The analysis of several types of catalysts for ozone decomposition

Veny Luvita1,2, Setijo Bismo1,* and Anto Tri Sugiarto2

1Laboratorium Intensifikasi Proses, Chemical Engineering, Faculty of Engineering, Universitas Indonesia, Kampus UI Depok 16424, Indonesia
2Technical Implementation for Instrumentation Development Unit – LIPI, Bandung, Indonesia

*Email: setijo.bismo@ui.ac.id

Abstract. There has been rapid technological development in the aspect of water and wastewater treatment, including the application of ozone technology, commonly known as Advanced Oxidation Processes (AOPs). This involves the use of ozone gas converted to oxygen and OH* radicals, which possess the capacity to degrade the unwanted compounds present, although there is need for performance optimization to enhance the ease of formation and decomposition. This process is faced with serious problems that require immediate attention, particularly the presence of excess ozone, which is harmful to the health of living things, especially humans. Ozone decomposition uses an MnOx active core catalyst with a nominal loading of 0–2%. As a comparison used catalyst supports such as Zeolite Alam Lampung (ZAL), Granular Activated Carbon (GAC) and Green Sand (GS) with diameter 18–100 mesh. However, the challenge is comprehensively attenuated by using catalysts possessing the capacity to degrade the excesses, and promote procedure optimization, subsequently enhancing conversion and decomposition. Furthermore, previous studies have demonstrated the potential to elevate the production of OH radicals, and it was also established that catalysts from natural origin are less expensive, easy to operate, highly selective and difficult to damage under various conditions. The result of this study is GAC is more effective and efficient compared to others for decomposition.

1. Introduction

Catalysts are substances with the capacity to increase the reaction rate to reach equilibrium, without reacting with the reactants. Furthermore, they are generally characterized by the ability to convert raw materials into desired products, with activeness obtained from a combination of chemical and mineralogical materials. Conversely, selectivity is defined as the ability of a catalyst to produce the desired products as one of the substances involved serves as a barrier in other processes, hence the need to examine each potential catalytic material (Nasikin, 2010).

About 3 factors are known to affect function during performance, including fluid flow, catalyst activity, and stability. These are possibly improved through the proper selection of components, materials and preparation methods needed to provide optimum surface area, due to the responsibility of catalytic active core towards the reaction principle. Furthermore, the first step to be taken in the design requires the selection of active components, which is performed on the basis of conductivity.
The use of Advanced Oxidation Processes (AOPs) involves adopting the right type of reactor, optimization, and the need for additional ozone decomposition, which particularly involves the use of catalysts. This causes an upsurge in demand, due to the excessive use of ozone in numerous industries. Furthermore, ozone is a powerful oxidant and disinfectant, used to eliminate unwanted chemical compounds, bacteria, and viruses (Koltunski E., Plumridge J., 2005).

The process of ozone decomposition involves the oxidation of complex organic compounds into simple units, leading to an improvement in biodegradability, and a decline in toxicity. This occurs directly and indirectly, through the activation of free radical hydroxide (OH ●), hydroperoxide radicals (HO2●), superoxide radical ions (O2-) and ozonide radical ions (O3-) formed in the process (Chu and Ching., 2003).

This research will compare the quality and performance of the catalyst with three support used Zeolite Alam Lampung (ZAL), Granular Activated Carbon (GAC) and Green Sand (GS). Performance of the catalyst is shown based on the conversion of ozone decomposition. Catalyst will be applied in a continuous fixed bed reactor in which ozone enter to the reactor and react with the catalyst.

2. Methodology
In this research are using 3 variables, namely independent variables, variables bound, and control variable. The independent variable in this study is the type of catalyst support namely Zeolite Alam Lampung (ZAL), Granular Activated Carbon (GAC) and Green Sand (GS), catalyst support diameter, namely 18-35 mesh, 35-60 mesh, and 60-100 mesh, and the nominal % loading of MnOx is 0% -w, 1% -w, and 2% -w. Dependent variable in this study the conversion produced by the catalyst and ozone concentration after bypassed the catalyst. The control variables of this study are atmospheric pressure, temperature space, the volume of catalyst used is 5 mL, and the ozone flow rate is 3 Lpm.

Scheme of the experiment can see in Fig 1. The experiment is using ozone generator system. Free air enters to the fixed bed reactor then the air will be converted into ozone. Ozone which out will go into the fixed bed reactor containing the catalyst. Inside the fixed bed reactor will occur ozone decomposition process, then the concentration of ozone will be tested using iodometric analysis method.

2
3. Result and Discussion

3.1. Catalytic ozonation

Catalytic ozonation is aimed at activating the ozone, characterized by an increase in selectivity and change in reaction rate, as well as reduced ozone consumption. This phase is classified as (1) homogeneous, typically involving the use of transition metals, expressed as the rate of OH’ radical formation or contaminant degradation, and (2) heterogeneous, which generally requires metal oxides, activated carbon and zeolites, which involves adsorption, reaction and desorption.

Activated Carbon is an oxidative or adsorptive material that assists in the decomposition of hydrophobic non-polar compounds present in water with ozone. Furthermore, the surface area possesses acid, represented by carbonyl, carboxyl, hydroxyl phenoleate, lactone and quinon, and also base groups, including ether and carbonyl (Laszlo et al., 2001). These collectively serve as a buffer in heterogeneous catalysts with several advantages, including high stability in acidic or basic media, and mechanical resistance resulting from the ease of recovery from the dispersed active phase through combustion, high surface area and porosity. This is also an inexpensive process, characterized by the ready market availability, and the stability of carbon in numerous conditions. This includes the procedure of methane or oxidation catalysis react ions, which is dependent on the nature of calcination/reduction.

Granular Carbon Active (GAC) is another catalyst widely used as a support, due to the intrinsic favorable adsorbent feature and the large surface area. In addition, they also possess an oxygen functional group that is possibly used as a catalyst for ozone decomposition, with the purpose of increasing the rate of conversion (Wang M. et al., 2014).

The process of ozone decomposition conducted by A. Pradyasti et al., (2017) involves the effective use of ZnO catalysts and GAC support, characterized by high conversion values using varied sizes and loading percentages. Meanwhile, the combination prepared with a size 60-100 mesh and a loading percentage of 2% -w, reached the highest conversion of 100% in 30 minutes. Hence, a relationship was established between both parameter and ozone conversion, where smaller ZnO catalyst exhibited easier dispersion potential, and a higher percentage comprised of more oxygen holes that enhance the modification to oxygen molecules.

3.2. Ozone decomposition reaction using a catalyst

Based on the problems above, there is need for adopting simple and inexpensive technological solution, including the use of catalysts as an alternative in the ozonation process, especially in cases where the contaminants are difficult to completely decompose. This approach accelerates the conversion of ozone to hydroxide radicals (OH*), which subsequently plays a role in the degradation reaction. Moreover, some examples of catalysts used include activated carbon, iron oxide, zeolite and manganese oxide.

The use of activated carbon in the ozonation process accelerates the formation of OH* and oxygen radicals responsible for the degradation of contaminants on the surface of the catalyst, subsequently leading to a decline in ozone demand. Furthermore, the effect of utilizing solid materials at an average rate varies greatly, including 0.25 mg/min. grams of catalyst for activated carbon and 0.02-0.25 mg/min. gram of catalyst for zeolites, while Al2O3 and SiO2 have the similar value of 0.01- 0.25 mg/min. gram of catalyst.

From Table 1 and 2, the ZAL and GS buffered catalysts have the highest performance on size 60-100 mesh with a nominal loading concentration of 1%. This is because the smaller size of catalyst will give the greater surface area of catalyst reacting. Buffer catalysts with a nominal loading concentration of 2% have lower performance than catalysts with a nominal loading of 1% because the catalyst has been saturated with the active core so that the buffer catalysts play less role in the ozone decomposition process (Rohimmahtunnissa Azhar, 2012).
Table 1. Ozone decomposition with Zeolite Alam Lampung (ZAL) catalyst.

| Decomposition (%) | Time (min)/MnOx Loading/Size (mesh) | 5 | 10 | 15 | 20 | 30 | 40 | 50 | 60 |
|-------------------|-----------------------------------|---|----|----|----|----|----|----|----|
| 0%/60-100         |                                   | 24.89 | 23.68 | 26.1 | 26.1 | 29.74 | 34.58 | 37 | 37.61 |
| 1%/60-100         |                                   | 73.35 | 70.92 | 70.92 | 72.14 | 77.59 | 78.19 | 75.77 | 76.98 |
| 2%/60-100         |                                   | 39.43 | 35.79 | 35.19 | 36.4 | 38.22 | 36.4 | 40.64 | 44.27 |
| 0%/35-60          |                                   | 22.77 | 26.73 | 26.73 | 24.75 | 21.78 | 21.78 | 24.2 | 26.24 |
| 1%/35-60          |                                   | 45.83 | 44.79 | 44.79 | 42.71 | 36.98 | 38.02 | 38.02 | 34.9 |
| 2%/35-60          |                                   | 22.51 | 22.51 | 23.62 | 25.28 | 25.83 | 30.26 | 31.37 | 38.01 |
| 0%/18-35          |                                   | 9.65 | 8.83 | 11.29 | 10.47 | 13.76 | 14.58 | 17.04 | 17.04 |
| 1%/18-35          |                                   | 26.13 | 26.13 | 21.62 | 16.22 | 10.81 | 10.81 | 10.81 | 11.26 |
| 2%/18-35          |                                   | 17.59 | 15.74 | 11.11 | 11.11 | 12.04 | 13.89 | 14.81 | 15.28 |

Table 2. Ozone decomposition with Green Sand (GS) catalyst.

| Decomposition (%) | Time (min)/MnOx Loading/Size (mesh) | 5 | 10 | 15 | 20 | 30 | 40 | 50 | 60 |
|-------------------|-----------------------------------|---|----|----|----|----|----|----|----|
| 0%/60-100         |                                   | 93.09 | 79.28 | 75.33 | 75.33 | 75.33 | 74.34 | 73.36 | 72.86 |
| 1%/60-100         |                                   | 100 | 100 | 100 | 100 | 98.03 | 94.08 | 89.14 | 86.18 |
| 2%/60-100         |                                   | 100 | 100 | 100 | 95.07 | 84.7 | 80.26 | 77.8 | 77.3 |
| 0%/35-60          |                                   | 48.87 | 33.22 | 33.22 | 34.26 | 35.83 | 37.91 | 39.48 | 38.96 |
| 1%/35-60          |                                   | 92.7 | 65.57 | 59.3 | 60.35 | 62.43 | 65.04 | 67.13 | 68.17 |
| 2%/35-60          |                                   | 79.52 | 52.4 | 54.61 | 57.38 | 62.92 | 62.36 | 65.68 | 63.47 |
| 0%/18-35          |                                   | 14.04 | 14.89 | 14.89 | 16.57 | 11.52 | 14.04 | 8.15 | 8.99 |
| 1%/18-35          |                                   | 32.65 | 17.78 | 16.91 | 17.78 | 15.6 | 19.1 | 20.85 | 21.72 |
| 2%/18-35          |                                   | 24.07 | 20.37 | 13.89 | 8.33 | 12.04 | 11.11 | 10.19 | 12.5 |

The performance of the GAC-supported catalyst is very high, see from Table 3, the catalyst has a percentage of 100% up to the 24th hour for the size of the catalyst support 35-60 mesh and 60-100 mesh with nominal loading concentrations from 0% to 2%.

Table 3. Ozone decomposition with Granular Active Carbon (GAC) catalyst.

| Decomposition (%) | Time (min)/MnOx Loading/Size (mesh) | 5 | 10 | 15 | 20 | 30 | 40 | 50 | 60 |
|-------------------|-----------------------------------|---|----|----|----|----|----|----|----|
| 0%/60-100         |                                   | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| 1%/60-100         |                                   | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| 2%/60-100         |                                   | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| 0%/35-60          |                                   | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| 1%/35-60          |                                   | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| 2%/35-60          |                                   | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| 0%/18-35          |                                   | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| 1%/18-35          |                                   | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| 2%/18-35          |                                   | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
Ozone used for industrial purposes is synthesized from pure oxygen through thermal, photochemical, chemical and electrochemical processes. Furthermore, they are created in the form of electrical discharges and particle flow, which is attained using the following reactions:

\[ \text{O}_2 + (e^-, h\nu, T) \rightarrow 2\text{O} (\text{O}_2^*) \]
\[ \text{O}_2 + \text{O} + \text{M} \rightarrow \text{O}_3 + \text{M} \]
\[ \text{O}_2^* + \text{O}_2 \rightarrow \text{O}_3 + \text{O} \]

In which: M is the third particle (Batakliev et al., 2014)

**Figure 2.** Structure of O₃ molecule.

\[ \text{HO}_2^* \leftrightarrow \text{O}_2^* + \text{H}^+ \]

**Figure 3.** Resonance structures of ozone.

The ozone structure is resonance stabilized, which is one of the reasons for its resistance against decomposition at low temperatures (Figure 2 and 3). At high temperatures, the decomposition reaction occurs spontaneously and very quickly, although the process is difficult and expensive as a result of the high energy requirement. The kinetics study of ozone thermal decomposition is also complicated by the fact that above a certain critical temperature the steady kinetic decomposition is transformed into explosion, subsequently passing to detonation (Rakovský et al., 2007). Ozone detonation is observed above 105 °C. The gaseous ozone is characterized by different times of half-life, depending on the temperature. The life time (half-life) of ozone at certain temperatures entails decomposition at 1.5 sec using a temperature of 250°C, and up to 3 days at room temperature, due to reduced resonance (Batakliev, et al., 2014).

Ozone decomposition reactions with activated carbon as a catalyst by Beltran et al., (2002) are stated as follows:

**Homogeneous decomposition:**

\[ \text{O}_3 + \text{OH}^- \rightarrow \text{HO}_2^- + \text{O}_2 \quad \text{(Eq. 1)} \]
\[ \text{O}_3 + \text{HO}_2^- \rightarrow \text{HO}_3^- + \text{O}_3^* \quad \text{(Eq. 2)} \]
\[ \text{O}_3 + \text{In} \rightarrow \text{O}_3^* + \text{In}^+ \quad \text{(Eq. 3)} \]
\[ \text{HO}_2^- \leftrightarrow \text{O}_2^* + \text{H}^+ \quad \text{(Eq. 4)} \]

Whereas heterogeneous decomposition on the reaction surface for pH 2 to 6 include:

\[ \text{O}_3 + \text{S} \leftrightarrow \text{O}_3^+ \text{S} \quad \text{(Eq. 5)} \]
\[ \text{O}_3^+ \text{S} \leftrightarrow \text{O}_3^- + \text{O}_2 \quad \text{(Eq. 6)} \]
\[ \text{O}_3 + \text{O-S} \leftrightarrow 2\text{O}_2 + \text{S} \quad \text{(Eq. 7)} \]

At the pH ≥ 6, the reaction formed are:

\[ \text{OH}^- + \text{S} \leftrightarrow \text{OH-S} \quad \text{(Eq. 8)} \]
\[ \text{O}_3 + \text{OH-S} \leftrightarrow \text{O}_3^+ \text{S} + \text{HO}^- \quad \text{(Eq. 9)} \]
\[ \text{O}_3^+ \text{S} + \text{HO}^- \leftrightarrow \text{O}_3^- + \text{O}_2 + \text{S} \quad \text{(Eq. 10)} \]
\[ \text{O}_3 + \text{O-S} \leftrightarrow \text{O}_3^+ \text{S} + \text{S} + \text{O}_2 \quad \text{(Eq. 11)} \]

**Homogeneous propagation and termination reactions:**

\[ \text{O}_3 + \text{O}_2^* \rightarrow \text{O}_3^+ + \text{O}_2 \quad \text{(Eq. 12)} \]
\[ \text{O}_3^* + \text{H}^+ \rightarrow \text{HO}_3^* \quad \text{(Eq. 13)} \]
\[ \text{HO}_3^* + \text{P} \rightarrow \text{HO}^+ + \text{O}_2 \quad \text{(Eq. 14)} \]
\[ \text{HO}^+ + \text{P} \rightarrow \text{End product} \quad \text{(Eq. 15)} \]
In which: $S$ is the catalyst surface and $i$ is the initiator. 

In this mechanism, reactions [1] to [4] and [12] to [15] constitute the homogeneous decomposition contribution to the total reaction rate, while reactions [5] to [11] are the steps of the surface chemical reaction involving adsorption, surface reactions and desorption processes. These reactions would be followed in the water phase by reactions [12] to [15] which support conclusions about the direct formation of free radicals in the water phase. In reactions [3] and [15], $In$ and $P$ account for the presence of initiating agents of ozone decomposition and scavengers of hydroxyl radicals, respectively (Beltran et al., 2002).

4. Conclusion
The processing of contamination/waste using advanced oxidation process with ozone decomposition catalyst is identified as an alternative. The best quality of the catalyst is seen from the greater surface area, pore volume, and the optimum pore diameter and actual loading composition will be even higher catalyst performance. This can be seen from the quality of GAC-supported catalysts. The performance of GAC supported MnOx catalysts is based on ozone decomposition conversion has the highest performance compared to ZAL and GS magnitude of conversion of 100% for 24 hours for the diameter of the catalyst buffer 35-100 mesh and nominal loading concentrations of 0-2%.

Acknowledgement
The authors are grateful to the financial support provided for this research by the University of Indonesia and by-research program of Indonesian Institute of Science.

References
[1] Pradyast A, Azhariyah A S, Karamah E F and Bismo S 2018 Preparation of zink oxides catalyst with activated carbon support for ozone decomposition. *IOP Conf. Series: Earth and Environmental Science* 105 012013
[2] Azhariyah A S, Pradyast A, Dianty A G and Bismo S 2018 Comparative study of activated carbon, natural zeolite, and green sand supports for CuOx and ZnO sites as ozone decomposition catalyst *IOP Conf. Series: Materials Science and Engineering* 334 012075
[3] Beltran F J, Rivas J, Alvarez Pand Montero-de-Espinosa R 2002 Kinetics of heterogeneous catalytic ozone decomposition in water on an activated carbon *Ozone Sci. Eng.* 24 227-37
[4] Gao G, Kang J, Shen J, Chen Z and Chu W 2016 Investigation on kinetics of heterogeneous catalytic ozone decomposition in aqueous solution over composite iron-manganese silicate oxides *Ozone Sci Eng.* 38 6
[5] Kasprzyk-Hordern B, Ziolek M and Nawrocki J 2003 Catalytic ozonation and methods on enhancing molecular ozone reaction in water treatment *Appl. Catal.* 46 639-69
[6] Koltunski E and Plumridge J 2005 *Ozone as a Disinfecting Agent in the Reuse of Wastewater* (Duebendorf, Switzerland: Ozonia Ltd)
[7] Yuan L, Chen Z, Liu Y and Liu Y 2011 Catalytic ozonation for the degradation of p-Chloronitrobenzene in aqueous solution by pumice. *Adv. Mater. Res.* 239-242 1123-8
[8] Nasikin M and Susanto B H 2010 Katalisis Heterogen. Universitas Indonesia.
[9] Chokshi N P, Bhutia H, Chotalia A, Kadiwala A and Ruparelia J P 2017 Heterogeneous catalytic ozonation of Reactive Black 5 with cobalt oxide. *Int. J. Chem. Tech Res.* 10(9) 402-9
[10] Zhu Q, Chen F, Guo S, Chen X and Chen J 2017 Variation of catalyst structure and catalytic activity during catalyst preparation for catalytic ozonation of heavy oil produced water *Water Air Soil Pollut.* 228 168.
[11] Rakovsky S K and Zaikov G E 2007 Kinetic and Mechanism of Ozone Reactions with Organic and Polymeric Compounds in Liquid Phase – 2nd edition (New York: Nova Sci. Publ., Inc.)
[12] Rohimmahtunnissa A and Setijo Bismo 2012 Studi Komparatif Zeolit Alam, Karbon Aktif dan Pasir Hijau sebagai Penyangga Katalis dengan Inti Aktif MnOx untuk Dekomposisi Ozon, Thesis submitted to the University of Indonesia.

[13] Batakliev T, Georgiev V, Anachkov M, Rakovsky S and Zaikov G E 2014 Ozone decomposition Interdiscip. Toxicol. 7(2) 47-59

[14] Wang M, Zhang P, Li J and Jiang C 2014 The effects of Mn loading on the structure and ozone decomposition activity of MnOx supported on activated carbon Chinese J. Catal. 35 335-41

[15] Li W 1998 Kinetics and Mechanism of Ozone Decomposition and Oxidation of Ethanol on Manganese Oxide Catalysts. Dissertation submitted to the Faculty of the Virginia Polytechnic Institute and State University