

# The Influence of Pre-cursor Materials on the Properties of Various Activated Carbons - Coresta Presentation 2006

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## **Abstract**

Activated carbon is a non-graphite form of carbon which can be produced from any carbonaceous raw material such as coal, lignite, wood, peat, coconut shell, petroleum coke, bones and fruit nuts. Although anthracite and bituminous coals are the major sources, activated carbon produced from the physical activation of coconut shells has traditionally been used within the tobacco industry.

Increasing records of droughts, diseases, pests, cultivation of palm trees in lieu of coconut trees and the devastating South East Asian earthquake; has caused the commercial availability of coconuts to hit record lows, more than twice in the last decade.

This study involves a thorough investigation of activated carbons derived from different precursor materials; and consequently their ability to reduce volatile aldehydes, hydrocarbons, ketones, phenolic compounds and semi-volatile bases in cigarette smoke; compared to coconut shell based material. In addition, important physical properties such as micropore and mesopore distribution, cyclohexane activity, moisture content, density and pH have also been reported. The advantages and disadvantages of each carbon type for potential use in cigarette filters are discussed.

## **Introduction**

The first references relating to the effective properties of charcoal date back to Ancient Egyptian times where it was primarily used for its medicinal purposes. Centuries later, carbon was still being used for the purification of beer and drinking water and by the late 19<sup>th</sup> century carbon was used on an industrial scale for the decolourisation and purification of sugar cane. However, it was not until the beginning of the First World War that the potential of activated carbon was first capitalised upon. The advent of gas warfare necessitated the development of suitable respiratory devices for personnel protection. During the late 1930's there was considerable industrial scale use of carbon for gaseous and liquid phase applications and new manufacturing processes had to be developed to suit the needs of the industry. Modern day uses of activated carbon are diverse to say the least, and this nanoporous material is certainly the most widely used sorbent due to its unique adsorption properties, attributed to its large micropore and mesopore volumes and the resulting extended surface area.<sup>1</sup>

World production capacity for activated carbon is concentrated among relatively few countries and manufacturers. For solely gas purification purposes there is a combined capacity of over 500,000 tonnes of activated carbon per year, the USA and China accounting for 50% of this

World total. Ten leading producers and their subsidiaries operate some 60% of the total capacity Worldwide. Calgon are the largest manufacturer producing 108,000 tonnes per year followed by Norit producing 69,000 tonnes and MeadWestVaco producing 55,000 tonnes, the remainder of activated carbons for gas purification purposes are manufactured by numerous, smaller carbon companies.<sup>2</sup>

World demand for activated carbon to cover all applications is forecast to expand around 5% per year through 2009 to over 1.2 million metric tonnes in 2010. The largest, most mature markets of North America, Western Europe and Japan, despite the slow growth, will continue to account for over half of the demand in 2010. The location of production has noticeably shifted from Western industrialised countries to China and South East Asian Countries, where there are lower associated raw material, energy and labour costs; it is in these markets where greater growth opportunities are expected to occur. In fact, China is expected to increase its share of the global market to around 15% in 2010. For the majority of developed nations, weak growth prospects will be associated with water treatment and motor vehicle applications, as these have been significantly exploited for many years. However, in developing markets, gains will be driven by increasing industrial output and a greater emphasis on environmental pollution for the removal of contaminants in both liquid and gas streams. As a consequence of these factors, several manufacturers have planned rapid expansions in order to meet this increased demand.

The availability of activated carbon for industrial use has much to do with accessing resources, renewing resources and processing to rigid specifications to control specific industrial applications. Almost any carbonaceous material with low organic volatile content, high in elementary carbon and sufficient chemical strength can be converted into activated carbon. However, typically only a handful of resources are used for activated carbon production, including several ranks of coal, peat, wood, fruit stones and nut shells, as well as coconut shells and some organic polymers. The key element in the success of an activated carbon is the reliability and constancy of the resource. Some carbonaceous materials provide mass yields that are so low typically less than 10%, as a result of volatile losses being so high, that their use is precluded. In some industrialised countries, there is interest in alternative raw materials such as oil mallee trees, rice hull ash, banana skins, straw and many organic waste materials. Collection from separated areas, transportation, bulk availability and seasonal variations in quality and availability are reasons why some of the above resources are not used.

In China, 60% of activated carbon production is based upon coal with wood being the second most commonly used pre-cursor. In Russia, activated carbon is manufactured from a selection of wood, coal and peat; this is in contrast to the production throughout Indonesia, Malaysia, the Philippines and Sri Lanka where the sole pre-cursor is based upon coconut shells. This variation in pre-cursor material results from associated costs of the raw material. Coconut shells and some other fruit nuts are agricultural solid waste products, which are available in large quantities; hence they are a very cost effective raw material for the preparation of activated carbons.<sup>3</sup>

Activated carbons predominately based upon coconut shell as a pre-cursor, have been traditionally used in cigarette filters since the 1950's in various products. The ability of activated carbon to reduce the levels of components in smoke is now well established. Japan was most notably the first market to use activated carbon in a major way, yet from this humble beginning

the use of carbon in cigarette filters has grown phenomenally and currently it is one of the fastest growing segments of the filter market. Global market data is very hard to obtain but results from a survey conducted by Filtrona in May 2003, identified there were 339 brand variants of carbon filtered cigarettes spanning across 59 countries.<sup>4</sup>

Due to the increasing demands on the current carbon resources and the predicted future rise in usage, it is essential that industries that rely on carbon as a primary raw material can find suitable alternatives to sustain their product range. With particular reference to the tobacco industry, a high proportion of our current and future product range will contain activated carbon and therefore this research project was implemented to establish the best possible equivalent to coconut shell based activated carbon for use in cigarette filters. It is also important to stress that activated carbons from different feed stocks will have different pore size distributions associated with them and possibly different adsorption properties with reference to coconut shell based materials, which could lead to more superior adsorption of components from cigarette smoke, and hence could result in a possible successor of coconut shell activated carbon.

### **Experimental**

There is no universal form of activated carbon that is capable of performing with the required efficiency for every industrial application. Instead, there are a range of commercially activated carbons available on the market as a result of intensive research and development programmes. The economics and availability of the parent materials are just as important as the desired internal pore volume (surface areas), the right type of porosity and surface chemistry. Close control of the activation process enables the production of a wide range of activated carbons with different physical and adsorptive properties, usually specified upon pore size distribution, adsorption capacity, surface area or other physical properties such as bulk density, ash content, pH value and particle size. For this investigation eight commercially available carbons were pre-selected according to internal surface area, this parameter being selected as a result of the influence it plays upon adsorption capacity. The carbon feed-stocks included coconut shell, wood, coal, peat, bamboo, almond shell, olive stone and a synthetic based carbon, all selected with surface areas in the range of 900 to 1200 m<sup>2</sup>g<sup>-1</sup>.

Filtrona has developed a reliable and reproducible method to evaluate a wide variety of granular materials for selectivity towards cigarette smoke. The analysis employs the use of specially formulated cigarettes, consisting of a 27 mm long filter, which in turn consists of a 10 mm segment of cellulose acetate capping the tobacco rod. In this study a fixed weight of dry carbon, 80 mg, was added to each cigarette and the cigarette completed by inserting an 8 mm length of non wrapped acetate to complete its construction. The non wrapped acetate material helps to give an effective seal downstream of the granular material and was always inserted into the cigarette so that the granular material formed a full cavity in the filter as shown in Figure 1.



**Figure 1: Schematic representation of the test cigarette incorporating a granular additive and the control cigarette consisting of an empty cavity**

Consequently, this led to a shorter recess in the mouth end of the filter for some activated carbons. Control cigarettes were prepared in the same manner with the exclusion of any carbon material. The only difference between the control and sample cigarettes was the bed of material produced by the individual activated carbon under study. All cigarettes were conditioned for 48 hours in the usual manner before smoking and all smoking procedures were carried out in accordance with standard ISO procedures. A range of Hoffman analytes were measured with boiling points in the range of -20 to 250°C; these include many of the well known toxicants such as volatile cyanides, aldehydes, ketones, hydrocarbons, semi-volatile bases and cresols and phenolic compounds.

In order to calculate the effectiveness of the carbon additive, the following equation (Equation 1) was employed to determine the percentage retention of the individual compounds of interest; where the greater retention values correspond to lower yield of components and therefore potentially lower risk to the smoker.

$$\% \text{ Retention} = \frac{\text{ControlCigaretteYield} - \text{TestCigaretteYield}}{\text{ControlCigaretteYield}} \times 100 \quad \text{Equation 1}$$

A range of significant physical tests were carried out on each of the individual carbons, which included bulk density, moisture content, activity measurements (this method measures the equilibrium weight increase given when the material is exposed to cyclohexane vapour in a desiccator) and pH of an aqueous extract which was carried out in accordance to the ASTM standard test method for the determination of pH of activated carbon (D3838-05). The results obtained from the study are displayed in Table 1.

Carbon Type	Moisture Content %	Density g/cm <sup>3</sup>	Cyclohexane Activity %	pH
Coconut	14.7	0.57	29.8	9.73
Almond	11.8	0.54	34.5	10.10
Bamboo	16.3	0.55	20.2	5.50
Coal	6.9	0.57	35.7	8.06
Olive	21.3	0.41	48.5	7.10
Peat	13.2	0.40	36.8	9.28
Synthetic	3.4	0.58	48.4	8.75
Wood	19.0	0.36	63.0	1.57

**Table 1: Physical Properties for each of the activated carbons studied**

It is evident from the data that the wood based carbon consisted of an acidic surface; most likely associated with residual acidic groups following the activation process. The remaining carbons were found to have alkaline surfaces, similar to coconut, with the exceptions of olive stone and bamboo based carbons which were found to be of neutral pH.

Adsorption isotherms, involving the controlled physical adsorption of nitrogen gas at 77K, which fills both the micro and meso porosity of carbons; makes it possible to quantitatively determine the pore size distribution of activated carbons. Adsorption isotherms were measured for each of the eight activated carbons; the results of which are shown below in Table 2.

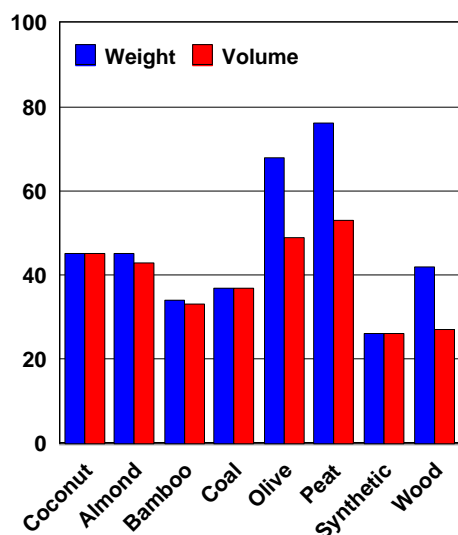
Carbon	Micropore Volume	Mesopore Volume
Type	<2 nm (ml g <sup>-1</sup> )	2 - 50 nm (ml g <sup>-1</sup> )
Coconut	0.341	0.084
Almond	0.333	0.142
Bamboo	0.230	0.116
Coal	0.407	0.318
Olive	0.589	0.423
Peat	0.380	0.148
Synthetic	0.166	0.270
Wood	0.504	0.608

**Table 2: Micropore and mesopore volumes determined from adsorption isotherms**

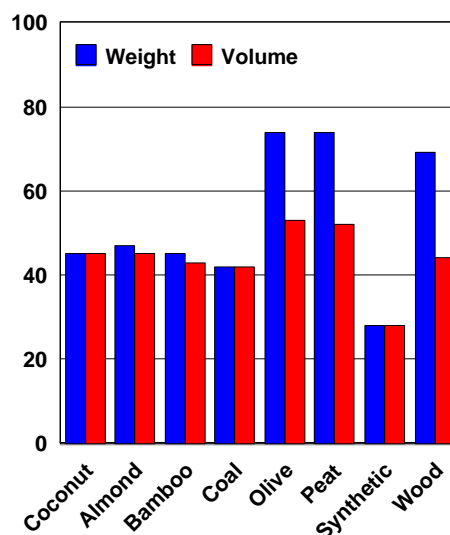
The results showed that the carbons were all typically microporous, with the exception of bamboo carbon, which was found to have a significantly lower micropore volume with respect to coconut shell based material. The variation observed in mesopore volume was much greater for the eight carbons. Coconut shell material was found to contain very few mesopores whilst the wood based carbon had a much greater content. It should be stressed that an optimised balance of both mesopores and micropores are required for efficient adsorption. Although, micropores play a significant role in the adsorption of gases and vapours, mesopores are also very influential as they act as transport pores, providing routes into the adsorbing material.

Chemical testing carried out in this study involved the use of a fixed weight of carbon for each test cigarette. However, a filter of fixed length and circumference has a fixed volume which is usually partly filled by fibrous material. Consequently, there is a limit to the maximum volume of granular material that can be added. Therefore, when comparing materials of different density it is important to consider comparisons between using equal volumes as well as equal weights. The following data plots illustrate retention values of the individual carbons based on equal weights and equal volumes basis.

The following two data plots (data plots 1 and 2) show the retention of the volatile cyanides, hydrogen cyanide and acrylonitrile and the retention of aldehydes respectively; which include the following six components acetaldehyde, acrolein, butyraldehyde, crotonaldehyde, formaldehyde and propionaldehyde.



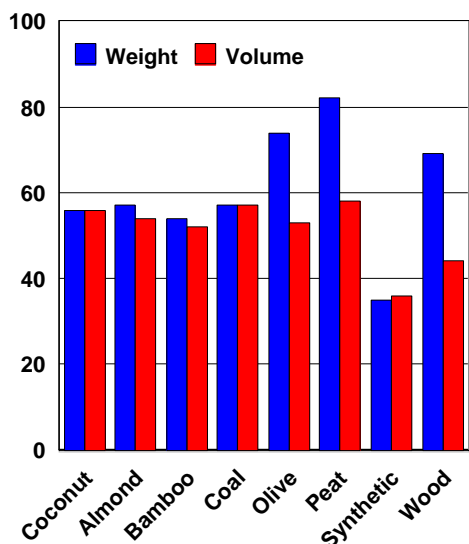
Plot 1: Retention of the volatile cyanides



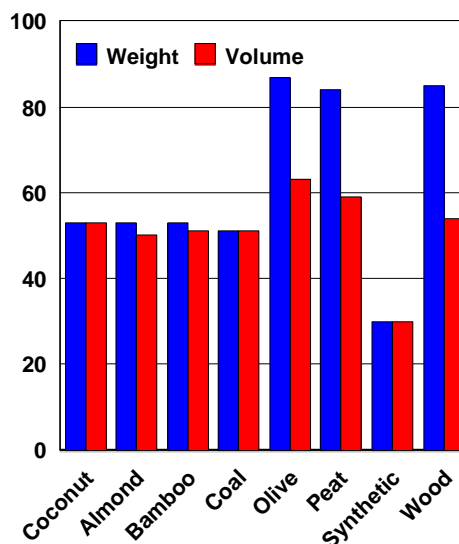
Plot 2: Retention of the aldehydes

The data plots for the respective removal of volatile cyanides and aldehydes illustrate that the retention efficiency of these components does vary depending upon the activated carbon feedstock used. It can be seen that almond shell, coal, bamboo and coconut are found to retain less volatile materials compared to olive stone and peat based feed-stocks. The results show that compared to coconut shell carbon (the industry standard), almond shell and coal based carbons are found to behave in a similar manner. The data for each of the carbon feedstocks is very similar for both the retention of volatile cyanides and aldehydes. This suggests in the majority of cases the carbon is not selective towards one or more components. However, this is contradictory to the results obtained for the wood based material, where the retention results for volatile cyanides are clearly lower than the data obtained for the retention of several aldehydes. This may be explained in terms of repulsion mechanism resulting from the acidic nature of both the carbon adsorbent and the cyanide adsorbate. In addition, although less notably, the bamboo based material was found to be slightly more active for the removal of aldehydes compared to the more volatile cyanide components. This could result from lower volatility materials being more difficult to adsorb and retain; hence they usually require granular materials incorporating a greater proportion of micropores. Retention data obtained using both olive and peat based activated carbons show increased efficiency of these materials for the removal of various cyanides and aldehydes compared to coconut shell material.

Similarities were also seen for the retention data corresponding to the removal of five hydrocarbons, 1, 3 butadiene, isoprene, benzene, toluene and styrene and two ketones, acetone and methyl ethyl ketone. The retention data is shown in data plots 3 and 4 below. The retention data for both hydrocarbons and ketones was found to be generally greater than the data obtained for the retention of volatile cyanides and aldehydes, suggesting that the carbons are more selective towards these types of compounds.

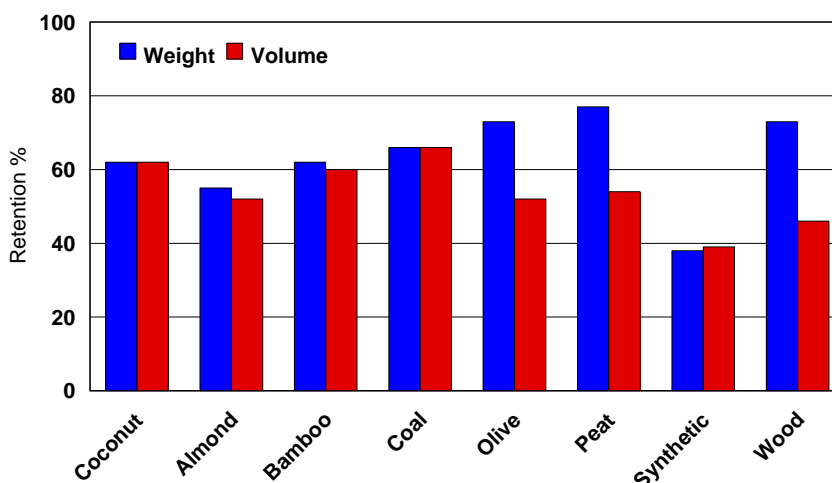


Plot 3: Retention of the hydrocarbons



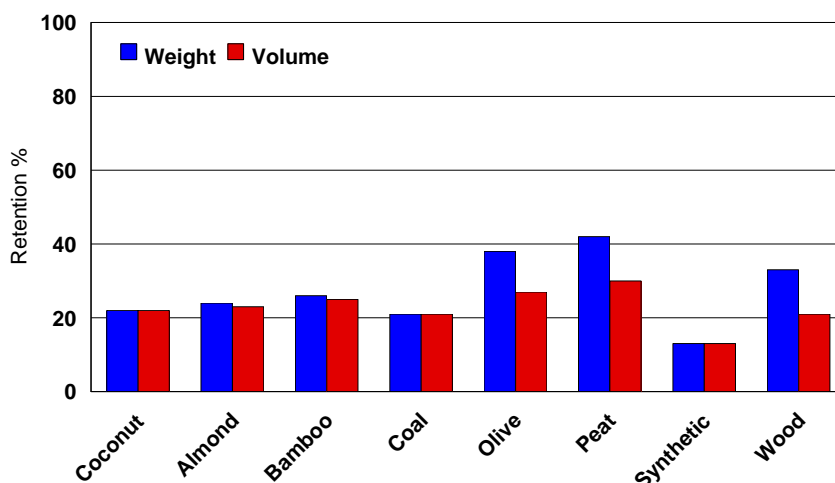
Plot 4: Retention of the ketones

For semi-volatile bases including both pyridine and quinoline the level of removal can depend upon the components boiling point as well as the availability of the adsorbent. As the boiling point of pyridine is 115°C, a significant amount of vapour which readily condenses is available for retention by carbon. Hence, the majority of pyridine present is available for removal, which commonly leads to significantly higher retentions of semi-volatiles than lesser volatile constituents; this behaviour is exemplified in the retention results shown in data plot 5.



Plot 5: Data plot for the retention of semi volatile bases

Smoking tests were also carried out for the retention of each of the eight activated carbons against phenol, ortho-cresol, meta-cresol and para-cresol, these were generalised using the term phenols. The results are depicted in data plot 6 shown below where the retention results are found to be significantly lower than the data obtained for other constituents of smoke. This is a result of phenols having lower volatilities than other components found in cigarette smoke. Consequently, their retention is dependent upon the amount of vapour present and not just the type of activated carbon.



Plot 6: Data plot for the retention of phenols

It should also be highlighted that cellulose acetate has high selectivity towards phenolic compounds and that the smoke in the test system we have used passes through an acetate filter segment, hence some of the available vapour may already have been removed before the smoke reaches the activated carbon.

## Conclusions

Following this investigation it can be concluded that activated carbon removes a wide range of volatile and semi-volatile compounds from cigarette smoke.

Activated carbons produced from raw materials, other than coconut shell, give significant activity towards cigarette smoke and may be alternatives for use in cigarette filters.

The adsorption profile for each of the activated carbon feed stocks studied are similar. This is principally true when the adsorption is focused on physical effects. However, factors such as surface chemistry can lead to significant changes in adsorption efficiency. The overall adsorption efficiency can be different from activated carbons from different feedstocks but other considerations such as availability, price, purity, dust levels etc must be evaluated before their use can be considered in cigarette filters.

- 1) H. Marsh, F. Rodríguez-Reinoso, *Activated Carbon*, Elsevier, (2006). H. Marsh, E. A. Heintz, F. Rodríguez-Reinoso, *Introduction to Carbon Technologies*, Publicaciones de la Universidad de Alicante, University of Alicante, (1997).
- 2) F. S. Baker, *British Carbon Group Conference - Carbon 2006*, The Robert Gordon University, Aberdeen, Scotland, (16<sup>th</sup>-21<sup>st</sup> July 2006).
- 3) Roskill, *The Economics of Activated Carbon*, Seventh Edition, Roskill Information Services, London, (2003).
- 4) Filtrona Filters Internal Report on Carbon Filters - (September 2003).

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