

TREATMENT OF SURFACTANTS IN THE FOAMING COLUMN

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Introduction

Nowadays, the processes where the interaction between gas and liquid occurs are very popular in the chemical engineering technology. Prevalence of them in the industry makes even slight improving of parameters of work very desirable. Foaming system was introduced a long time ago as the way of increasing the efficacy. Presently, it can be one of options for cleaning the large amounts of the polluted exhaust gas because the heat and mass exchange is especially efficient in the two-phase systems like a dynamic foam environment.

Several kinds of foam, with totally different properties and hydraulic parameters exist. The most famous are foams created using surfactants, three-state foams and unstable foams generated using only kinetic energy of the gas flow. It must be emphasized that foams created without any surfactants are the most desirable from the environmental point of view. The experiments using this kind of foam, generated from gases and pure water only were reported in the previous works^{1–3}.

On the further stages of the research the possibility of foaming system application for the dusty, polluted gas or the treatment of special kind of wastewater will be investigated. Some of contaminants show the surface-active character, they can change and extremely enhance the foaming properties of the purified solution.

Foams

Foams are unstable colloidal mixtures, which contain prevailing part of gas by volume. The initial distribution of liquid in foam depends on the manner in which the foam was produced. Foams can be divided into two categories, homogenous and pneumatic forms, depending on the method of generation⁴. *Static foams* (also called homogenous, stable or standing foams) are produced by vigorous agitation of solutions. The initial distribution of liquid is homogenous. *Pneumatic foams* (also called dynamic foams) are produced by bubbling of gas through the solution, as the bubbling proceeds, foam increases its length (until the gas supply is shut off) and the profile of liquid fraction develops. Such foam is drier at the top (liquid fraction is lower) and wetter in the lower part. Pneumatic foams are always in contact with the

foaming solution (in the static foams there is a time lag before some liquid appears in the bottom of the column). They also have some steady state height and the same amount of foam is produced as destroyed.

Pure liquids cannot foam unless the foaming agent (surfactant) is added in the case of typical static foams. The shaking of the sample of the water can become its purity test. Pneumatic foam can be created by a pure liquid using the kinetic energy of flowing gas. Foam can be easily created using dispersion technique – shaking or whipping the liquid with gas, which is immiscible in that liquid. The general ways to create foam are whipping, injection, sparging, shaking, aspiration or compressed air foams generation^{5,6}.

Properties of foam depend on composition of the solution, eventual surfactant, eventual contaminants, foam formation, and foam maintenance (temperature, pressure, etc.). General rules concerning the flow and apparatus-construction limits for foam environment creation are: a) linear velocity of substrate gas for whole apparatus cross-section (V_C): 0.1–4.0 m s⁻¹, b) gas velocity in the diffuser hole (V_D): 10–20 m s⁻¹, c) diffuser's perforation level: 5–20 % of whole shelf area^{7,8}. Foaming leads to the intensification of the processes between gas and liquid phase, especially those, this proceed on the inter-phase surfaces. The contact area is much larger than in typical bubbling process⁹. The three zones above the diffuser's shelves in the apparatus can be distinguished:

- the lowest one: bubbling in the thin liquid layer,
- middle: foam zone,
- upper: splash zone.

Experimental set-up

The main reactor vessel of the foaming system is depicted in Figs. 1. It consists of a cylindrical, polyacrylate column of 50 mm diameter. A ceramic diffuser made of Al₂O₃ was placed perpendicularly to the flow direction of media.

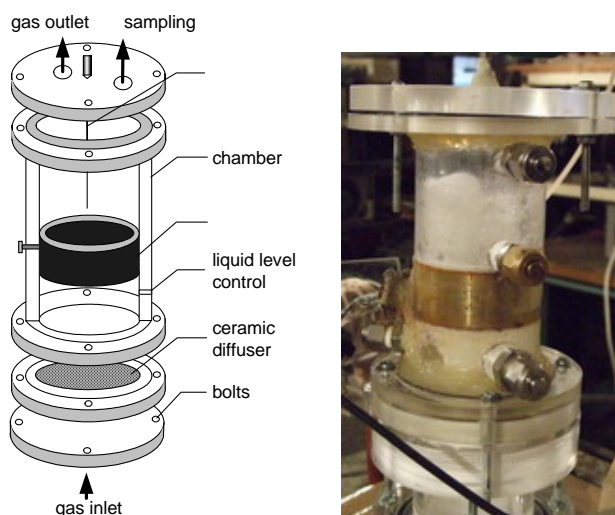


Fig. 1. Scheme of foaming vessel and its photograph during the foaming process

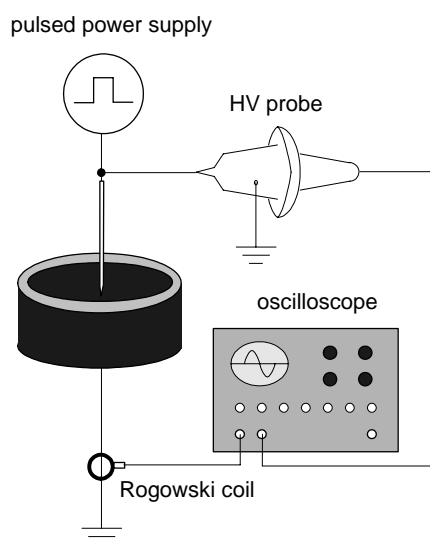


Fig. 2. Experimental apparatus

The central high voltage (HV) electrode of 1.5 mm diameter was placed inside the cylindrical, grounded electrode (40 mm of diameter, 30 mm of height) in homogenous foam zone, above the diffuser.

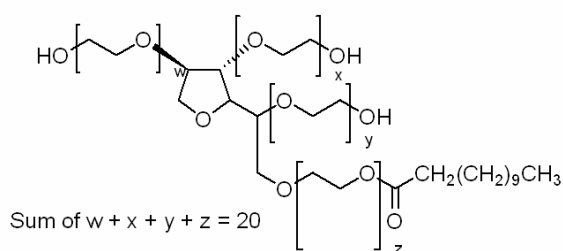
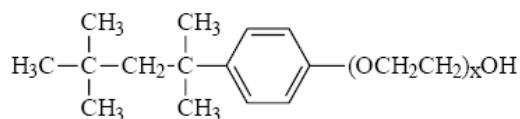
The electrical circuit is shown in Fig. 2. Blumlein type pulsed power source consisted of coaxial cables (RG-8U) for charging energy, triggered spark gap switch and switch triggering system. The pulse width of output voltage depended on the length of coaxial cable. In the performed experiments the pulse width of voltage was 50 ns, which corresponded to the cable length of 5 m. Surfactant-supported foam was uniform, with 1–2 mm diameter bubbles.

Results and discussion

Many kinds of the surface-active foaming materials can be distinguished. They can be particles of dust, liquid crystals, polymers or specific cations or anions from inorganic salts. Some of them can cause foaming in very low concentrations, even 10^{-9} M (ref.¹⁰). Large-molecule, nonionic surfactants do not dissociate into ions in aqueous solutions. They have plenty domestic, medical and industrial applications as mild and non-denaturing detergents. Showing excellent chemical stability, are good solvents of moderate foaming properties but they also have a tendency to bioaccumulation and can be harmful for aquatic organisms.

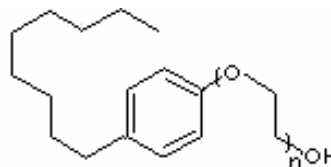
Tween® 20 (polyoxyethylene sorbitan monolaurate), which chemical structure is presented in Fig. 3, is yellow, viscous liquid miscible with water and used in the biotechnology, textile production and food industry.

Triton X-100 (polyoxyethylene octyl phenyl ether) is very stable non-ionic detergent soluble in water, benzene, toluene, xylene, trichloroethylene, ethylene glycol, ethyl ether, ethanol, isopropanol, and ethylene dichloride. At 10 % (v/v) in water, it gives a clear to slightly hazy solution, from clear to slightly yellow in appearance¹¹. It absorbs in UV region at 280 nm. Triton X-100 is relatively non-toxic and

Fig. 3. Chemical structure of Tween® 20 (ref.¹¹)

$$x = 9-10$$

Fig. 4. Chemical structure of TRITON-100

Fig. 5. Chemical structure of Polyoxyethylene Nonylphenyl Ether (PN5NPE)¹³

widely used in biochemical procedures. Its chemical structure is presented in Fig. 4.

Polyoxyethylene (5) nonyl phenyl ether (P5NPE, NE), (Fig. 5) is the large molecule nonionic surfactant playing important role in nanotechnology and biochemistry, but it also occurs to be a skin sensitizer, sometimes causing allergies¹².

For the experiment, 0.025 % water solution of Tween® 20, P5NPE, and Triton X-100 were prepared. 50 ml of the solutions were dosed into the foaming apparatus. Oxygen gas flow rate was fixed to 1.0 l min^{-1} . Change of COD (Chemical Oxygen Demand) during the treatment by the electrical discharge in foam was monitored for each pollutant. COD was measured using HACH spectrometer and COD 2720 method at 620 nm wavelength. The average energy per pulse ranged from 2 to 4 mJ. After 20 minutes of treatment at 30 Hz and 17 kV discharge voltage, 53 %, 87 %, 58 % COD removal efficiencies for Tween® 20, P5NPE, and Triton X-100 were achieved, respectively. The experimental data are summarized in Fig. 6.

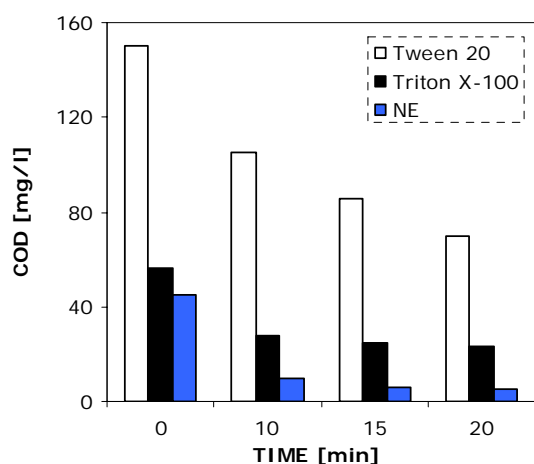


Fig. 6. Change of COD in dependence on the treatment time

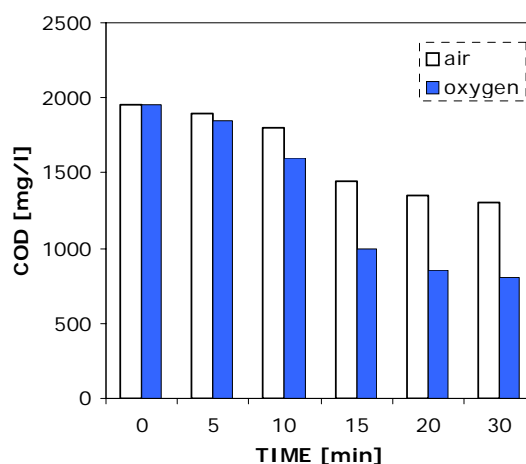


Fig. 8. Removal of COD in SDS solution and ethyl violet residues in dependence on the substrate gas

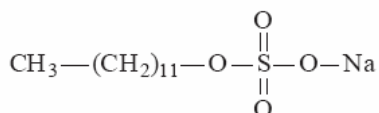


Fig. 7. Chemical structure of dodecyl sodium sulfate

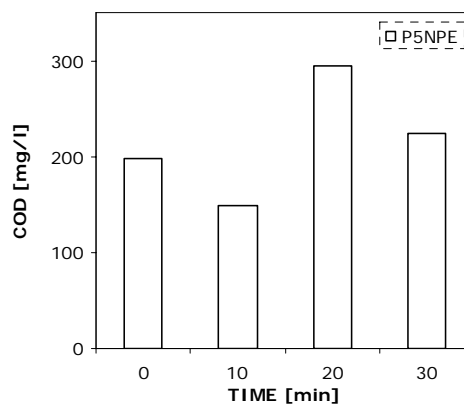


Fig. 9. COD in dependence on the treatment time at low pulse energy (P5NPE)

Dodecyl sodium sulfate (SDS, Lauryl sulfate sodium salt, Fig. 7) is a white powder soluble in water giving colorless liquid. This anionic detergent is widely used in molecular biology, drug and food industry, ceramics, and in methane hydrate formation^{14–16}.

In the experiment with SDS, 58 % reduction of COD was observed after 30 min of treatment of 15 ml solution of SDS surfactant (0.05 g l^{-1}) and residues of cationic dye: ethyl violet (Fig. 8) at 0.3 l min^{-1} oxygen flow. EV is highly pH-sensitive dye, which reacts mostly via OH reaction route.

For the lower pulse energies after the COD reduction in the first 10 minutes, the rapid increase of COD, sometimes exceeding the primary untreated value was observed. For instance, in the case of P5NPE solution, 30 minutes treatment time led to 13 % increase in COD comparing the initial value (Fig. 9).

After initial decrease in COD, what may suggest breaking the large molecule compound, further application of the electrical discharge promoted the unwanted reaction paths and formation of some other large-molecule species. In such condition, attempt of SDS and EV residues solution treatment due to complicated chemical structure of both compounds caused rapid increase of COD even by 30 times during the first 10 minutes and then slow decrease of this value, which after 30 minutes was still 15 times higher than untreated one.

In all observed cases, there was a visible decrease in the foamability of the treated solutions and in the last 5 minutes of treatment the bubbling prevailed over the foaming phenomenon.

Conclusions

Various active species as ozone, hydrogen peroxide and OH radicals were formed during the electrical discharge in the foaming column.

Treatment of pollutants and oxidants' formation was performed in the same reaction zone in the apparatus.

53 %, 87 %, 58 %, 58 % COD removal efficiency was achieved for Tween® 20, P5NPE, Triton X-100 and SDS, respectively. However, decreasing of the pulse energy led to the increase in COD of the solutions.

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