The Influence of Different Filter Parameters on the Semivolatile Composition of Mainstream Smoke*

by

K. Formella, Th. Braumann and H. Elmenhorst

Research and Development, Rothmans Produktions GmbH
2800 Bremen, Germany

SUMMARY

The semivolatile fraction of cigarette smoke contains the most important aroma and taste compounds which contribute to the smoker's enjoyment. Obviously, the semivolatile composition is strongly affected by cigarette filters and consequently by the material which is used for filter manufacturing. We have studied the effect of cellulose acetate and polypropylene as filter material on the smoke semivolatiles. Further, the effect of other parameters like pressure drop and the use of additives has been investigated. Smoke condensate was collected on a Cambridge filter pad, the semivolatiles were evaporated using a headspace apparatus and subsequently collected in a cold trap. Semivolatile analyses were performed by high-resolution GC/MS. The cellulose acetate filter, due to its polar structure, selectively retains polar compounds such as phenols and furans while the non-polar polypropylene filter shows a non-selective retention behaviour. The addition to polypropylene filters of a polar compound such as triacetin, which is used as plasticiser in the manufacturing of cellulose acetate filters, does not affect the retention behaviour towards the semivolatiles.

ZUSAMMENFASSUNG

Die halbflüchtigen Substanzen im Zigarettenrauch enthalten die wichtigsten Geschmacksstoffe, die zum Rauchgenuß beitragen. Die Zusammensetzung dieser Rauch-

fraktion wird durch den Zigarettenfilter und damit auch durch das Material, das zur Filterherstellung benutzt wird, beeinflusst. Wir haben den Einfluß von Celluloseacetat und Polypropylen als Filtermaterial auf die Zusammensetzung der halbflüchtigen Substanzen untersucht. Von weiterem Interesse war der Einfluß anderer Parameter, wie Zugwiderstand und Zugabe von polaren Stoffen auf die Filtercharakteristik. Das Rauchkondensat wurde auf Cambridge-Filtern gesammelt, die halbflüchtigen Substanzen wurden mit einer „Headspace“-Vorrichtung verdampft und nachfolgend in einer Kältefalle aufgefangen. Die Analyse der halbflüchtigen Substanzen erfolgte durch Gaschromatographie (GC), die Identifizierung einzelner Substanzen wurde durch Massenspektrometrie (MS) vorgenommen. Der Celluloseacetatfilter hält wegen seiner polaren Struktur selektiv polare Bestandteile wie Phenole und Furane zurück, während der nicht-polare Polypropylenfilter nicht-selektives Verhalten zeigt. Die Zugabe eines polaren Stoffes wie Triacetin, das als Weichmacher bei der Produktion von Celluloseacetatfiltern eingesetzt wird, zum Polypropylenfilter beeinflusst das Retentionsverhalten gegenüber den schwerflüchtigen Substanzen nicht.

RESUME

La fraction semi-volatile de la fumée de cigarettes contient les substances les plus importantes pour l'arôme et le goût qui contribuent au plaisir du fumeur. La composition des matières semi-volatiles dépend largement du filtre ainsi que des substances utilisées pour la fabrication des filtres. Nous avons étudié l'effet de l'acétocellulose et du polypropylène, matières utilisées pour la fabrication de filtres, sur la composition des matières semi-volatiles. En outre,

* Received: 17th January 1992 – accepted: 27th October 1992 Presented, in part, at the 44th Tobacco Chemists' Research Conference, Winston Salem, North Carolina, 1990.

nous avons examiné d'autres paramètres tels que la résistance au tirage et l'addition de substances polaires. Le condensat de fumée a été collecté sur filtres Cambridge, les composants semi-volatils ont été évaporés à l'aide d'un appareil headspace et ensuite isolés par précipitation à froid. Les composants semi-volatils ont été analysés par chromatographie en phase gazeuse et par spectrométrie de masse. Grâce à sa structure polaire, le filtre en acétocellulose retient sélectivement des composants polaires tels que les phénols et les furanes, tandis que le filtre en polypropylène non-polaire est non-sélectif. L'addition d'une substance polaire au filtres en polypropylène telle que le triacétin, utilisée comme plastifiant dans la fabrication de filtre en acétocellulose, n'influence pas la rétention de composants semi-volatils.

INTRODUCTION

The semivolatile fraction of cigarette mainstream smoke contains most of those chemical substances, which possess distinct aroma and taste properties thus contributing to the smoker's enjoyment. The semivolatile composition is of course different for different cigarettes strongly depending on the tobacco blends used as well as the cigarette design. But nevertheless it can be stated that this is a very complex chemical mixture, which contributes to the smoker's pleasure.

Mainstream smoke semivolatile composition is of course strongly affected by cigarette filters. Some compounds due to their chemical nature interact more with a filter material than others thus being retained to a greater extent. The retention is dependent on the affinity between the filter material and the chemical compound to be retained and on the number of active filtration sites within the filters. We were interested in the alteration of smoke semivolatile composition effected by the variation of special filter parameters to demonstrate how the technological modification of cigarette design can influence the aroma and taste properties of the modified product.

A main interest of our work was to study the effect of different filter materials on the semivolatile composition. Cellulose acetate is the standard filter material used for a long time in many countries because of its favourable filtration characteristics and its ease of production.

An alternative filter material is polypropylene. Advantages of polypropylene are the lower tow weight, the lower costs of the raw material and the good availability. Additionally, according to US-Patent 4.811745, no further additives are necessary for the polypropylene to be a suitable filter material in contrast to cellulose acetate which needs the addition of plasticisers such as triacetin. The advantages of polypropylene are evident and therefore it is worthwhile to study polypropylene as an alternative to cellulose acetate for practical reasons. If one considers the chemical structure of both materials, which are presented in Figure 1, it is reasonable to expect that the mainstream smoke composition of cigarettes with cellulose acetate and polypropylene filters would be different. Cellulose acetate has a polar structure which possess a

Figure 1a.
Chemical structure of filter materials: cellulose acetate.

Figure 1b.
Chemical structure of filter materials: polypropylene.

high affinity to polar smoke constituents. There is also a possibility of interaction with smoke components which have hydrogen-donor/acceptor functionalities. In contrast, polypropylene has an unpolar, completely hydrophobic structure. The filtration characteristics of each material should be different. To what extent these differences affect the aroma and taste has to be studied.

Another point of interest was the influence of filter pressure drop on the semivolatile composition for cigarettes manufactured with both cellulose acetate and polypropylene filters. As mentioned above, the filter pressure drop is a measure of filter retention capacity. For our investigations we had cellulose acetate and polypropylene filters with two different pressure drops available. Pressure drops were matched between the different filter materials. The last item of our study was the influence of the addition of the polar compound triacetin to the polypropylene filters on the semivolatile composition. Triacetin addition could alter the filter characteristics of polypropylene so that the retention capacity for polar compounds is enhanced in comparison to non-treated polypropylene filters.

EXPERIMENTAL

The mainstream smoke semivolatiles of six cigarette samples with different filters were investigated. The tobacco was a typical English flue-cured blend. Samples 1 and 2 were cigarettes with low and high pressure drop cellulose acetate filters (cigarette pressure drop: 110 and 130 mm W. G.*). Samples 3 and 5 were cigarettes with

* CORESTA - unit

low and high pressure drop polypropylene filters (cigarette pressure drop: 110 and 130 mm W.G.) and samples 4 and 6 were the polypropylene samples 3 and 5 treated with 1 % of triacetin on the filter. Smoke semivolatile analysis was carried out according to the scheme given in Figure 2:

Figure 2.
Experimental procedure to analyse smoke semivolatiles.

Smoking of cigarette samples under DIN/ISO-conditions
Heating of Cambridge filter pads in a Dynamic Headspace Apparatus
Trapping of the semivolatile fraction evaporating from the Cambridge filter pads
Separation and identification of the semivolatile fraction by GC/MS
Statistical evaluation of the data
Result: semivolatile components which show significantly different concentrations for two samples

Cigarette samples were smoked on a rotary smoking machine under DIN/ISO-conditions. The condensate was trapped on a Cambridge filter pad, which was subsequently heated in a Dynamic Headspace Apparatus under Helium up to a temperature of approximately 200 °C. The semivolatiles evaporating under these condi-

tions were trapped in a cold trap at the temperature of liquid nitrogen. The trapped semivolatiles were analysed by GC with FID. The equipment used and the analytical conditions were as follows:

Gas-chromatograph:	Carlo Erba GC 4160 (FID) Siemens Sichromat (coupled to MS)
Column:	Fused silica capillary column coated with OV-351
Column geometry:	50 m lenght × 0.32 mm ID
Carrier gas:	Helium (flow rate 250 mm/s)
Injection part temperature:	270 °C
Split ratio:	1:40
Temperature programme:	50–240 °C with 3 °C/min
Sample size:	2µl
Mass spectrometer:	Finnigan 311 A
Electron energy:	70 eV
Emission current:	2 mA
Resolution:	1000 amu
Mass range:	35–500 amu
Scan:	2.5 s
Interface temperature:	270 °C

The procedure was repeated for each sample at least three times. From these three individual gas chromatograms a “mean” gas chromatogram was calculated and the standard deviation for all individual GC peaks in the three gas chromatograms were determined. Subsequently, the “mean” chromatograms were compared and those compounds which showed a statistically significant difference in intensity were selected for identification by GC/MS. Sophisticated computer programmes for this type of statistical evaluation were developed by ourselves.

A typical gas chromatogram of cigarette mainstream smoke semivolatiles gives approximately 350 peaks. It is of course possible to identify all peaks by MS, but as we were only interested in differences between the semivolatile composition of two samples due to special modifications like filter type etc., we performed semivolatile analyses as described above sparing the relatively time

Table 1.
Smoke Chemistry.

Sample	Filter material	Cigarette pressure drop (mm W.G.*)	PMWNF** (mg/cig.)	Nicotine (mg/cig.)	CO (mg/cig.)	Puff number	Filter nicotine retention (%)
1	Cellulose acetate	110	16.9	1.65	17.0	10.0	34.8
2	Cellulose acetate	130	15.2	1.54	16.0	10.2	39.1
3	Polypropylene	110	19.4	1.84	16.1	10.2	32.2
4	Polypropylene + 1% triacetin	110	18.6	1.68	16.6	10.1	32.7
5	Polypropylene	130	17.6	1.67	16.6	10.3	39.2
6	Polypropylene + 1% triacetin	130	17.6	1.62	16.6	10.1	38.6

* CORESTA unit.

** Particulate matter water nicotine free

consuming step of identifying every peak by mass spectrometry.

The yields of the individual semivolatile compounds were expressed in mg/g burnt tobacco. From our experience this is the optimal way to compare cigarette samples with different particulate matter water nicotine free (PMWNF) yields. The amount of burnt tobacco per cigarette was determined by weighing the cigarettes before smoking and the butts after smoking.

RESULTS AND DISCUSSION

The results of routine smoke analyses are given in Table 1. As expected for the cigarettes with cellulose acetate filters, sample 2 with the higher pressure drop filter gives lower readings for PMWNF and nicotine than sample 1. There also seems to be a small influence on the CO yield.

The same trend is true for PMWNF and nicotine yields of the polypropylene filter samples 3 and 5.

The addition of triacetin to the polypropylene filter seems to have only minor effects on the PMWNF and nicotine yields (Samples 3 and 4), if at all.

The CO yield of the polypropylene filter cigarettes seems to be unaffected by pressure drop or by triacetin addition. The puff numbers are very similar for all samples. Filter retention is only affected by pressure drop and seems to be independent of filter material.

The differences in smoke semivolatile composition of samples 1 and 2 both with cellulose acetate filter are shown in Figure 3. We found different concentrations for eight compounds of which four were identified. Most of the compounds identified are oxygen containing polar substances. This finding may be explained by the higher number of active filtration sites in the high pressure drop cellulose acetate filter which can interact with these smoke constituents. Since the differences between samples are small, one would, however, expect only minor taste differences, if at all.

The differences in semivolatile composition of samples 1 and 3 with cellulose acetate and polypropylene filters having low pressure drop are presented in Figure 4. There were 14 differences in yields. For each of these compounds the yield is higher for the polypropylene sample. All 14 compounds are polar ones with at least one oxygen atom including very different types of substances such as carbonylic compounds (ketones, aldehydes, lactones), heterocyclic compounds like furans and phenols. This finding is plausible if one considers the different chemical structure of the filters. Although polar compounds are retained by polypropylene filters to a certain extent, the interaction forces between the substances and the cellulose acetate are stronger and thus the retention is higher. All compounds mentioned in the Figure 4 have special aroma and taste qualities but it is very difficult to predict

Figure 3.
Smoke semivolatiles of cigarettes containing cellulose acetate filter with different pressure drop.

Figure 4.
Smoke semivolatiles of cigarettes with cellulose acetate and polypropylene filters (low pressure drop).

cigarette taste only from the knowledge of the chemical composition of mainstream smoke. If one considers the taste properties, e.g. of phenol and o-cresol, which occur in an approximately 50 % higher concentration in the polypropylene sample than in the cellulose acetate sample, it is possible that this sample tastes harsher. Even more differences (22) were found in mainstream smoke semivolatile composition of cellulose acetate and polypropylene samples with high pressure drop (Figure 5). We could identify principally the same classes of substances as for the lower pressure drop cigarettes plus nitrogen containing heterocycles like an amine and a pyrrole. Again, phenol and o-cresol were found with the highest yield. To predict taste differences for the high

Figure 5.
Smoke semivolatiles of cigarettes with cellulose acetate and polypropylene filters (high pressure drop).

pressure drop samples is even more complicated than for the low pressure drop samples because more chemical differences could be identified. It is again possible that the smoke of the polypropylene sample possesses a harsher character and more impact.

In Figure 6 the yields of the identified semivolatile compounds for the low pressure drop polypropylene sample in comparison with those of the high pressure drop polypropylene sample are listed. Except for the phenol and the o-cresol, the values are very similar. This indicates that the filter efficiency of polypropylene filters for a polar smoke compound is independent of pressure drop and therefore of filter density per unit. This finding might be explained by the hydrophobic structure of polypropylene as the interaction of the material with the polar smoke compounds is poor and an increase of filter material per unit does not affect the number of active filtration sites as it would be the case for cellulose acetate. The addition of triacetin to the polypropylene filters had no effect on the smoke semivolatile composition compared to cigarettes with untreated filters. The only differences we could detect both for the samples with high and low pressure drop were the occurrence of tri- and diacetin in the smoke of the triacetin treated samples. Diacetin is always present in the technical triacetin used for the filter treatment. Our hypothesis to alter the

Figure 6.
Smoke semivolatiles of cigarettes containing polypropylene filter with different pressure drop.

filtration characteristics of polypropylene by adding a polar liquid with a high boiling point could therefore not be confirmed. It would have been possible to increase the amount of triacetin added to the filter but since it was shown that triacetin is transferred to the mainstream smoke even at 1 % addition, it has to be expected that this would occur to a greater extent at higher triacetin loadings. Major disadvantages for the taste quality of mainstream smoke can therefore not be excluded.

CONCLUSION

From the results presented in the study we can draw the following conclusions:

- Cellulose acetate filters show selectively a higher filtration efficiency for polar smoke compounds than the polypropylene filters used in this study.
- There is an indication that selective filtration of cellulose acetate filters varies when the pressure drop is modified.
- Pressure drop differences do not seem to influence smoke composition of cigarettes with polypropylene filters.
- The addition of triacetin to the polypropylene filters has no effect on the smoke composition.

Besides the above results our study clearly shows the importance of smoke semivolatile analyses for the assessment of technological modifications of cigarettes such as different filter materials. From the results of routine smoke analyses, e.g. PMWNF and nicotine, the samples used in our investigations would have been rather similar even with the different filters. Smoke semivolatile analyses, however, can give useful hints on possible differences in the taste quality. Since cigarette smoke is very complex mixture with a number of gaseous components, e. g. low molecular organic acids, which are not covered by this analysis, the semivolatile analysis alone cannot be used to predict cigarette taste but it is a useful tool to investigate cigarette smoke in more detail.

Authors' address:

*Rothmans Produktions GmbH,
Forschung und Entwicklung,
Postfach 10 79 05,
W-2800 Bremen 1, Germany.*