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Research paper

Prediction of by-Products from Wet Air Oxidation Module for Sludge Treatment of Produced Water

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Abstract

This study presents and verifies the deep-well wet air oxidation (WAO) reaction model for treating organic sludge (among the various by-products discharged from produced water treatment facilities) for recycling, and predicts the reaction characteristics. The deep-well WAO reaction model is established theoretically and a simulation model is developed. The validity of the simulation model is examined by comparing the modeled pressure change inside the reactor with that given by a model developed in a previous study. In terms of the pressure profile inside the reactor, the developed simulation model shows a 2.3% difference from the previously proposed model. It is confirmed that the increase in reaction pressure and residence time inside the deep-well WAO reactor improves organic decomposition by increasing the oxygen mass transfer rate in water containing such organics.

Keywords: *Wet air oxidation, Deep well reactor, Producer water, Sludge treatment, by-product*

1. Introduction

The treatment of oil, gas, and environmental waste generates produced water, which contains a complex mixture of organic and inorganic compounds. The criteria for the use and treatment of such produced water are being reinforced to reduce its environmental impact, and various types of treatment technology are under development. In particular, for the treatment of organic waste with significant environmental impact, physical, chemical, and biological treatment methods such as filters, membrane separation, dissolved air precipitation, chemical oxidation, and aerobic treatment have been developed.

Previously, Rajab et al. [1] examined the performance of the forward osmosis process for treating produced water, and demonstrated the possibility of dissolved organics removal. Shokrollahzadeh et al. [2] oxidized produced water separated from the gas flow in an Iranian gas refinery using hydrogen peroxide, ozone, and calcium hypochlorite, for reuse as fire-fighting water. Further, Dwyer and Mcdonald [3] demonstrated that the oxidation method using ozone removes more organics than the membrane separation method when treating water produced by an oil and gas extraction process in the Four Corners area of New Mexico. However, Ahmadun et al. [4] reported difficulty in removing dissolved elements such as acetic acid from produced water using current technology, and stated that these types of technology incur high initial and operation costs for produced water treatment while also producing hazardous sludge.

The wet air oxidation (WAO) reaction has been investigated for treatment of organic waste occurring in the produced water treatment process. In experiments on the tubular-flow-type WAO reaction for the treatment of wastewater containing phenol, a non-biodegradable substance. However, the ground installation conditions for the existing WAO reactor are limited, because pressurization power is required to maintain a high pressure; thus, the life cycle operation cost is high.

To address such problems, the deep-well WAO reactor, which can dramatically reduce the power cost, has been attracting growing research attention. Gran-Heedfeld et al. [5] have reported that the COD can be reduced by 65□90% when the temperature of the lower part of the reactor is 280□C, based on numerical calculations concerning a deep-well WAO reactor for wastewater.

Kodra and Balakotaiah [6] have examined the effects of the organic waste concentration, the amount of oxygen injected into the reactor, the inlet pressure, and the reactor length on the organic waste decomposition rate in a steady-state deep-well reactor, through numerical calculation of the WAO wastewater reaction.

The aim of this study is to develop reaction characteristic prediction software that can be utilized for the design and operation optimization of a deep-well WAO reaction plant for treating the organics of produced water. A method to treat these organics using the deep-well tubular-flow-type WAO reactor is proposed, and a simulation model is developed based on related theories to predict the reaction characteristics. The simulation model feasibility is then examined through comparison with a previously developed model. The design and operation variables that significantly affect the conversion rate of the reaction in the deep-well WAO reactor are assessed

2. Analysis Model

2.1. WAO Reaction in Deep-Well Reactor

Various methods are available to treat the dispersed oil, grease, soluble organics, suspended particles and sand, dissolved gas, and salt contained in produced water. In this study, the WAO method

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to treat the organics present in produced water is proposed. An outline of the overall process is shown in Fig. 1.

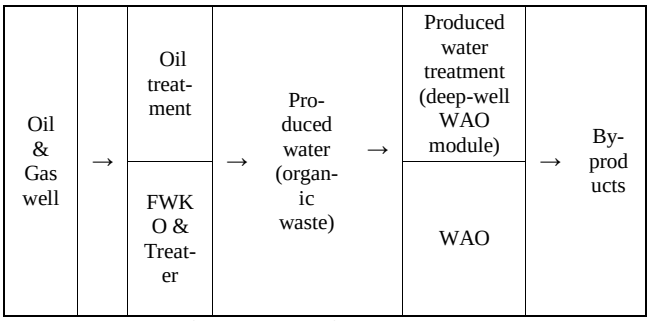
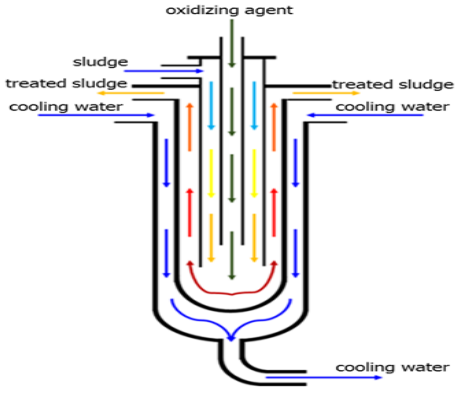


Fig. 1: Application of WAO method for treating produced water (FWKO: Free water knocks out).

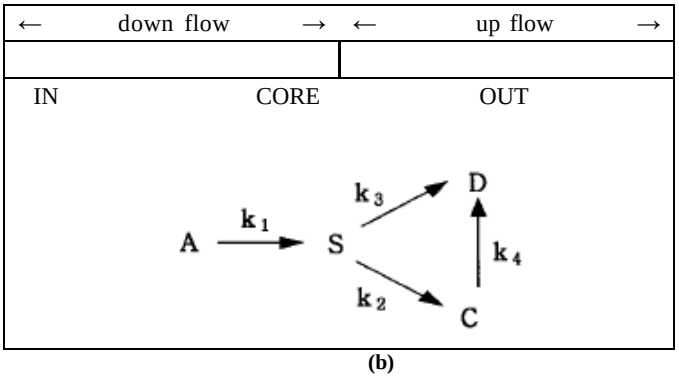
The WAO method is mainly used for treating organic wastewater, because it effectively decomposes organic waste. However, the WAO reaction, which is usually performed under high-temperature (T) and high-pressure (p) conditions, is expensive to operate. To reduce this inefficiency, a deep-well reactor has been developed, which uses the head p inside the tube to establish the p required for the reaction. This is achieved by installing the reactor underground. WAO converts liquid substances into by-product gas or water by oxidizing them with a liquid oxidizer converted from gaseous oxidizer in a p range of 10-200 atm and a T range of 120-350°C.

To treat typical organic waste, a reactor with a length of 1,200-3,000 m capable of achieving subcritical p conditions is employed. The deep-well WAO reactor considered in this study was 1,500 m long and consisted of three coaxial tubes (inner, middle, and outer), as shown in Fig. 2(a). Organic waste flows to the bottom of the reactor through the inner tube. The reaction begins when the oxidizing agent is injected in the vicinity of the reactor bottom. The WAO reaction generates heat, and the reaction product flows to the reactor top through the middle tube, causing heat transfer between the organic waste in the inner tube and the cooling water in the outer tube.

Fig. 2(b) shows the organic waste decomposition route in the deep-well WAO reactor, where the k terms are reaction rate constants. The down and up flows of the deep-well WAO reactor are considered. At the reactor bottom, where the oxidizing agent is injected, hydrolysis reaction occurs in the down flow, with A substances such as sludge being converted into liquefied organic substances (S). In the up flow, oxidation reaction mostly occurs. The S substances that can be easily decomposed are directly converted into carbon dioxide and water (D) by the oxidation reaction. Most organic substances that cannot be easily decomposed are converted into organic acids (C), an intermediate substance, and remain as liquids; however, some are decomposed into the final product, D. Depending on the oxidizing-agent ejection location, C and D products can also be confirmed in the down flow.



(a)



(b)

Fig. 2: (a) Deep-well wet oxidation reactor and (b) organic waste decomposition route.

According to Lixiong et al. [7] and Bernal et al. [8], the hydrolysis and oxidation reactions of organic waste are first-order reactions. When an excessive amount of oxygen is supplied, the following decomposition formulas are obtained, as the dependency on the oxygen concentration is excluded:

$$k_i = k_{0_i} e^{E_i/RT} \tag{2.1}$$

$$r_S = \frac{dC_S}{dt} = k_1 C_A - (k_2 + k_3) C_S \tag{2.2}$$

$$r_C = \frac{dC_C}{dt} = k_2 C_S - k_4 C_C \tag{2.3}$$

Here, the subscripts have the same meanings as above, C is the concentration, and t is time. The reaction rate constants, k_1 , k_2 , k_3 , and k_4 , have certain values according to the reaction. They vary depending on T and can be determined via the Arrhenius equation:

$$k_i = k_{0_i} e^{E_i/RT} \tag{2.4}$$

Note that *k* is unrelated to *C*, but is dependent on *T*, to a degree that can be determined from the Arrhenius equation, in which *k* is taken as a constant considering the temperature pre-exponential factor (k_{0_i}), the activation energy (*E*), and gas constant (*R*).

2.2. Establishment of Simulation Model

In the deep-well WAO reactor, the hydrostatic pressure head varies depending on the reactor depth, causing the T and p conditions to vary continuously. In other words, as the decomposition conditions for the target substance are determined by the location in the reactor, an analysis model that considers the decomposition characteristics of the target substance is required. In addition, the thermodynamic and physical properties of each substance must be accurately reflected to improve the accuracy of the simulation model. It is important to select an appropriate thermodynamic model, because the mixture phase behavior varies depending on the applied physical properties.

To establish the simulation model, the *A* substances were regarded as the dissolved state. As for the *S* substances, decomposition to *D* or *C* through the oxidation reaction was considered. In addition, although sludge and intermediate substances contain numerous mixed components, they were regarded as a single substance for simulation. The average C, H, O, and N contents of the organic materials were analyzed and *S* was assumed to be $C_5H_7O_2N$ (ethyl cyanoacetate) based on previous studies. *C* was assumed to be $C_2H_4O_2$ (acetic acid) only. Although many organic acids such as acetic, propionic, and butyric acids are actually produced, most are known to be derived from $C_2H_4O_2$. *D* was assumed to be CO_2, H_2O, and HNO_3. The oxidation reaction of $C_5H_7O_2N$ is a continuous parallel reaction including three basic reactions, which can be expressed as follows:

$$C_5H_7O_2N + 7O_2 \xrightarrow{k_1} 5CO_2 + 3H_2O + HNO_3,$$
$$C_5H_7O_2N + 5O_2 \xrightarrow{k_2} C_2H_4O_2 + 3CO_2 + H_2O + HNO_3,$$
$$C_2H_4O_2 + 2O_2 \xrightarrow{k_3} 2CO_2 + 2H_2O.$$

In the case of a continuous parallel reaction, the compositions of the intermediate and final substances vary depending on the reaction conditions such as T and the residence time. The reaction rate equations can be defined from the reaction mechanism, as follows. (Here, the oxidation reaction is regarded as a first-order reaction with a reaction degree (n) of 1.)

$$r_{C_5H_7O_2N} = (k_1 + k_2)C^n_{C_5H_7O_2N} = (k_{0_1}e^{-\frac{E_1}{RT}} + k_{0_2}e^{-\frac{E_2}{RT}})C^n_{C_5H_7O_2N} \quad (2.5)$$

$$r_{C_2H_4O_2N} = k_3C^n_{C_2H_4O_2N} - k_2C^n_{C_5H_7O_2N} = k_{0_3}e^{-\frac{E_3}{RT}}C^n_{C_2H_4O_2N} - k_{0_2}e^{-\frac{E_2}{RT}}C^n_{C_5H_7O_2N} \quad (2.6)$$

The value of k was calculated through equation (2.4) using the k_{0_i} and E data derived by Ahn [9] under the WAO conditions (180–240°C and 3.04 MPa) of the perfectly stirred reaction system.

In general, the non-random two-liquid (NRTL) model is used to design a wastewater treatment process. Previously, Olsson and Zacchi used the NRTL equation for gas-liquid and liquid-liquid equilibrium calculations to treat seven hazardous organic compound condensates from Kraft mill wastes [10]. Further, Randa *et al.* used the NRTL equation to calculate the mass balance and mixture properties in a process simulation for carboxylic acid recovery from wastewater [11]. Therefore, the NRTL model was used in this study to simulate decomposition of the organic substance ($C_5H_7O_2N$) by the deep-well WAO reactor

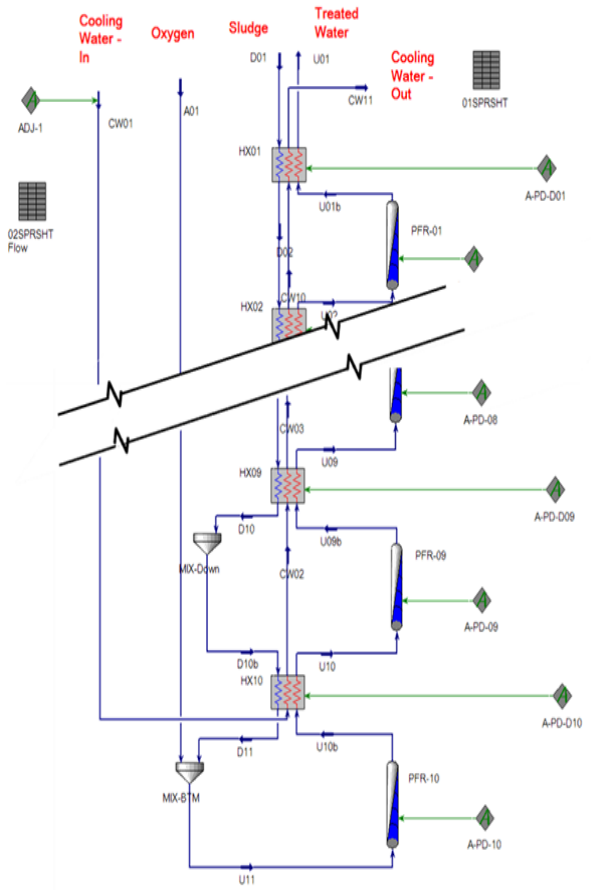


Fig.3. Simulation model of simplified deep-well wet oxidation reactor with HYSYS blocks.

The library of HYSYS V10, the process simulation software program used in this study, does not include the deep-well WAO reactor. Therefore, a model similar to the deep-well WAO reactor was simulated using two units, as shown in Fig. 3. The HYSYS blocks and streams used here are summarized in Table 1.

The system in which the up flow, down flow, and heat exchange of the cooling medium occur was expressed as a multi-stream heat exchanger, whereas the system in which the oxidation reaction occurs in the middle tube was expressed as a PFR. As the heat transfer between the oxidizing agent that flows down from the top of the reactor and the down flow is negligible, a mixer was used to mix the oxidizing agent with organic wastewater and to inject the mixed flow into the reactor.

In the reactor model, the p at each location must be derived by calculating the total pressure drop using the flow velocity and density values obtained from the simulation. The total pressure drop Δp_{total} is the sum of the static, momentum, and frictional pressure drops (Δp_{static}, Δp_{mom}, and Δp_{frict}, respectively), as follows:

$$p_{total} = \Delta p_{static} + \Delta p_{mom} + \Delta p_{frict} \quad (2.7)$$

As p varies with the elevation head in the deep-well reactor, the reactor was divided into ten units of 150 m. Then, Δp_{total} was calculated by inputting equation (2.7) into a spreadsheet so that the calculated Δp_{total} values were then set for entry into each reactor model.

Table 1: Blocks used in Aspen HYSYS

Category		HYSYS Model	
		Block	Name
Stream			
- Oxidizing agent flow	Oxidizing agent	Stream	A01
- Down flow	Organic wastewater	Stream	D01–D11
- Up flow	Treated wastewater	Stream	U01–U11
- Cooling medium flow	Cooling water	Stream	CW01–CW11
Model			
- Deep-well reactor	Reactor	PFR	PFR01–PFR10
	Multi-stream heat exchanger	LNG Exchanger	HX01–HX10
	Mixer	Mixer	MIX–BTM

To verify the deep-well WAO reactor simulation model, the mathematical model developed by Kodra and Balakotaiah [6] was compared with the simulation model developed using HYSYS in this study, using the calculated p, density, and organic waste conversion. Note that the flow rate at each location in the reactor is affected by T. In other words, after T is determined, changes in the flow rate, density, and p can be calculated according to the volume velocity for the reference T. Therefore, the T values in the literature [6] were taken as the initial values for comparing the calculated density and p values.

In this study, the input conditions of the deep-well WAO rector model were set to be identical to those of Ref. [6], as detailed in Table 2. The p and conversion rate calculated from the reactor model were compared with the calculation results of Kodra and Balakotaiah [6] for verification. Then, the factors affecting organic waste decomposition were analyzed using the verified model.

Table 2: Input values used in simulation model

Items		Value
Reaction-stream inlet velocity	m/s	0.5
Inlet temperature	°C	20.0
Inlet pressure	MPa	2
Weight fraction of organics in feed	wt.%	1.0

Reactor length	m	1,500
Reaction zone (oxygen injection)	m	1,500
Excess of oxygen injected in reaction mixture	mol%	10.0
Heat transfer coefficient	W·m²/K	2.0

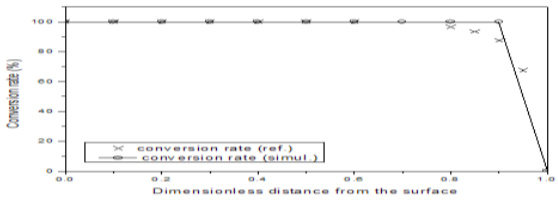
3. Results and Discussion

3.1. Deep-Well WAO Reactor Model Verification

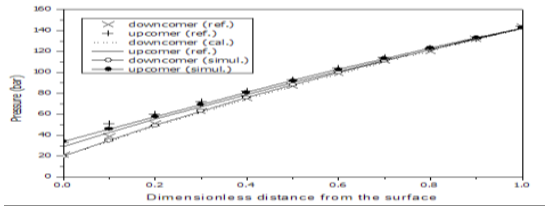
To verify the WAO reactor model, the calculated *p*, and conversion rate values of the simulation model developed using HYSYS were compared with those of the mathematical model developed by Kodra and Balakotaiah, as shown in Fig. 5. Here, "ref." represents the Kodra and Balakotaiah model while "simul." represents the simulation model developed in this study.

In the deep-well WAO reactor simulation model, the *p* change can be calculated through iterative calculation on the HYSYS spreadsheet using the *T* values set above and the density and flow velocity values calculated based on the *T* values. These *p* change values were set to be entered for each location in the reactor model through the HYSYS spreadsheet. Fig. 5(a) shows the *p* values according to the location in the reactor calculated through iterative calculation. At locations closer to the reactor bottom, the *p* was high due to the increase in the hydrostatic *p* head of the reaction mixture. As the up-flow *p* was approximately 1.4 MPa higher than the down-flow *p*, it was concluded that additional pressurization is not required during operation of the deep-well reactor, but the *p* generated by the pump is required during the reactor initiation to reach the critical condition. The error of the simul. model was 2.3% compared to the ref. model.

Fig. 5(b) shows the organic conversion rate results in the reactor. As oxygen was injected into the reactor bottom and the oxidation reaction was initiated near the critical point, most organics were decomposed at the reactor bottom (dimensionless distance of 0.6–1 from the surface); this yielded a conversion rate of 100%. For locations closer to the reactor bottom, the increasing *T* and *p* approached the critical point. In this instance, water with a weakened hydrogen bond increases the solubility of the polar organic substance and the maintained liquid state increases the oxygen solubility, making it possible to meet the minimum oxygen requirement. Furthermore, the high-*T* condition increases the diffusion coefficient of oxygen and the *k* of the oxidation reaction. In other words, the high-T, high- *p* critical condition at the reactor bottom increases the oxygen mass transfer rate in the pollutant-containing water, thereby decomposing most organics into CO_2 and low-molecular-weight organic acids during oxidation. The conversion rate difference at the reactor bottom for the ref. and simul. model was 1.6%, a low error.



(**a**) Pressure

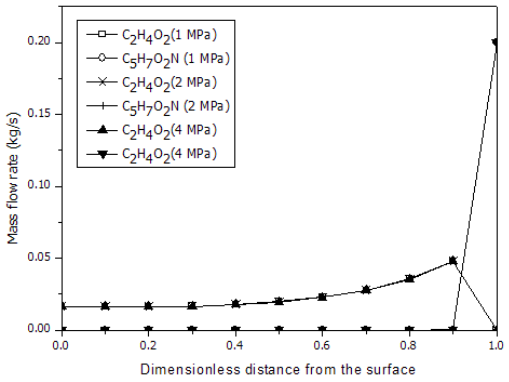


(**b**) Conversion rate

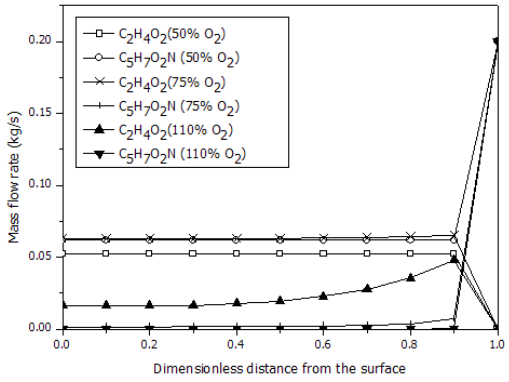
Fig. 5: Characteristics profiles of deep-well WAO reactor.

3.2. Influence Factor Analysis

Fig. 6(a) shows the $C_5H_7O_2N$ and $C_2H_4O_2$ up-flow flow rates according to the inlet *p*. When the inlet *p* was set to 1, 2, and 3 MPa, the *p* values at the reactor bottom were 13.3, 14.3, and 16.3 MPa, respectively, and most organics were decomposed at locations 1,380 m from the inlet. Changes in the inlet *p* do not appear to affect the reaction significantly, because the reaction *p* is sufficiently high. Fig. 6(b) shows the $C_5H_7O_2N$ and $C_2H_4O_2$ up-flow flow rates when the oxygen injection rate was 50%, 75%, and 110%. When the oxygen injection rates were 50% and 75%, 69% and 99% of the $C_5H_7O_2N$ was decomposed, while 0% and 3% of $C_2H_4O_2$ (created via $C_5H_7O_2N$ decomposition) was decomposed. This is because the conditions for $C_5H_7O_2N$ and $C_2H_4O_2$ decomposition could not be met, when the injected oxygen requirement was not met. When the oxygen injection rate was 110%, 100% of the $C_5H_7O_2N$ and 66% of the $C_2H_4O_2$ was decomposed. Thus, even when the oxygen requirement for complete decomposition was surpassed, there were cases for which the conversion rate is low. This appears to be because the efficiency of mass transfer through the gas-liquid contact is low. Therefore, it is necessary to optimize the operation conditions by simultaneously changing the *p*, and oxygen amount to improve the gas-liquid contact efficiency.



(a)



(b)

Fig. 6: Influence of (a) feed p, and (b) oxygen content on C2H4O2, C5H7O2N decomposition.

4. Conclusion

In this study, the deep-well wet air oxidation (WAO) reaction model for treating the organic sludge discharged from produced water treatment facilities for recycling was proposed and verified, and its characteristics were analyzed.

For the pressure and conversion rate profiles in the reactor, the simulation model developed of this study exhibited 2.3%, and 1.6% differences compared to the results given by a model developed in a previous study, indicating that the accuracy can be improved by modifying the density and pressure models according to the multiphase flow. In addition, it was confirmed that the decomposition

of organics and organic acids in the deep-well WAO reaction is proportional to the inlet pressure.
It is expected that the proposed reaction model can be effectively applied to the treatment of organic sludge contained in produced water.

Acknowledgement

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