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Possibilities of VOC Treatment in Cylindrical Foaming Reactor

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Abstract

The possibility of the treatment of VOC in the cylindrical foaming reactor is presented. About 55 mg/l of H₂O₂ and 20 ppm of O₃ were formed within the foam as an effect of the electrical discharges in oxygen. The experiments evaluating the absorption range of acetaldehyde within foam formed with pure water and additionally with the solution of surfactant in pure water were performed. The influence of the electrical discharge on the absorption and on the decomposition of acetaldehyde was observed.

1. Introduction of the foaming system

The problems of accretive devastation of natural environment and the increasing emissions of pollutants gain recently much attention of the authorities and local communities. It is necessary to develop new, environmentally safe techniques of production of goods, and also of recycling and utilization of wastes.

In this paper a foaming system is proposed. Despite of the small amount of required liquid, foaming column could be applied not only for polluted gas treatment but also for specific type of water and wastewater purification. The electrical discharge might be applied directly in foam, partly consisted of pollutant. Foaming column became the generator of various oxidants and the reaction vessel in the same time. The losses of oxidants in the providing system could be reduced.

Foam belongs to the special colloids group [1,2]. It can be generated in various ways in dependence of the required structure. On the base of those qualities foams are categorized as homogenous, (standing) and pneumatic (dynamic) foams [3], which both ensure the significant expansion of the contact surface between gaseous and liquid phases.

The most of foams are produced using the surface active compounds. However, foams created without any surfactants were very desirable from the environmental point of view. The experiments using this kind of foam, generated from gas and pure water only were performed as well as with the addition of the surface active substance to improve the absorption, to lower the gas flow limits and to avoid the pressure losses.

Pneumatic foam in presented experiments was 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 [4]. The linear velocity of substrate gas for whole apparatus cross-section for dynamic foam should range 0.1-4.0 m/s, the gas velocity in the diffuser hole - 10-20 m/s, and 5-20% perforation of whole shelf area of the diffuser is advised.

2. Acetaldehyde as a substrate for technology and as an undesired pollutant in environment.

The treatment methods of ethanal

Acetaldehyde was first produced commercially in the United States in 1916. Nowadays, it is manufactured by the oxidation of ethylene with a palladium catalyst and by the catalytic hydration of acetylene.

Acetaldehyde is used in various branches of the industry as a chemical intermediate and basic substance for the production of acetic acid, pyridine and pyridine bases, peracetic acid, butylene glycol, esters, flavor and fragrance acetals, paraldehyde, metaldehyde, phenolic and urea resins, antioxidants, polymers, and various halogenated derivatives. It is also a common compound in manufacturing of aniline dyes, synthetic rubber, silver mirrors, fuel compositions, disinfectants, drugs, perfumes, explosives, pesticides, and room air deodorizers. Acetaldehyde is used as a fungicide, substrate of food flavorings, preservatives, lacquers and varnishes, photographic chemicals as well [5, 6].

Properties of acetaldehyde are presented in Table 1 and its molecular structure is depicted in Fig.1A.

Tab.1. Properties of acetaldehyde.

Name/Formula:	Acetaldehyde, Ethanal, acetic aldehyde, ethyl aldehyde, CH ₃ CHO, NCI-C56326
Physical Properties	Volatile, flammable, clear, colorless liquid, miscible in water, alcohol, ether, benzene, gasoline, solvent naphtha, toluene, xylene, turpentine, acetone, and other common organic solvents
Odor	Pungent, suffocating (in low concentration- fruity) odor, detectable at 0.0068 to 1000 ppm
Molar Weight	44.05
Specific Gravity	0.78 - 0.79
Vapour Density	1.52 (air = 1.0)
Vapour Pressure	740 mmHg at 20 °C
Melting Point	of -123.5°C
Boiling Point	20.2 to 20.8°C
Flash Point	-38 °C
Autoignition Temperature	185 °C
Stability	A highly reactive compound that undergoes numerous condensation, addition, and polymerization reactions (autopolymerization with metals (iron) or acids (concentrated sulfuric acid)). It oxidizes readily to form corrosive acetic acid.
Toxicity Data	LD ₅₀ oral (rat) 661 mg/kg
Major Hazards	Highly flammable liquid, its vapor is explosive in the concentration range 4 to 66% in air. Irritating to the eyes and respiratory system.

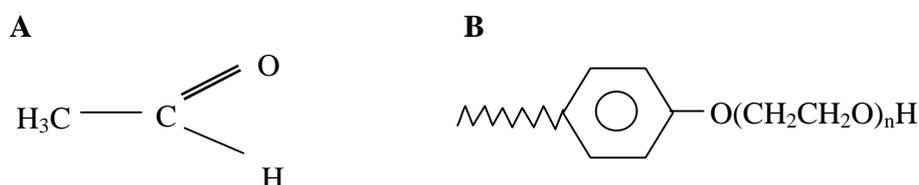


Fig.1. The structure of acetaldehyde (A) and Tritron X-100, n=9,10 (B).

Acetaldehyde is considered as a mutagen and possible human carcinogen [5-7]. Exposure to acetaldehyde by inhalation is irritating to the respiratory tract and mucous membranes; this substance is a narcotic and the chronic exposure can produce symptoms similar to alcoholism. Ingestion of acetaldehyde may cause severe irritation of the digestive tract. Ethanal causes irritation upon skin contact and eye burns.

Above premises gave an additional propulsion for research centers to study on the removal of acetaldehyde from exhaust gases and wastewaters.

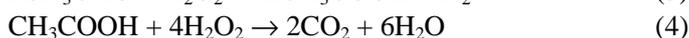
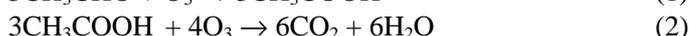
Acetaldehyde decomposes above 400°C to form mainly methane and carbon monoxide, however thermal methods with large volumes seemed to be quite costly.

Various attempts of immobilization and treatment of acetaldehyde have been done. The amorphous silica [8], activated carbon with about 13% adsorption efficiency [9] and the polymer filters [10] were used to limit the concentration of acetaldehyde in the outlet fluid. Interesting solution based on biodegradation of ethanal in packed column with immobilized activated sludge gel was presented by Ibrahim et al. [11].

Other direction was the photodecomposition using surfactants and organic solvents, which amplified the overall decay rate [12]. The photon dissociation of acetaldehyde was described by [13, 14] with indicating

formaldehyde, methylhydroperoxide, CO as the products generated mainly via free radical channel. Those results were partly confirmed by the report based on acetaldehyde reactions with hydroxyl radicals [15].

In this paper a new method of absorption of acetaldehyde within foam is introduced. Additionally, the oxidants were formed in foam as an effect of electrical discharge [16] and the results of combination of electrical discharge and absorption in foaming apparatus were analyzed. The ideal treatment process of acetaldehyde using generated oxidants could be described by the equations (1-4) :



3. Experimental apparatus

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

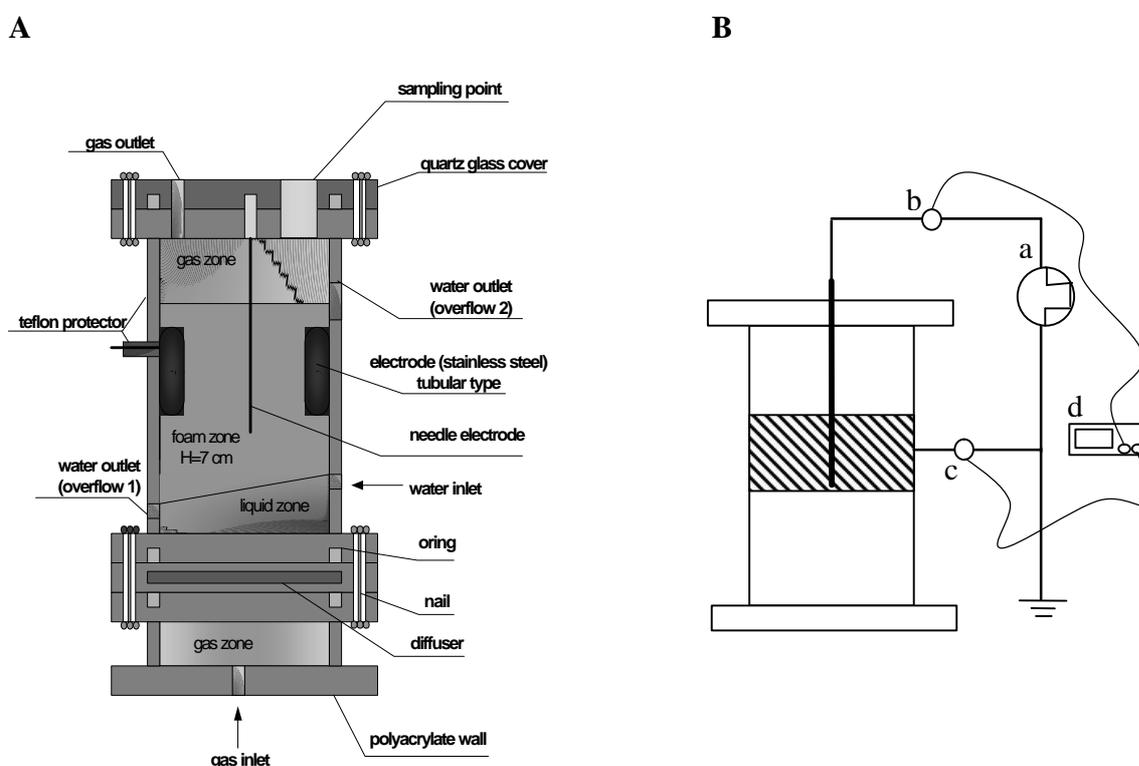


Fig. 2. Cylindrical foaming column (A) and the electrical circuit (B), (a- pulse power source, b- high voltage probe, c-current probe, d-oscilloscope).

Main reactor, depicted in Fig. 2A was a cylindrical column ($D_{in}=50$ mm, $L=200$ mm). The ceramic diffuser type IA-500 was placed inside the apparatus. Stainless steel electrodes were located in the homogenous foam zone, above the diffuser. The inner electrode ($d_{out}=1.5$ mm) was placed inside the outer electrode ($d_{in}=40$ mm, $l=30$ mm).

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 (1 ml/500 ml H_2O) and Triton X-100 (1ml/300ml H_2O)

was used as a substrate liquid. Substrate gases were air, oxygen and acetaldehyde with nitrogen as a carrying gas.

The electrical circuit is presented in Fig.2B. 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.

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).

3. Results and discussion

Dynamic foam was formed in the reactor. Average diameter of the single bubble in foam ranged from 1 mm to 5 mm. The diameters of the bubbles tended to be bigger in the case of the lack of the surfactant, with increasing the distance from the diffuser and with increasing the substrate gas flow as well. Dosing of the additional amount of water caused the bubble diameter to decrease. Foam with surfactant was stable. Natural decay of foam formed with Triton X-100 took more than 5 minutes whereas decay of dynamic foam without surface active compound took place immediately after the gas flow was shut down.

Several types of non- uniform discharges were obtained within dynamic foam. The typical electrical characteristics of the discharge and its photo taken from the top- side of the reactor in oxygen and pure water are shown in Fig.3.

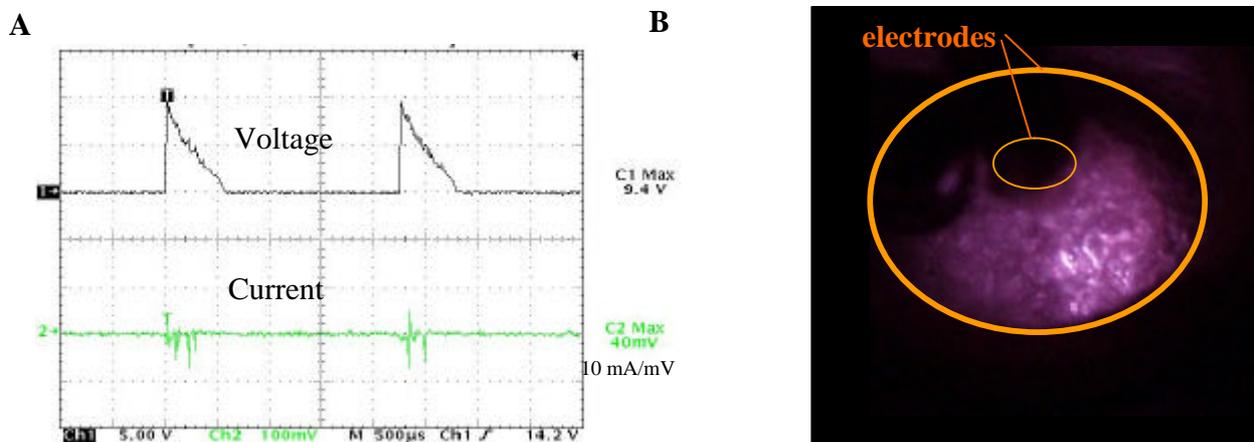


Fig. 3. Typical applied voltage and current waveforms of the electrical discharge in foam (A), and the photograph of the discharge (B). Oxygen flow rate 5 l/min, total power (including losses) 40 W.

The measurements were performed to confirm the presence of hydrogen peroxide and gaseous ozone generated by the electrical discharge. The concentrations of hydrogen peroxide in cylindrical column in the case of air without and with the addition of the common surfactant are depicted in Fig. 4. The small amount of gaseous ozone was also detected.

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. In the case of addition of surfactant the oxidants concentration decreased within the

same flow limits as without the addition of surface active compound. In the case of long term experiment added surfactant was gradually decomposed by formed oxidants and foam stability decreased.

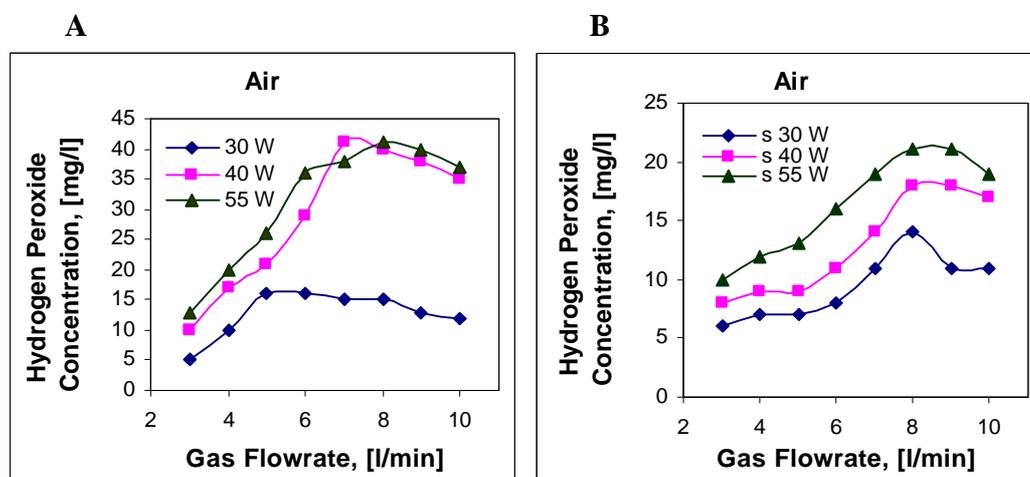


Fig.4. The hydrogen peroxide concentration in dependence on the gas flow without (A) and with the common surfactant (B), (power losses included).

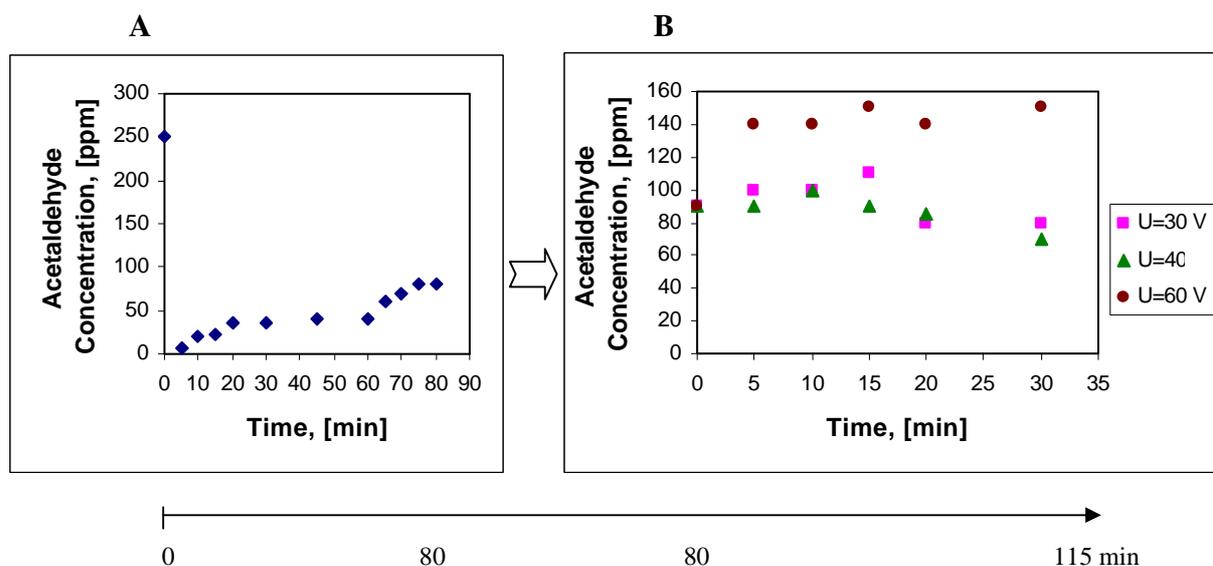


Fig.5. The absorption of acetaldehyde within foam with addition of Tritron X-100 versus time (A) and change in acetaldehyde concentration after application of electrical discharge to the saturated solution (B), (power losses included).

The process of absorption of acetaldehyde within foam without and with addition of Tritron 100 X was studied. The example of the one absorption cycle with 5 ml of the solution of surfactant in pure water is presented in Fig.5. In that case air-acetaldehyde in nitrogen gas flow rate was 1,2 l/min and initial concentration of ethanal was 250 ppm. After the 80 minutes of saturation time, the electrical discharge was applied. The proceeding of electrical discharge caused the releasing of acetaldehyde absorbed before and decomposition of the surfactant then gradually concentration of CH_3CHO decreased. The absorption process in presence of

Tritron was much more efficient than in the case of pure water only because of hydrophobic nature of acetaldehyde molecule.

4. 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 common surfactant and Tritron X-100.

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 acetaldehyde could be absorbed within the foam. The superposition effect of combining the absorption process with the electrical discharge was not fully confirmed. The absorption was improved when the surfactant was dosed to the substrate liquid.

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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