Prototype of Ozone Generator for Industrial Wastewater Treatment: Some Kinetics and Performance Aspects

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Abstract

The second generation of ozone generator has been designed to be low energy consumption, by using coaxial electrode configuration and working at moderately high AC voltage (about 15 kilovolts/50 – 60 Hz). Other advantage of the equipment are its interesting performance, which can be used in atmospheric pressure and ambient temperature (around of 28 - 30 °C), either for air compression treatment or preparation of ozone from technical oxygen without additional complicated cleaning or advanced gas treatment process.

There are several interesting elements to be reported, such as: the role and relatively constricted range of operating temperature in corona discharge chamber as well as for ozone production or energy consumption during conversion of oxygen.

Introduction

The treatment of hazardous organic wastewater is typically carried out in a continuous reactor or converter, to convert to other less dangerous compounds than the origin. This conversion takes place in a reactor through a given complicated and specific mechanism and stage, depend on the operating condition or chemical and physical parameters of wastewater being treated. In this case, the main parameters are temperature, pH and pollutants concentration.

In Indonesia, many industries conservatively still use conventional biological processes, especially activated sludge process, to remove the pollutants in wastewater, which can be decomposed or converted biologically to another molecules or species as the specific purpose of microorganism. This biological change obviously involves very complicated and protracted biochemical reactions and therefore needs specific enzymatic catalysts which has protein and specific molecules or ions in its structure, such as functional groups and metallic ions, carbohydrate, and nucleotide. Most of them are produced as a result of microorganic metabolism in activated sludge.

In the contrary to biochemical reactions, chemical processes being applied in wastewater
treatment plant are generally independent to any specific catalyst. These chemical reactions are fast and spontaneous, therefore the waste treatment may be controlled by mass and momentum transfer. Meanwhile, waste treatment based on chemical processes have not been applied broadly in Indonesia, mainly for wastewater treatment, such as: (a) rapid oxidation (using strong oxidator such as peroxide and or ozone), (b) adsorption (simultaneous physisorption and chemisorption), and (c) ion exchange (1), (2), (3), (4).

Chemical waste treatment method may be chosen as an alternative because of its process is much faster than biological waste treatment. Besides, it needs less space than biological waste treatment. However, the chemical waste treatment still has considerable obstacles due to its high cost and complicated operation and maintenance, such as corrosion, fouling formation or precipitation.

Wastewater treatment technology through oxidation process with ozone (O₃), or ozonation, is one of potential choices to be developed in Indonesia. On the other hand, based on studies and field investigation, ozonation process gives a satisfaction result for removal of toxic and dangerous organic compound including phenolic compound (phenol and its derivatives), cyanide, chlorohydrocarbons, complex aromatics and pesticides from industrial wastewater. As a strong oxidator for treatment process, the main obstruction of its application in industrial scale is its preparation, since ozone can not be stored or even transported, therefore it must be generated on site. Engineering concept of ozone generator (ozonator) prototype, which is compatible for wastewater treatment, is reported in the first part of this study. This prototype is designed with coaxial electrode configuration to work in moderately high AC voltage, that is at 15 kilovolts and frequency about 50 – 60 Hz, with low energy consumption. Another advantages of this equipment is its performance, which can be used in atmospheric pressure and ambient temperature (around 28-30 °C), either for treated air compression (from air compressor) or technical oxygen (from gas bottled) without additional complicated cleaning or treatment process.

A performance test applied to the prototype of ozonator results in an optimal operating conditions for ozone formation as oxidator for waste treatment. Experimental results consist of the role of operating temperature in ozonator, productivity of ozonator, and energy consumption for ozone production (equivalent to oxygen conversion). Additionally, as the result of continuation study, several results of basic kinetics study on ozone production as a function of equilibrium reaction with oxygen will also be reported.

Results of performance test and ozonator kinetics give information and description more clearly about performance of ozone production from new equipment, either related with physical parameters or chemical parameters.

**Design Of Ozonator**

The research has been emphasized on the design of ozonator, considering many factors in wastewater treatment process plan, such as ozone productivity, operating condition, energy consumption, and so on. Ozonator design is shown schematically in Figure 1.

The equation for ozonator design is based on equation proposed by Rice and Browning (5):
\[
\frac{y_{\text{ozon}}}{A_{el}} = \frac{k_o \cdot f \cdot V_p}{t_{md}}
\]  

where:

- \(y_{\text{ozon}}/A_{el}\) = ozone yield per area of electrode (at optimum condition)
- \(k_o\) = productivity constant
- \(f\) = current frequency, Hertz
- \(\varepsilon\) = dielectric constant of moving dielectric medium
- \(V_p\) = peak potential between two electrode (discharge gap), Volt
- \(t_{md}\) = dielectric medium thickness, m.

Hence, peak potential between two electrodes can be calculated by equation,

\[
V_p = k_v \cdot p \cdot g
\]

where:

- \(k_v\) = potential change constant as an effect of gas pressure
- \(p\) = gas pressure between two electrode, bar
- \(g\) = distance/gap between two electrode, m.

Some special criteria in the design of this process equipment are: (1). least fouling formation potential (precipitation, and algae formation), (2). good operability with low operating and maintenance cost, and (3). Least potential of new pollutant problems or new pollutant molecule productions.

**Research Methodology And Analysis**

Analysis of ozone content (as a total oxidant) in aqueous solution is based on iodometry method (starch-potassium iodide). As a strong oxidation agent, ozone will oxidize iodide ion from KI solution obtaining iodine (I\(_2\)) in yellow-dark brown KI solution (KI\(_3\)). This free iodine is then titrated with hypo solution (sodium thiosulfate, Na\(_2\)S\(_2\)O\(_3\),5H\(_2\)O) and used starch as indicator.
The choice of the method is based on analysis technique done by Day and Underwood and Freeman (6), (7), (8), (9), (10). In this case, modification of iodometry method is made to find a standard method of ozone determination in water. Basically this method is very close to classical iodometry method, which is oxidizing of iodide ion to iodine by ozone in buffer solution of potassium iodide. The pH solution is maintained at 2 with sulphuric acid, and free iodine is titrated by sodium thiosulfate. Oxidation reaction scheme of ozone with potassium iodide may be abridged as:

\[ O_3 + 2I^- + H_2O \rightarrow I_2 + O_2 + 2OH^- \]  \hspace{1cm} (3)

Free iodine in KI solution is then titrated by sodium thiosulfate:

\[ I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-} \]  \hspace{1cm} (4)

Research method of ozonator productivity may be shown schematically as the following figure:

![Scheme of experiment of ozone productivity](image)

Figure 2. Scheme of experiment of ozone productivity

Procedure of data collecting and productivity analysis are carried out in the following steps:

- KI solution is placed in gas washing bottle (bubbler) consists of upstream and downstream with 200-mL each, then ozonator is turned on. Oxygen valve is opened to allow oxygen flow to ozonator, and therefore mixture of ozon/O_2 is passed through bubbler with variation of flow rate, electrical potential and temperature. Electrical current in amperemeter (AC) is noted as well as the time needed for KI solution exchange (in downstream) to bright yellow is reached.
- Sample for titration is taken when the colour of KI solution in downstream changed from clear to bright yellow.
- Add 10 ml of H_2SO_4 (2N) and amylum to sample before being titrated with Na_2S_2O_3.5H_2O, and the color of sample solution become dark blue (it is indicated that there is I_2 in solution).
- Titration process is stopped when dark blue sample solution is disappeared. Volume of titrant is noted.
- The same treatment is also done for upstream and downstream.
Experimental Results and Discussion

(a). Effect of Temperature.

The effect of operating temperature (moving dielectric and cooling water temperature) for several of air flow rate through ozonator is shown in Figure 3.

![Figure 3. Ozonator productivity performance as a function of temperature at V_{PT3} = 220 volt](image)

For the three types of oxygen flow rate, the increment in temperature will affect the increment of ozone production. Figure 3 shows that the optimum ozone production lies on the temperature of 28 – 30 °C. As the temperature increase after 30 °C, ozone production will decrease. This phenomenon occurs due to ozone decomposition at higher temperature. This working temperature is preferable for Indonesian tropical climate than those of commercial ozonator with optimum working temperature of –45 to –60 °C (2), and (4).

(b). Effect of Oxygen Flow Rate.

Productivity of ozonator will augment with the increasing of air feed flow rate as shown in Figure 4. The increment of air flow rate to ozonator will increase the oxygen content in feed gas and therefore will increase the productivity of ozone (equilibrium reaction will move to the direction of ozone formation).

![Figure 4. Ozonator productivity performance as a function of O_2 feed flow rate at T = 30 °C, V_{PT3} = 220 volt](image)
(c). Effect of Energy Consumption.

The role of energy on ozonator productivity can be replaced by electrical potential on ozonator, with the assumption that flow of current in ozonator is constant as shown in Figure 5. From the figure 5, it can be demonstrated that ozonator productivity is directly proportional to energy consumption of ozonator which in average is relatively small, between 7 – 35 Watt (in the voltage range of 150 – 220 VAC) and ozone production is in the range 8 – 22 kWh/kg-ozone. Ozone production of commercial ozonator in industry is of 23.3 kWh/kg-ozone (5), which is higher than designed or prototype of ozonator. It indicates that the designed ozonator is more efficient and more benefit than the commercial ones.

![Graph showing the relationship between energy consumption and ozonator productivity.](image)

\[ y = 0.0039x^2 - 1.2417x + 107.72 \]
\[ R^2 = 0.9826 \]

Figure 5. Ozonator productivity performance as a function of energy consumption at T = 30 °C, Q O₂ = 400 L/h

(d) Activation Energy of Monomolecular Equilibrium Reaction.

Activation energy investigation of ozone formation reaction is based on this elementary reaction (2), (5):

\[ 3O_2 \rightleftharpoons 2O_3, \quad \Delta H^0 = +283,508 \text{ kJ/mol} \]  

(5)

If \( k_j \) is a function of \( T \), then activation energy \( (E_A) \) of equilibrium reaction to the right direction can be calculated by equation.

\[ k_1 = f(T) = A \exp(-E_A/RT) \]  

(6)

The value of \( k_1 \) can be calculated by substitution of Classius-Clayperon equation:

\[ d\ln K/dT = \Delta H^0 / RT^2 \]  

(7)

to equation of residence time of plug flow reactor which is equivalent to space-time. From the calculation result, optimum \( E_A \) at oxygen feed flow rate of 400 L/h is 8.195 kJ/mole.

(e). Residence Time of Plug Flow Reactor.

Residence time in ozonator as a function of temperature is shown in Figure 6.
As feed gas flow rate is increased, the residence time is decreased according to the less contact time of oxygen in ozonator, and hence less availability oxygen to be reacted in ozone formation chamber (corona discharge). In general, this means that fluid residence time in reactor is becoming smaller. For any gas flow rate to the ozonator, it can be seen that optimum residence time lies on temperature of about 28 – 30 °C.

Concluding Remarks

Ozone production will increase with temperature, as reaction of ozone formation reaction is endothermic. However, for the operating temperature higher than 30 °C, ozone production will decrease due to the decomposition of ozone at high temperature. Optimum operating temperature of ozonator is about 28 – 30 °C, and this temperature is very appropriate for tropical country like Indonesia. It seems clearly that the operating temperature is better than commercial ozonator.

Ozone production will increase as the increasing of the air feed flow rate due to the availability of oxygen to be converted in ozonator. Ozone production will also increase as the electric potential for ozone formation is increase. This situation fits to the ozonator working rule that is producing ozone by high voltage:

- The increment of feed flow rate will increase ozone production and ozonator energy consumption as well. Optimum feed flow rate is at Q = 400 L/h, with activation energy \((E_A) \pm 8.195 \text{ kJ/mole}\), and energy consumption is around 8 - 22 kWh/kg ozone.
- Residence time of plug flow reactor is influenced by oxygen feed flow rate. The higher the oxygen feed flow rate, the shorter the residence time.

References


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