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DISCHARGE IN FOAM BUBBLES**

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ABSTRACT

The method of generation of hydroxyl peroxide and ozone using the cylindrical foaming apparatus are presented in this paper. High concentration of H_2O_2 and low concentration of ozone were obtained as a result of the electrical discharge in humid foam environment. Despite of the small amount of required liquid, this system could be applied not only for polluted gas treatment but also for specific type of water and wastewater purification.

INTRODUCTION

The treatment of increasing amount of exhausted gases and wastewaters as same as gaining water of the certain quality became a severe problem of the present times. The Advanced Oxidation Technologies, acquired popularity and reliance in above areas. The application of ozone (O_3), hydrogen peroxide (H_2O_2) or OH radicals could be fruitful for the removal of many kinds of pollutants.

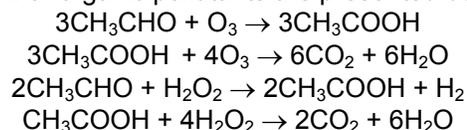
Ozone is traditionally generated in dry oxygen or air as a result of barrier or surface discharge between two electrodes (where one at least is covered by dielectric layer) using devices called ozonizers [1]. The huge energy losses take place during the ozone generation and its transportation process. The ozone's lifetime is short and O_3 decomposes during its transportation, so it cannot be stored and must be produced in the place of application. Despite of costs, ozone already replaced chlorine installation in the paper industry [2] and the

biggest installations for ozone generation were built for this peculiar purpose.

Hydrogen peroxide is manufactured in large amounts by the chemical and electrochemical methods. It can be stored and dosed separately during the treatment process. H_2O_2 is usually combined with the other treatment methods e.g. with ozone to enhance the OH radicals formation. Current techniques are based on "in situ" ozone generation and the separate addition of hydrogen peroxide to the reaction zone. Some researchers however, try to avoid the transportation losses by the designing new kinds of reactors, which allow for simultaneous generation of various oxidants in the same reaction zone [3,4].

The electrical discharge might be applied directly in foam, partly consisted of pollutant. Foaming column became the various oxidants generator and the reaction vessel in the same time. The losses of oxidants in the providing system could be reduced. The operation spectrum of such an installation can be widened because of superposition effect.

The examples of chemical reactions of active oxidants with organic pollutants are presented below:



Foam is a kind of the colloidal structure, the highly concentrated dispersions of gas in a two-phase

system with a gas phase as a dispersed phase and the liquid matrix (dispersion medium or continuous phase) [5,6].

Foam properties and the size of the bubbles depend on several factors, e.g. composition of the solution, eventual surfactant, eventual contaminants, foam formation and environment.

Foams can be divided into two categories depending on the method of generation [7]:

- homogenous, (standing) foams
- pneumatic (dynamic) foams

During the foam production, several transition structures can occur. The foam density is decreasing with the height of the apparatus. Two extreme types of foam structures are: sphere and polyhedral foam.

The most of foams are produced using the surface-active compounds. However, foams created without any surfactants were the most desirable from the environmental point of view.

Pneumatic foam without surfactant could be formed without the addition of any foaming agents using only the gas kinetic energy, keeping the strict conditions of the medium flow and using the diffusers. Co-current flow, when gas and liquid flow through the same diffuser's hole, allowed for the appropriate inside-area usage, [8,9].

The general rules concerning the flow and the apparatus-construction limits for the foam environment creation are presented below:

- Linear velocity of substrate gas for whole apparatus cross-section (VC): 0.1-4.0 m/s,
- Gas velocity in the diffuser hole (VD): 10-20 m/s,
- Diffuser's perforation level: 5-20% of whole shelf area.

Bistron mentioned that in the dynamic foam conditions, the increasing of inter-phase surface leads to the significant increasing (comparing with typical bubbling process) of mass and heat exchange coefficients.

In this paper the foaming system was proposed, the discharge occurred in the humid environment- foam. The experiments using both kinds of foam were performed. The generation of oxidants was observed.

Additionally, the significant expansion of the surface of contact between gaseous and liquid phase was noted. Both of phases can consist partly of the polluted medium, which makes possible the applications for various purposes (including the exhaust gas treatment).

NOMENCLATURE

Acetaldehyde, Foam, Hydrogen Peroxide, Ozone

EXPERIMENTAL SET-UP

The set-up consisted of the foaming sub-system (gas and liquid providing), the electrical discharge sub-system and the chemical analysis sub-system.

Main reactor, presented in Fig.1. was a cylindrical, polyacrylate column ($D_{in}=50$ mm, $L=200$ mm). The apparatus was designed to maintain the appropriate flow of media, which is necessary for dynamic, surfactant-free foam formation. The column was connected to the liquid and gas providing system. In the performed

investigations pure water or pure water with addition of common surfactant (1ml/500ml H_2O) was used as a substrate liquid. Substrate gases were air, oxygen and acetaldehyde with nitrogen as a carrying gas.

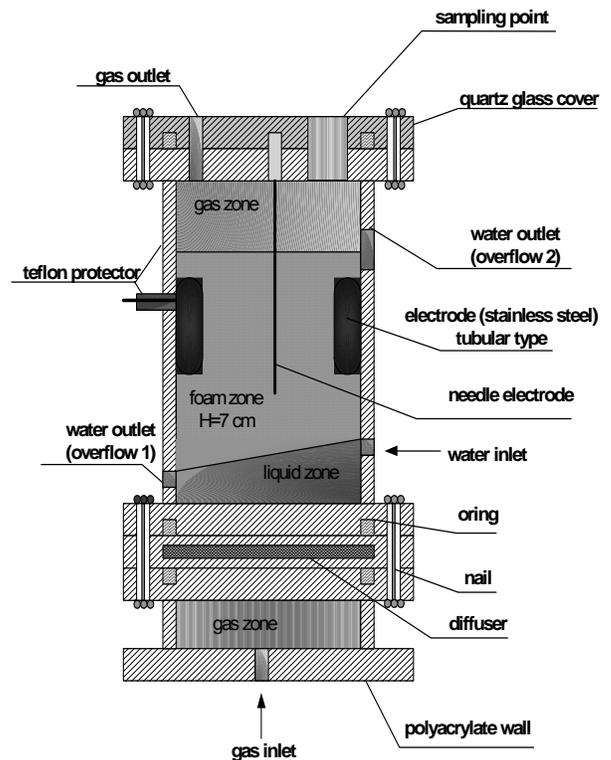


Fig. 1. Cylindrical foaming column.

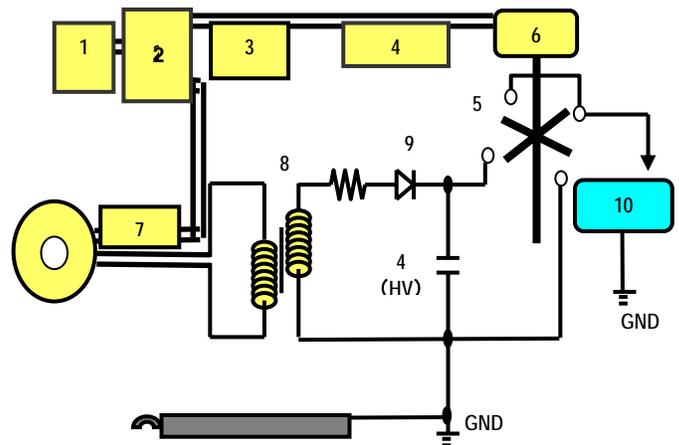


Fig. 2. Electrical circuit.

- (1- AC 100V, 2- breaker, 3- switch, 4- capacitor,
- 5- rotary spark gap, 6- motor, 7- switch, 8- transformer,
- 9- diode (10kΩ), 10- reactor).

A ceramic diffuser (type IA-500 of mainly aluminum oxide) was placed perpendicularly to the flow direction of media. Gas was added in the lowest part of the apparatus using the gas inlet. Gas was uniformly

distributed during passing through the diffuser. Initially, small amount of liquid was dosed on its surface. The droplets of liquid were carried by the gas through the diffuser and the foam zone was formed in the column.

The electrodes were located in homogenous foam zone, above the diffuser. The inner electrode (stainless steel tube $d_{out}=1.5$ mm) was placed inside the outer electrode (stainless steel ring $d_{in}=40$ mm, $l=30$ mm).

Quartz glass window was put on the top of the apparatus.

The electrical circuit is presented in Fig.2. The pulse power source was operated at 250 Hz. The discharge voltage and current were measured using the high voltage probe (Tektronix, model P6015A) and the current probe (Tektronix, model P6021) with an oscilloscope (Tektronix, model TDS 644A), respectively.

The discharge pictures were taken using the digital camera Olympus Camedia X-2.

Chemical measurements and analytical system

Measurements of concentrations of gaseous hydrogen peroxide (H_2O_2), gaseous ozone O_3 , and acetaldehyde were performed during the experiment.

The hydrogen peroxide concentration was determined using Hydrogen Peroxide Test Kit (HACH, Model HYP-1). Thiosulfate titration of the sample (liquid after discharge application, mixed with specially formulated starch-iodide reagent used in hydrogen peroxide tests and with ammonium molybdate reagent) was performed in a low pH (pH=3.5) condition.

The ozone concentration in the outlet gas was measured using the GASTEC and KITAGAWA ozone gas probes. Outlet gas was collected in the gasbags and sampled.

The acetaldehyde concentration was measured using GASTEC and KITAGAWA acetaldehyde gas probes and gas chromatography (SHIMADZU GC-14B).

RESULTS AND DISCUSSION

Foam Structure in the Reactor

The construction of the apparatus assured the creation of dynamic foam.

Average diameter of single bubble in foam ranged from 1 mm to 5 mm. The diameters of bubbles tended to be bigger (connecting to each other and then sharing their lamella) with increasing the distance from the diffuser and with increasing the substrate gas flow as well. The dosing of the additional amount of water caused the bubble diameter to decrease.

Electrical Properties of the Discharge

Generally, several types of discharges were obtained in dynamic foam. The discharges however, were not totally uniform. The photo of the discharge in foam from the backside of the column is presented in Fig.3. Typical applied voltage and current waveforms for various substrate gases are shown in Fig.4. The photos of the discharge in various gases, taken from the topside of the column are presented in Fig. 5.

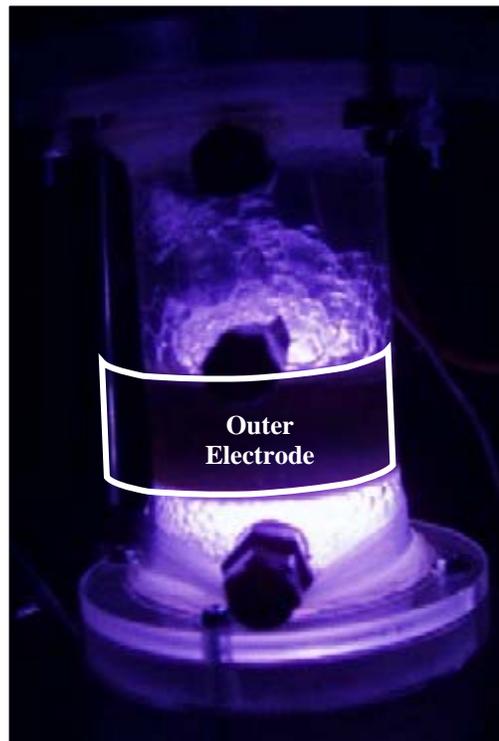
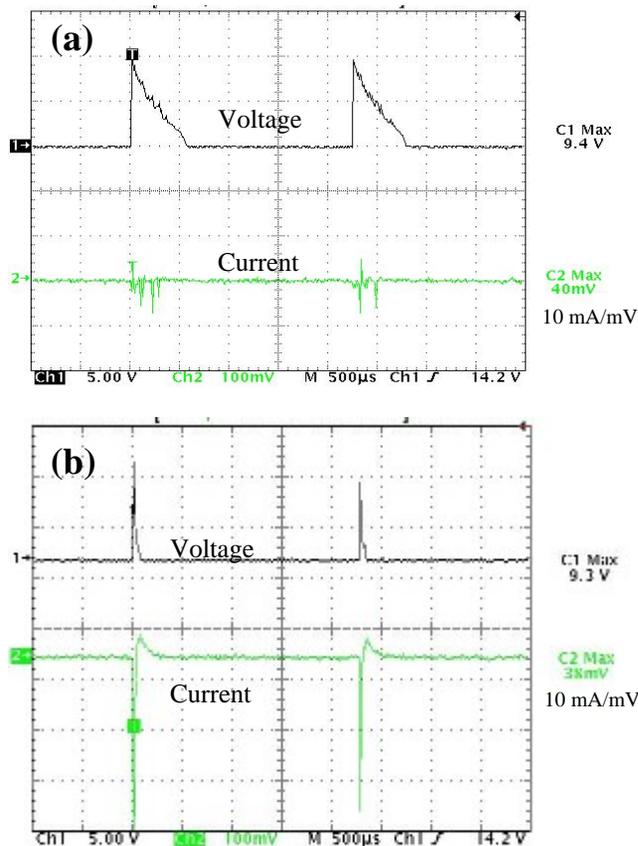


Fig. 3. The photo of the discharge in foam. Gas flow rate 5 l/min, acetaldehyde (40 ppm) in nitrogen, total power 60 W.



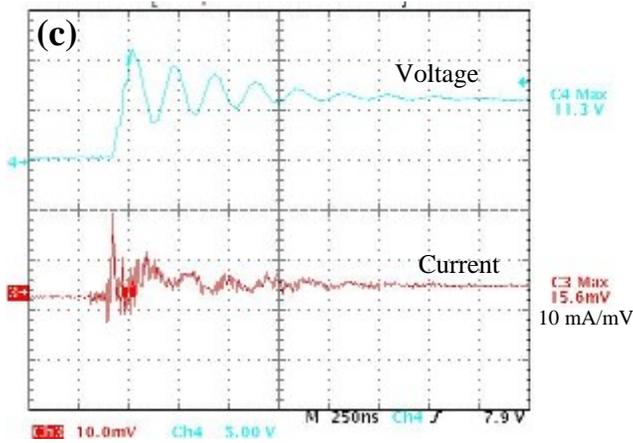


Fig. 4. Typical applied voltage and current waveforms of the discharge in oxygen (a), air (b) and acetaldehyde (40 ppm) in nitrogen (c). Gas flow rate 5 l/min, total power 40 W.

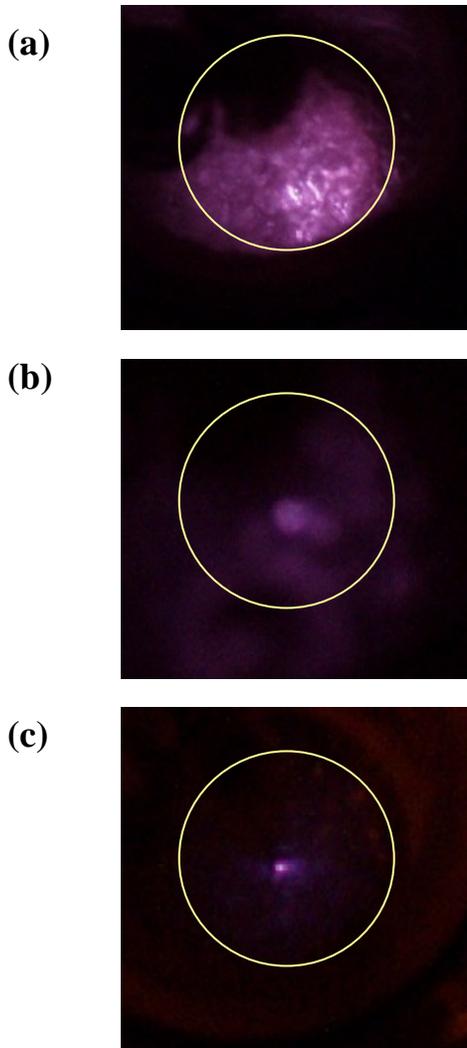


Fig. 5. Photos of the discharge in oxygen (a), air (b) and acetaldehyde (40 ppm) in nitrogen (c). Gas flow rate 5 l/min, total power 40 W.

The discharge intensity was increased with the increasing of applied voltage and the gas flow rate.

Oxidants' Formation

Proceeding of various reactions' chains, leading to the formation of several oxidants was expected in the humid environment [10]. The generation of hydrogen peroxide, hydroxyl radicals, gaseous and dissolved ozone was possible in foam during the competitive, sequential reactions. The measurements were performed to confirm the presence of hydrogen peroxide and gaseous ozone.

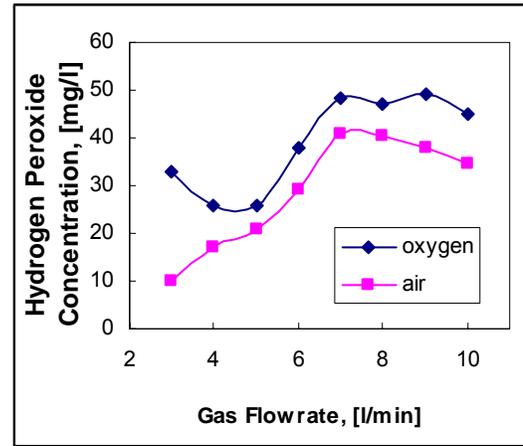


Fig.6. The hydrogen peroxide concentration in dependence on the gas flow. Total power 40 W.

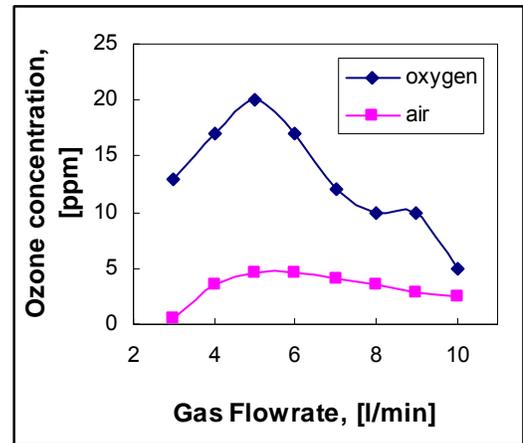


Fig.7. The ozone concentration in dependence on the gas flow. Total power 40 W.

The concentration of hydrogen peroxide in cylindrical column was shown in Fig. 6. The amount of H₂O₂ ranged 55 mg/l and was highest for the limits of gas flow where foam was most stable and uniform. Slightly higher values were obtained for oxygen. The small amount of gaseous ozone was also detected. The ozone concentration in dependence on the gas flow rate is shown in Fig. 7.

Generally, with the higher applied voltage, the concentration of oxidants increased as expected. For the relatively low gas flow rate for the formation of foam in the column, only low concentration of hydrogen peroxide was achieved. With slight increasing, concentration of oxidants tended to increase as well. In the accordance to the literature data, in a low gas flow rate it is easier to generate multi-channel discharges. Thus, the volume, where the active species are generated is more extended than in the case of one arc channel. With the high gas flow rate the discharge character changed, the arcing phenomena took place and the concentration of oxidants decreased.

CONCLUSIONS

An apparatus based on the discharge in the foam was designed.

Foam was obtained without the dosing of the surface-active substances keeping the strict conditions of the gas flow rate and with the addition of surfactant.

The high amount of hydrogen peroxide and low amount of gaseous ozone were formed within foam. The combination of various kinds of oxidants makes foam belong to the Advanced Oxidation Processes.

The foaming system allows obtaining various species in one compact apparatus, potentially even directly in the polluted medium and it connects in one body the advantages of oxidants' generator and the reaction vessel.

ACKNOWLEDGMENTS

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