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Modification of filtering materials with aerogel for improvement of oil mist separation

Introduction

Separation of oil/gas dispersion is a problem emerging in many branches of industry: e.g. chemical, petrochemical, mechanical or food [Leith *et al.*, 1996; Boundy *et al.*, 2000]. Air containing the dispersed oil phase (mist) occurs in machining and cutting operations, engine closed crankcase ventilation and compressed gas cleaning. This is particularly important in factories operating in colder climates, where contaminated air may be recirculated through the building to reduce heating costs. The significance of this problem stems from the fact that many liquids used in industrial processes are characterized by properties harmful both for humans and other living organisms. Among all droplets size spectrum, so-called nanodroplets should be specified, which on account of their size can penetrate the respiratory system. Drops of this size range are particularly difficult to remove. Frequently used method is the oil sorption on the solid material.

Traditional sorbents are based on inorganic materials, organic porous polymers or natural materials. Sorption might be used to remove oil vapor as well as condensed oils from the air. The limiting factor is sorption capacity. Inertial mechanisms, used e.g. in screen impactors or cyclones, are widely used as the simplest way to remove oil mist both in the laboratory and industrial scale. While they are sufficient to reduce the oil amount according to requirements for most workstations, they are not effective in removing droplets of smaller diameter. The inertia of droplets decreases with their mass, and thus with their diameter. To remove oil nanodroplets, filtering in coalescence filters is required. Although filters used in oil/gas separation are widely used, there is still need for improvement of their properties.

In order to render the surface properties of materials a variety of modification methods could be applied, which generally can be divided into chemical and physicochemical methods. Chemical methods rely on performing changes in the chemical composition of the surface (etching, chemical reactions on the surface). Physicochemical methods allow the influence on surface morphology, like a change of the texture and increase/decrease of roughness (deposition, coating, vaccination).

The primary objective of modification is to increase the separation efficiency by intensification of the surface phenomena (e.g.: wettability). The use of oleophobic materials may, in theory, reduce saturation as the oil will not fully wet the surface, but it is more likely to allow collected oil to be re-suspended and re-entrained into the gas stream [Mullins *et al.*, 2014]. Unlike in dust filtration, mist filters generally decrease in separation efficiency over time (in diffusion dominated collection regimes). In the case of oleophilic material, droplets are being collected and spread out over the fiber surface, thus forming a thin film [Roe, 1975]. This leads to increase of fiber diameter and a decrease of filter efficiency. However in few works (e.g.: [Conder and Liew, 1989]) have been reported an increase in efficiency of oleophilic materials with loading.

In Jakubiak *S. et al.*, [2016] work hydrothermal method of ZnO structure growth, with plasma pre-treatment, was used to obtain fibrous filter media with the high specific surface area and high porosity. The development of zinc oxide rods allowed to achieve improved filtration efficiencies in aerosol and water dispersion filtration tests. Although filtration efficiency for aerosol particles

with a diameter of 0.2 μm increased by 30%, the material gives no advantage against PP nonwoven when particles larger than most penetrating particle size (MPPS) range are being filtered.

Recent studies [Brochocka *A. et al.*, 2013] focuses on modification PP electret melt-blown nonwovens to improve their filtration efficiency by adding modifiers with various electrostatic potentials to the polymer material. A greater improvement in electret filtration efficiency was seen for nonwoven modification with perlite beads (positive) and positive corona discharge than for amber beads (negative) and positive corona discharge. When the modifiers used in PP nonwovens had the same sign as the corona discharge, their electrostatic potential increased.

Werner and Jackiewicz, [2015] showed aerosol filtration results on charged and uncharged polypropylene filtering materials with various air velocity and morphology (mean fiber diameter). Analyzing the influence of the process conditions turned out that in the case of lower aerosol velocity the filter performance is better (higher nanoparticles separation efficiency and lower pressure drop). It was proven that electric charges on fiber enhance the separation efficiency without great increase in pressure drop. Although electret filters are more effective, material loses its advantage in case of long-time filtration and during filtration of liquids that does not have an electrostatic charge.

To improve the adsorption capacity of feather fibers, sodium pyrosulfite ($\text{Na}_2\text{S}_2\text{O}_5$) was used to modify the feather fiber in order to improve its Pb^{2+} adsorption capacity [Wang *et al.*, 2015]. It is found that Pb^{2+} adsorption capacity of the feather fiber increased after being modified by $\text{Na}_2\text{S}_2\text{O}_5$. Modified feather/PP filter cartridge exhibited higher Pb^{2+} adsorption capacity than feather/PP filter cartridge and pure PP filter cartridge in the whole dynamic adsorption process.

This research is based on filter modification using aerogel spheres to improve oil mist separation on filtering materials. This modification provides an improvement in sorption and in surface phenomena.

Aerogels are organosilicon structures, synthesized in two-step sol-gel process. First, the precursor is mixed with methanol and the oxalic acid solution, so the water of the acid solution promotes the hydrolysis reaction – acid step. After set amount of time, the ammonium hydroxide solution is slowly added, where the alkaline medium favors the condensation of silanols, increasing the reaction rate and forming a sol – basic step. Aerogels are highly porous solid materials with very low density (and hence low weight) and good thermal insulation. Due to its hierarchic porosity (in micro- and nanoscale), aerogels are highly effective as sorbents, used to absorb oils and other mineral and organic liquids. Aerogels with methyltrimethoxysilane (MTMS) used as a precursor has hydrophobic, oleophilic and oil-sorptive properties [Yun *S. et al.*, 2014]. That is why it was chosen for filtering materials modification.

Materials and methods

Polypropylene filtering materials, with mean fiber diameter 5 μm , produced by melt-blown technology were used in the modification. This method allowed us to obtain materials with repeatable structure [Gradoń *et al.*, 2005; Podgórski *et al.*, 2011]. Filter modification is a multi-step process. Right after acid and base step of sol-gel reaction (described above), filter sample is placed into reactive solution,

and thus filter fibers are covered by condensing alcogel. Then, the wet structure of alcogel is changed into aerogel by drying sequence. Appropriate drying method prevents pore collapse, shrinking of the structure and thus keeps high porosity of aerogel. As a result aerogel coating is obtained on the surface of the fiber in the whole volume of the filter. Modification occurs for different MTMS:methanol ratios (1:10, 1:15 and 1:25). MTMS: oxalic acid: ammonium hydroxide ratio was 1:4:4 for all modifications – based on [Rao *et al.*, 2006]. The volume of reactive solution and size of modified filter was the same for all modifications. It means that a number of aerogel decreases in series 1:10, 1:15, 1:25. Filters were weighed before and after modification to measure the amount of deposited aerogel. Modified filters were imaged by SEM. Filtering materials were wounded on a core (total filtration surface equal to 77 [cm²]) and tested for its filtration properties.

The efficiency of oil mist separation (in respect to droplets with diameter 0.2-10 µm) of filters modified with aerogels has been investigated, by means of HFP 2000 filter test system designed by PALAS GmbH, Germany. Scheme of the experimental set-up is presented in Fig. 1. The main element of this test-bench is a horizontal channel – 2 with a holder where the investigated filter is placed – 1. Gas (air) flow rate in the channel is controlled by the software. Droplets of di-ethyl-hexyl-sebacat (DEHS), commonly used oil for filter testing, are generated by means of the generator PLG 2000 – 3. The concentration of liquid aerosol was about 40 g/h. The tests were accomplished at gas face velocity $u = 0.2$ m/s, flow rate $Q = 92$ l/min at an ambient average temperature of 22°C. The loading of each filter with droplets took 24 hours. During this period the efficiency and pressure drop were measured three times: at the beginning of loading, after 4 hours and after 24 hours. Every measurement has been repeated three times.

The scheme of a test bench for nanodroplets filtration has been showed in Fig. 2. *MFP Nano Plus*, a new advanced test bench was designed and developed by the German manufacturer PALAS in cooperation with the Faculty of Chemical and Process Engineering of Warsaw University of Technology. The test bench is equipped with a compressor. The *UGF 2000* generator was used to produce well-defined di-ethyl-hexyl-sebacat (DEHS) oil nano-mist. The efficiencies of the filters were obtained by measuring the particles concentration before (upstream) and after (downstream) the filter using the SMPS system (scanning mobility particle sizer). Each filter has been tested in the sequence of three upstream and three downstream measurements; with duration of 380 seconds (320 sec of particles loading and 60 sec of pause between tests). Such a long time of single experiment is required to ensure a reliability of nanodroplets measurement. Tests after 4 and 24 hours were not presented, due to lack of changes in pressure drop and fractional efficiency during nanodroplets loading.

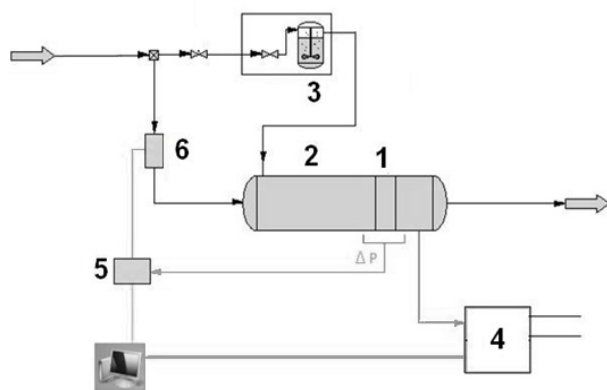


Fig. 1. Scheme of the experimental set-up for investigation of the dynamics of filter efficiency and pressure drop. 1 – filter holder, 2 – horizontal channel, 3 – nebulizer PLG 2000, 4 – particle counter, 5 – control unit, 6 – pump

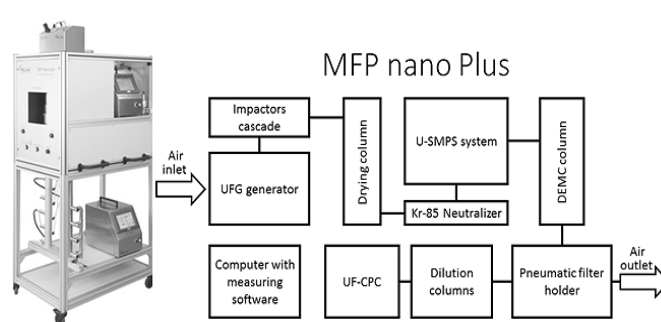


Fig. 2. Scheme of test bench for nanodroplets filtration

The tests were accomplished at gas face velocity $u = 0.1$ m/s, flow rate of $Q = 60$ l/min, at an ambient average temperature of 22°C. Oil mist nanodroplets were generated from 0.03% solution of DEHS in pure isopropanol.

Results and discussion

Different types of modifications have been tested. This paper presents the most promising results.

Fig. 3 shows SEM picture of native filtering material before (A) and after 24h of oil mist filtration as well as filtering material modified with MTMS aerogel before (C) and after 24h of oil mist filtration (D). In the case of native material after filtration (B), fibers are connected by liquid bridges, which are even more visible in case of aerogel modified filter (D). It is clearly visible that fibers are quite uniformly coated and oil is sorbed in pores of aerogel spheres. Sorption prevents re-suspension of collected oil. In some places aerogel agglomerated and created larger clusters.

All samples, from different MTMS: methanol ratios, look similar while taking into account inner parts of the filter. The main difference is an amount of deposited aerogel spheres during modification (Fig. 4). In the case of sample 1:10, 0.0038 g of aerogel was deposited on 1 cm². As expected, on the other samples less aerogel amount was deposited: 1:15 – 0.0024 g/cm² and 0.0016 g/cm². In the case of 1:10 ratio, more aerogel particles accumulated on filter surface (Fig. 5). That is due to faster gelation of aerogel during the sol-gel process, thus a portion of aerogel remained on the filter surface. In the case of 1:15 and 1:25 ratios, no surface accumulation was observed. Thus most of the aerogel particles penetrated inwards filter. Each aerogel sphere is highly porous structure.

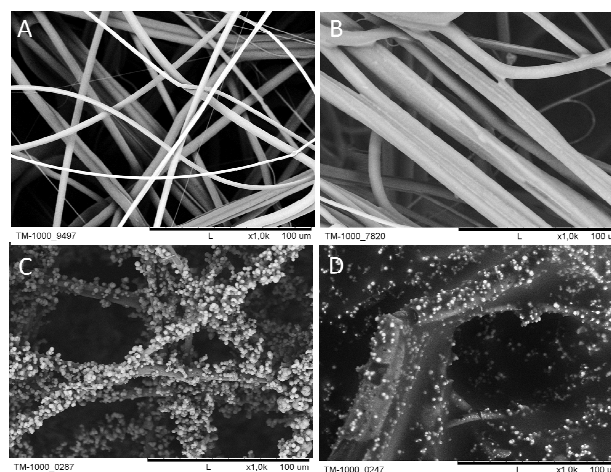


Fig. 3. SEM picture of filtering materials: A – unmodified; B – unmodified after oil filtration (24h); C – modified with aerogel (1:15); D – modified with aerogel after oil filtration (24h)

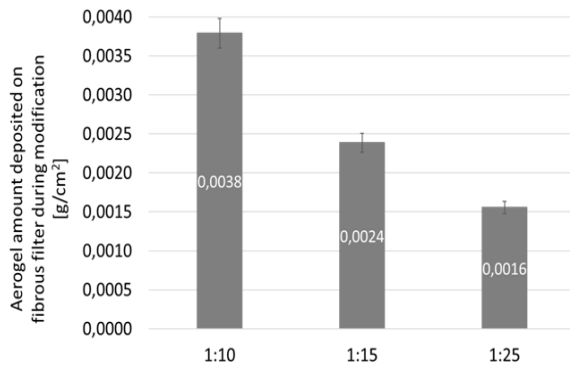


Fig. 4. Amount of aerogel deposited on filtering material during modification

However, filtration tests showed discrepancies that may be related to the inner structure of modified filter. To confirm this connection more characterization will be conducted in future phases of the research.

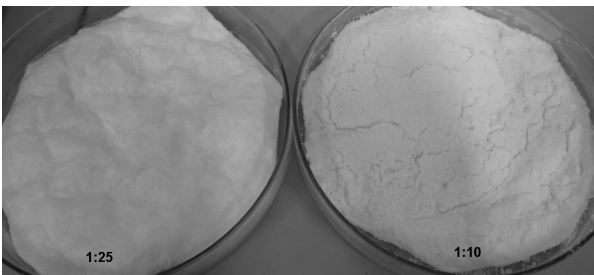


Fig. 5. Picture of the outer surface of filtering material modified with aerogel

Fig. 6 presents fractional efficiency of filtering materials modified with aerogel particles with different MTMS: methanol ratios. During filtration of nanodroplets (Fig. 6 A), the 1:15 sample also gave the best results. Filter with this modification reaches 100% efficiency for droplet diameter of 20 nm and approximately 50% for 220 nm. Samples 1:10 and 1:25 gave similar fractional efficiency curves. For smallest droplet diameters their efficiency was above 90% and decrease to approximately 40% for droplets of 200 nm diameter. Unmodified filter shows fractional efficiency above 80% for 20 nm and 20% for 200 nm droplet diameter. Fig. 6 A shows that efficiency for modified filter sample is 20-40% higher for all sizes of nanodroplets.

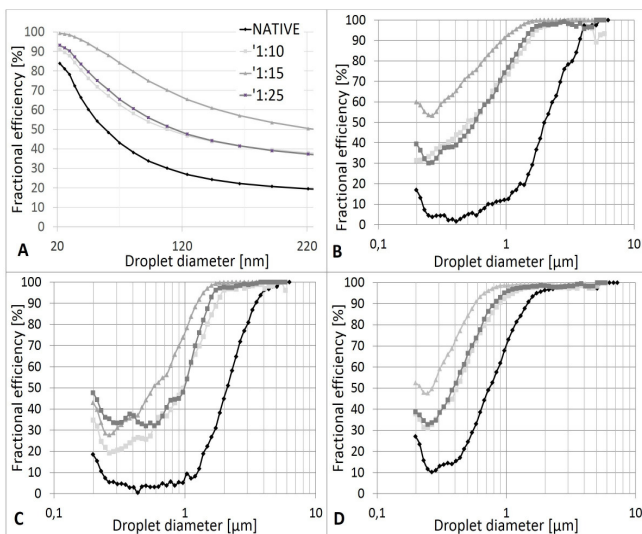


Fig. 6. The fractional efficiency of aerogel modified filtering materials at different MTMS: methanol ratios. Filtration of aerosol at the beginning of nano aerosol filtration – A; Filtration of aerosol in microscale: B – at the beginning of load, C – after 4 hours, D – after 24 hours

At the beginning of filtration test of aerosol in micro scale (0 h) sample 1:15 gave the best results (Fig. 6 B). Samples with ratios 1:10 and 1:25 gave similar, lower fractional efficiency. The fractional efficiency of unmodified (NATIVE) filtering material is the lowest for the whole range of droplet diameter. After 4 hours (Fig. 6 C) fractional efficiency is decreasing for all samples. Nevertheless modified samples have approximately 4÷5 times better fractional efficiency for droplets range 0.5÷1 µm than a unmodified filter. After 24 hours (Fig. 6 D) situation is similar to that at the beginning of the test. The best results were obtained for 1:15 sample, although efficiency decreased approximately 10% for the smallest droplets during the test. For this sample, efficiency reaches 100% for particles around 1 µm. Also 1:10 and 1:25 samples gave similar results. Fractional efficiency for the smallest droplets is around 30÷40% and above 90% for droplets diameter around 1 µm. Native filter efficiency for smallest droplets is between 10÷25% and reaches approximately 70% for droplet size 1 µm. The increase of fractional efficiency, between 4 and 24 h of loading indicates that the oil sorption capacity of material was not reached.

Although the amount of aerogel was the biggest in sample 1:10, the highest fractional efficiency was obtained for sample 1:15. In the case of sample 1:10 some part of aerogel did not penetrate inwards and accumulated on the filter surface (Fig. 5). This may have an influence on separation efficiency. This efficiency is dependent on dominant deposition mechanism. For biggest droplets, the predominant mechanisms are interception and inertia forces. Those mechanisms lose their importance for smaller droplets. For droplets of diameter size close to 0.2 µm the diffusion mechanism begins to dominate, thus increase of efficiency. Fig. 5 B, C, D shows that lowest efficiency is obtained for particles between 0.3 and 0.6 µm. In the case of nanodroplets (Fig. 6 A), higher efficiency for the smallest diameter size is related to the strong influence of Brownian motion. Unlike to the work of *Jakubiak. et al.* [2016] presented modification improves the fractional efficiency of droplets larger than MPPS.

Fig. 7. presents droplet diameter which is separated with different filtration efficiency (50, 80, and 95%) on filtering materials modified with aerogel at different MTMS: methanol ratios. While on the native filter 50% filtration efficiency is reached for droplets around 2 µm and 95% for 4 µm, for modified samples it is respectively about 0.4, 0.9 and 1.4 µm depending on MTMS: methanol ratio (at the beginning of load). The best result was obtained for sample 1:15, where in every case the droplet diameter was more than twice smaller than one obtained for the native filter.

General retention of filtering materials modified with aerogel with different MTMS: methanol ratios was measured during filtration (Fig. 8.). At the beginning, general retention for the unmodified filter is around 10%. For all modified samples growth of retention was observed. The best result was obtained for sample 1:15 – 70%. For other modifications value was between 40 and 50%. While after 4h general retention for the native filter was approximately the same, it decreased for modified filters: 1:10 – 37%, 1:15 – 50%, 1:25 – 43%. After 24 h, general retention was around 55÷60% for samples 1:10 and 1:25, over 70% for sample 1:15 and 33% for native filter.

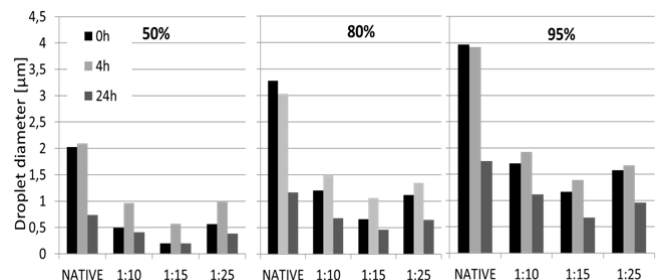


Fig. 7. Droplet diameter separated with different filtration efficiency for filtering materials modified with aerogel at different MTMS: methanol ratios

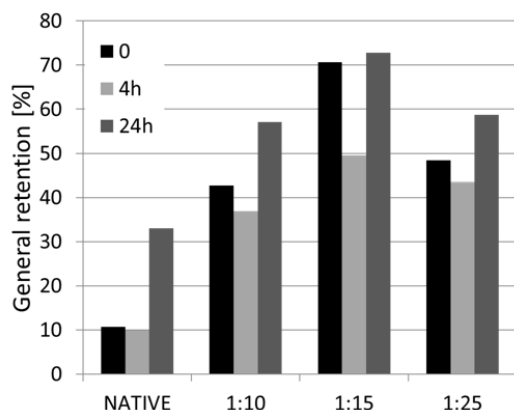


Fig. 8. General retention of filtering materials modified with aerogel with different MTMS: methanol ratios

During each test, the pressure drop was measured. Results are presented in Fig. 9. In the case of filter modified with aerogel with MTMS: methanol ratio 1:15, the biggest pressure drop was observed. At the beginning of the test pressure drop was 245 Pa, increased to 314 Pa after 4 h and finally reached 1789 Pa after 24 h. Filter modified with ratio 1:25 starts with pressure drop equal to 200 Pa and stayed that way for next 4 h. After 24 h pressure drop reached 1233 Pa. The smallest pressure drop among all modified filters was observed for 1:10 MTMS: methanol ratio, although the amount of aerogel in the solution was the biggest. It is 140 Pa at the beginning of load, 152 Pa after 4 h and approximately 1160 after 24 h. It may be related to the aerogel accumulation on the filter surface, but more tests are required. Similar results were obtained during nanodroplets filtration. The highest pressure drop was measured for 1:15 sample – 158 Pa, smaller for 1:25 – 67 Pa and for 1:10 – around 60 Pa. In all cases, the pressure drop for the unmodified filter was the lowest: 59 Pa at the beginning of the process, 102 Pa after 4 hours and 303 Pa after 24 hours. At the beginning of nanodroplets, filtration pressure drop for native filtering material was around 24 Pa. Pressure drop measurements correlates with separation efficiency tests. With the highest fractional efficiency comes the highest pressure drop. This may indicate that the increased amount of aerogel spheres deposited on fibers in the material volume (that may cause pressure drop) influencing better the increase of separation efficiency.

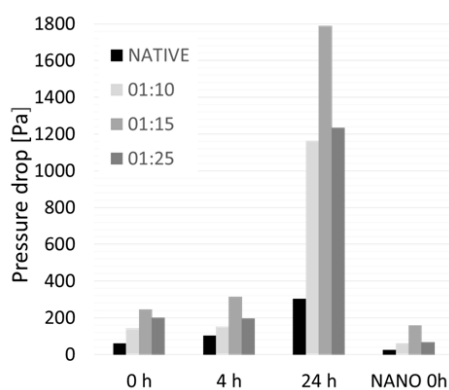


Fig. 9. Pressure drop for filtering materials modified with aerogel with different MTMS: methanol ratios. Filtration of aerosol in microscale: at the beginning of loading, after 4 and 24 hours. Filtration of nano aerosol was conducted at the beginning of loading.

Calculations of the relative pressure drop of filtering materials indicate that during 24h of oil filtration the biggest growth was observed for sample 1:10 – 8.29 times. For sample 1:15 relative pressure drop grow 7.3 times and for 1:25 – 6.165. The growth of relative pressure drop of native material was 5.13 times higher.

This result correlates with those shown in Fig. 4. The bigger amount of aerogel was deposited on the material, the greater oil sorption properties the filter has and thus the more significant growth of relative pressure drop is observed.

Summary and conclusions

Modification of filtering materials with MTMS aerogel improves oil mist separation both in micro- and nanoscale. The best fractional efficiency and general retention were obtained for MTMS: methanol ratio at 1:15. Same separation efficiency was obtained for droplets of more than twice smaller diameter than in the case of the unmodified filter.

This modification also gave the biggest pressure drop. This may indicate the biggest amount of aerogel spheres in the volume of the filter. Samples 1:10 and 1:25 gave similar separation efficiency and pressure drop, although the amount of aerogel was bigger in 1:10 sample. It may be related to faster gelation and accumulation of aerogel on filter surface in case of ratio 1:10. Sample 1:10 gave also the biggest relative pressure drop growth.

The best way is to find the modification with high separation efficiency and relatively small pressure drop. Research on obtaining the best filter properties are in progress. Although, this modification may be a promising way to obtain filtering materials for ventilation systems and purification of compressed gas streams in various branches of industry.

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