SSPT 54 - Mueller - Application of a modal reactor for efficiency testing of potential filter additives

Authors: MUELLER C.; INTORP M.

Application of a modal reactor for efficiency testing of potential filter additives.

Christian Mueller and Michael Intorp
Imperial Tobacco Limited, Industry & Scientific Affairs, Albert-Einstein-Ring 7, D-22761 Hamburg, Germany

Summary

For the development of potentially reduced exposure products ('PREPS'), there is a demand for a quick and inexpensive pre-check methodology to access the effect of potential filter additives on certain constituents of mainstream cigarette smoke.

In this work a simple model reactor for this purpose is described that generally allows an estimation of the performance of filter additives towards selected Hoffmann Analytes (nitriles, aldehydes, ketones, aromatic hydrocarbons) in mainstream cigarette smoke - without preparing cigarette test pieces.

The effect of a series of aluminosilicates and charcoal on the level of 20 vapour phase constituents is demonstrated for a monitor cigarette on a 12 mg/cig. tar level.

For this methodology, total cigarette smoke is passed through a layer of the respective filter additive and is sampled using a glass syringe. An aliquot is subsequently analysed by GC-FID. Physical characteristics of the materials are given and the effects observed are briefly discussed on a molecular basis (e.g. adsorption and/or interaction of total cigarette smoke with reactive surface centres). For one material, the findings from the reactor model are compared with those from prototype cigarettes.

Although the reactor model discussed in this study cannot simulate the behaviour of an additive incorporated in a cigarette filter, the model allows a time and cost-saving estimation of the filter performance of potential filter additives.

Introduction

Mainstream cigarette smoke is a complex dynamic system composed of both particulate phase and vapour phase. For the design of potentially reduced exposure products ('PREPS'), innovative new materials play a key role as potential filter additives for selective reduction of certain constituents of mainstream cigarette smoke that have been identified by the public health communities as potentially harmful [1-3].

In order to assess the filtration performance of a new filter additive, it is most appropriate to produce prototype cigarettes comprising the respective material. However, this procedure is relatively costly and time-consuming, especially when checking a wide range of different materials. For this reason, a quick and inexpensive pre-check methodology has been developed for the assessment of potential filter additives. A glass container with defined dimensions equipped with a glass frit was used as a model reactor that can be filled with the respective material. Twenty Monitor cigarettes were smoked under ISO conditions and the total mainstream smoke of all cigarettes was directed through a layer of the filter additive. Subsequently, the vapour phase was collected in a glass syringe and the composition of an aliquote was analysed by GC-FID. The chemical analysis was focussed on certain nitriles (acrylonitrile, acetonitrile, hydrogen cyanide), aldehydes (acetaldehyde, acrolein, propionaldehyde, *iso*-butyraldehyde), ketones (acetone, 2-butanone, 3-buten-2-one, diacetyl), aromatics (benzene, toluene, styrene), furans (furan, 2-methylfuran, 2,5-dimethylfuran), unsaturated hydrocarbons (1,3-butadiene, isoprene) and methanol, most of them being included in the so called “Hoffmann”-list.

The use of silica gel and aluminosilicates has been described in the literature and recent patents before [4-6]. For this work, charcoal and a two series of different aluminosilicates have been checked for their behaviour towards twenty vapour phase constituents of mainstream cigarette smoke.

Experimental

Numerous GC methods are available for the analytical determination of organic vapour phase compounds. These methods have been reported in the literature and many CORESTA presentations [4, 7-11]. As a rule, they have not been validated by international joint experiments. However, they are suitable to describe developments in cigarette design by analytical means.

For the determination of the organic compounds mentioned above in the vapour phase of mainstream cigarette smoke, 20 cigarettes are smoked on a rotary smoking machine according to ISO 3308 [11]. 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 × 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.

Studied Material

The adsorbent materials tested in this study were from commercial sources. Some of their physical properties are listed in Table 1. When smoking 20 Monitor cigarettes, about 1000 mg of the adsorbent were filled into the glass reactor.

Table 1: Physical characteristics of aluminosilicates, Al_2O_3 extrudate and charcoal.

Material		SiO_2 content [%]	Surface area [m^2/g]
Aluminosilicates	1	1.3	286
	2	5.6	377
	3	9.5	413
	4	19.8	430
	5 (HT)	1.7	216
	5 (HT)	5.5	318
	5 (HT)	10.1	362
	5 (HT)	19.8	407
Al_2O_3 Extrudate		traces	201
Charcoal		traces	1100

As shown in Table 1, two series of aluminosilicates have been tested covering a SiO_2 content between 1 and 20%. Materials 5 to 8 were subject to a post-synthesis hydrothermal treatment (HT) which results in an increase of surface acidity compared to the standard materials 1 to 4 [12]. In addition, an alumina extrudate and standard charcoal were tested. The surface areas were determined by BET measurements. For the aluminosilicates, the surface areas increase with increasing silica content.

Results and Discussion

The filtration performances of adsorbents were compared using the vapour phase component deliveries per cigarette. By comparison with the deliveries of an empty reactor, the total percent reduction for each vapour phase compound measured due to the filtration by each particular adsorbent was determined.

Each of the percent reduction values was statistically evaluated, and if a significant percent reduction of a particular vapour phase compound was noted, that amount of reduction is listed in Tables 2 and 3. If the percent reduction was deemed insignificant (smaller than 30% and 3 RSD), it is shown as a blank.

Table 2: Effects of potential filter additives on the delivery of mainstream vapour phase components of a Monitor cigarette. Percent reduction, only statistically significant figures given (> 3 RSD; bold numbers: reduction > 30%; blank: reduction not statistically significant)

Material	1	2	3	4	Extruc
1,3-Butadiene					
Isoprene					
Acetaldehyde	-16	-18	-17	-16	-18
Propionaldehyde	-37	-48	-37	-36	-32
i-Butyraldehyde	-56	-73	-57	-51	-30

Acrolein	-43	-58	-35	-38	-29
Acetone	-27	-41	-37	-52	-31
2-Butanone	-38	-61	-54	-68	-36
2-Buten-3-on	-52	-68	-56	-61	-31
Diacetyl	-85	-88	-90	-81	-46
Acrylonitrile	-34	-40	-42	-46	-23
Acetonitrile	-24	-31	-34	-42	-24
Hydrogen cyanide	-89	-99	-86	-84	-55
Benzene					
Toluene	-19	-16	-19	-18	
Styrene	-50	-50	-58	-55	
Methanol	-48	-68	-63	-70	-40
Furan					
2-Methylfuran					
2,5-Dimethylfuran	-15				-14

Table 3: Effects of potential filter additives on the delivery of mainstream vapour phase components of a Monitor cigarette. Percent reduction, only statistically significant figures given.

Material	1	2	3	4	Extruc
1,3-Butadiene					-83
Isoprene					-95
Acetaldehyde		-22	-24	-32	-69
Propionaldehyde	-30	-42	-46	-64	-93
i-Butyraldehyde	-47	-58	-60	-81	-95
Acrolein	-33	-42	-52	-73	-95
Acetone	-20	-35	-39	-77	-95
2-Butanone	-29	-50	-50	-92	-98
2-Buten-3-on	-40	-49	-56	-85	-99
Diacetyl	-83	-84	-84	-95	-98
Acrylonitrile	-23	-38	-42	-67	-96
Acetonitrile	-17	-29	-33	-61	-87
Hydrogen cyanide	-92	-90	-91	-98	-97
Benzene			-15	-14	-97
Toluene		-20	-25	-35	-96
Styrene		-42	-50	-77	-86
Methanol	-35	-56	-49	-86	-83
Furan					-86
2-Methylfuran			-20	-32	-97
2,5-Dimethylfuran		-17	-22	-35	-97

Unsaturated hydrocarbons

For 1,3-butadiene and isoprene a significant reduction was observed for charcoal only.

Aldehydes and ketones

For aldehydes (acetaldehyde, propionaldehyde, *i*-butyraldehyde, acrolein – Figure 1) and ketones (acetone, 2-butanone, 3-buten-2-one, diacetyl – Figure 2), significant reduction has been observed for all materials tested. Especially within the series of materials 5-8 (HT) and charcoal, a trend to higher reduction with higher surface area and higher surface acidity, respectively, was observed.

Figure 1: Effects of potential filter additives on the aldehyde deliveries of mainstream vapour phase of a Monitor cigarette. Percent deliveries, grey data points indicate non-significant figures.

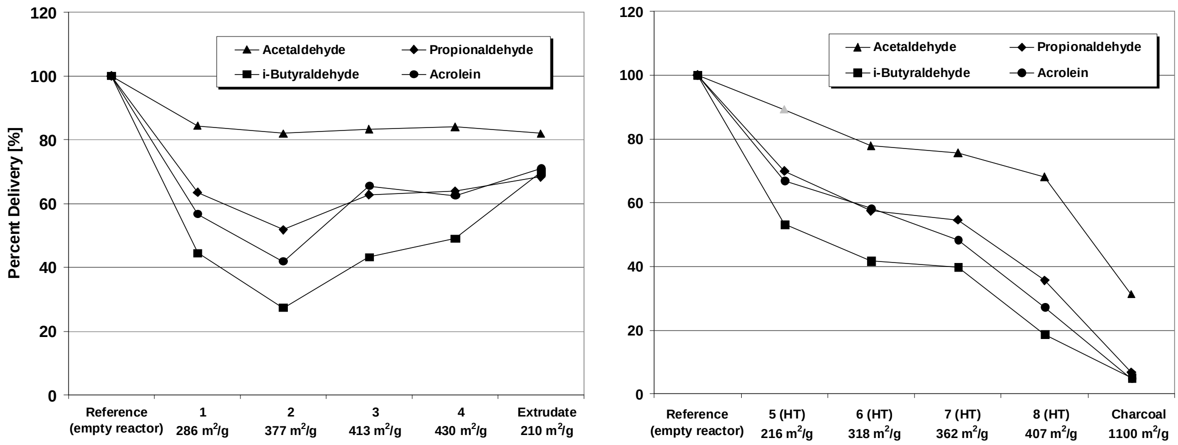
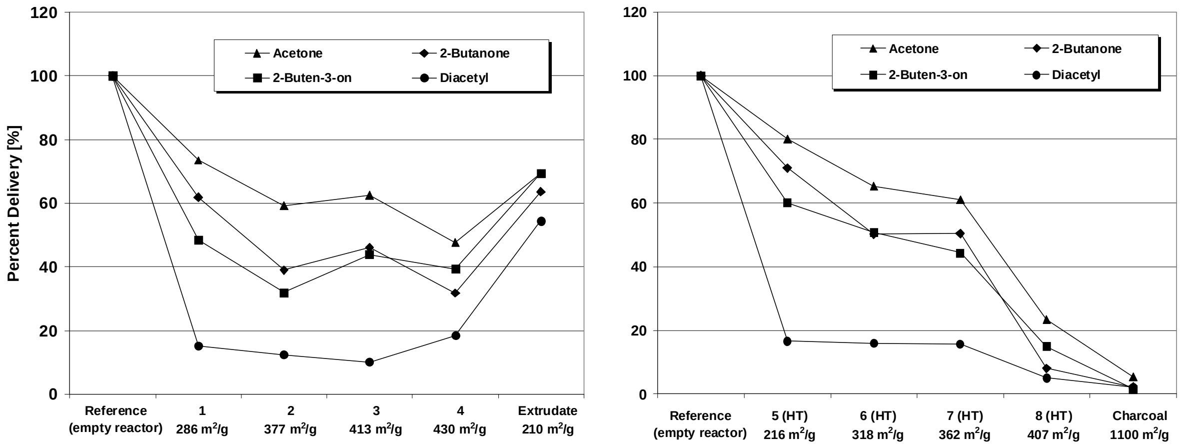


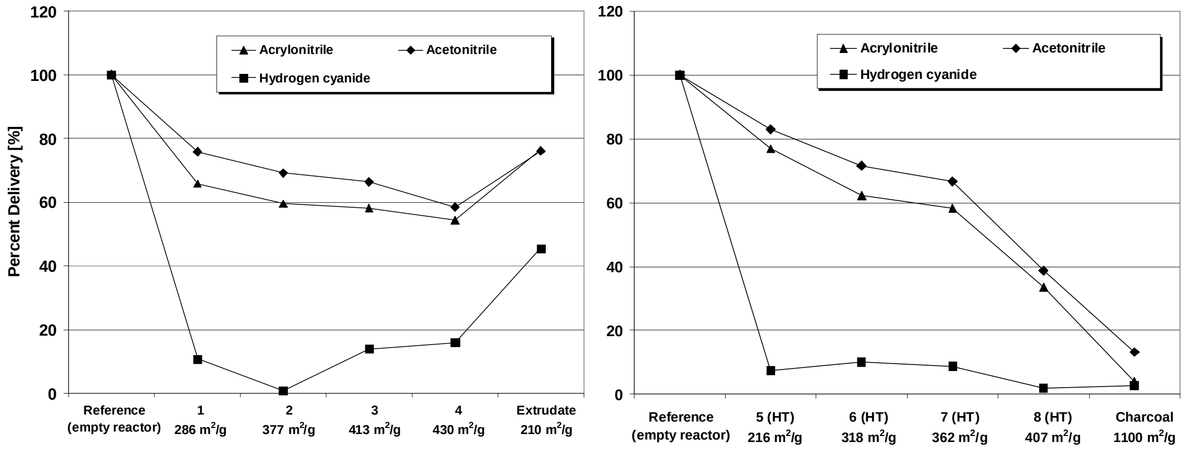
Figure 2: Effects of potential filter additives on the ketone deliveries of mainstream vapour phase of a Monitor cigarette.



Nitriles

For acrylonitrile, acetonitrile and hydrogen cyanide, significant reduction has been observed for all materials tested (Figure 3). Remarkable reductions have been observed for hydrogen cyanide.

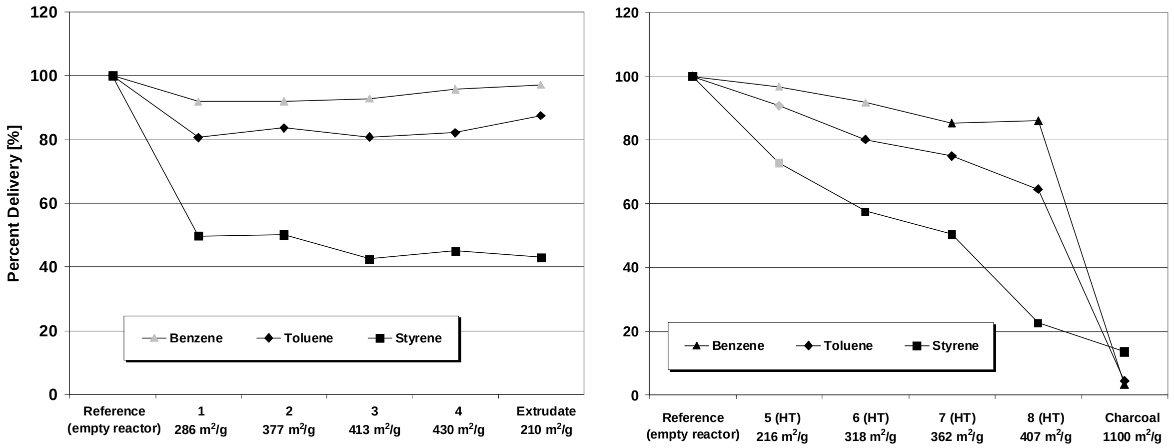
Figure 3: Effects of potential filter additives on the nitrile deliveries of mainstream vapour phase of a Monitor cigarette.



Aromatic hydrocarbons

For aromatic hydrocarbons (benzene, toluene, styrene), a reduction of 86% and higher was found for charcoal only. Within the HT-series of aluminosilicates (materials 5-8), higher reduction was observed with increasing surface acidity (Figure 4).

Figure 4: Effects of potential filter additives on the deliveries of aromatic hydrocarbons of mainstream vapour phase of a Monitor cigarette. Percent deliveries, grey data points indicate non-significant figures.



Other vapour phase constituents

For methanol, significant reduction was observed for all aluminosilicates as well as for charcoal. In case of furan, 2-methylfuran and 2,5-dimethylfuran, reduction by charcoal was 86% and higher; the aluminosilicates showed no remarkable effect.

Charcoal significantly reduces all of the vapour phase components observed. These results are expected since the charcoal has a high surface area and diversified surface activity [13].

In comparison, the aluminosilicates, although having a much lower surface area, still show significant and selective reduction for polar compounds such as aldehydes, ketones, and nitriles. All of the vapour phase compounds reduced by aluminosilicates have, in common, hydrogen-bondable oxygen or nitrogen atoms. The filtration performance for these compounds is most likely the result of hydrogen bonding between Si-OH and O or N atoms with lone electron pairs. An increase of surface acidity seems to intensify this interaction.

Prototype cigarettes

In addition to reactor model testing, the alumina extrudate was fit into a polyethylene tube and has been incorporated into a cigarette filter using the Burghart "Multi Segment Maker". Table 4 summarises the statistically significant percent reduction of this prototype cigarette in comparison to the reference cigarette (empty tube). The percentage reductions observed for the prototype cigarettes are still significant but less apparent than for the model reactor.

Table 4: Effects of alumina extrudates on the delivery of mainstream vapour phase components of a Monitor cigarette (significant percent reduction).

Material	**Al_2O_3 Extrudate Reactor Model**	**Al_2O_3 Extrudate Prototype Cigarette**
Acetaldehyde	-18	-11
Propionaldehyde	-32	-9
i-Butyraldehyde	-30	-25
Acrolein	-29	-18
Acetone	-31	-16
2-Butanone	-36	-23
2-Buten-3-on	-31	-24
Diacetyl	-46	-33
Acrylonitrile	-23	-23
Acetonitrile	-24	-14
Hydrogen cyanide	-55	-31
Toluene		-12
Methanol	-40	-31
2,5-Dimethylfuran	-14	

The results obtained with prototype cigarettes comprising the aluminosilicate extrudate confirm the findings from the reactor model.

Conclusion

The reactor model discussed in this study cannot exactly simulate the behaviour of an additive incorporated in a cigarette filter. However, this model allows a time and cost-saving estimation of the filter performance of potential filter additives and clearly shows strong correlation between physical properties and filter efficiency.

References

[1] B. Fisher: “Unraveling smoke. Smoke chemistry: a series”, Tob. Reporter, 129, No. 9, September 2000.

[2] C.L. Brown: “The design of Cigarettes”, Celanese Acetate LLC, January 4, 2000.

[3] T.W. George, C.H. Keith: “The selective filtration of tobacco smoke” in Tobacco and tobacco smoke, edited by E. Wynder and D. Hoffmann, Academic Press, 577-609 (1969).

[4] C.E. Thomas, K.B. Koller: „Puff-by-puff mainstream smoke analyses by multiplex gas chromatography-mass spectrometry”, Beitr. Tabakforsch. Int. 19, 345-351 (2001).

[5] Patent US 2005/0133048, J.A. Fournier, Z. Luan (June 23, 2005).

[6] Patent US 2005/0133051, Z. Luan, D.I. Gee, J. Nepomuceno, S. Zhuang, J.A. Fournier (June 23, 2005).

[7] L. Xue, C.E. Thomas, K.B. Koller: “Mainstream Smoke Gas Phase Filtration Performance of Adsorption Materials Evaluated with A Puff-by-puff Multiplex GC/MS Method”, TSRC presentation No. 80, Greensboro, 2001.

[8] H.-J. Klimisch, H. Wernicke, K. Meißner: „Gaschromatographische Bestimmung von Isopren, Acetaldehyd und Acrolein aus der Gasphase von Cigarettenrauch“, Beitr. Tabakforsch. Int., 8 (6), 350-353 (1976).

[9] K.D. Brunnemann, M.R. Kagan, J.E. Cox, D. Hoffmann: **„**Analysis of 1,3-butadiene and other selected gas-phase components in cigarette mainstream and sidestream smoke by gas chromatography-mass selective detection**“,** Carcinogenesis 11 (10), 1863-1868 (1990).

[10] F. Omori, N. Higashi, M. Chida, Y. Sone, S. Suhara: „Internal Standard-based Analytical Method for Tobacco Smoke Vapor Phase Components“, Beitr. Tabakforsch. Int., 18 (4), 131-146 (1999).

[11] M. Intorp: “Studies on alternative analytical methods for the determination of organic compounds in the gas phase of mainstream cigarette smoke”, CORESTA congress presentation, New Orleans, 2002.

[12] W. Daniell, U. Schubert, R. Glöckler, A. Meyer, K. Noweck, H. Knözinger: **„**Enhanced surface acidity in mixed alumina-silicas: a low-temparature FTIR study”, Appl. Catal. A, 196, 247-260 (2000).

[13] J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, J.J.M. Orfao: „Modification of the surface chemistry of activated carbons“, Carbon 37, 1379-1389 (1999).