

ACTIVATED CARBON FIBERS - PAST, PRESENT, AND FUTURE

by

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Introduction

In this paper the background to the development of activated carbon fibers (ACFs) is reviewed, and then some of the recent progress of the past several years is discussed. Finally, a glimpse of the future for this field is provided which builds on some very recent results produced in our group.

The ACFs were first developed in the period of 1969-72 and made available in developmental quantities at that time. Since then, Nippon Kynol, the current manufacturer, has developed a number of niche markets which today have resulted in a multi-million dollar industry. Surprisingly, it is only in the last several years that a number of researchers have begun to examine this very interesting family of materials as witness the number of papers on ACFs in this Symposium.

It should be noted that the ACFs are currently priced in the range of \$100/lb and hence hardly compete with the activated carbon granules (ACGs) which are available for \$1.00/lb. and less. Hence, the ACFs only find commercial application in those areas where the unique textile forms of the ACFs permit use based on the greatly improved contact efficiency of the fibers. For the future, we have recently shown that we can prepare ACFs at a cost much closer to that of ACGs. Hence, one would anticipate a major market opportunity not only as a replacement of ACGs, but also from the creation of many new markets which are not available to ACGs because of the need for containment.

Past (1963 - 1975)

In 1963, at the Carborundum Co. we first showed that we could prepare crosslinked phenolic (phenol formaldehyde) fibers by spinning from a Novolac melt and then curing with $\text{HCl} + \text{CH}_2\text{O}$.⁽¹⁾ This fiber could be processed into a wide range of textile forms by conventional methods. It also displayed an outstanding flame resistance. In 1969 we commercialized this fiber under the trade name Kynol as a potentially low cost textile for use in highly aggressive environments.

More pertinent to this article, we showed in 1968 that we could produce a range of high surface area ACFs by heating the Kynol in steam 700 - 900°C (See Figure 1).⁽²⁾ By 1971 we began to make developmental quantities available commercially in the USA and also a joint venture company in Japan, Nippon Kynol Inc. In 1974, commercial development was transferred to Nippon Kynol and the program was terminated at the Carborundum Company.

During the period of 1968 - 74, we made considerable progress in developing and characterizing the ACFs. Thus, we were able to finalize on three ACFs with nominal surface areas of 1500, 2000 and 2500m²/g. The 2500m²/g ACF was shown to have the highest capacity, but was also the

most brittle. Considerable work was carried out to determine possible advantages over ACGs. It was found that for similar surface areas the ACFs displayed an almost 2x increase in breakthrough times over ACGs for removal of phenol or butane.⁽³⁾ The ACFs could be reactivated in situ by electrical resistance heating at 100 - 200°C (See Table 1). It was also shown that the modestly acidic pore surface of the ACFs could be converted to a basic surface by heating in ammonia at 600 - 900°C.⁽⁴⁾ Finally, it was found that high surface fibers (600m²/g) could be obtained by etching at much lower temperatures of 450°C to produce an activated phenolic fiber (APF).⁽⁴⁾ These fibers appeared to have a smaller pore size distribution, but could be made at somewhat lower cost than the ACFs.

Present (1990 - 94)

Starting in about 1990 we initiated a program at the University of Illinois to develop a far better understanding of the nature of activated carbons. Our intent was that we would not only develop a more predictive capability concerning the adsorption characteristics of ACFs, but that this could also lead to design of much lower cost fiber based systems that would be cost competitive to ACGs. Our expectation was that with a greatly improved understanding of the kinetics of adsorption and of contact efficiencies we would be able to design low cost systems that would be capable of removing trace contaminants in the low parts per billion (ppb) range.

Initially our efforts focused on pursuing possible leads from the work of the early 1970's. Thus we found that we could chemically convert the pore surface of the ACFs to a much wider range of chemistries (See Figure 2).⁽⁵⁾ As a result of these studies it became apparent that we could tailor the pore surface chemistry to be much more acidic or basic or more polar or relatively neutral. Several papers have already been published showing the utility of chemically tailored surfaces for selective removal of VOCs⁽⁶⁾ and of H₂O.⁽⁷⁾ The role of surface area and pore size and shape has also been examined in far greater depth particularly with respect to the dramatic changes in separation of contaminants at high versus low concentrations.⁽⁸⁾ A critical component of this study has been our ability to directly access the porosity in ACFs using Scanning Tunneling Microscopy (STM).⁽⁹⁾ As a result of these studies we are now able to directly measure the microporosity dimensions and correlate these measurements with the adsorption characteristics of the ACFs. All of these issues are discussed in far greater detail in the ensuing paper by Daley, et al.

The earlier work on the APFs has also been reexamined during the last several years and the conditions for reproducible manufacture have been identified. (See Figure 3) We have also shown that the APFs have modestly improved wear resistance over the ACFs.⁽⁴⁾ As might be expected the microporosity is smaller (in the range of 5 - 7Å as compared to 10 - 13Å for ACF 1500). The potential for design of molecular sieve-like carbon is clearly a possibility from this work.

Future (1996 -)

One of the most exciting aspects of our program has been the recent announcement that we had developed a low cost alternative to ACFs.⁽¹⁰⁾

This was accomplished by coating glass fibers with a phenolic resin. Activation of the phenolic coating can be carried out by any one of a number of techniques normally used for ACFs. Thus, for the first time one has access to a very low cost activated fiber assembly. Typically, phenolic resins are available for 60 - 70¢/lb while the glass fiber, depending on its product form, can cost well under a dollar for non-wovens and somewhat higher for woven textiles. In order to maintain flexibility of the final textile we limit the percentage of phenolic resin to ~30% by volume in the case of woven textiles. With non-woven textiles, paper or felt we can go to much higher loadings of phenolic resin. This may appear to be a limitation in terms of the amount of activated material for a given volume. However, we find that the contact efficiency is greatly improved compared to ACFs which of course are significantly better than ACGs (See Figure 4). Obviously reactivation of the spent assembly would be much faster than with ACFs. From preliminary tests the glass fibers coated with activated carbon can be reactivated by electrical resistance heating at 100 - 200°C or by use of steam at 120 - 170°C.

An important advantage of the activated, glass coated textile is the greatly improved wear resistance of this material. We believe that this arises from the fact that the coating provides protection to the glass fiber surface, which otherwise would be very sensitive to damage.

As a result of our recent announcement concerning this development we have had a number of inquiries from industry concerning commercial availability and utility. Currently, we have identified a number of companies that would be interested in participating in those aspects of the manufacture of this new product where they have a core competency. We are also starting to talk to companies that would be interested in acting as product form assemblers. In the new environment in industry, which requires focusing on one's core business, few companies appear willing to embrace the entire spectrum of activities required for commercial development of a new product. On the other hand, this product appears to lend itself to the establishment of a virtual business involving 3-4 companies to manufacture the product. With such an approach, only a minimal investment in manufacturing and scale-up would be required. A similar argument can be made for product assembly.

One area that we are examining carefully is that of chemical warfare including nerve gases. Up to now, gas masks that depend on ACGs have been in use for the past 50 years. However they are cumbersome and expensive and because of the acidic nature of the pore surface are not as effective against most of the toxic agents which are also acidic. It would seem that fabric which is easily deployed as a hood over the head and shoulders would provide very low cost protection against most all of the chemical warfare agents. To further enhance the adsorption capacity it would be important to activate in such a way that the pores are basic and would bind the toxic chemicals more tightly. If indeed all this proves to be correct, we may have available for the first time the ultimate defense against chemical warfare and one that would discourage future use of such methods by terrorists.

Other directions that we are now beginning to pursue is the use of these new activated assemblies as catalyst supports. We also plan to revisit some of our earlier work of 28 years ago on hyperfilters based on activated membranes⁽¹¹⁾ and on ion exchange fibers⁽¹²⁾ which are tailored to remove specific metal contaminants.

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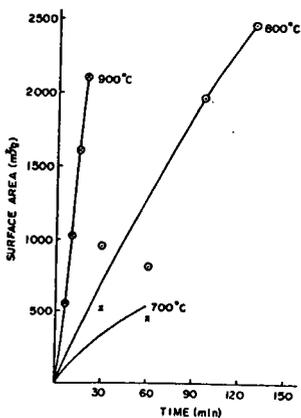


Fig. 1
Steam Activation of Carbonized Kynol Fibers

Sample	PAC Before Adsorption (mg/g)	Reactivation Time (min)	Current (amp)	PAC After Reactivation (mg/g)	Capacity Regain (%)
1	139	10	3	88	66.5
2	140	10	4	---	---
3	153	10	5	46	38.0
4	131	10	2	113	86.0
5	160	10	1	94	52.5

Table 1
Effect of Current Strength on Phenol Adsorption Capacity Regain in Electrical Reactivation

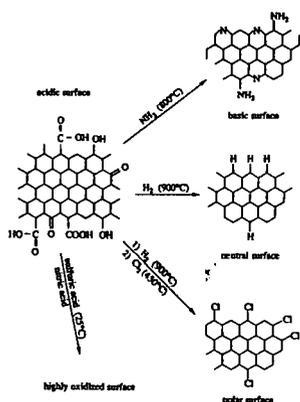


Fig. 2
Chemical Treatment of ACFs Produces a Number of Different Surface Chemistries

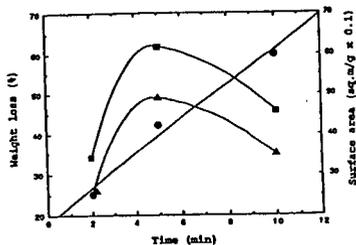


Figure 3
Heating Phenolic on Hot Plate at 450°C for Increasing Times
circle- wt loss (%)
square- Langmuir S.A.
triangle- B.E.T. S.A.

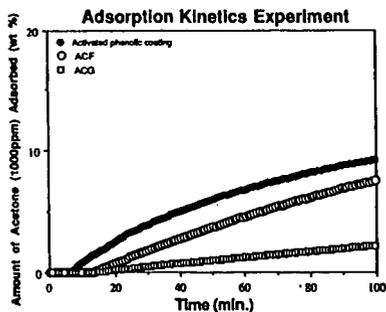


Figure 4
Comparison of Adsorption Kinetics of ACG, ACF, and Activated Phenolic Coating