Efficient Compact Micro DBD Plasma Reactor for Ozone Generation for Industrial Application in Liquid and Gas Phase Systems

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Abstract—Ozone is well known as a powerful, fast reacting oxidant. Ozone based processes produce no by-product residual as non-reacted ozone decomposes to molecular oxygen. Therefore an application of ozone is widely accepted as one of the main approaches for a Sustainable and Clean Technologies development.

There are number of technologies which require ozone to be delivered to specific points of a production network or reactors construction. Due to space constraints, high reactivity and short life time of ozone the use of ozone generators even of a bench top scale is practically limited. This requires development of mini/micro scale ozone generator which can be directly incorporated into production units.

Our report presents a feasibility study of a new micro scale rector for ozone generation (MROG). Data on MROG calibration and indigo decomposition at different operation conditions are presented.

At selected operation conditions with residence time of 0.25 s the process of ozone generation is not limited by reaction rate and the amount of ozone produced is a function of power applied. It was shown that the MROG is capable to produce ozone at voltage level starting from 3.5kV with ozone concentration of 5.28×10^{-6} (mol/L) at 5kV. This is in line with data presented on numerical investigation for a MROG. It was shown that in compare to a conventional ozone generator, MROG has lower power consumption at low voltages and atmospheric pressure.

The MROG construction makes it applicable for both submerged and dry systems. With a robust compact design MROG can be used as an integrated module for production lines of high complexity.

Keywords—DBD, micro reactor, ozone, plasma.

I. INTRODUCTION

OZONE is an inorganic compound that consists of three oxygen atoms arranged in a linear structure. It occurs naturally in the earth's atmosphere when oxygen activated by UV light, it can also be produced in thunderstorms and other types of electrical discharges [1]. It is artificially produced in photocopiers, electric motors, etc.

Ozone is known as a powerful oxidant [2], [3] with an oxidation potential of 2.07 V. It has been successfully used in varies applications including bacteria, algae, spores killing and vanishing volatile organic compounds, odor treatment,

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enhancing fertilization and water treatment [4].

Conventionally, non-thermal corona discharges are one of the most common ways to produce ozone at large scale [5]. In general, industrial corona reactors are not flexible in operation and usually produce ozone in excess that is expensive to be disposed. Ozone production at industrial scale of corona reactors requires specialized high voltage power generators and dedicated physical infrastructure [6]. Large scale unit operation at relatively high current and voltage results to high power consumption. This makes ozone production energy intensive.

All notes above lead to high capital investment and limit wide ozone application for industrial use.

Electric discharge approaches for ozone production usually accompanied by formation of some intermediate species of oxygen - oxygen radicals and ions [7]. These intermediate species has a life time similar to a short ozone recombination time. Therefore ozone based processes are considered as a clean technology with high attention given for further development and application.

Practically, there are number of ozone involved applications require ozone to be delivered to specific points along the production pipe network. However, due to constraints of modern chemical reactor construction -- high reactivity and short ozone life time -- the use of standard ozone generators with a single point of ozone injection to the reaction volume is limited [5], [8]. This demands development of mini/micro scale ozone generation units that can be directly incorporated into a certain points of pipeline or reaction volume.

Miniaturized dielectric barrier discharge (DBD) plasma reactors are good alternative to corona one. DBD plasma reactors can operate at atmospheric pressure, at room temperature, use air as a feed gas and ignite plasma at lower voltage in compare to corona reactors.

Our research aimed to develop a low power consumption DBD plasma reactor with possibility to *in-situ* ozone generation to the liquids of interest. Our report presents a feasibility study of a new micro scale rector for ozone generation (MROG).

II. NUMERICAL ANALYSIS OF DBD DOWNSCALING PROCESS

In a plasma discharge the electric field transfers energy to the charged particles, a small portion of this energy is consumed in elastic collisions that increase the gas temperature and the rest is spent on increasing the internal

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energy of atoms and molecules. This energy transfer can be accounted for with the heat transfer equation:

$$\rho_m C_p \left[\frac{\partial T}{\partial t} + (v \cdot \nabla T) \right] = k\nabla^2 T + \sigma E^2 + S_{jE} \qquad (1)$$

where C_p is the specific heat (at constant pressure) and k is the thermal conductivity of the fluid. On the left hand side, there are the accumulation and convection terms. The first term on the right hand side is the thermal diffusivity term, the second term is the Joule heating term, and the third term is the source of heat, S_{jE} which will be ignored in the present analysis because it does not scale with any spatial parameters, it depends on the densities of the particular atomic or molecular system under consideration which cannot be known a priori [9]. Following the application of the electric field, the temperature field reaches a stationary state in a time of the order of $t = (\rho_m C_p l^2)/k$. For an oxygen discharge with a gas density, $\rho_m = 1.3$ Kg/m^3, Cp of around 0.92 KJ/Kg K and $k = 2.6 \times 10^{-2}$ W/(m K) at Tg=300 K, the relaxation time is of the order of 4 milliseconds.

The relationship between heat convection and heat diffusion is given by the Peclet number

$$\left| \rho_m C_p (v \cdot \nabla) T / k\nabla^2 T \right| \approx P_e = \rho_m C_p v l / k \approx 10^{-2} \qquad (2)$$

Which for a micro DBD reactor it turns out to be a small number, which means diffusion dominates over convection. Therefore, in steady state (when $\partial T/\partial t = 0$ and the l.h.s of (1) vanishes) the temperature equation reduces to the Poisson's equation, with Joule heating as the energy source

$$|k\nabla^2 T| = -\sigma \langle E^2 \rangle \qquad (3)$$

An order of magnitude estimate of the incremental temperature rise inside the DBD plasma reactor can be made by substituting for the electric field in (3) to obtain

$$kT/l^2 \approx \sigma V^2 / 2l^2 \qquad (4)$$

where V is the amplitude of the applied voltage.

It can be seen that the temperature increment does not depend on any spatial parameter directly, but since the reduced electric field (E/N) is an invariant of the discharge -it is kept constant- then in order to keep the reduced field constant, the external applied voltage must be decreased as the dimensions of the system are reduced. As it follows from (4) the reduction in scale demands a reduction in voltage, and in turn, an effective reduction in the temperature increment is expected.

This implies that micro DBD plasma reactors can operate at much lower temperatures than their conventional counterparts. This is an important feature that could reduce the operative costs of these micro devices, and in the case of an oxygen discharge this is a very attractive feature for ozone production which is favored at low temperatures [9].

In addition, decreasing the external voltage to meet the temperature demand helps in maintaining the discharge in a regime of low power consumption.

III. DBD PLASMA UNIT

Fig. 1 presents a principal diagram of PEEK made DBD plasma unit which consists of a pair of parallel circular copper electrodes 28mm in diameter. Each electrode is covered by a dielectric barrier, made of 140μm thick glass. The pair forms a gap of 300μm for plasma operation. The plasma unit has inlet through the central hole of the rod. Gas further flows to the inter electrode gap. After plasma treatment an ozone containing mixture exits the inter electrode gap via arrangement of axial nozzles and overfills the plasma unit chamber to be delivered into ambient.
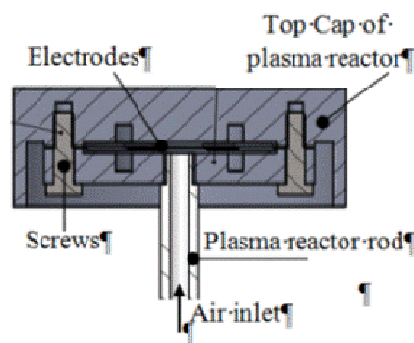

Fig. 1 Diagram of the plasma unit

IV. THE EXPERIMENTAL SETUP

The core of experimental setup, Fig. 2, is a 2L of volume cylindrical stainless steel reactor with the plasma unit coupled with the diffuser and incorporated at the bottom of the reactor.

Gas inlet made through the bottom flange of the cylindrical reactor and outlet is done through the top flange. Powering cables were connected to the plasma unit via isolated ports. Voltage level and frequency readings were done with application of high voltage (HV) probe and the oscillator.

V. MATERIALS AND METHODS

The plasma unit was powered by the custom made 500W power supply at 5 kV and 50 kHz. In order to characterize the power supply a high voltage probe TES TEC HVP-15 HF was used in combination with a computer controlled Picoscope ADC-212 oscilloscope. Current measurement was done with application of Tecpel DCM-033 Digital Clamp Meter.

The ozone concentration was measured by the indigo method [10]. This method is widely accepted as very sensitive, precise and fast approach for ozone measurement. Ozone decolorizes the indigo solution by cleavage of indigo bonds. The reaction leads to formation of a colorless product.

The calculation of ozone concentration using the indigo reagent is based on a ratio where 1 mol of decolorized indigo is equal to 1 mol of ozone detected, assuming that the applied potassium indigo trisulfonate was pure. The decolorization value was measured using a spectrophotometer DR 2800 Hach-Lange.

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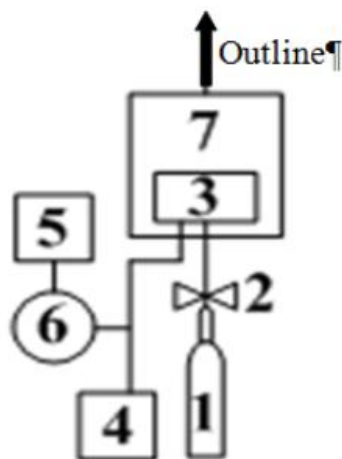Vol:8, No:1, 2014

Fig. 2 Principal diagram of the setup and the measurement system 1 - gas cylinder, 2 - gas regulator, 3 - plasma unit, 4 - HV power supply, 5 - oscilloscope, 6 - High Voltage probe, 7 - reactor

The change in light absorbance at 600nm indicates the amount of indigo reacted which is proportional to the ozone concentration. Equation (5) presents calculation of indigo concentration in the stock solution

$$C_{ss} = \frac{m_{pi}}{mw_{pi}} \times \frac{1}{V_T} \qquad (5)$$

where C_{ss} is the concentration of stock solution (mol/L), m_{pi} is the mass of potassium indigo (g), mw_{pi} is the molecular weight of potassium indigo (g/mol) and V_T is the total volume of the mixture (L).

Stock indigo solution (SIS) was prepared by mixing 0.385 g of potassium indigo trisulfonate and 0.5ml of concentrated phosphoric acid in 500 ml of distilled water (DIW). The working solution (WS) was prepared by diluting of 20ml SIS in 1-L of DIW with addition 10g of sodium dihydrogen phosphate and 7ml of concentrated phosphoric acid. Equation (6) shows the calculation of the indigo concentration in the WS

$$C_{ws} = \frac{C_{ss} \times V_{iw}}{V_T} \qquad (6)$$

where C_{ws} is the concentration of the working solution (mol/L), V_{iw} is the volume of indigo in the working solution (L).

Ozone concentrations were determined by using a calibration curve. Calibration solutions (CS) were prepared by diluting 5ml of WS into several volumes of DIW (5ml, 10ml, 15ml, 20ml, and 25ml). The calculation of the indigo concentration in a CS (C_{cs}) was done in accordance to (7). To perform the calibration, the absorbance of a set of CS's was plotted against indigo concentration

$$C_{cs} = \frac{C_{ws} \times V_{ic}}{V_T} \qquad (7)$$

where V_{ic} is the volume of indigo in the calibration solution

(L). The SIS used in this work was a fresh solution applied straight after synthesis. The remaining stock was stored in dark and cold condition to prevent degradation. Basically, the degradation can be characterized by a reduction in absorbance below 80% of the initial value, which typically happens within 3-4 months of storage.

During experimentation the ozone concentration was measured both in the water and gas phase as function of air flow rate at fixed voltage level and at different voltage with stable air flow rate.

Measurement of ozone content in the gas phase is conducted by flushing the ozone containing mixture coming from outlet of reactor through indigo solution with use of a washing flask for a given time. The change in absorbance of indigo solution before and after ozone containing mixture bubbling gave the concentration of the ozone in the gas phase.

For ozone concentration measurement in the liquid phase we have applied in-house developed approach. The 4mL of ozone contained water sample was taken from the reactor to the syringe preloaded with 4mL of indigo solution. After a sample loading syringe content was mixed up by vibration for 5 minutes followed by analysis on spectrophotometer. Dilution 1/1 factor was taken into account. The change in absorbance of indigo solution before and after sampling gave the concentration of the ozone in the liquid phase.

VI. RESULTS AND DISCUSSION

Fig. 3 plots CS series against absorbance at 600 nm using a fixed volume of WS (5mL) diluted in different proportions with DIW to obtain the calibration curve.
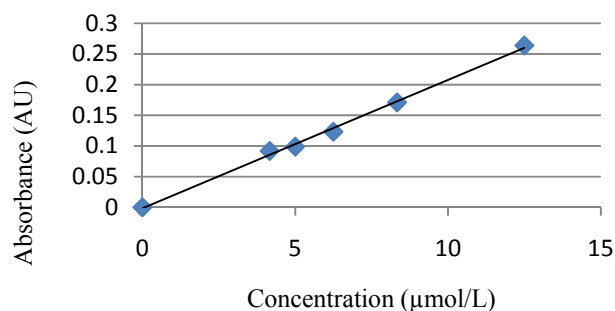

Fig. 3 Calibration curve of ozone concentration

The PEEK made plasma unit investigated in this research was designed to work at voltage up to 6 kV. From our experimental experience an optimal "safe" voltage level for this type of unit is 4kV.

Therefore investigation of air flow rate influence to the ozone productivity carried out at 4 kV. Reactor was filled with 1.5 L of DIW. Ozone production time was set to 2 minutes.

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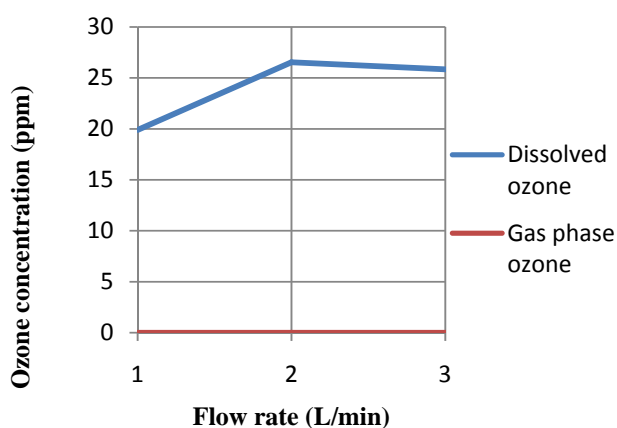International Journal of Chemical and Molecular Engineering
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Fig. 4 Ozone concentrations at different air flow rates

It was found for applied conditions, Fig. 4, that maximum ozone production level reached 26 ppm at air flow rate of 2 L/min. At lower flow rate, 1 L/min, the process of ozone production was limited by mass transfer of oxygen. At higher air flow rate, 3 L/min the level of dissolved ozone is practically constant.

It is important to note that for this experimental set ozone was not detected in the gas phase. This can be described by fast ozone diffusion to the water [11] and by the method of ozone injection. Ozone was introduced to the DIW in form of bubbles with 800 μm diameter. Smaller bubbles remain longer in the balk of the liquid in provide large gas-liquid contact area which significantly enhances ozone dissolving process.

To estimate an energy consumption basic equation for power (7) and energy (8) were applied.

$$P = VI \qquad (8)$$

where P is power (W), V - voltage level (V), I - current (A).

For applied voltage V = 4 kV and measured current of 25 mA the power was equal to 100 W.

$$E = P\Delta t \qquad (9)$$

where E is energy (kW*h), P is power (kW), Δt is period of plasma treatment (hour).

From our experimental data an energy consumption for selected conditions was equal to 3.3×10^{-3} (kW*h).

In order to characterize the plasma unit ozone productivity as function of voltage level the extended voltage range at 2 L/min of air flow rate was applied. The experimentation started from optimal 4kV level and ended up at 5kV. The range from the top was limited by technical characteristics of the power supply available. Treatment time was set to 2 minutes. Reactor was loaded with 1.5L of DIW.

It was found that concentration of dissolved ozone was stable at 26ppm over the tested range of voltage. The gas phase ozone was first detected at 4.4kV. The maximum 52ppm of gas phase ozone concentration was obtained at 4.8kV and it was at the same level up to 5kV.

Experimental data shown that at power consumption of 4×10^{-3} (kW*h) the unit was able to produce 78ppm of ozone in total. To avoid ozone production in excess for air flow rate of 2 L/min the voltage level should not exceed 4.4kV.

VII. CONCLUSION

With feasibility study of the DBD microplasma unit detailed above, we have proven that the plasma unit of new design is able to generate ozone while immersed. We have demonstrated that our experimental data is in good agreement with the numerical analysis of DBD downscaling in terms of lower power consumption for effective ozone production.

The unit operation conditions were optimized for different air flow rates and voltage levels to obtain high dissolved ozone concentration and avoid ozone off-gas.

This study contributes to development and industrial application of plasma micro reactors and to evolution of ozone based techniques within the mainstream of clean technologies.

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