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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.

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 regulations 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

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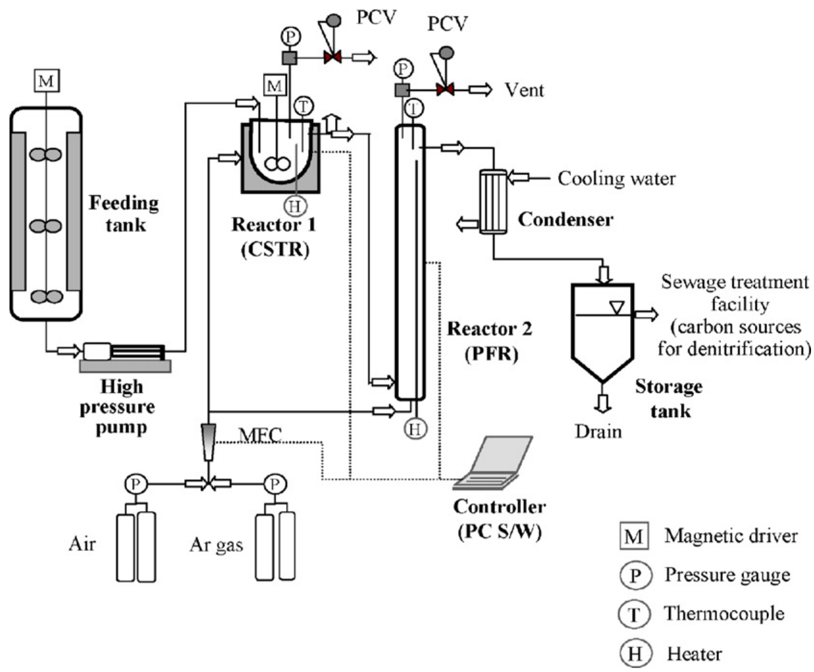

Fig. 1. Schematic of the lab-scale wet air oxidation process.

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