

EVALUATION OF MICROPOROUS CARBON FILTERS AS CATALYSTS FOR OZONE DECOMPOSITION¹

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ABSTRACT

Ozone is produced in small quantities in photocopiers and laser printers in the workplace and large quantities in industrial waste water treatment facilities. Carbon filters are commonly used to decompose this unwanted ozone. The three most important factors in producing a filter for this purpose are flow properties, efficiency, and cost.

Most ozone decomposition applications require very low back-pressure at modest flow rates. The tradeoff between the number of pores and the size of the pores will be discussed. Typical unfiltered emissions in the workplace are approximately 1 ppm. The maximum permissible exposure limit, PEL, for worker exposure to ozone is 0.1 ppm over 8 hours. Several methods have been examined to increase the efficiency of ozone decomposition. Carbon surfaces were modified with catalysts, the surface activated, and the surface area was increased, in attempts to decompose ozone more effectively. Methods to reduce both the processing and raw material costs were investigated. Several sources of microporous carbon were investigated as ozone decomposition catalysts. Cheaper processing routes including macropore templating, faster drying and extracting methods were also studied.

INTRODUCTION

Ozone, an allotrope of oxygen, present in the upper atmosphere (ozonosphere) plays a critical role in radiative balance. However, ozone is a toxic gas with a pungent odor when present in the troposphere and is considered a health hazard. The Occupational Safety and Health Administration (OSHA) has established a maximum permissible exposure limit (PEL) of 0.1 ppm in an 8 hour period.

There are many sources of exposure to ozone in the workplace. Ozone is generated by high voltage discharge wires found in laser printers and photocopiers. Other common uses for ozone include waste water treatment, medical and dental instrument sterilization, drinking water purification, industrial oxidation processes, bleaching, and as a bactericide in swimming pools. Carbon filters are often used to minimize worker exposure to ozone.

When designing a filter to decompose unwanted ozone, there are three requirements for most commercial applications. The first requirement is that production costs of the filter be minimal. Many applications require large quantities of filters and may have to be changed out often. The relatively low PEL also requires the filters to have a very high ozone decomposition efficiency. Finally, current applications tend to use small, low power fans to move air through the filters. Low back-pressure is required to prevent over heating and prevent build-up of the toxic and potentially explosive ozone. In this paper, we will discuss two porous carbon filters that satisfy all of these requirements.

The TAK2 is a commercially available carbon filter used to decompose ozone produced during laser printer operation. Without these filters the ozone concentration would exceed the federal standard for worker exposure. The TAK2 has a geometric surface area of approximately

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10^{-6} m²/g and a BET surface area of approximately 10^3 m²/g. The filter has 0.8 mm diameter straight channels through the 10 mm thickness.

EXPERIMENTAL PROCEDURES

Filter Synthesis and Processing

It was postulated that a low density emulsion derived carbon foam without straight through channels would have a higher efficiency of ozone decomposition than the TAK2. Several high pore volume commercially available reticulated vitreous carbons (RVC) were evaluated. Although there was no straight path for the ozone to readily pass through, the RVC filters exhibited very poor efficiencies. This was later attributed to low BET surface areas. High surface area (>300 m²/g) and low density (60 mg/cc) resorcinol-formaldehyde (RF) polymer emulsion derived carbon foams were also examined. The efficiencies of these filters were very high. However, backpressures were shown to be prohibitively high for the applications discussed above. Theoretically, a thin enough emulsion derived filter would have an acceptably low backpressure. Unfortunately, the structural integrity of these materials is substantially decreased at less than 3 mm thick. It was then decided to investigate methods to introduce channels into the RF emulsion to reduce the backpressure, but still take advantage of the high surface area.

Two channel forming methods were investigated: stamping and molding. Also, two different templates, giving different channel sizes, were used to do the stamping or molding: a bed of pins (BOP) and a bed of nails (BON). The BOP template consists of a 73 by 75 matrix in a 4900 mm² area of pins (Dressmaker, 0.76 mm dia by 31 mm long) supported by two layers of stainless steel mesh. A third layer of mesh was used to aid the removal of the template from the cured emulsion. The BON template is of similar design except that it has only a 71 by 71 matrix in a 5400 mm² area of blunt tip nails (1.17 mm dia by 42 mm long).

Early tests revealed several interesting facts. First, attempts to stamp a cured or partially cured RF polymer emulsion with the BON template resulted in complete collapse of the emulsion microstructure and macrostructure. This was presumably due to the blunt tips of the nails since stamping a partially cured RF emulsion (24 hours) with the BOP template had favorable results. Second, the pins in the BOP template were too close together for it to be used as a mold. This was demonstrated by the fact that a freshly prepared RF emulsion could be poured into a pan and the BON template set down in the emulsion allowing the emulsion to flow between the nails and removed after partial cure of the polymer. When the BOP template was used in this procedure, the partially cured polymer cannot be removed without completely breaking-up. Two out of the four permutations were found to provide favorable filter materials: stamping with the BOP template and molding with the BON template.

Bed of Nails (BON) Filter

A low density resorcinol-formaldehyde (RF) emulsion (60 mg/cc) was prepared as previously described.² All chemicals were used without further purification. Some RF emulsions were prepared with decahydronaphthalene (Decalin) recovered from previous emulsions and purified by distillation. The emulsion was either poured into a 265 mm by 375 mm glass pan or several 152 mm diameter crystalizing dishes. A bed of nails molding template with blunt ends was then gently placed into the freshly made emulsion. It was then covered left at room temperature for twenty-four hours. After this period of time the stamp was gently removed using a screen surrounding the nails to allow removal of the bed.

Bed of Pins (BOP) Filter

A low density RF emulsion (60 mg/cc) was prepared as previously described. The emulsion was either poured into a 265 mm by 375 mm glass pan or several 152 mm diameter crystalizing

dishes. After allowing the filter to sit at room temperature for 24 hours, a BOP template was stamped into the partially cured polymer. The pointed ends of the pins resulted in an easier entry into the emulsion. The BOP was gently removed immediately after stamping. A BON stamped at the same time as the BOP crushed the emulsion due to blunt nail ends. Likewise, the larger number of pins per area (compared to nails) resulted in break-up of the emulsion when the molding procedure was attempted.

Drying

After 48 hours at room temperature, the covered emulsion was placed in a forced air convection oven at 50°C for a period of one to three days. The temperature was raised to 65°C for two days. After complete removal of the pore former, a low density monolith was obtained.

Carbonization and Activation

The cured emulsions were placed into a carbonization furnace. The temperature is ramped at a rate of 2°C/min to 300°C and held for 2 hours. The ramp rate was reduced to 1°C/min and the temperature increased to 370°C and held for 5 hours. A final ramp of 2°C/min was used up to 1100°C. The temperature was held under argon atmosphere for five hours and then allowed to cool down. The whole carbonization step lasted thirty hours.

A group of carbon samples was then activated to increase the surface area. The samples were placed in the activation furnace and heated to 800°C under flowing nitrogen at 2 liters per minute. The inlet gas was switched from nitrogen to carbon dioxide and the temperature held at a constant 800°C for a period of two to four hours. After cooling back to room temperature under nitrogen, volumetric shrinkage and mass losses were determined. The whole step took up to seven hours.

Ozone Decomposition Efficiency Evaluation

Dry compressed air (12 psi) was passed through an ENMET Corporation ozone generator (UV light) at 8 liters per minute to produce approximately 15 ppm of ozone. The ozone then has one of two paths to follow: a three way valve allows the ozone to either bypass the filter and bubble into a potassium iodide solution to form iodine and oxygen or pass through the sample holder and be destroyed by the carbon filter. The 38 mm diameter carbon sample disk, bounded by an o-ring to help prevent leakage around the edge of the filter, was held between two separate 115 mm long, 38 mm diameter glass tubes. The glass tubes were butted-up against the filter and 51 mm diameter heat shrink tubing was collapsed around the two glass tube ends, o-ring and filter. Electrochemical sensors from the ENMET Toxic Gas Detection Systems were used to measure ozone concentrations between 0.001 to 0.300 ppm. The sensors were determined to be flow rate sensitive and calibrated accordingly. ENMET ozone detector tubes were used for calibration and measurement of the concentration of ozone between 0.025 and 1000 ppm.

In order to determine the flow through the apparatus a mass flow meter (Tylan Corporation, model FC-260) measured the average flow rate. Baratron pressure transducers from MKS Instruments Inc., are used to measure pressure up to 1000 torr on either side of the carbon filters for the determination of back pressure.

RESULTS AND DISCUSSION

Efficiencies

As described in the experimental section, cylindrical shaped channels are introduced into the BOP filters from a stamped bed of pins and the BON filters are molded from a bed of nails. A low density and high surface area resorcinol/formaldehyde polymer emulsion is used as the substrate for the stamping and molding procedures. Following carbonization, the ozone decomposition efficiency and BET surface area of the BOP and BON carbon filters was

determined and is listed in Table I below. Brunauer, Emmett, and Teller (BET) surface area measurements were conducted on a Micromeritics ASAP 2400 using nitrogen as the adsorption gas at -196°C. Efficiencies were calculated as shown in Equation 1. Following carbonization, the filters were activated at 800°C for 2 hours in flowing CO₂. These activations are known to increase the surface area. Efficiencies and surface areas were measured again. The second activation was almost twice as long as the first, 3.5 hours at 800°C in flowing CO₂. Also included in Table I is the efficiency for a commercially available TAK2 filter.

$$\frac{\text{input of ozone}}{\text{output of ozone}} \times 100 = \text{Efficiency} \quad (1)$$

Table I. BET surface area and efficiency³ results for 5 mm thick carbon filters.

Filter Number	Percent Efficiency			BET Surface Area (m ² /g)	
	Before Activation	First Activation	Second Activation	Before Activation	First Activation
TAK2	99				
BON					
29*	27	78	89	175	
69	92			467	
71	87	90			
BOP					
31	85	92	98	274	413
46	86	92		390	373
69	64	87		358	1546
71	86	97		358	657

* Dried slowly over several weeks.

Filter thickness plays a role in determining the efficiency of ozone decomposition. In order to compare the efficiencies of various filters, ozone output concentration was measured after sanding off layers of the carbon filters to obtain a variety of thicknesses. These output concentrations were converted to percent efficiencies according to Equation 1. The BOP filters were not sanded because they were already approximately 4.5 mm thick.

The effect of stamping or molding on the surface of the channel was examined. Although the macrostructure of the RF emulsion appears intact, SEM micrographs show substantial collapse of the microstructure. This is explained by the fact that we are forcing the pins into a partially cured polymer below its glass transition temperature. Since there is a high pore volume, the microstructure just closes in on itself. This collapse results in a rougher channel wall of a BOP filter compared to the the wall of a BON filter. Even for a BON filter with a higher surface area, the efficiency is lower than for a BOP filter. This is also in agreement with the TAK2 filters having very rough channel walls and high efficiencies. Stamping and molding templates with longer pins and nails will allow preparation of thicker filters with higher efficiencies.

Economic Analysis for RF Derived Carbon Ozone Filters

The economic evaluation part of this study was undertaken to see how close we could come to beating the cost of the commercially available TAK2 filter. The TAK2 retails for approximately \$12.00. Unfortunately, we do not know anything about how it is produced. So, direct comparison is difficult, but we have an upper bound. The cost of the various elements are broken out for a

variety of production capacities, channel forming methods, and drying operations as shown in Table II. Details concerning each of the cost elements are provided below.

Costs are based on quotes for bulk materials free on board (f.o.b.), although transportation is included. Because it is assumed that 50% less material is required in molding than in stamping, material costs are lower for molded channel forming because less material is needed. Bulk pricing is based on 400000 quantity production. Although some of the experimental volumetric shrinkages are higher, filters are assumed to lose 50% of their volume during processing in all cases. A defect fraction of 0.05 is assumed during production.

Costs for equipment f.o.b. are quotes. Installed costs for equipment include: 1) cost of equipment purchase, 2) shipping and installation, 3) engineering, site preparation, and auxiliary facilities, 4) insurance, sales taxes, construction overhead, and 5) contingency and fee.

Equipment costs are estimated by multiplying f.o.b. costs by a Lang factor, which approximates the totality of all costs listed above. For most solids operations, a factor of 3.9 is used.⁴ This factor is used to derive all installed equipment costs; exceptions are: molds and stamping molds, 1.5; freeze drier, 5; vacuum oven, 5; and SCCO2 unit.^{7,5} In calculating the cost per unit of the filters, installation costs are distributed evenly over a 10 year period.

Labor required for operation of each piece of equipment is estimated based upon the amount of supervision required. The salary cost for each worker, \$29,000/year, is calculated using the mean salary for chemical plant workers in mid-1982⁵. The figure is adjusted using the CE Plant Cost Index for August of 1994.^{6,7} Overhead, which includes worker benefits, social security, unemployment insurance, and other compensation paid to workers, is estimated at 60% of direct salaries.⁴

Table II. Production cost estimates for 400,000 filters per year.

	Raw Materials	Installed Equipment	Labor and Overhead	Maintenance and Repair	Other Costs*	Total Cost	Cost/unit
<i>Stamped</i>							
Conv. Oven	397476	1610310	371200	86322.6	103402	1119432	2.80
Freeze Drier	397476	2729350	417600	179465	143664	1411141	3.53
SCCO2**	397476	3179350	417600	215465	156264	1504741	3.76
Vacuum Oven	397476	1954350	371200	106965	114230	1185307	2.96
<i>Molded</i>							
Conv. Oven	149053	8001660	348000	149553	235377	1682150	4.21
Freeze Drier	149053	9120700	394400	242696	275639	1973859	4.93
SCCO2**	149053	9570700	394400	278696	288239	2067459	5.17
Vacuum Oven	149053	8345700	348000	170196	246205	1748025	4.37

The cheapest filter we calculated is stamped and dried in a conventional oven. This filter is estimated to cost \$2.80 to produce, with 400,000 filters produced per year. The economy of scale is significant in carbon filter production.

As shown in Table II, raw materials is the largest contribution to the overall production cost of the carbon filters. Raw materials for stamped filters are twice as much as molded due to approximately 50% compression during the stamping operation as it is currently performed. We feel this is an area that substantial improvements can be made, thus lowering the cost of stamped filters.

Flow Properties

The flow properties of both the BOP⁸ and BON filters (approximately 37 mm diameter) were investigated up to 8 lpm. High precision MKS Baratron pressure transducers located on either side of the filters were used to determine the pressure difference. No backpressure (<1 mm H₂O) could be detected for the BOP, BON or TAK2 filters. Emulsion filters with no through holes exhibited substantial backpressures and were thus disregarded in spite of their high efficiency of ozone decomposition. It should also be noted that the BOP filter thickness did not exceed 5mm. Thicker BOP filters may exhibit small, but not prohibitive backpressure.

CONCLUSIONS

Catalytic ozone decomposing carbon filters have been prepared. Process cost improvements for preparing carbon filters were achieved using an emulsion derived carbon foam with straight through channels. The economics of producing these filters has been projected to be approximately \$2.80 per filter, competitive with existing TAK2 filters selling at \$12.00 retail. The lower back-pressures required by photocopiers and laser printers was achieved by either stamping or molding processes. Finally, the efficiency of several of the carbon filters we have prepared were as good as currently used filters. We are currently investigating a variety of alternative applications for these engineered porous filter materials.

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²W.R Even, R.W. Crocker, M.C. Hunter, N.C. Yang, and T.J. Headly, "Surface and Near Surface Structure in Carbon Microcellular Materials Produced From Organic Aerogels and Xerogels," Proceedings of the International Symposium on Aerogels (ISA4), Berkeley, CA, September 1994.

³Efficiencies are adjusted to 5 mm thickness.

⁴Ulrich, G.D., A Guide to Chemical Engineering Process Design and Economics, John Wiley & Sons, New York, 1984.

⁵SCCO₂ operations do not include solvent exchange costs.

⁶*Chemical Engineering*, August 1994.

⁷*Chemical Engineering*, January 10, 1983.

⁸BOP thicknesses did not exceed 5 mm.

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