Morphology characterization of lignocellulosic materials in ozone based degradation

A P Siswanto¹*, M E Yulianto¹, D Handayani¹, E F Sapatra¹, I Yuniarti¹, R A S Imamsyah¹
¹Department of Industrial Technology, Diponegoro University, Semarang, Indonesia

E-mail: anggun.siswanto@live.undip.ac.id

Abstract. Oil-rich plants are widely cultivated as raw materials for the biofuel industry in developing countries. However, this plant is mainly also a potential source for food supply. Therefore, the supply of food crops and oil competes, making a solution to this conflict very desirable. Technological developments aimed at contributing to an increase in food and fuel supply to meet market demand is the next step in increasing existing food and oil production. Renewable energy is renewable energy and, if managed properly, these resources will not be used up. Renewable energy types include biomass, geothermal, solar energy, water energy, wind energy, and ocean energy. This method promises an economical and environmentally friendly process. Ozone is a strong oxidant for potential use in the degradation process of lignocellulosic materials. This can be produced by air flow through a plasma micro-reactor. Utilization of water as a solvent will produce a solution that is rich in ozone. This research aims to develop a degradation scheme for lignocellulosic materials using an ozonolysis reactor. The novelty of this research is the use of ozone in dissolved water for the degradation of lignocellulosic materials. Water is used as a solvent for ozone dissolving where water molecules with dissolved ozone can be separated into OH radicals which are very reactive oxidants.

1. Introduction
The energy needs of petroleum fuels in various countries in the world in recent years have increased sharply, not only in developed countries, but also in developing countries including Indonesia. Petroleum fuels in the future, is currently developing new and renewable energy sources that are environmentally friendly. Renewable energy is energy that can be approved and approved to be managed well, the resources will not be used up. Renewable energy types Updated biomass, geothermal, solar energy, air energy, wind energy, and ocean energy. Ethanol is a biofuel, and has good prospects as a substitute for liquid and gasohol fuels with raw materials that can be supportive, environmentally friendly, and very beneficial for the microeconomics of a farmer-based community.

Ozone that cannot be revised will re-form molecules [1]. This method promises economic and environmentally friendly processes. Ozone is a strong oxidant for potential use in the degradation process of lignocellulosic material. This can be done by the flow of air through a plasma micro-reactor. Utilization of water as a solvent will produce a solution that is rich in ozone. Plasma has promising advantages because of its low energy consumption, conversion in atmospheric pressure, and high conversion [2]. Maintenance using a plasma micro-reactor is usually carried out at atmospheric pressure

* To whom any correspondence should be addressed.
which contributes to economic efficiency. Does not require process under vacuum conditions. Because of this, it is easier to process a reaction.

This research develops lignocellulose degradation materials using an ozonolysis reactor. The novelty of this research is the use of ozone in dissolved water for the degradation of lignocellulosic material. Water is used as a solvent for ozone dissolving where water molecules with dissolved ozone can become OH radicals which are very reactive oxidants. These molecules are expected to attack carbon double bonds in the structure of the lignocellulose molecule. This process is similar to the Criegee interaction which explains the completion of esters at the ozone junction. The benefit of this new technology is that there are no by-products left after ozonolysis treatment.

2. Methodology

2.1. Ozonolysis treatment

Raw materials in the form of lignocellulosic materials were pre-treated using the size reduction method. The raw material was processed first then treated by ozonolysis. The ozone concentration is adjusted to the capacity of the ozone generator it has. Variables included: ratio of distilled water and weight of lignocellulosic materials was 1:20, room temperature and ambient pressure, duration ozonolysis (5; 10; 15; 20; 25; 30 minutes).

2.2. Morphology analysis

Morphological test of lignocellulosic materials after ozonolysis using the Scanning Electron Microscope (SEM) method. This test aims to determine qualitatively lignocellulosic materials after the ozonolysis process. Ozonolysis of carbon double bonds is well explained by the Criegee mechanism, shown in Fig. 1. The reaction takes place in three different stages namely (Reaction I) the formation of "primary ozonide", (Reaction II) "primary ozonide" decomposition into becarbonyl compounds and "carbonyl oxides", (Reaction III) insertion of carbonyl oxides into the structure of carbonyl compounds. It was reported that during the decomposition stage (Reaction II), selective fission occurs with chemical bonds. Oxygen bonds (O-O) and carbon bonds (C = C) split where the stronger bond (C-O) remains intact [3].

![Figure 1. Criegee mechanism](image)

Ozone technology has been specifically applied to study its effects on carbon double bonds from biodiesel [1] and in the field of detoxification of phorbol ester [4, 5]. Ozone is expected to attack carbon double bonds (C = C) in the phorbol ester structure which can cause molecular recombination. The division of a double bond is predicted to modify the strength of the configuration molecule. As a result,
the modified phorbol ester is produced by changing the activation power as a tumor promoter after ozonolysis.

3. Result and discussion
Investigation of the effects of ozonolysis in biodiesel, especially on carbon double bonds under extreme operating conditions, has been reported [1]. Methanol and dichloromethane are used as solvents with triethylamine as a catalyst where ozonolysis is carried out at -75°C. This study aims to analyze the molecular structure of soy methyl as biodiesel samples after ozonolysis. Fourier Transform Infrared Spectroscopy (FTIR), Gas Chromatography (GC) and Gas Chromatography-Mass Spectrometry (GC-MS) are used for structural analysis. A 90% reduction in the number of double bonds in the mixture is produced after 2 hours of ozonolysis. A theoretically predicted ozonolysis ester product was found. This shows that chemical-based reactions in combination with ozone treatment affect the configuration of the double bond. Further experiments to the ambient temperature are recommended to meet the requirements of industrial processes.

3.1. Plasma application in ozone production
Plasma refers to an electrically neutral ionized gas, the same amount of positively and negatively charged ions, and is often defined as the fourth state of matter. Ionized gas is produced from oscillations which are considered as compressed electric waves, similar to sound waves [6]. Langmuir also stated that: "Except near the electrode, where there is a casing that contains very few electrons, ionized gas contains approximately the same number of ions and electrons so that the resulting space charge is very small. We will use the name plasma to describe this region containing a balanced charge of ions and electrons "Plasma envelope is defined as the transition region separating plasma and its boundaries. Unlike plasma and its boundaries, the characteristics of the plasma envelope are typical which give impetus to the movement of charged particles" [7]. Fig. 2 shows the plasma phase compared to the phases of other substances.

Figure 2. Various state of matters [8]

Nehra et al [9] have summarized various types of non-thermal plasma reactors. Corona release, plasma jets of atmospheric pressure and dielectric barrier discharge are described. Corona release is the first type of plasma reactor. Typically, this reactor release is produced from a pair of asymmetrical electrodes with a DC voltage that is continuously lit or pulsed. The homogeneous electrode configuration is surrounded by the electric field that is generated. Atmospheric pressure plasma jets create radio frequency interference during ignition release. This speeds up the free electrons from the central electrode so that energetic collisions in the feed gas occur quickly.
3.2. Dielectric barrier discharge plasma reactor
Another class of plasma reactors, Dielectric barrier discharge (DBD) is also non-thermal. DBD is called a silent discharge, because a typical discharge is generated from AC power, and operates under atmospheric pressure and moderate gas temperatures. Fig. 3 shows the configuration of a non-thermal plasma reactor.

![Configuration of non-thermal plasma reactor](image)

**Figure 3.** Configuration of non-thermal plasma reactor [9, 10].

Typically, DBD reactors consist of two metal parallel electrodes separated by a small gap in between. To ignite plasma, gas is passed through the electrodes and induced by an electric current. Various gases can be used to produce plasma such as helium, neon, argon and air. DBD plasma can consist of independent current filaments, which are micro-discharges [11]. The occurrence of micro-release in the DBD configuration develops because it reaches an electric field strong enough in the reactor gap to exceed the point of damage. This micro-release is homogeneously distributed on the dielectric surface in nanosecond duration [12].

3.3. Ozonolysis treatment in lignocellulosic materials
Ozone is an inorganic compound consisting of three oxygen atoms arranged in a linear structure. It is colourless, partially soluble in water and usually conductive in the form of gas. It occurs naturally in the Earth's atmosphere when oxygen is activated by UV light and is also produced in storms [13, 14]. In addition, ozone produced artificially can be found in copiers, electric motors, etc. Ozone is known as a strong oxidant with an oxidation potential of 2.07 V [14, 15]. Table 1 presents the oxidation potential of various oxidant agents.

| Oxidant                  | Oxidation Potential (V) |
|--------------------------|-------------------------|
| Fluorine                 | 3.06                    |
| Hydroxyl free radicals   | 2.80                    |
| Atomic oxygen            | 2.42                    |
| Ozone                    | 2.07                    |
| Permanganate             | 1.67                    |
| Chlorine                 | 1.36                    |
| Oxygen                   | 1.23                    |
| Hypochlorite             | 0.94                    |

Table 1. Oxidation Potential of Various Oxidant [13]
Lignin is recognized as an outer layer of cell structure that is polymerized into hemicellulose and cellulose. Agricultural waste, food waste and organic industrial waste mainly contain lignocellulosic material [16, 17]. Hemicellulose is cellulose which can be used for many industrial products such as enzymes, biofuels, organic acids and food additives. This compound is known for its sugar-based chemical composition, and therefore can be used as a source of economic value [18, 16]. Fig. 4 illustrates the biological structure of lignocellulosic material.

![Cross sectional view of lignocellulosic structure](image)

**Figure 4.** Cross sectional view of lignocellulosic structure [18].

The process of lignin degradation is highly desirable to biologically access hemicellulose and cellulose layers. The presence of ether bonds in the lignin structure limits this process. This results in lignin insusceptibility during conventional biodegradation approaches such as enzymatic and chemical treatments [17-20]. Fig. 5 shows the images of Scanning Electromagnetic Microscope (SEM) on the lignocellulosic materials.

![SEM images of lignocellulosic samples](image)

**Figure 5.** SEM images of lignocellulosic samples.

Studies on the use of ozonolysis in the treatment of lignin compounds have been conducted for decades [21-23]. Vidal and Molinier [23] have studied lignin ozonolysis to improve the digestion of sawdust. They found that the accessibility of enzymes to the experimental substrate was improved during ozonolysis. Unfortunately, a high voltage input, 15-33 kV is needed during ozone generation. These high-power supply requirements have associated high processing costs. Subsequently, laboratory-scale experiments were carried out in 350 ml of a gas washer by Wu et al [21] with a modern ozone generator. Ozone is used in the pre-treatment stage of hydrogen production using barley straw as a raw material.
4. Conclusion
Ozone is known by its high oxidation potential which make it as one of the strongest oxidant. There are several ways of producing ozone in which Dielectric Barrier Discharge Plasma Reactor was applied in this research. The application of ozone in lignocellulosic materials was studied and showed that the lignocellulosic materials is susceptible to ozone.

5. References

[1] Baber T M 2005 Biomacromolecules 6 1334
[2] Zimmerman W B, Lozano P J H and Bandulasena H H 2010 J. Sewerage & Water
[3] Criegee R 1975 Angew. Chem. Internat. Edit. 14 745
[4] Diwani G I E, S A E Rafei and Hawash S I 2011 Adv. Applied Sci. Res. 2 221
[5] S Kongmany, H Matsuura, M Furuta, S Okuda, K Imamura, Y Maeda 2013 J. Phys.: Conf. Ser. 441 012006
[6] Langmuir I 1928 Proc. Natl. Acad. Sci. USA, 14 628
[7] Fridman A 2008 Cambridge University Press
[8] Cheng H H, C S Shing, W Y Chi and H D Lit 2007 J. Environ. Eng. Manage. 17 427
[9] Nehra V, A Kumar and H K Dwivedi 2008 Int. J. Eng. 2
[10] Wu Z, Z Pengyan, T Lin, Z Duo, W Ailing and G Xingang 2012 Adv. in Biomed Eng.
[11] Kogelschatz U, Eliasson B and Egli W 1997 J. Phys. IV 7
[12] Wagner H E, Brandenburg R, Kozlov K V, Sonnenfeld A, Michel P and Behnke J F 2003 Vacuum 71 417
[13] Barlow P J 1994 Watertec Engineering Pty Ltd
[14] Franken L 2005 Food Safety and Security at Kansas State University
[15] Babikov D, Kendrick B K, Walker R B and Pack R T 2003 J. Chem. Phys. 119
[16] Chuck C J, Parker H J, Jenkins R W and Donnelly J 2013 Bioresour. Technol. 143 549
[17] Palmqvist E and Hahn H B 2000 Bioresour. Technol. 74 25
[18] Mussatto S I and Teixeira J A 2010 Formates Research Center 2
[19] Malgorzata M, Jadwiga S O and Anna M 2012 Fibres Text. in East. Eur. 20 191
[20] Wu J, Upreti S and Ein M F 2013b Int. J. Hydrog. Energy 38 10270
[21] Wu J, Ein M F and Upreti S 2013a Bioresour. Technol. 144 344
[22] Nouwezem R, Borredon M E, Parisi J P and Gaset A 1993 Bioresour. Tech. 45 43
[23] Vidal P F and Molinier J 1988 Biomass 16 1