THE INFLUENCE OF CIGARETTE DESIGN ON THE AGEING OF CARBON FILTERS

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SUMMARY

Coconut shell based activated carbon is still the most powerful tool for retaining the various constituents from mainstream cigarette smoke. Several authors have reported on the reduction of carbon activity as a function of storage time and conditions. Previous work indicates that the formation of acetic acid by hydrolysis from triacetin plays only a minor role but a higher storage temperature leads to a faster de-activation of those micropores which can adsorb the smaller gas phase components. This is most likely due to the increasing mobility of compounds originating from the tobacco blend and the packaging material.

This study looks at a set of product parameters such as blend style, filter design and tar level of the test cigarettes. Packed samples have been stored at room temperature and at 40° Celsius. To assess the effect of aging on carbon activity a set of 20 vapour phase constituents and some semi-volatile smoke components, e.g. phenols, have been measured under ISO smoking conditions over a period of 6 months. Additionally the rate of plasticizer hydrolysis has been measured as a function of time by analysing the acetic acid contents in the filter tips.

The present investigation demonstrates that a set of selected vapour phase compounds is sufficient for monitoring the activity of carbon in cigarette filters over a period of time. This study also confirms the influence of storage conditions on deactivation of active carbon but also demonstrates that the effect of aging can be kept at a tolerable level by choosing an appropriate set of product properties

INTRODUCTION

The positive effects of activated carbon in cigarette filters on the retention of several vapour phase compounds have been repeatedly confirmed [1-3]. The resulting reduced exposure of smokers to such smoke constituents by measuring the related biomarkers in human body fluids has recently been reported [4]. Besides a higher production complexity and higher costs for charcoal filters against mono-acetate filters, several other drawbacks have been reported such as the deactivation of the

carbon and a faster formation of acetic acid [5, 6, 7, 11]. Both could limit the shelf-life of products made with carbon filters and could influence the taste or consumer's acceptance. Most of the work was done with a carbon loading of 20 to 50 mg per filter tip. The co-authors assumed in a recent presentation that a higher carbon loading (about 80 mg) could minimize the loss of retention ability [6]. In an earlier publication P. Ceschini demonstrated a constant activity over a period of 6 months after a freshly-activated carbon had reached its equilibrium moisture level. This was done with hand-filled cavity filters and a high loading of about 150 mg per tip.

Several explanations for the deactivation process have been discussed [5, 6, 7, 11]. Apparently the deactivation process can be separated into a short term and long term effect of adsorbing volatile compounds via vapour phase. As with any other high surface material it can promote the decomposition of substances. The function of carbon as a catalyst has been proposed for the triacetin hydrolysis. The short term deactivation occurs if highly-activated material comes into contact with the tobacco rod. When using charcoal with water content below equilibrium, it starts to suck water from the tobacco rod immediately after passing the filter attachment part of the cigarette maker. A rapid uptake of water can observed within a few hours after manufacturing and takes up to 2 weeks to complete [4, 8].

Therefore carbon at its equilibrium moisture content of about 6%, or even at higher moisture of 10 – 12%, is commonly used for cigarette filters to avoid any drying effect of the tobacco rod. The higher moisture content of the coconut shell carbon particles has no negative effect on the adsorption capacity of organic volatile compounds.

The medium to long term deactivation will always occur because of the nature of the material, which is an effective broad-band adsorbent for nearly all types of volatiles. The objective of this study was to look at some design parameters like blend style and filter design type, e.g. cavity against "dalmation", and their effect on the adsorption capability over a period of 6 months. In addition we wanted to know if the aging process can lead to major changes in taste and smell of the test samples.

SUMMARY OF THE EXPERIMENT

The experimental work was conducted in a joint project between Filtrona FTC and Imperial Tobacco. Filtrona UK manufactured the filter rods and cigarettes were made and packed at Imperial Tobacco in Germany. FTC performed testing for tar, nicotine, carbon monoxide, water, cyanide, formaldehyde & phenolic compounds in cigarette smoke along with acetic acid in filter tips removed from packaged cigarettes. Imperial conducted analysis of TNCO, vapour phase constituents and aliphatic acids in smoke.

Overview of Analytical Methods

Smoke analysis of tar, nicotine and carbon monoxide was conducted in accordance with the ISO standards 3402, 4387, 8454, 10315 and 10362.

Vapour phase compounds

For the determination of the organic compounds in the vapour phase of mainstream cigarette smoke, 20 cigarettes are smoked on a rotary smoking machine according to ISO 3308. The WTPM is not collected on a cambridge filter pad but the total mainstream smoke is passed through a glass reactor containing about 1000 mg of the respective additive. Part of the vapour phase is collected in a glass syringe. A special valve system allows sampling of individual puffs from different cigarettes for vapour phase analysis.

Prior to injection, a 6 ml sample loop is filled with a vapour phase aliquot and the organics are then separated using a 60 m x 0.32 mm DB Wax capillary column.

After FID detection the organic vapour phase components are quantified using appropriate GC software and the internal standard method (internal standard: certified mixture of CH_4 in N_2). For calibration, the individual gas phase components are injected into a special glass flask using a gas-tight syringe and mixed by shaking with glass beads. An aliquot of the calibration mix is injected into the sample loop using a gas-tight syringe.

Phenolic compounds

Cigarettes are smoked under standard conditions and the cigarette smoke condensate collected on a Cambridge filter pad as described in ISO 4387:2000. This condensate is extracted as per the water and nicotine determinations described in ISO 10315:2000 & ISO 10362-1:1999, and this extract is analysed directly by liquid chromatography with fluorescent detection.

Hydrogen cyanide & Formaldehyde

Cigarettes are smoked into a modified Cambridge Filter smoke trap containing silica gel to trap the Formaldehyde and Hydrogen Cyanide. After smoking the traps are extracted with deionised water and the amounts of Formaldehyde and Hydrogen Cyanide determined using an AA3 continuous flow analyser.

For Formaldehyde the sample is washed automatically with dichloromethane to remove interfering material and then reacts with sulphur dioxide and rosaniline to produce methyl sulphonic acid whose absorbance is measured at 570 nm.

For Hydrogen Cyanide the cyanide is converted to cyanogen chloride by reaction with chloramine-T and then reacts with a pyridine/pyrazolone solution to form a coloured compound measured at 540 nm.

Acetic acid in filter rods (FTC)

The method for acetic acid analysis in filter tips involves the extraction of 20 tips by shaking in 200mL of potassium dihydrogen orthophosphate buffered mobile phase for 3 hours. Samples are centrifuged before analysis by liquid chromatography (LC) with ultra-violet detection (UV). For full details see [7].

Anions and organic acids in filter tips, tobacco and mainstream smoke (ITG)

The filter tips of 5 cigarettes were slit open and extracted for 30 minutes using 20 mL of de-ionised water (Milli-Q quality). The tobacco of two cigarettes was extracted for 30 minutes using 50 mL of de-ionised water. The extracts were filtered with a 0.22 µm membrane filter and diluted 1:10 with de-ionised water.

20 cigarettes were smoked on a smoking machine with electrostatic precipitation of the total particulate matter (TPM). The TPM was dissolved in 80 mL of de-ionised water, the extracts were filtered (0.22 µm membrane filters) and diluted 1 : 5 with de-ionised water. Analysis was performed using the following conditions after injecting 10 µL of extraction solution:

Analytical columns:	Dionex AG11 4 x 50 mm pre-column, AS11 4 x 250 mm analytical column, ATC-3 9 x 24 mm trap column.
Eluent:	0.20 – 35 mmol NaOH (gradient programme)
Eluent flow rate:	1.50 mL/min. (738 psi)
Suppressor:	Dionex SRS-ULTRA, chemical suppression
Detector:	Dionex CD 25 conductivity detector.

Identification of anions and organic acids was based on their retention time; quantification was performed via peak areas by an external standard technique. Three replicate measurements were performed.

Material Studied

A) Samples for analytical evaluation

Filter tips: A 25 mm mono-acetate filter (AC) and two charcoal filters (DA = Dalmation, CA = Cavity) were manufactured at Filtrona UK. The carbon loading was 82.5 mg and 85 mg for the DA and CA filter. Pressure drop (75 mmWG) was adjusted by filter tow selection in order to achieve comparable tar and nicotine retention.

For all charcoal filters we used one batch of PICA FA 60 10 H carbon; a commercial 30/70 mesh grade with 60 % CCl4 activity and 10 % moisture content.

An American Blend (AB) and a Virginia Blend (VB) at a comparable tobacco nicotine level of 2 % were processed in ITG's pilot plant without added tobacco ingredients.

Cigarette samples with 93 mm length (25 mm filter and 69 mm rod length) and 24.5 mm circumference were made on a Protos 90 maker at 2 degrees of filter ventilation (0 % FV and 50 % FV) by using online perforation.
All cigarettes were packed, randomized and split into two portions for both laboratories. Samples were stored at 20 and 40 degrees Celsius and 60 +/- 5 % relative humidity over a period of 6 months.
In total there were 24 samples for smoke analysis (2 blends with 3 filters at 2 degrees of ventilation stored at 2 different temperatures).

B) Cigarettes for sensory evaluation

We decided to use newly manufactured cigarettes for the fresh sample. Filter rods and cigarettes were reproduced within the accepted tolerances for all physical and chemical parameters. For the aged sample, packaged cigarettes of the American Blend version with the Dalmation filter in KS format at a ventilation level of 50 % (6 mg tar) were stored at room temperature for more than one year.

The smell comparison was performed in a special session. Smell assessment was done immediately after the panellists had randomly opened the packaged test samples. The taste evaluation was conducted by trained people (descriptive panel) by using the in-house standard procedure.

RESULTS AND DISCUSSION

Analytical evaluation

The TNCO figures as shown in table 1 were comparable for different filter types. Data remained constant over the aging period except nicotine which decreased in average by 8 %.

Table 1: TNCO yields in mg/cig of fresh VB test samples

FV	0%			50%		
Filter	AC	CA	DA	AC	CA	DA
puffs	9,5	9,2	9,5	10,3	10,4	10,6
tar	14,2	14,8	14,8	8,1	8,7	8,5
nicotine	1,17	1,20	1,24	0,81	0,85	0,86
CO	12,8	13,4	13,7	6,1	6,8	6,5

Carbon activity was assessed by calculating the relative retention for the total vapour phase (TVP, calculated from 20 substances as shown in figure 2) and for the single substances against the acetate filter as a standard. For TVP and for most of the single compounds we found a small (5 - 10%) but

insignificant reduction of carbon activity at room temperature over a period of 6 months (figure 1). Consequently we found no effect as a result of the different design parameters.

Figure 1: Influence of aging on total vapour phase (comparison of blend style for DA filter) and Benzene (comparison of filter type for Virginia blend)

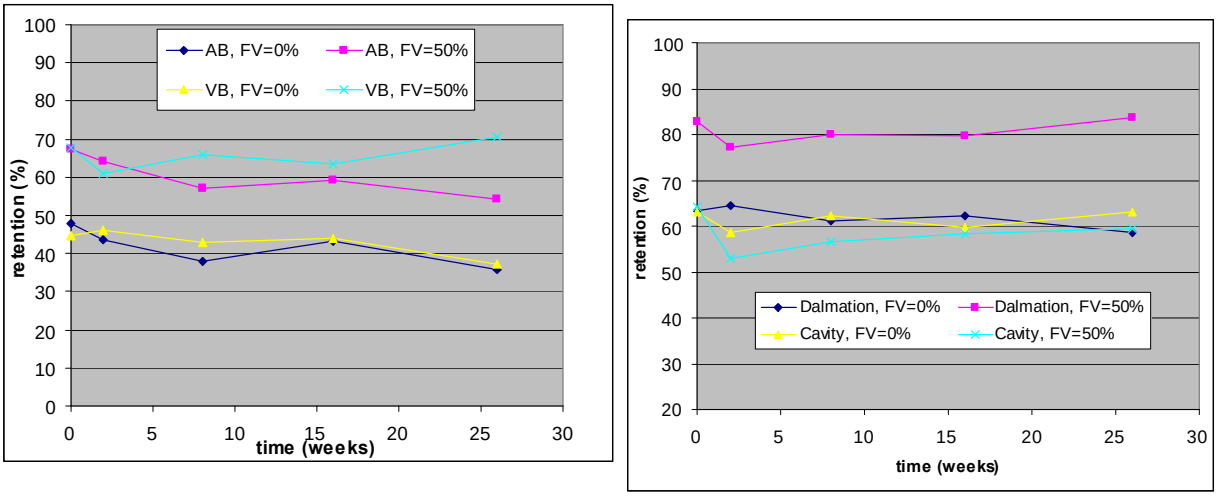
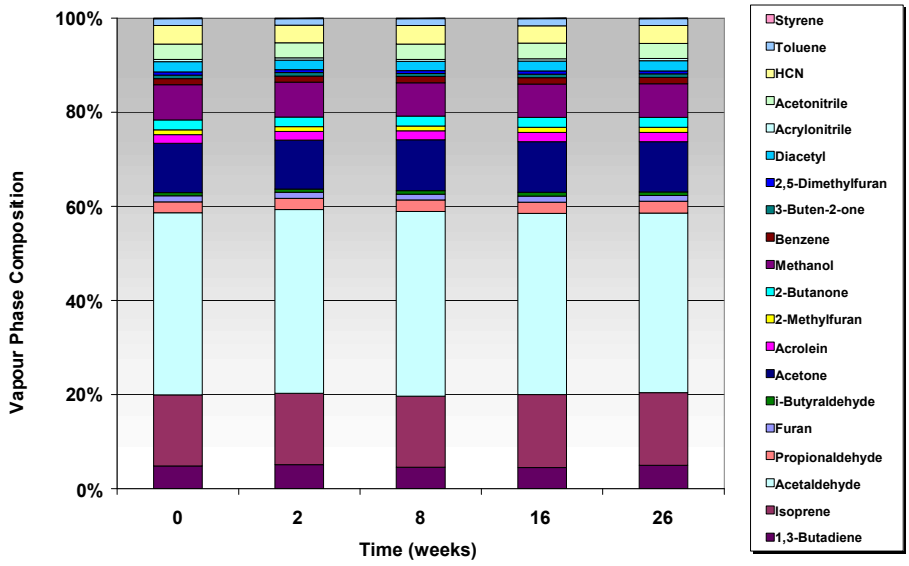


Figure 2: Influence of aging on the relative vapour phase composition



We also calculated retention data for subsets of the 20 compounds but found no differences. From the single substances Benzene and Toluene were good markers for the carbon activity because of the high retention capability and low standard deviations.

Effect of aging on other smoke constituents

For formaldehyde no clear trend could be observed, this was due to the higher standard deviations. The phenols showed a small but insignificant trend towards lower smoke yields during aging.

Influence of storage conditions

Although we found no significant carbon activity reduction for most of the vapour phase constituents (below 5 % for all design parameters) at room temperature (RT) the higher temperature of 40° Celsius led to a small but significant lower activity of 8 % (average of all samples). Again no differences between design parameters were significant (range from 5 to 10 % lower activity against RT). This is in good agreement with previous results and can be explained by an increased mobility of e. g. volatile compounds from the tobacco column. The effect of higher storage temperature on the acetic content in carbon filter tips is much more pronounced: from week 8 to week 26 the acetic acid level in both carbon filter was found to be 35 % higher than in filters stored at room temperature. If acetic acid played a major role in deactivation we would expect a much greater activity decrease than found in this study.

Acetic acid content in carbon filter tips and their transfer into smoke

The measured acetic acid content for all samples is in good agreement with previously reported data [6, 7]. Again we found a steep increase during the first 8 weeks of storage and after week 10 the curves flatten out showing a clear ranking of Dalmation > Cavity > Acetate. Of course filter ventilation had no influence and the Virginia blend showed a small but insignificant trend towards higher levels.

Because the acetic content in carbon filters can become 5 to 10 times higher compared with acetate filters we wanted to know if differences in smoke can be observed and whether this has an influence on taste and consumer's acceptance (see sensory evaluation). For comparison we also looked at formic acid which was detected in the carbon filters. There are very few published data for aliphatic acids of charcoal filter cigarettes available. Lakritz *et. al.* [9] and Morie [10] reported levels of 200 – 250 µ/cig for non-ventilated carbon filter cigarettes which were equal to or slightly lower than samples with mono-acetate filter (220 – 300 µ/cig).

Table 3: Acetic and formic acid in smoke [ISO regimen] of aged samples with blend AB

sample	filter type	filter ventilation FV [%]	Acetic acid [µ/cig]	Formic acid [µ/cig]
AB-AC-0-RT	AC	0	229	78
AB-DA-0-RT	DA	0	183	70
AB-AC-50-RT	AC	50	100	27
AB-DA-50-RT	DA	50	87	31

It is obvious that the higher acetic acid content in carbon filters has no influence on smoke transfer.

Table 4: Acetic acid in tobacco, filter tips and smoke; samples for sensory evaluation

sample*)	age [weeks]	filter type	FV [%]	tobacco [µ/tob]	filter [µ/tip]	total [µ/cig]	smoke [µ/cig]
Acetate "fresh"	4	AC	55	1218	416	1634	75
Carbon "fresh"	4	DA	55	596	1156	1752	54
Carbon "aged"	60	DA	55	593	1766	2359	48

*) American blend AB, KS format, 83 mg carbon per tip

Because of the similar, or even slightly lower, transfer of acetic and formic acid into smoke for cigarettes with carbon filters in comparison to cigarettes with acetate filters we looked at the total balance of acetic acid (free and in salt form [10]) in the tobacco rod and the filter tip. Surprisingly we found significantly lower levels in the tobacco rod of cigarette with carbon filters. (table 4 [8]). This is in contradiction to the findings from the working group on triacetin analysis. They recently postulated the hydrolysis of triacetin as being the source for increased acetic acid levels in carbon filters. To explain our results we had to assume a migration of free acids or even of the responding salts from the rod onto the carbon containing filter plug. However such a proposed mechanism might also be questionable. To fully understand the matter future work has to be done.

Sensory Evaluation

The results of the 1st session (smell assessment) are:

- 83 % of the panellists noticed a sour smell right after opening the pack,
- After they had taken them out of the pack, 75 % of the panellists described the smell of the aged cigarettes as smelling like "cut grass" whereas the smell of fresh samples was described as being more tobacco-like (terms like mouldy, musty and smoky).
- When smoking the samples no significant difference was found.

The results of the descriptive panel were similar for the smell difference before smoking. The taste of the mainstream smoke of the fresh samples was described to be more intense, sharper and of having more total strength.

These taste differences between fresh and aged samples were also found for samples with mono-acetate filters. The sour smell can be due to the elevated level of acetic acid in the aged filter tips. Taking into account the difference in age of about 15 months and the assessment by educated specialists we believe that there is only little relevance for consumer's acceptance of charcoal filter products.

CONCLUSION

In this study the overall loss of carbon activity in highly-loaded charcoal filters did not exceed 10 per cent over a period of 6 months. The increase of acetic acid content in filter tips over the storage time and the effect of storage at higher temperature were able to be confirmed. But the smoke transfer rates of the low molecular weight organic acids showed no significant difference in comparison to cigarettes with mono-acetate filters. This is in good agreement with the sensory evaluation of aged products against fresh samples: a slight acid smell is noticeable right after opening the pack but no negative effect on taste occurs other than that also known for products without carbon filters. From this study and the previously presented data we can conclude that carbon activity can be kept at a sufficient level over a period of at least 6 months if the carbon loading is high enough and the level of available volatile compounds for adsorption is low e.g. by avoiding elevated temperature during storage.

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