24thABCM International Congress of Mechanical Engineering
December 3-8, 2017, Curitiba, PR, Brazil

COBEM-2017-2290
CONTROLLED ATMOSPHERE OZONE GENERATOR

Camila Santana Silva Matos
Lucas Ramalho Oliveira
Programa de Pós-graduação em Mecatrônica, Universidade Federal da Bahia, BA, Brazil
ss.camila@hotmail.com
lucasengmeca@gmail.com

Luiz Carlos Simões Soares Junior
Universidade Federal do Recôncavo da Bahia, BA, Brazil
lcsimoes@ufrb.edu.br

Iuri Muniz Pepe
Programa de Pós-graduação em Mecatrônica, Laboratório de Propriedade Ópticas, Universidade Federal da Bahia, BA, Brazil
lapo.if@gmail.com

Abstract. *Ozone is a strong oxidizing agent and in O_3 alkenes presence, initiates a cleavage reaction called ozonolysis. In this chemical reaction multiple C-C bonds are replaced by double bonds with oxygen (oxidation). Ozone can significantly reduce the testing time in oxidation measurements. Although there are several commercial devices employed to produce the ozone as well as to measure its concentration, ozone controlled generation is still a challenge. This paper describes the development of a device capable of supply a controlled ozone atmosphere to be employed during oxidation tests. The device is composed of an ozone generator Corona type, an absorption cell to measure ozone concentration along with two systems used for signal conditioning and data acquisition. The proposed ozone detector uses visible light absorption trough an LED, as the light source, along with a photodiode, as a photodetector.*

Keywords: *generation, ozone, oxidation, sensor, concentration*

1. INTRODUCTION

The ozone, according to Georgiev et al., 2015, due to its high oxidative potential, can be used for sterilization, disinfection, deodorization, among other things. In order to adequate the ozone for each type of application, defining its concentration is required. Several methods have been developed to measure ozone concentration, such as electrochemical, chemical and ultraviolet (UV absorption).

According to Raknees et al., 1996, ozone concentration measurement by electrochemical method measures the current produced in an electrolytic cell, composed of an anode and a cathode. The current passes through iodine, remaining from a previous chemical reaction. In the chemical method ozone is inserted in Potassium Iodide, producing Iodine. The Iodine is measured as a function of the sodium thiosulphate concentration that indirectly leads to O_3 concentration. In ultraviolet technique the light transmission intensity is determined; ultraviolet light passes through ozone molecules that absorb part of this radiation. This method is based on the portion of the ultraviolet spectrum that is absorbed by the ozone molecules, obeying the Beer-Labert law.

The ultraviolet light transmission phenomenon can be also observed on certain bands of the visible light because ozone absorbs radiation from 200 nm up to about 700 nm. According to Brion et al., 2007, there is four main ozone absorption regions know as Hartley band, Huggins band, Chappuis band and Wulf system. The Hartley band, within the UV region, has the highest ozone absorption, therefore more useful for measuring low O_3 concentrations, ranging from 200 nm to 310 nm, with absorption peak at 253.7 nm. The range from 550 to 650 nm, called Chappuis band, shows that ozone absorbs visible light, however, generally the sensitivity of the detector must be increased, since the absorption coefficient in that band is smaller than in Hartley band. Generally, this band is used to measure higher ozone concentrations.

Considering Chappuis band applications, Flowes and Wayne (1981) developed an apparatus that uses visible light to measure low concentrations of ozone using an LED, emitting at 584 nm, a photodetector and a 0.10 m absorption cell, attesting that greater paths allow smaller concentrations measuring. In the work developed by O'keeffe et al., 2007, an optical path of 1.50 m was used with an LED, emitting at 590 nm, along with a photodiode to measure ozone in higher concentrations compared to Flowes and Wayne. In the research carried out by Teranishi et al., 2011, a 0.50 m absorption cell, an LED at 609 nm and a photodiode were utilized to measure concentrations from 7.3 x 10^{-3} to 70.4 x 10^{-3} kg/m^{-3}. Furthermore, the device developed by Jodpimai et al., 2016, measured the ozone using an LED at 605 nm, with a 0.70 m absorption cell and a photodiode. In this last example, O_3 concentration was manually controlled.

The aim of this project is to develop and test a system capable of producing a controlled ozone atmosphere and measure its concentration. An LED will emit light in the visible bandwidth, at 603 nm, a photodiode and an absorption cell of 0.50 m, are integrated into an ozone generation system. The absorption method in the visible light was chosen due low cost with parts easily found in the local market. The proposed device will be used to analyze the oxidative stability of biofuels, where the ozone is injected in order to reduce oxidation time.

2. MEASUREMENT PROCEDURE

The experiment was carried out based on Beer-Lambert's law, see Eq. (1). The transmitted light is denoted by *I* – light not absorbed by matter, which in this case is the O_3, and I_0 is the incident light intensity, i.e., light coming from the light source and reaching the detector with no ozone interaction. Thus, the transmitted light intensity is the incident light intensity I_0 multiplied by an exponential term, raised to the ozone absorption cross-section, σ, along with the optical path length, l, and the ozone concentration inside the optical cell, c.

$$I(\lambda) = I_0(\lambda)e^{-\sigma lc} \tag{1}$$

Ozone concentration derives from sample transmittance or absorbance, manipulating Eq. (1). The transmittance, defined in Eq. (2), is the ratio between the transmitted and the incident light. The absorbance, Eq. (3), is the amount of light absorbed by the ozone, which is defined by the natural logarithm of the transmittance. The absorbance can also be represented according to Eq. (4) as a linear function.

$$T = \frac{I}{I_0} \tag{2}$$

$$A = -ln(T) \tag{3}$$

$$A = \sigma cl \tag{4}$$

If one knows transmittance and absorbance the actual ozone concentration can be calculated using Eq. (5). The absorption cell length is given in meters (m) and according Brion et al., 2007 the ozone absorption cross-section is 5.23 x 10^{-25} m². To convert the concentration units to kg/m³ one can use the ratio between the ozone molar mass, 47.998 x 10^{-3} kg/mol and the Avogadro number, 6.02 x 10^{23} molecule/mol, according to Eq. (5).

$$c = -\frac{1}{\sigma l}\frac{M}{N}ln\left(\frac{I(\lambda)}{I_0(\lambda)}\right) \tag{5}$$

3. EXPERIMENTAL PROCEDURE

The controlled ozone atmosphere generator is composed of a corona-type O_3 generator, a PWM circuit, an Erlenmeyer flask, a homemade absorption cell; containing an LED as a visible light source, a linear optical path and a silicon photodiode as light detector; a signal conditioning system, and a data acquisition system. The apparatus is shown in Fig. 1.

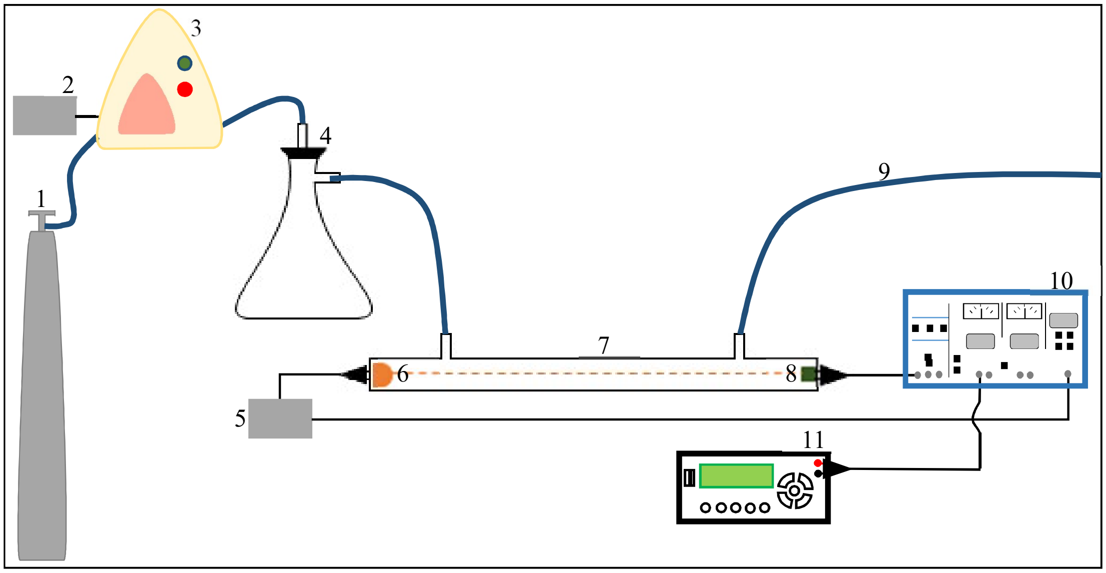

Figure 1. Schematic diagram of the developed apparatus. (1) Oxygen, (2) PWM circuit, (3) Ozone generator, (4) Erlenmeyer flask, (5) Current source, (6) LED, (7) Absorption cell, (8) Photodiode, 9) Ozone, (10) Lock-In, (11) Bench Multimeter.

The ozone generator is a Vigor® model Y605, the Erlenmeyer flask works as a reservoir used to vary the ozone concentration, the absorption cell is composed of a polyvinyl chloride (PVC) pipe used as optical path with 1.27×10^{-2} m diameter, which has a 603 nm LED in one of its ends, and a BPW34 photodiode at the opposite side. At the tube ends, two connections were mounted perpendicular to the sensing device, one serves as a gas inlet and the other as outlet. A pulsed current source was developed to power the LED, which has its wavelength within the Chappuis band. The current source is featured allowing the control of the light intensity and frequency. A Stanford Research Systems® Lock-In, model SR530, was employed to perform the signal conditioning, and hence, the transmitted light can be properly measured. The data is, then, collected through a Rigol® DM3062 digital multimeter.

All the tests were carried out according to the following procedure: at the beginning, pure oxygen is inserted inside the cell and the light intensity of free-ozone cell is measured for 10 s (100% transmittance). Then, the ozone generator is turned on allowing O_3 pass throughout the absorption cell, and new measurements are performed.

During the first round of testing, the PWM circuit and the Erlenmeyer flask were removed from the apparatus and the effect of the optical path on the absorbance was evaluated. In this case, five different tube lengths rating 1.00, 0.75, 0.50, 0.25 and 0.10 m were used as optical pass. Oxygen was inserted in the five cells for 10 seconds and then the ozone generator was turned on for a period of 120 seconds. After that time, the O_3 generator was turned off, awaiting the complete dispersion of the ozone inside the cell through the outlet connection.

In the second round of tests, the 0.5 m cell was used and the system response was evaluated as a function of the relative concentration and the generator duty cycles of 17%, 33%, 50 %, 75% and 83%. The ozone concentration was controlled by varying this parameter (duty cycle) through the PWM circuit. Using an on-off period of 30 s for the PWM driver, varying this driver duty-cycle and mixing ozone and O_2 inside the Erlenmeyer flask, it was possible to manipulate the ozone concentration inside the absorption cell.

4. RESULTS AND DISCUSSIONS

In the first round of testing, for a constant ozone concentration, it was observed that as the length of the absorption cell increased, the transmittance decreased. Since the ozone generator was kept on for 120 s for each investigated absorption cells, it was possible to detect the decrease in the transmittance, the stabilization of the ozone concentration and, 20 s after the generator is turned off transmittance returns to 100%. In Fig. 2, the transmittance is shown for each tested absorption cells. Notice that the shorter the absorption cell length the higher its transmittance is. This result is in accordance to Beer-Lambert law.

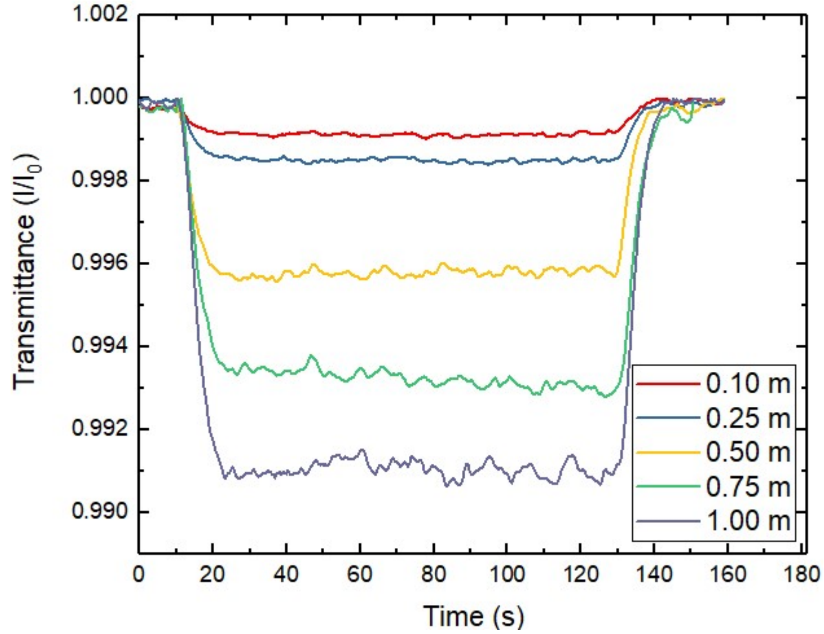

Figure 2. Transmittance (I/I_0) versus time (s)

When ozone concentration inside the absorption cells is below a certain limit, observed transmittance variation is small for all tested cells, independently of its length. In this case, the exponential function described by Beer-Lambert law becomes approximately a linear function.

According Beer-Lambert law absorbance is a function starting at zero, since there is no absorption when O_3 concentration is null. Based on Eq. (4), when the concentration and the absorption cross-section are constant, the variation of the absorbance occurs only when the absorption length varies. By making the cell bigger, the absorbance fatally increases. This linear behavior is shown in Fig. 3.

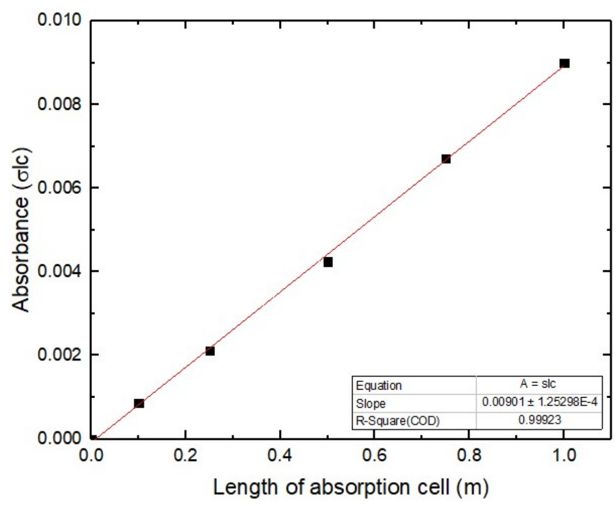

Figure 3. Absorbance (σcl) versus length of absorption cell (m)

From the first round of tests was verified that the length of 0.50 m was the best choice for the absorption cell, despite the fact that 0.10, 0.25 and 0.50 m lengths have presented close results regarding O_3 concentration. While optical paths of 0.75 and 1.00 m show certain discrepancy on measuring O_3 concentration. However, 0.50 m optical length presented a better responsiveness and resolution on concentration. In the second round of testing, in addition to the 0.50 m tube the PWM circuit was used to vary the ozone generator duty cycle, as well as an Erlenmeyer flask used to store the produced ozone.

Using the relationship between absorbance and optical length it's possible to corelate angular coefficient, obtained in Fig. 3, with the term *σc*, given by Eq. (4). The ozone absorption cross-section, *σ*, is 5.23 x 10^{-25} m² so the ozone concentration used in this measurement can be calculated and is given by 1.40 x 10^{-3} kg/m³. This concentration is more than ten thousand times bigger than O_3 concentration considered air quality guideline by World Health Organization (WHO), 2005.

In the second round, measurements were carried out changing the duty cycle in order to vary the ozone concentration. For 17% duty cycle, the quantity of ozone circulating inside the Erlenmeyer flask is less than the volume of oxygen, creating a lower O_3 concentration atmosphere, leading to lower absorption and higher transmittance. As expected with other duty cycles, more O_3 was present inside the Erlenmeyer flask, increasing in concentration. The results are shown in Fig. 4.

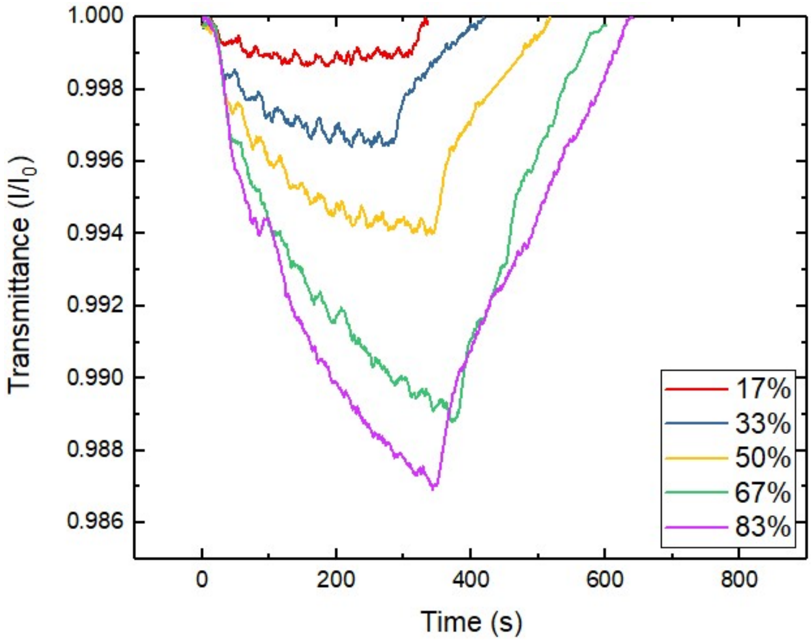

Figure 4. Variation of transmittance for different duty cycles

5. CONCLUSIONS

Using a commercial ozone generator and a PWM drive circuit was possible produce different O_3 concentrations inside an Erlenmeyer flask and measure those different concentrations using a homemade absorption cell. The developed device, based on an LED emitting visible light at 603 nm, used a silicon photodiode as light absorption detector. Different optical path lengths were tested but better responsiveness and concentration resolution was obtained with the 0.5 m cell. Absorbance and transmittance for ozone inside the cells could be determined from experimental data. Keeping the ozone concentration constant and varying the optical path length of the absorption cells shows a Beer-Lambert behavior.

6. ACKNOWLEDGEMENTS

The presented work was supported by the team working at Laboratório de Propriedades Ópticas (LaPO) - UFBA and by its coordinator, professor Dr. Iuri Pepe, who remarkably contributed to the success of the present project. The acknowledgment must also be extended to Leandro Rozário, José Alejandro Moreno, Marcus Lima, who played an essential role in all the development path. Finally, many thanks to Coordenação de Aperfeiçoamento de Ensino Superior (Capes) that provided the financial support.

7. REFERENCES

Brion, J., Chakir, A., Charbonnier, J., Daumont, D., Parisse, C., & Malicet, J. (1998). "Absorption spectra measurements for the ozone molecule in the 350–830 nm region." *Journal of atmospheric chemistry*, *30*(2), 291-299.

Fowles, M., & Wayne, R. P. (1981). Ozone monitor using an LED source. *Journal of Physics E: Scientific Instruments*, *14*(10), 1143.

Georgiev, V. F., Batakliev, T. T., Anachkov, M. P., & Rakovski, S. K. (2015). “Study of ozonated olive oil: monitoring of the ozone absorption and analysis of the obtained functional groups.” *Ozone: Science & Engineering*, *37*(1), 55-61.

Jodpimai, S., Boonduang, S., & Limsuwan, P. (2016). “Inline ozone concentration measurement by a visible absorption method at wavelength 605 nm.” *Sensors and Actuators B: Chemical*, *222*, 8-14.

O’keeffe, S., Fitzpatrick, C., & Lewis, E. (2007). “An optical fibre based ultra violet and visible absorption spectroscopy system for ozone concentration monitoring.” *Sensors and Actuators B: Chemical*, *125*(2), 372-378.

Rakness, K.; Gordon, G.; Langlais, B.; Masschelein, W.; Matsumoto, N.; Richard, Y.; Robson, C.; & Somiya, I. (1996). “Guideline for measurement of ozone concentration in the process gas from an ozone generator.” *Ozone: Science & Engineering*.

Teranishi, K., Shimomura, N., & Itoh, H. (2010). “Measurement of Ozone Concentration Based on Visible Photo-Absorption Method.” In *Proc. 12th Int. Symp. High Pressure, Low Temperature Plasma Chem* (Vol. 2, pp. 325-328).

WHO, 2005. “Air quality guidelines – global update 2005”. 10 Out. 2017 <http://www.who.int/phe/health_topics/outdoorair/outdoorair_aqg/en/>.

8. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.