



## Filtrona Technology Centre

### **The Adsorption of Various Smoke Compounds by Activated Carbon**

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#### **Summary**

The ability of a porous material to adsorb compounds from gas or liquid streams is often related to a number of physical properties of the material such as surface area, pore size distribution and to some extent the nature and surface functionality of the material. A number of methods are used by carbon suppliers to measure the overall adsorption capacity or activity of carbon by measuring the adsorption of compounds such as carbon tetrachloride, butane, iodine or molasses. Commonly for carbons used in gas applications the carbon tetrachloride or butane activity would be quoted and for carbons meant for liquid applications iodine number or molasses number used. How do such measurements that often rely on adsorption only relate to activity in cigarette smoke? In such a complex mixture as cigarette smoke carbon activity is often measured as the average retention of a range of vapour phase compounds. But how does the chemistry and volatility of compounds in smoke affect the adsorption by carbon?

Measurements of adsorption isotherms for coconut shell carbon have been carried out for a range of smoke compounds to see how these compounds are adsorbed by carbon. Data will be presented on the adsorption of a range of compounds and how the volatility and chemical nature of the compounds affects the levels of adsorption. In particular the adsorption and possible chemisorptions of acetic acid by carbon will be discussed.

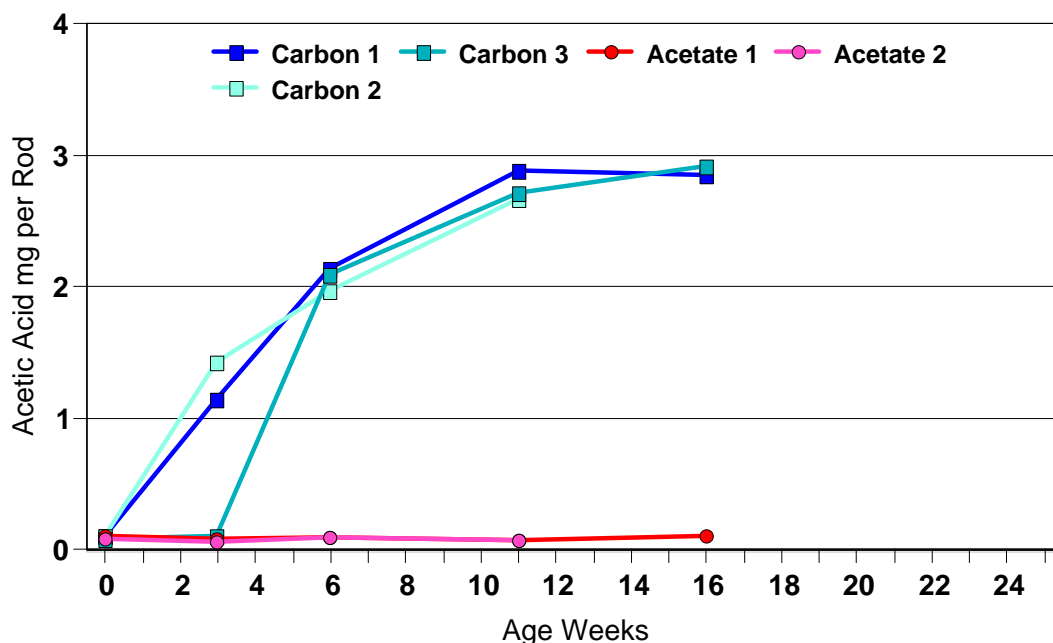
### **The Adsorption of Various Smoke Compounds by Activated Carbon**

The ability of a porous material to adsorb compounds from gas or liquid streams is often related to a number of properties of the material such as surface area, pore size distribution and to some extent the nature and surface functionality of the material. In general the adsorbability of a compound by carbon, increases with, increasing molecular weight, a higher number of functional groups such as double bonds or halogen compounds and increasing polarisability of the molecule. A number of methods are used by carbon suppliers to

measure the overall adsorption capacity or activity of carbon by measuring the adsorption of compounds such as carbon tetrachloride, butane, iodine or molasses. Commonly for carbons used in gas applications the carbon tetrachloride or butane activity would be quoted and for carbons meant for liquid applications iodine number or molasses number used.

The situation is much more complex for cigarette smoke. A very complex mixture is presented to the carbon and the carbon is often already partly loaded with previously adsorbed material such as volatiles from the filter including plasticiser and plasticiser hydrolysis products and volatiles from tobacco in an assembled cigarette. Previous work has shown that the ability of activated carbon to reduce compounds in smoke is reduced the longer the filters are stored before use. Greater deactivation is usually given for cigarette storage than for filter storage. Triacetin may be involved in the deactivation of carbon but during rod storage some degree of hydrolysis of the Triacetin occurs for all filter types. This rate of the hydrolysis is faster for rods containing carbon than for monoacetate rods<sup>1</sup> with the temperature and time of storage affecting the amount of acetic acid generated.

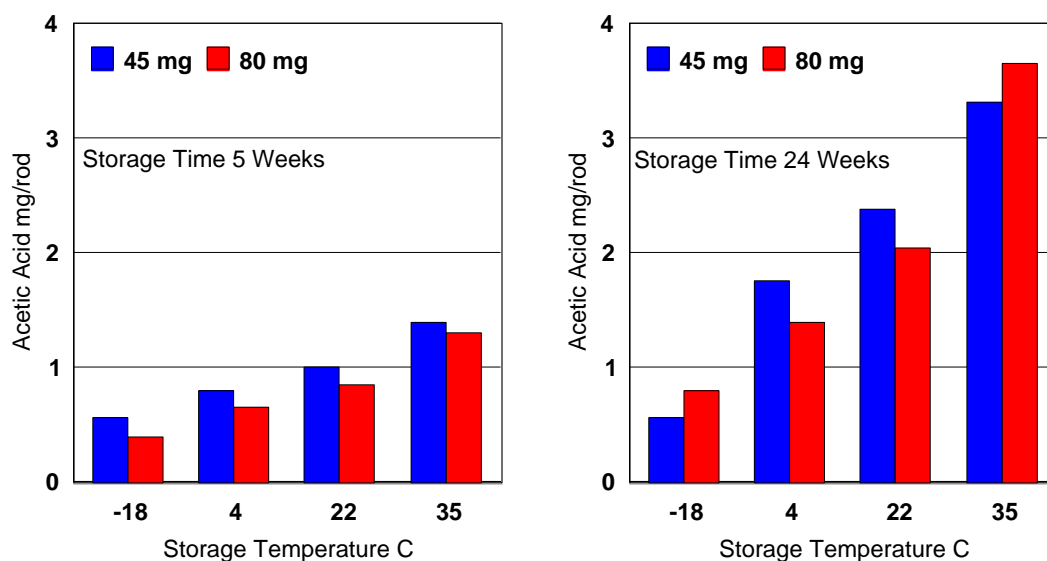
The difference in acetic acid generation for filters containing carbon with that for a monoacetate filter is shown in figure 1. In this example the carbon filter is a carbon on tow filter containing about 4mg of carbon per millimetre of filter length. All the filters were stored under standard laboratory conditions of 22 C and 60% RH. It can be seen that the acetate filters maintain a low and relatively constant amount of acetic acid around 0.1 mg per rod. Whereas, the acetic acid level of the carbon filter rods increase quite steadily as they are stored and after about 6 weeks the acetic acid level is about 2 mg per rod and after about 3 months this has increased to about 3 mg per rod for the examples shown below.



*Figure 1 Acetic Acid Generation in Carbon and Acetate Filters*

During storage some carbon filter rods give an initial increase in acetic acid but others seem to take 2 or 3 weeks before the generation of acid starts at an appreciable rate. At this point in time it is not clear why this difference occurs. Generally the amount of acetic acid increases as storage time increases for periods

of up to about 6 months. After this time the levels of acetic acid reach a constant value or start to decline slightly. As previously mentioned the time and temperature of storage also affects the levels of acetic acid in filter rods. Figure 2 shows a



*Figure 2 Effects of Temperature and Time on Acetic Acid Levels*

comparison of carbon on tow dual filter rods with different levels of carbon, 45 and 80 mg per filter. These filters were stored at a range of temperatures from -18 to 35 C for periods of up to six months. It can be seen that the higher the temperature of storage the greater the amount of acetic acid generated. This is as perhaps expected as the rate of most chemical reactions including hydrolysis is faster at higher temperatures. Despite the acetic acid generated an odour of vinegar is very rarely found on carbon filters so what happens to the acetic acid generated?

To evaluate how carbon adsorbs and desorbs different compounds simple adsorption and desorption experiments have been carried out using various compounds found in smoke and cyclohexane which is used in our laboratory as a standard material to measure the activity of carbon. The compounds that have been studied are acetaldehyde boiling point 21C, acetone boiling point 56C, cyclohexane boiling point 81C, water boiling point 100C, toluene boiling point 111C, acetic acid boiling point 119C and styrene boiling point 145C. These give a range of boiling points from acetaldehyde in the vapour phase fraction up to styrene that would be considered part of the semi-volatile fraction in smoke. Tests were carried out using coconut shell carbon that had been dried overnight at 105C in an air circulating oven. Approximately 5g of dry carbon was accurately weighed and placed in a shallow glass crucible with a sintered glass base. This crucible was placed in a small desiccator containing a reservoir of the liquid under test. The crucible was removed and weighed periodically and weight increase expressed as a percentage of the initial weight of carbon. Four replicate determinations were carried out for each test. Most of the experiments were carried out for a period of 2 to 3 days or until equilibrium weight was established. Desorption was measured using the same crucibles removed from the desiccator and placed in an air flow and again weighed periodically.

Under these test conditions the adsorption of the carbon is measured at the equilibrium vapour pressure of the chemical under test. The data is plotted showing percentage weight increase against time as shown in figure 3. It can be seen that acetaldehyde, acetone, cyclohexane and toluene gives the expected adsorption behaviour with a rapid adsorption of the material reaching constant values of 31%, 31%, 30% and 35% respectively. Water seems to adsorb more slowly and finally reaches a constant value of about 27% after 3 days. The adsorption of styrene takes longer but does reach a constant value of around 40% after 3 days.

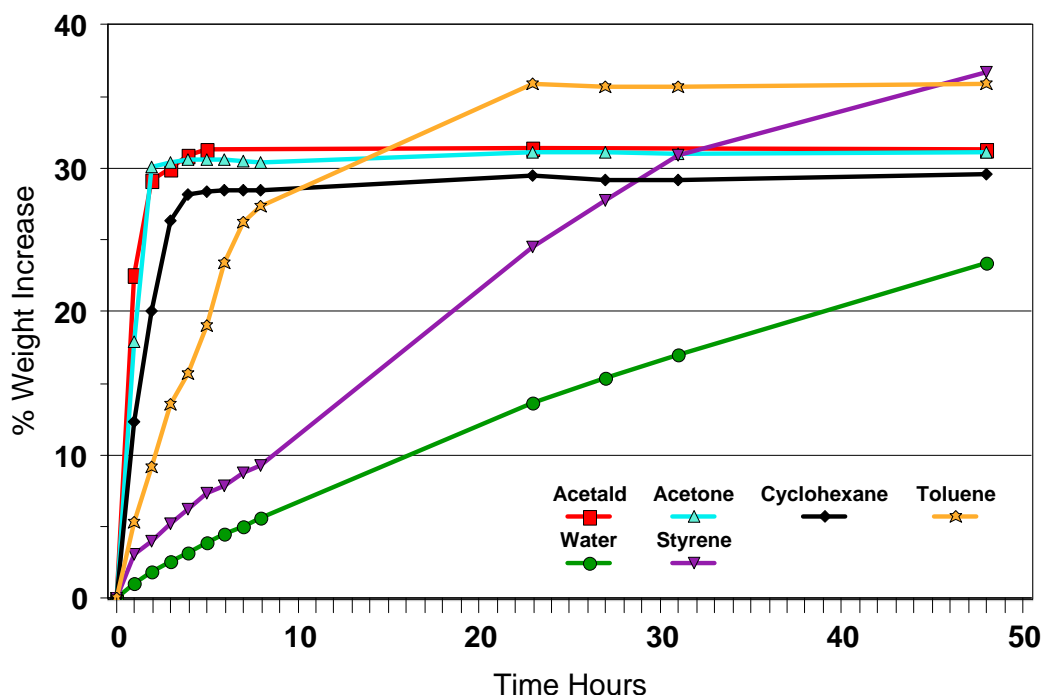


Figure 3 Adsorption of Various Compounds

Looking now at desorption, figure 4 below, gives the plot for the organic compounds studied. All show rapid initial desorption and as perhaps may be expected the rate of desorption seems to be mainly governed by the boiling point of the material under test. Over a two day test period acetaldehyde with the lowest boiling point is almost totally desorbed but styrene with the highest boiling point remains on the carbon and only about 6 to 7% of the adsorbed styrene is lost to the atmosphere. The rate and amount of desorption seems to depend entirely on the boiling point of the material which suggests that the adsorption of these compounds is caused by weak physical interactions and very little chemical effects are contributing to the adsorption. As the surface of carbon is relatively inert this is what would be expected. But what happens in then case of acetic acid?

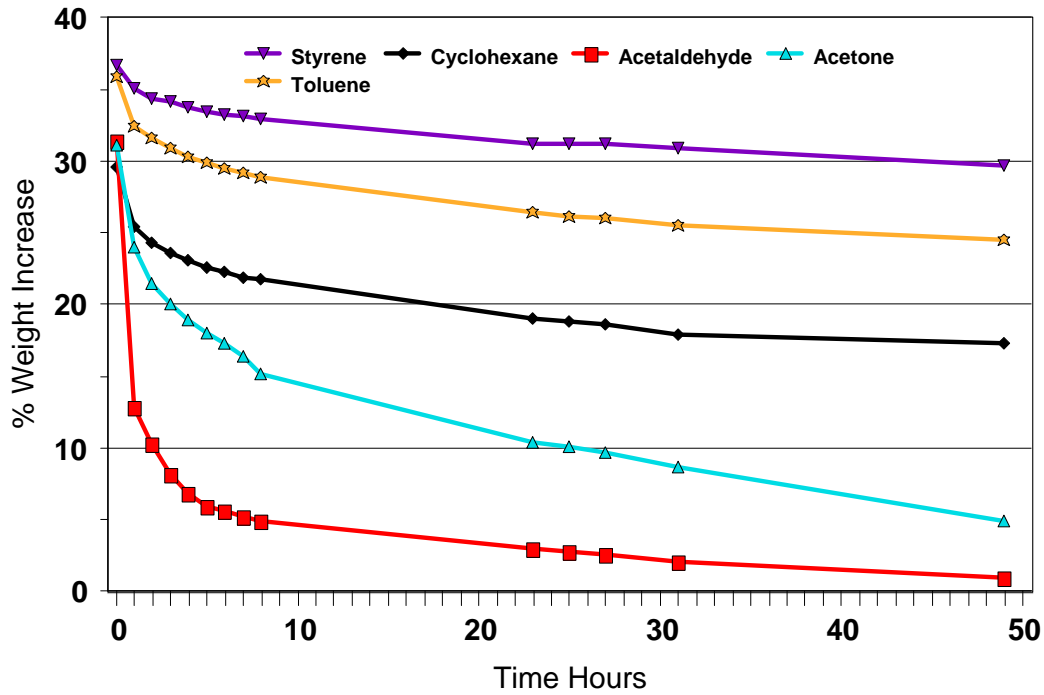


Figure 4 Desorption of Various Compounds

During rod storage the carbon is continually exposed to small amounts of acetic acid generated by the hydrolysis of triacetin. It is well known that coconut carbon is alkaline in nature and a water extract usually has a pH in the range 9 to 10. Therefore acetic acid should give some reaction and so the adsorption may not be typical as it may be expected to be given by a mixture of physical and chemical effects. Under the same conditions as the proceeding work figure 5 for the adsorption of acetic acid is shown below.

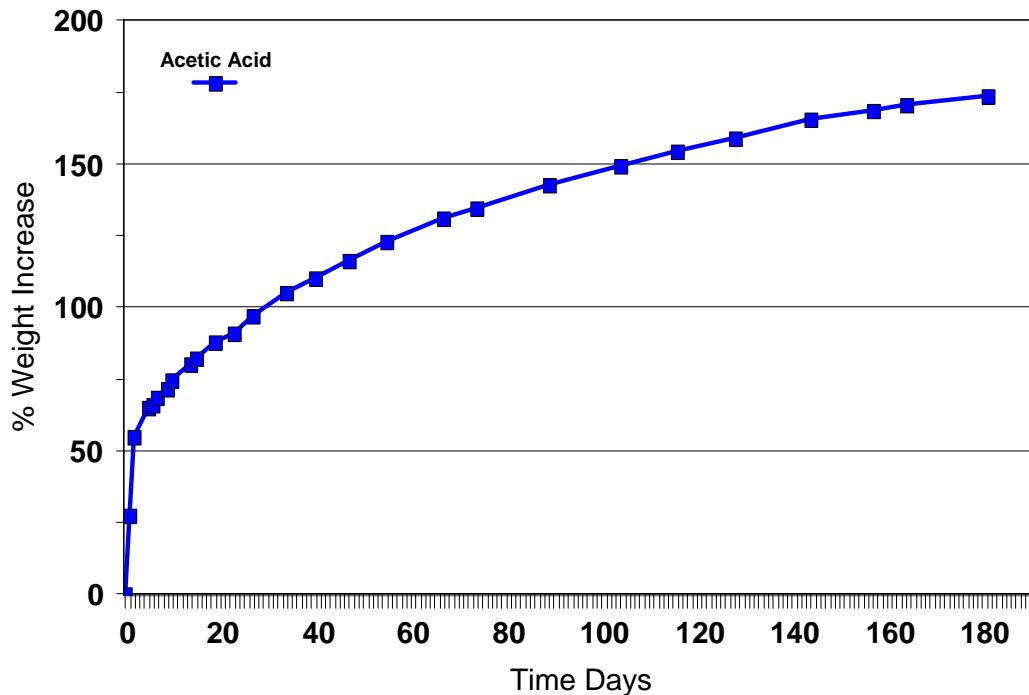
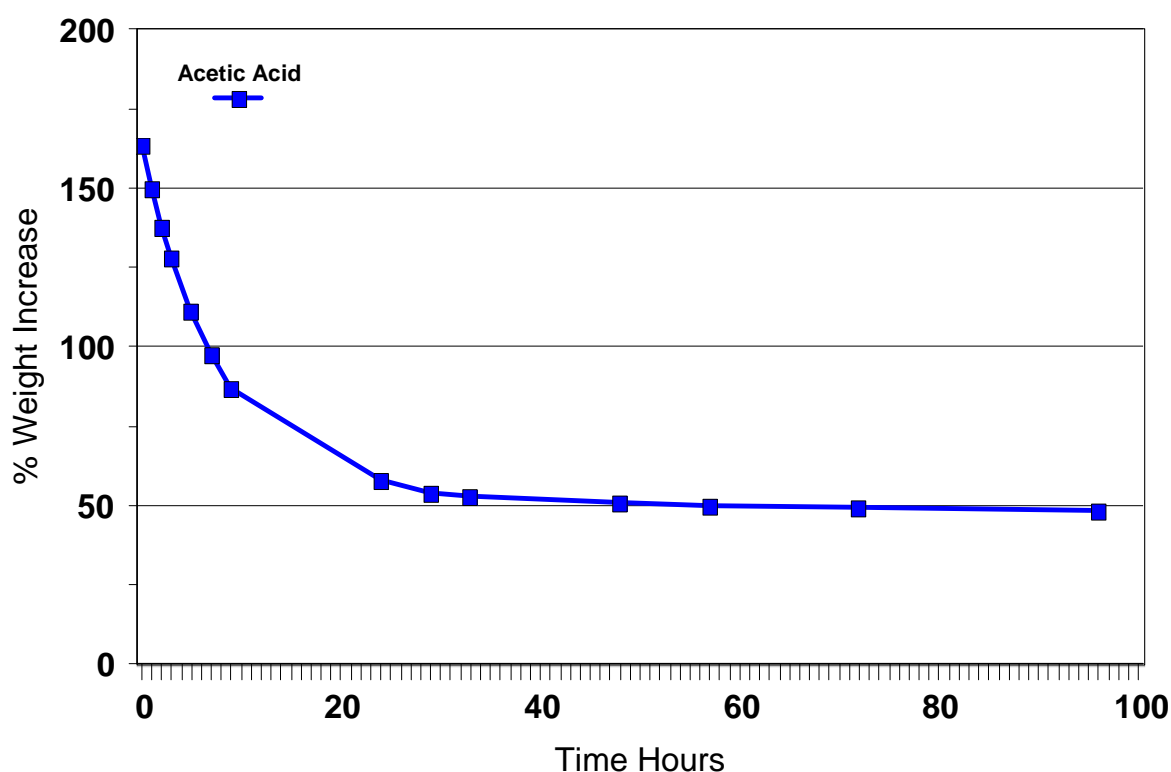


Figure 5 Adsorption of Acetic Acid

It is immediately apparent that the timescale and amount of the adsorption is very much higher than the previous compounds. A weight increase to over 50% is given in the first 2 days of testing followed by a reasonably steady rise for many weeks giving a weight increase of over 150% in a 6 month period. After this time the experiment was terminated even though an equilibrium weight had not been reached. During this experiment the outside surface of the carbon appeared wet so that perhaps the acetic acid was being collected on the outside surface of the carbon as well as on the inner surface.

However, it does suggest that carbon in a filter rod stored for some months can easily adsorb all of the acetic acid generated and this perhaps explains why although much larger amounts of acetic acid are measured in filter rods containing carbon no odour of acetic acid is usually detected. The desorption curve for acetic acid is shown in figure 6.



*Figure 6 Desorption of Acetic Acid*

The desorption seems to be similar to the previous desorption curves except that the amount of acetic acid remaining on the carbon is perhaps higher than would be expected from the boiling point alone. The boiling point of acetic acid is lower than styrene and slightly higher than toluene but after 50 hours of desorption the carbon only retains between 25 and 30 % of these compounds whereas about 50% of the acetic acid remains on the carbon. This apparently stronger binding of some of the acetic acid to the carbon could be due to some of the acetic acid under going chemisorption on the alkaline coconut shell carbon. It is probable that any chemisorption is less reversible than the normal physical adsorption so that some of the acetic acid may be so strongly bound to the carbon that it could not be displaced by any smoke compounds when the cigarette is smoked.

During storage of carbon filter rods acetic acid is generated and adsorbed and perhaps chemisorbed by the carbon. After storage the rods would be assembled into cigarettes and the cigarettes then smoked. So how does the acetic acid in the filter rod affect the performance of the carbon as far as adsorption of smoke vapour phase compounds is concerned? To measure this effect carbon loaded with different levels of acetic acid have been tested during smoking for retention of a range of vapour phase smoke compounds. Briefly the method used<sup>2,3</sup> involved hand preparing filters filled with carbon containing different levels of acetic acid and comparing these cigarettes with a control cigarette. The carbon was loaded with 0, 10, 50 or 100% of acetic acid by weight. Figure 7 shown below gives a comparison of the retention of 12 vapour phase compounds for the untreated carbon and carbon loaded with different levels of acetic acid.

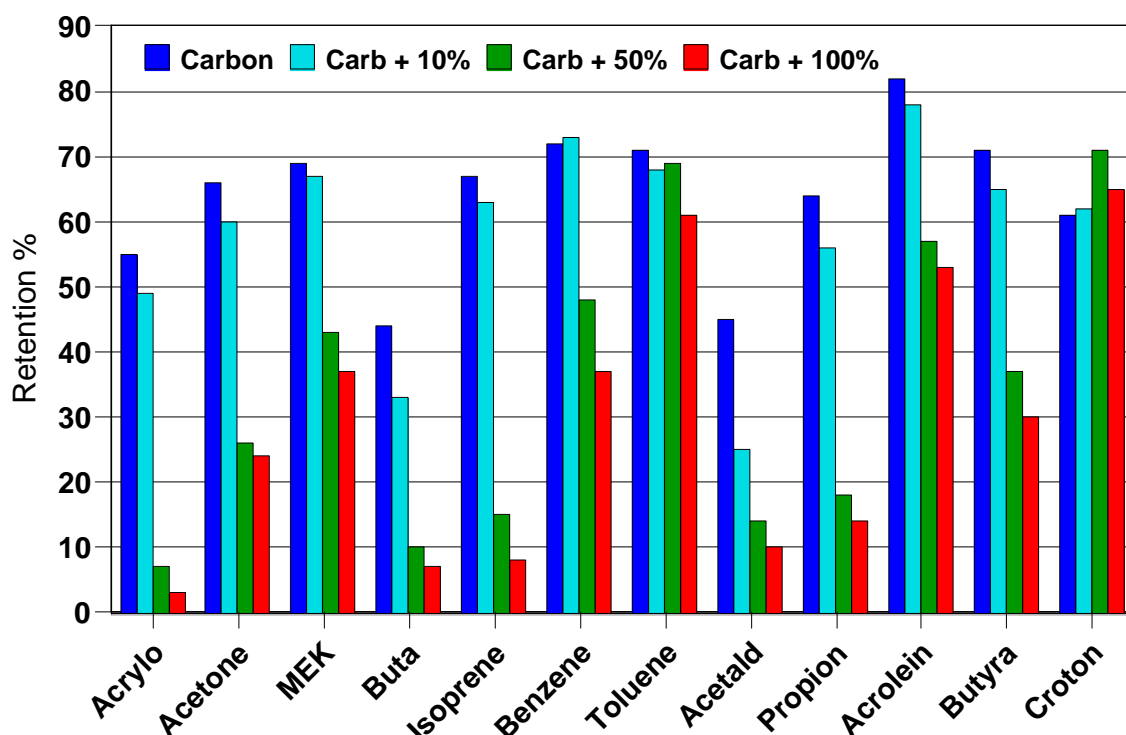


Figure 7 Vapour Phase Retentions

The difference in performance between the carbon loaded with acetic acid and the untreated, 0% loaded, carbon gives an indication of the effect of the acetic acid on the ability of the carbon to adsorb vapour phase compounds from the smoke. The weight of carbon used was calculated to give the same weight of dry carbon in the filter. It can be seen that very high acetic acid loadings, 50 and 100%, seem to considerably reduce the retention of the majority of the vapour phase compounds. In contrast the 10% acetic acid loading has much less effect on the retention of the carbon. In practise of course the relative amounts of carbon and triacetin in a filter rod and the amount of acetic acid generated would tend to give samples with less than 10% acetic acid on the carbon. It should also be noted that in this work only the effect of acetic acid was determined, in practice carbon in a filter could contain acetic acid and a range of other compounds adsorbed from the filter and/or the tobacco. Looking at some of the compounds tested in more detail it can be seen that in general the boiling point of the compound to be adsorbed seems to have a large

effect on the amount reduction in retention given by the carbon loaded with acetic acid. The retention of the most volatile material 1, 3 butadiene is slightly reduced even for the 10% loaded carbon and significantly reduced for the 50 and 100% loaded carbon. But for the least volatile hydrocarbon, toluene, the presence of acetic acid on the carbon does not seem to have a significant effect at any of the acetic acid loadings tested and even the 100% loading only gives a small reduction in the retention of toluene from smoke. In general for aldehydes the higher the boiling point of the aldehyde the lower any effect seen from the loading of acetic acid on the carbon. But as mentioned earlier the adsorption by carbon can also be affected by functional groups such as double bonds. This may be why acrolein has a higher retention than butyraldehyde despite having a lower boiling point. As for the hydrocarbons the compound with a boiling point near that of acetic acid crotonaldehyde, which also has a double bond, does not show any reduction in retention for acetic acid loaded carbons. The most volatile aldehyde, acetaldehyde, shows significant reduction in retention for any of the acetic acid loadings studied.

The work shows that the Coconut shell carbon typically used in cigarette filters has the capacity for the adsorption of very high levels of acetic acid. Carbon containing the levels of acetic that may be practically found in cigarette filters does not show significant deactivation towards smoke compounds. Deactivation of carbon in cigarettes is an extremely complex phenomenon and is probably due to contributions from a number of causes. Carbon can adsorb low levels of compounds during storage and still show significant activity towards cigarette smoke.

## References

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- 2) The Influence of Pre-cursor Materials on the Properties of Various Activated Carbons, N C Thompson and M J Taylor CORESTA Congress Paris 2006
- 3) The Activity of Different Carbon Weights in a Cigarette Filter and the Effects of Triacetin, J Walker and M J Taylor CORESTA Study Group Meeting Korea 2007

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