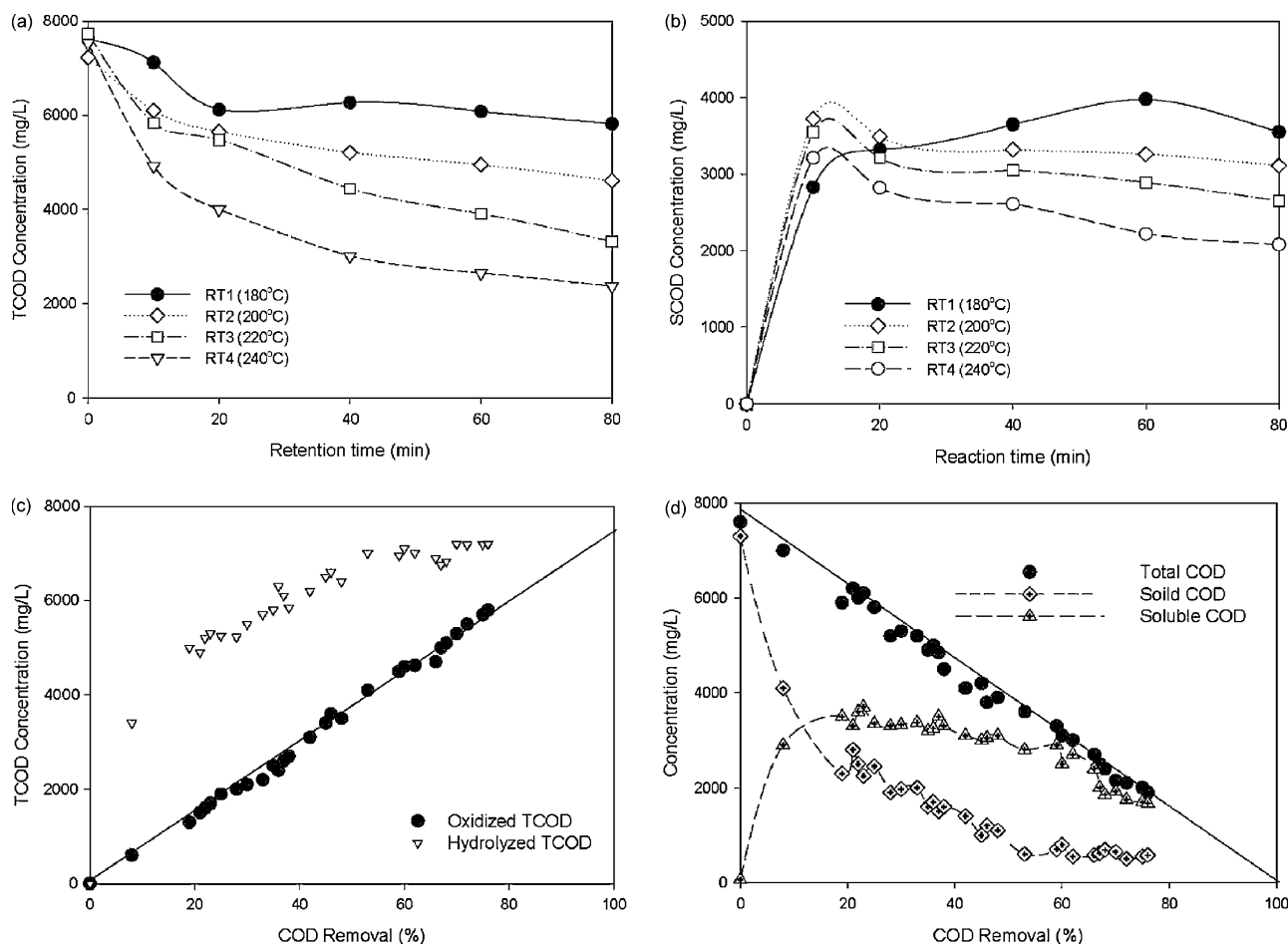

Fig. 2. (a–d) Effect of reaction temperature on biodegradation of organic compounds.

slowly with time for all the RTs except RT1. The WAO, in general, accelerates the thermal hydrolysis reaction capable of liquidizing volatile organic solids at the initial stage of reaction. The liquidized organic compounds are then converted to organic acids as intermediates by the sequential oxidation reaction, or decomposed into CO_2 and water [2,15,16]. Based on the results of SCOD with various temperatures, the thermal hydrolysis reaction was completed within 10 min of reaction time under the reaction temperature higher than 200 °C. This implies that the higher reaction temperature can increase the oxidation rate of liquidized organic compounds.

The oxidized TCOD and hydrolyzed TCOD were calculated by subtracting the final TCOD and the remained solid TCOD from the initial TCOD, respectively. As shown in Fig. 2(c), the degradation rate of the hydrolyzed TCOD was faster than that of the oxidized TCOD at the early stage and consequently the oxidation reaction was the rate-limiting step when both degradation efficiencies were similar (about 20%). This result was similar to the one from Shanableh [17]. Fig. 2(d) shows COD concentrations of total, solid, and soluble, along with the COD removal. Since the solid and soluble COD values crossed over, the oxidation reaction acted as the main reaction. Shanableh [17] reported that approximately 65% of the organic solids were hydrolyzed by the time 40% COD removal was achieved. At below 40% COD removal, oxidation rather than thermal hydrolysis was the rate-limiting step. All the results show that the accumulated hydrolyzed COD was depleted through oxidation, following the exhaustion of hydrolyzable organic solids.

3.2. Effects of reaction temperature on SS removal efficiency and organic acids formation

For the effects of the reaction temperature and time on the SS concentration of sludge, 700 mL of sludge was injected, and the initial SS concentration was around 6150 mg/L. After 10 min reaction time, the SS removal efficiency over 50% was observed for all the RTs [Fig. 3(a)]. The SS concentration for RT2, RT3, and RT4 was 1920, 1720, and 1570 mg/L, respectively, indicating the decomposition efficiencies of 68.3–74.4%. The formation of organic acids was increased rapidly at the reaction time of 10 min, with the increasing reaction temperature [Fig. 3(b)]. The concentration of organic acids for RT1 (180 °C) was increased continuously throughout the reaction time, showing 488 mg/L at the reaction time of 80 min, whereas those for RT2, RT3, and RT4 were increased at relatively slower slopes than the initial stages. When the reaction time reached 80 min, the organic acids concentration for RT2, RT3, and RT4 was 589, 631, and 688 mg/L, respectively. The higher the reaction temperature, the more organic acids formed as intermediates, is also in a good agreement with some previous studies [15,18]. Furthermore, the effects of reaction temperature and time on the formation of organic acids were shown closely related to the change of SCOD concentrations [Fig. 2(b)]. The SCOD concentration was increased significantly at the initial stage of reaction and the liquefied organic compounds were oxidized to organic acids, and the conversion rate of SCOD to organic acids was decreased with the reaction time. However, the formation of organic acids was increased gradually by the subsequent oxidation reaction with the reaction temperature increased.

Table 2 demonstrates organic acid, acetic acid, and propionic acid at 40 min reaction time under various reaction temperatures. As the reaction temperature was increased, the concentration of organic and acetic acid was increased. There was no formation of propionic acid when the reaction temperature was 180 °C and 13.5 mg/L formed at 240 °C, indicating the maximum formation of propionic acid at below 3% of organic acids. Since the acetic acid among low molecular weight organic acids produced as intermediates was stable, it was shown significantly difficult to be
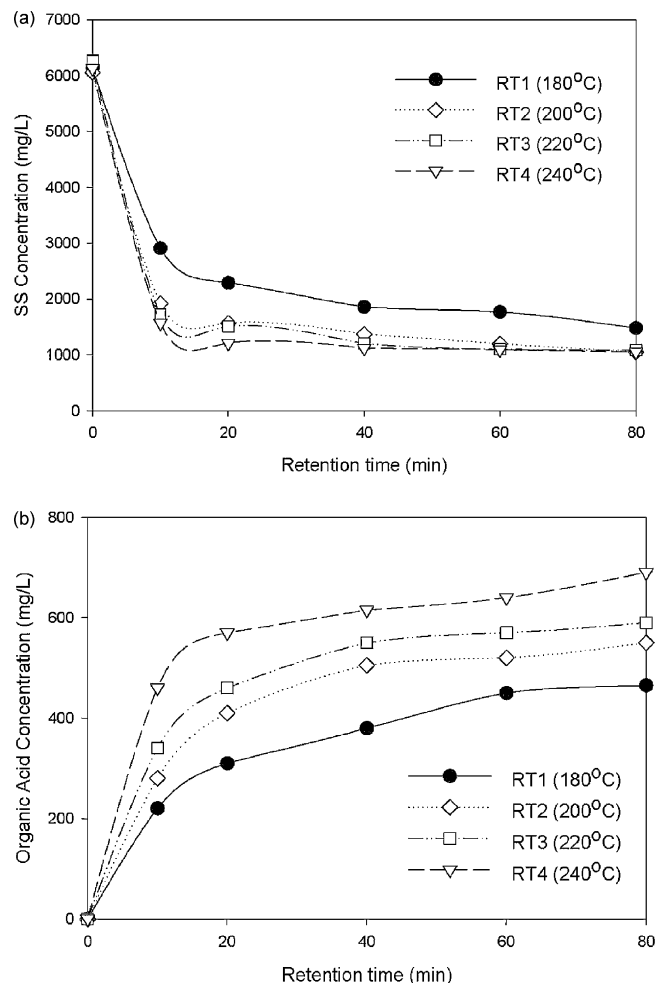

Fig. 3. Effect of reaction temperature on SS (a) and organic acid (b) concentrations.

biodegraded under the wet oxidation reaction [17,19]. The initial thermal hydrolysis reaction was for the rapid conversion of high molecular weight organic acids into low molecular weight or liquefied organic acids. However, the oxidation rate after liquefaction was relatively slower than the thermal hydrolysis reaction, depending on the oxygen transfer rate in water [7,9].

3.3. Effects of reaction pressure on degradation of organic compounds

In general, the reaction pressure in wet air oxidation process plays important roles in maintaining liquid phase and increasing oxidant's solubility. Consequently, the reaction pressure can increase the reaction rate and restrain the loss of latent heat from evaporation [20]. The effect of reaction pressure (RP) on the organic compound degradation was investigated at 240 °C reaction temperature, for 80 min reaction time, and with 1.0 mL/min of air flow

Table 2
Changes of organic, acetic, and propionic acids (mg/L) at different reaction temperatures (reaction time: 40 min)

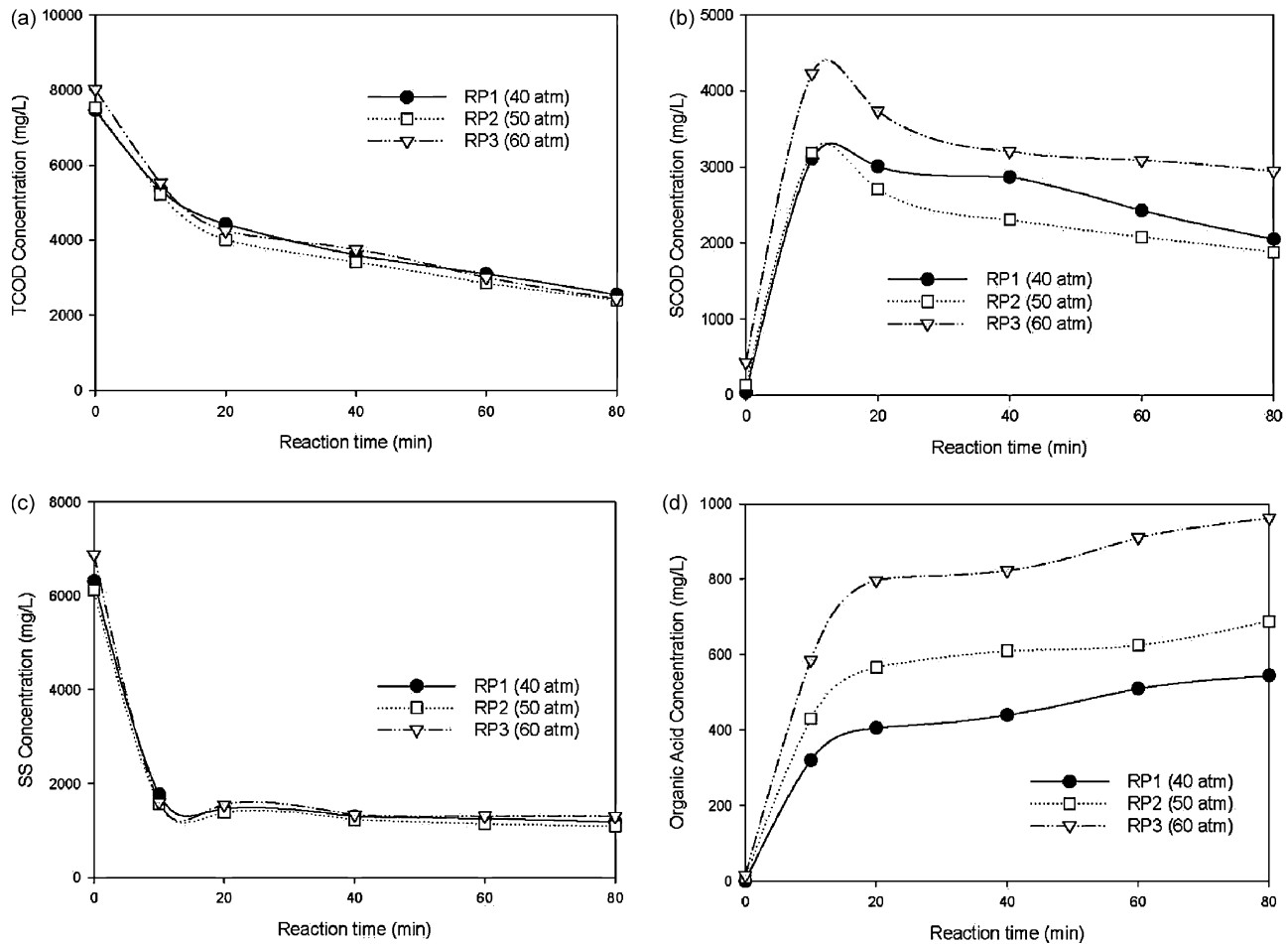|	Temperature (°C)	Organic acids	Acetic acid	Propionic acid
RT1	180	400	105	0
RT2	200	546	307	3.6
RT3	220	576	447	12.6
RT4	240	620	603	13.5

Fig. 4. (a–d) Effect of reaction pressure on biodegradation of organic compounds.

rate. The initial TCOD concentration ranged from 7420 mg/L to 8020 mg/L was decreased dramatically at the early stage of reaction, for all the experimental conditions [Fig. 4(a)]. When the reaction time was 80 min, removal efficiencies for TCOD were 64, 67, and 70% for RP1, RP2, and RP3, respectively. There was almost no significant relationship between the reaction pressure and the degradation rate of TCOD. The increase of reaction pressure from 40 atm to 60 atm did not affect liquefaction efficiencies for organic compounds at the thermal hydrolysis reaction step due to the negligible effect of pressure, related to the oxygen transfer rate, on the reaction. On the other hand, the conversion rate of SCOD was increased with the reaction pressure [Fig. 4(b)]. This result implies that the increase of pressure resulted in the increase of oxygen transfer rate and accelerated the solubility of oxidants, leading to the increase of the liquefaction reaction rate. As shown in Fig. 4(c) and (d), the change of reaction pressure did not cause the change of SS degradation rates but the concentration of organic acids was increased significantly as the reaction pressure increased. This result further implies that the increased reaction pressure can accelerate the organic acids formation by improving the oxygen transfer rate for the liquefaction reaction.

3.4. Effects of oxidant dose on degradation of organic compounds

In order to evaluate the effect of oxidant dose (OD), the air flow rate was varied from 0 L/min to 3.0 L/min at the fixed reaction temperature and pressure, 240 °C and 50 atm. In addition, the

argon gas as an inactivated compound was added to investigate the degradation rate under the anoxic condition. For OD1 operated under the anoxic condition, there was little change of TCOD concentration with reaction temperature and time. When the air was injected, on the other hand, the TCOD concentration during the initial reaction was decreased significantly but the degradation rates became relatively slow after the 20 min reaction time [Fig. 5(a)]. The SCOD concentration, however, was sharply increased at the early stage of reaction, similar to the results obtained above. The production rate of SCOD under the anoxic condition was slightly increased because of the progress of thermal hydrolysis reaction only [Fig. 5(b)]. With the injection of air, however, the liquefaction and oxidation of organic compounds were increased when the oxidant dose was at 3.0 L/min. This result implies that the increase of oxidant dose can improve the oxygen transfer rate in water, resulting in the increase of the degradation rate of organic compounds and the production rate of intermediates.

Based on the result from Fig. 3(c), the actual SCOD production was calculated as 860 mg-SCOD/g-SS by excluding the SCOD concentration degraded by oxidation. The increase of oxidant dose affected the degradation efficiency for volatile suspended solids except the inorganic compounds but with insignificant effect on the liquefaction of suspended solids. As shown in Fig. 5(d), the formation of organic acids was increased with the oxidant dose but at >2.0 L/min (OD5) with almost no difference from OD4.
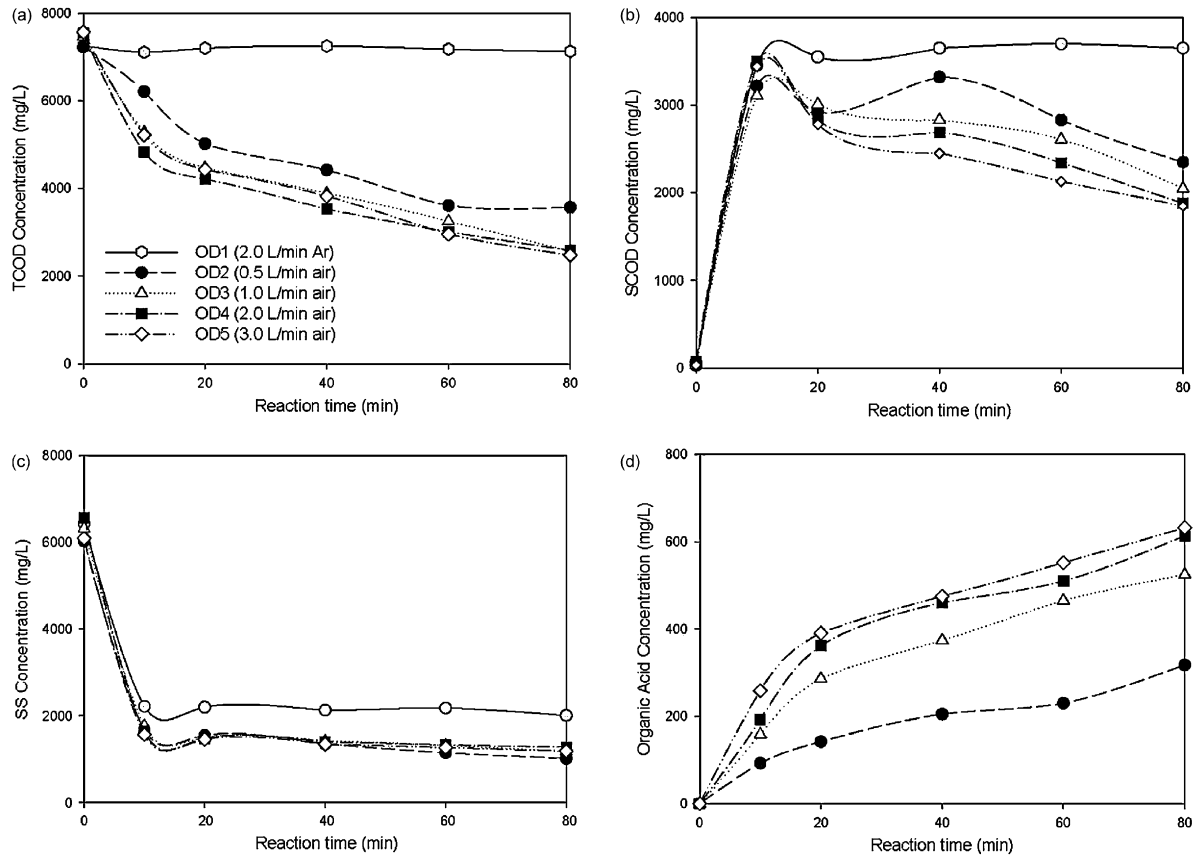
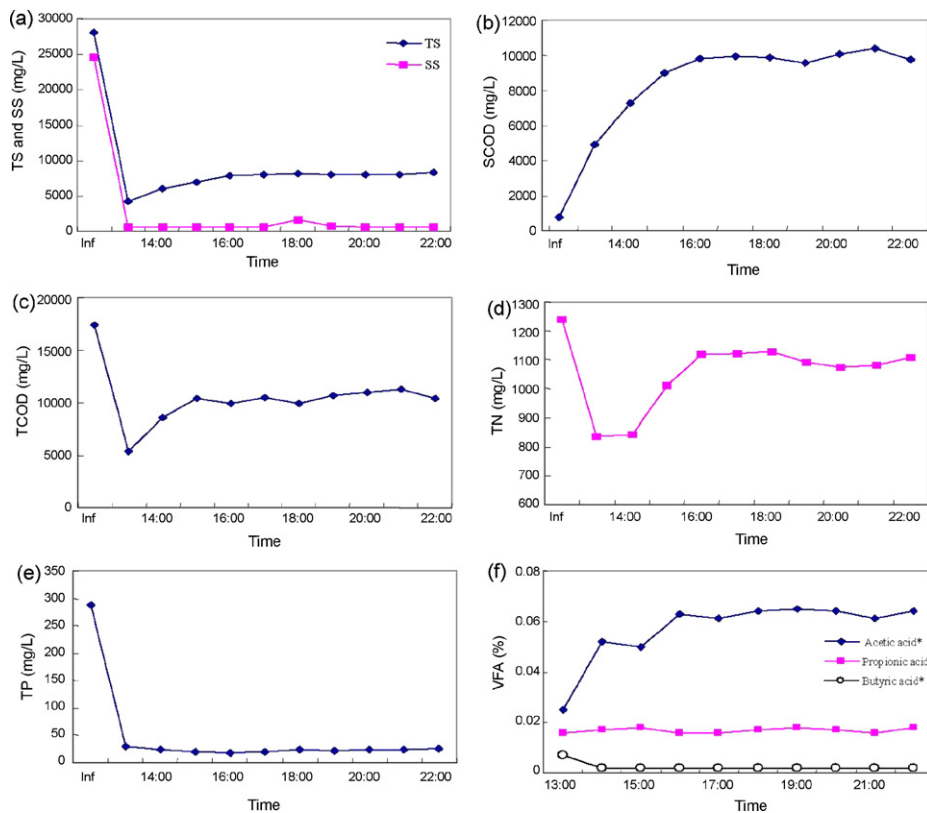**Fig. 5.** (a–d) Effect of oxidant dose on biodegradation of organic compounds.

Fig. 6. Profiles of TS and SS (a), SCOD (b), TCOD (c), TN (d), TP (e), and VFAs (f) during 12-h monitoring of operation.

$CO_2 + H_2O + NH_4$: 2,370 mg/L (27.8%)

Q : 110 L/day
TCOD : 8,510 mg/L
$TCOD_L$: 936 g/day
→
L-WAO
Temp. 200 °C
HRT 40 min
→
Q : 110 L/day
TCOD : 6,140 mg/L
$TCOD_L$: 675 g/day (72.2%)

$CO_2 + H_2O$ ... : 3,160 mg/L (37.1%)

Q : 110 L/day
TCOD : 8,510 mg/L
$TCOD_L$: 936 g/day
→
L-WAO
Temp. 240 °C
HRT 40 min
→
Q : 110 L/day
TCOD : 5,350 mg/L
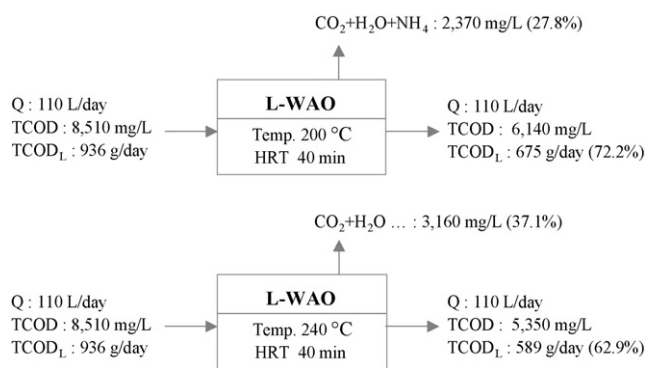$TCOD_L$: 589 g/day (62.9%)

Fig. 7. Mass balance for COD during WAO process operated at two different reaction temperatures.

3.5. Operation of 12-h monitoring

In order to investigate SS removal, SCOD increase, and organic acids formation over time, a 12-h real-time monitoring was performed under the operational conditions of 60 min, 220 °C, <30 atm, and 50% SOR. The influent concentration of TS, TCOD, TN, and TP was 2.8%, 17440 mg/L, 1238 mg/L, and 288 mg/L, respectively. It took approximately 3 h (09:00–12:00) to increase the temperature to 220 °C after heating, while the pressure was stably kept at 30 atm during the whole operation. Sampling was performed in every hour from 13:00 when the system reached the steady state. Fig. 6 shows changes in TS, SS, SCOD, TCOD, TN, TP, and VFAs concentrations during the 12-h monitoring. The TS was shown the stable removal efficiency with the average of higher than 74% for more than 10 h. The concentration of SCOD was increased to approximately 10,000 mg/L, 13-fold higher than the initial concentration (768 mg/L), during the operation. The removal efficiency for TCOD and the TN concentration in effluent were approximately 44% and 1100 mg/L, respectively, implying that TCOD and TN were removed insignificantly in the WAO. The TP was shown 92% removal efficiency when liquefied and the acetic acid among VFAs was observed increased by 0.025–0.065%.

3.6. Mass balance

Fig. 7 shows the mass balance in relation to the COD, following the continuous experiment conducted at the reaction temperature of 200 °C and 240 °C, respectively. For the WAO process with the reaction temperature of 200 °C and the reaction time of 40 min, the remained COD load was 72.2% and the rest (27.8%) was decomposed into CO_2, H_2O, etc., whereas for the process with 240 °C reaction temperature, the remaining COD was 62.9% and the rest (37.1%) decomposed, for the same influx COD load of 936 g/day (100%).

4. Conclusions

In order to investigate operational factors in a sewage sludge reduction technology applying the sub-critical wet oxidation pro-cess, experiments were performed using the thickened sludge taken from a municipal wastewater treatment facility. The influence of such factors as reaction temperature and time, reaction pressure, and oxidant dose on the sludge reduction was considered. The reaction temperature directly affected the thermal hydrolysis reaction rather than the oxidation reaction, and the formation of organic acids was increased with the increase of reaction temperature. Most solids were rapidly liquefied under the wet air oxidation and most organic acids as intermediates were converted into acetic acid. The reaction pressure and oxidant dose were not shown with significant effects on the liquefaction of organic solids, but increased the solubility of oxidizing agents, subsequently speeding up the liquefaction reaction.

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