

# Effect of Mesoporous Catalysts on the Mainstream Tobacco Smoke of 3R4F and 1R5F Reference Cigarettes

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**Abstract:** The effect of three synthesised mesoporous catalysts (a SBA-15 and two MCM-41) on the smoke of two reference tobaccos (1R5F and 3R4F) has been studied. Mixtures of the catalysts and each tobacco were smoked under the ISO 3388 standard conditions. The gaseous compounds and the particulate matter condensed in the filter tip (TPM-F) and in a trap located downstream (TPM-T) from the mainstream smoke were analysed separately. The results obtained show that these catalysts directly mixed with tobacco are capable of reducing the yield of most of the compounds studied in the mainstream tobacco smoke. SBA-15 is a better additive for reducing the amount of the compounds analysed in 1R5F and 3R4F tobaccos, both in the liquid fraction (TPM-F and TPM-T) and in the gas fraction. The effect of the studied catalysts is higher on the full-flavour cigarette than on the ultra-low one. As an example, the reductions observed for CO and nicotine in TPM-T from 3R4F as a consequence of the SBA-15 addition were 46% and 77%, respectively. Thus, although the three checked materials are able to provide noticeable reductions, the best is the one having the higher size of pores (SBA-15).

**Keywords:** Tobacco, Tar, CO, SBA-15, MCM-41, Reduction

## 1. Introduction

Tobacco smoking is a controversial issue of great concern for people and the Departments of Health of many countries (WHO). There is a large amount of data available in the literature regarding the composition of smoke and the influence of the variables in the smoking process. The type of paper and filter (1), the type of tobacco and the smoking regimes (2, 3), the cigarette design (1) and the tobacco packing (4), among other variables, are responsible for a wide variation in the results reported that must be carefully analysed in order to obtain adequate conclusions.

The complexities of the chemistry of smoke, where more than 5000 compounds have been identified (5), and of the smoking process, where several processes are overlapped, make this topic especially interesting. During the smoking of a cigarette several mechanisms occur, which cause the generation of tobacco smoke. These mechanisms include: pyrolysis/distillation, combustion, pyrosynthesis, condensation and dilution, which contribute to the formation of the mixture of the forming compounds of tobacco smoke (6,

7). Predominant mechanisms are pyrolysis/distillation, in the range of temperature of around 200-600°C, and combustion, where the temperature is in the range of around 700-950°C. These processes generate the so-called mainstream tobacco smoke.

According to Baker and Bishop (5), at least 60 compounds have been identified as toxic and carcinogenic. Potentially harmful smoke constituents have been identified and reviewed by several authors (8, 9).

In this context, reference cigarettes play an important role in the research on this topic since they allow the replication and comparison of experiments in different laboratories (10, 11). The University of Kentucky is providing such references since 1968. The 1R5F reference tobacco represents an ultra-low tobacco. It delivers approximately 1.67 mg/cigarette of tar, 0.16 mg/cigarette of nicotine and 2.08 TPM mg/cigarette, and 2.95 mg/cigarette using the FTC (Federal Trade Commission) method (<http://www2.ca.uky.edu/refcig/>), whereas the 3R4F represents a typical American “full flavour” cigarette, yielding typically 9.4 mg/cigarette of tar, 0.7 mg/cigarette of nicotine 11 mg/cigarette of TPM, and 12.0 mg/cigarette of CO, under

ISO condition and according to the supplier.

The use of aluminosilicates as tobacco additives with different purposes has been described by several authors; as an example, studies describing the use of additives which are added to the filter or directly to tobacco. Meier and Siegmann demonstrated that zeolite catalysts on tobacco provide a good means to reduce the level of toxic compounds in tobacco smoke (12). The use of other aluminosilicates has also been described, as in the case of MCM-48 materials, which have been proposed for reducing polycyclic aromatic hydrocarbons (PAHs) in the mainstream tobacco smoke (13). Other studies describe cigarette filters with carbon nanotubes or with activated carbon and NaY zeolite (14, 15). As an example, Xu *et al.* (15) described the use of materials such as zeolites NaY and ZSM5 in the filter, as well as SBA-15 and MCM-48. These materials are used as selective adsorbents because they favour the removing of specific nitrosamines of tobacco. In the same way, the use of oxide-iron particles for removing CO has been described by Li and Hajaligol (16). Vesna *et al.* (17) reported on the effect of the CuZSM5 zeolite on the reduction of PAHs in tobacco smoke, and Lin *et al.* (18) studied the strong effect of ferric zeolites in reducing the specific tobacco nitrosamines in the tobacco smoke. Deng *et al.* (19) studied the effect of titanate nanosheets and nanotubes and reported significant reductions of harmful compounds in tobacco. Zeolites, as well as MCM-41, SBA-15 and their modified analogues have also been studied because their ability for efficiently adsorb and catalytically degrade volatile nitrosamines from tobacco due to their special pore structure (20). In this way, Lin *et al.* (20) have studied the effect of different molecular sieve materials on the elimination of specific tobacco nitrosamines. In that study, these authors tested A, ZSM5 and USY type zeolites as well as mesoporous materials such as MCM-41 and SBA-15, and they concluded that the mesoporous materials were the more effective in reducing such compounds.

According with Lin *et al.* (20), there are three possible mechanisms for explaining the removal of tobacco smoke nitrosamines by porous additives. The first one considers that the additive particles are distributed on tobacco rod as "straw spreading on lawn", and their fiber-like morphology permits intercept the particles passed by. The second proposed model suggest that the crystalline catalyst particles, with spherical-like morphologies, could locate on the leaf as "separated stones in lawn", thus with lower ability for the reduction of nitrosamines, that usually rebounds from these particles. Finally, according with the third model, some particles of smoke could be trapped in the cavities of the catalysts, which would be distributed in the tobacco rod "as a rubble". The higher activity of the SBA-15 for intercepting the particulate matter in smoke as compared to crystalline zeolites was mainly attributed to the fiber-like structure morphology of this material leading to a better distribution on the tobacco strands.

Our research group has studied the effect of three commercial zeolites (HUSY, H $\beta$  and HZSM-5) and an own-synthesized Al-MCM-41 catalyst when mixed with a

commercial tobacco brand of cigarettes in order to study the modifications in the components of the tobacco smoke (21). We have also studied the effect of Al-MCM-41 on the thermal decomposition behaviour of tobacco (22), as well as the efficiency of solvent extraction for template removal in the synthesis of MCM-41 to be used as tobacco additive for smoke toxicity reduction (23). The results obtained in these works showed that some zeolites and Al-MCM41 were able to reduce to some extent the yields of some known toxic and carcinogenic compounds studied in the mainstream of cigarettes smoke. Especially interesting was the case of the Al-MCM-41 catalyst.

The objective of this work is to study the effect of three catalysts which were prepared in our laboratories, and whose application for reducing tobacco toxicity is protected by a patent (24, 25), on two reference tobaccos. Cigarettes prepared with the references directly mixed with the catalysts were smoked under the ISO 3308 smoking conditions. 33 compounds were identified and quantified in the vapour fraction and 84 in the particulate matter. The effect on the yields of these compounds when these catalysts were used as tobacco additives in order to reduce the tobacco harmful effects is also shown in the present work.

## 2. Experimental

### 2.1. Catalysts Used

Three different catalysts were synthesised, and their effect on the yield of several compounds appearing in the mainstream smoke obtained from cigarettes prepared with their mixtures with two reference tobaccos has been studied. The catalysts are mesoporous aluminosilicates and have been prepared according with the standard procedures described in the bibliography. The first catalyst is a SBA-15 with a fiber-like morphology, and has been synthesised as has been proposed by Zhang *et al.* (26) by the reaction of a triblock poly(ethylene oxide)-b-poly(propyleneoxide)-b-poly(ethylene oxide) copolymer with TEOS in the presence of an aqueous HCl solution. The obtained SBA-15 (C1 catalyst, according with the nomenclature employed in this work) had a noticeably high pore size in comparison with other mesoporous materials (see Table 1). The other two catalysts (C2 and C3) are MCM-41 samples obtained by different synthesis routes, both of them with sphere-like or granular shapes. C2 catalyst was prepared at room temperature using a polymeric version of ethyl silicate as a source of silica, as was described by Gaydhankar (27), followed by a post-synthesis modification for to obtained the aluminum-containing mesoporous MCM-41 material (28). The third catalyst was obtained according with the sol-gel approach at room temperature proposed by Aguado *et al.* (29), followed by an ionic interchange step with Na<sup>+</sup>. The corresponding textural properties and acidity are shown in Table 1. More details about the synthesis can be found in the patents where the use of these catalysts is covered (24, 25).

**Table 1.** Characteristics of the catalysts

Catalyst	BET area <sup>1</sup> (m <sup>2</sup> /g)	Pore volume <sup>2</sup> (cm <sup>3</sup> /g)	Pore size <sup>3</sup> (nm)	Acidity <sup>4</sup> (mmol/g)
C1 (SBA-15)	757.2	1.051	6.2	0.0
C2 (MCM-41)	923	0.74	2.9	0.3
C3 (MCM-41)	1213	0.81	2.4	0.4

1. N<sub>2</sub> adsorption isotherms, BET method

2. N<sub>2</sub> adsorption isotherms, measured at P/P<sub>0</sub> = 0.995

3. N<sub>2</sub> adsorption isotherms, BJH method

4. TDP of NH<sub>3</sub>

## 2.2. Reference Cigarettes

In this work, two reference cigarettes (3R4F and 1R5F) provided by the University of Kentucky (Reference Cigarette Program, College of Agriculture, <http://www2.ca.uky.edu/refcig/>) have been used in order to check the behaviour of the studied catalysts. The blend specifications for these cigarettes, according to the supplier, are shown in Table 2A and 2B. The percentages are referred to the sum of the masses of the different tobaccos mixed in the cigarette (i.e., Flue cured, Burley, Maryland, Oriental and Reconstituted, for 3R4F). 3R4F (Table 2A) is a "full flavour", filtered, American blended reference cigarette, whereas 1R5F (Table 2B) is an ultra-low yield reference cigarette.

**Table 2A.** Blend summary of 3R4F tobacco

Flue-cured	*35.41%
Burley	21.62%
Oriental	12.07%
Maryland	1.35%
Reconstituted (Schweitzer)	29.55%
Glycerine	2.67%
Isosweet (sugar)	6.41%

\*Wet weight basis

**Table 2B.** Blend summary of 1R5F tobacco

Flue-cured	*5.75%
Flue-cured puffed	19.50%
Burley	42.25%
Burley puffed	10.50%
Turkish	7.00%
Reconstituted sheet	15.00%
Glycerine	2.80%
Invert sugar	5.30%

\*Wet weight basis

## 2.3. Smoking Experiments

Before performing the smoking experiments, 200 cigarettes of each sample were disassembled and the tobacco, the filter and the paper were weighed separately. The tobacco was tumbled and mixed and then the cigarettes were reassembled in the original tubes. The cigarettes were conditioned for at least 48 h at 22°C and relative humidity of 60%.

Cigarettes were prepared with mixtures of tobacco and catalyst and smoked in a smoking machine described elsewhere (4, 20). The results obtained for the composition of the gaseous and condensed products were compared with

those corresponding to the standard cigarettes with no catalyst added. In order to obtain similar characteristics of the cigarette packing and conditioning, the reference cigarettes were prepared following the same procedure (i.e.: disassembling the cigarettes and reassembling them as described above).

The smoking machine employed allows five cigarettes to be smoked simultaneously and the pressure of aspiration of the machine was never higher than 1.5kPa. Ten cigarettes were smoked for each experiment. The puff volume was 35 mL, taken for 2.0 seconds, with a puff frequency of 60 seconds, according to the ISO 3308. The cigarettes were placed in the ports of the smoking machine, ensuring that the ventilating holes were not blocked. The standard butt length, to which cigarettes shall be marked, must be over 23 mm of length.

The condensable products retained in the filter of the cigarette and in the trap (filter fibre glass, EPM2000 Circles, 47mm, Acefesa) placed before the Tedlar bag, were extracted with isopropanol (99.9% purity, Fluka) as solvent and analysed by GC/MS using a HP-5MS column. Before and after each experiment the filter tips and the traps were weighed. The difference has been called TPM-F (total particulate matter condensed in the filters) and TPM-T (total particulate matter condensed in the traps).

The amount of smoked tobacco was determined as the difference between the initial amount of tobacco contained in each cigarette and the amount of tobacco remaining in the butt after the smoking process was finished.

The analysis of the content of CO and CO<sub>2</sub> in the gas-fraction was carried out by GC-TCD using a CTR I column. The rest of non-condensed products were analysed by GC-FID using a GAS-PRO column. Standards gaseous mixtures of CO<sub>2</sub> and CO (Reference 501670) and of gaseous hydrocarbons (References 501816, 22567 and 501662) supplied by Scott Specialty Gases were used to identify and quantify these compounds in the tobacco smoke. The nicotine standard (99.9% purity) was from Merk. Other compounds such as benzene (Ref. 21803.291) and toluene (Ref. 1.08325.1000) were from VWR while acetaldehyde (Ref. 00070), furan (Ref. 185922) and acetonitrile (Ref. 34967) were supplied by Sigma. 33 and 84 compounds were identified and analysed in the fraction collected in the Tedlar bags and in the TPM (both, TPM-F and TPM-T), respectively. The analysis and quantification of the compounds have been carried as described elsewhere (4). Standard deviations lower than 20% were obtained for all the compounds analysed.

### 3. Results and Discussion

#### 3.1. Preliminary Analysis

Table 3 shows the number of puffs, the actual weight percentage of catalyst mixed with tobacco, the amount of smoked tobacco in the smoking runs and the total particulate matter condensed in filters and traps (TPM-F and TPM-T), both expressed as milligrams per gram of smoked tobacco. TPM-F and TPM-T have been chemically analysed to adequately evaluate the activity of the catalyst and to know the

actual change in quantity and composition of the total smoke generated. Table 3 reflects that, in all cases, the addition of the studied catalysts reduces the yield of TPM, even though in some cases the number of puffs increases as does the amount of tobacco smoked. Mixtures of 1R5F and C3 have not been considered because, as demonstrated in the following sections, the results obtained showed that C1 is better than C2 and C3 in order to reduce tobacco toxicity, and the effect of the catalysts is more noticeable when they are mixed with the full flavour 3R4F than with the ultra-low 1R5F.

**Table 3.** Number of puffs, amount of catalysts added, amount of smoked tobacco, TPM-F, TPM-T and TPM-F+TPM-T for the different experiments

Sample	Number of puffs	Catalyst (%w/w)	Smoked tobacco (g)	TPM-F (mg/g smoked tobacco)	TPM-T (mg/g smoked tobacco)	TPM-F + TPM-T (mg/g smoked tobacco)
1R5F	7	0.0	6.19	25.2	3.56	28.8
1R5F+C1	8	5.6	6.32	9.34	0.99	10.3
1R5F+C2	8	5.2	6.32	18.4	3.03	21.5
3R4F	9	0.0	6.78	29.6	11.5	41.0
3R4F+C1	9	5.6	6.64	10.4	2.26	12.7
3R4F+C2	9.7	5.6	6.44	17.5	5.70	23.1
3R4F+C3	10	5.8	6.47	21.1	4.98	26.0

Table 4 shows the amounts of nicotine, CO and tar reported by the supplier (11, <http://www2.ca.uky.edu/refcig/>) and that obtained in the present work. The values are quite comparable, especially when taking into account that the cigarettes smoked in the present work have been emptied and refilled following the same procedure as in the case of the cigarettes including the catalysts, in order to have an adequate reference to

establish the effect of the catalyst. Moreover, the butt length is different in both cases (35 mm in the reported results for reference cigarettes and 23.5 mm in the present work), although the number of puffs is the same. These results enhance the importance and the need for treating the reference cigarettes in exactly the same way as the catalyst added cigarettes.

**Table 4.** Nicotine, carbon monoxide and tar yields in the mainstream smoke of the reference cigarettes 1R5F and 3R4F reported by the supplier and obtained in the present work

Sample	Nicotine (mg/cigarette)	CO (mg/cigarette)	Tar (mg/cigarette)
1R5F (Supplier)	0.16	2.95	1.67
1R5F	0.14	4.30	1.47
3R4F (Supplier)	0.73	12.0	9.40
3R4F	0.65	11.0	7.40

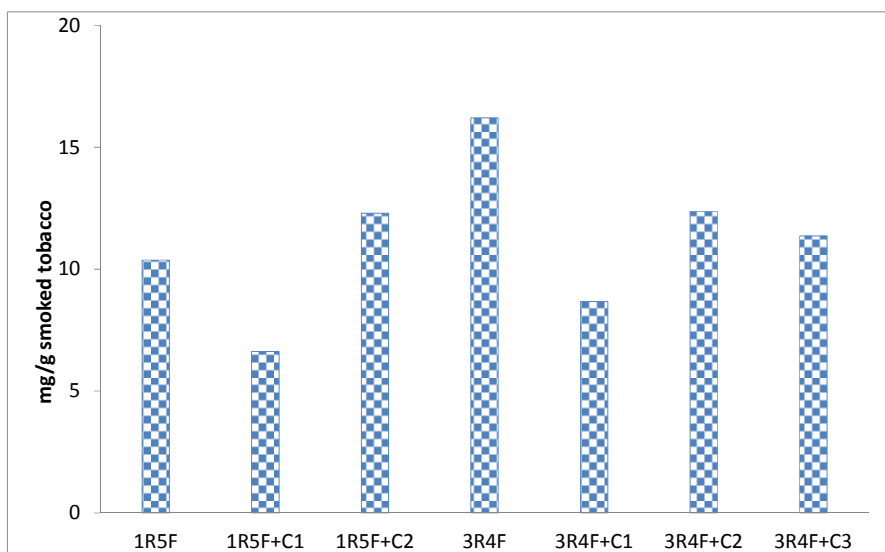
As pointed out above, according to Table 3, the amount of TPM-F and TPM-T obtained is lowered when both standard tobaccos are mixed with the catalysts studied in this work. The percentages of reduction obtained [% reduction =  $100 \times (\text{yield obtained with no catalyst} - \text{yield obtained with catalyst}) / (\text{yield obtained with no catalyst})$ ] for total TPM in the case of the 1R5F cigarette are in the range of 25-64%. Moreover, C1 permits to obtain higher reductions than C2 and higher for TPM-T than for TPM-F, reaching values of 72% and 63%, respectively. In the case of the 3R4F cigarette, the results obtained are better, thus showing the great influence of the tobacco characteristics on the behaviour of the catalysts, and the need for carrying out specific studies in each particular case. As can be seen, the percentages of total TPM reduction provided by the catalysts are in the range of 36-69%, and they are also higher for TPM-T (50-80%) than for TPM-F, and are also the highest for C1 (65-80%). The reductions obtained

when C3 was added are lower than that obtained with C2 for TPM-F and total TPM, and slightly higher for TPM-T. Thus, the case of catalyst C1 is particularly interesting because it permits to obtain very high reductions in TPM, especially in TPM-T for both studied references (i.e., 80% for 3R4F and 72% for 1R5F). As Table 3 reflects, the amount of particulate matter retained by the filters is very similar for both types of reference tobaccos, though the main difference is in the amount retained in the traps. As expected, that corresponding to the 1R5F is much lower as corresponds to an ultra-light tobacco.

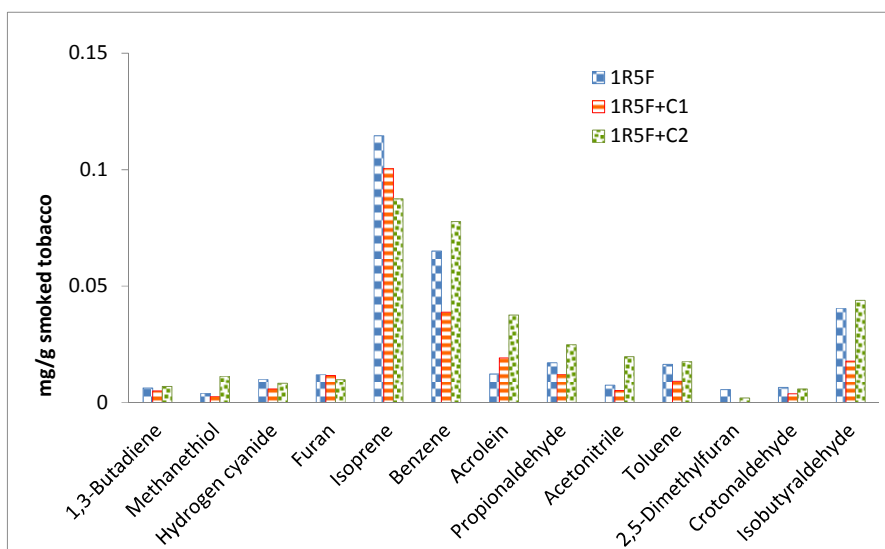
#### 3.2 Analysis of the Vapour Phase

Tables A1 and A2 of the Appendix show the yield of the 33 compounds identified and quantified in the gaseous fraction obtained from the experiments corresponding to the 1R5F and 3R4F systems, respectively (i.e., different mixtures of tobacco

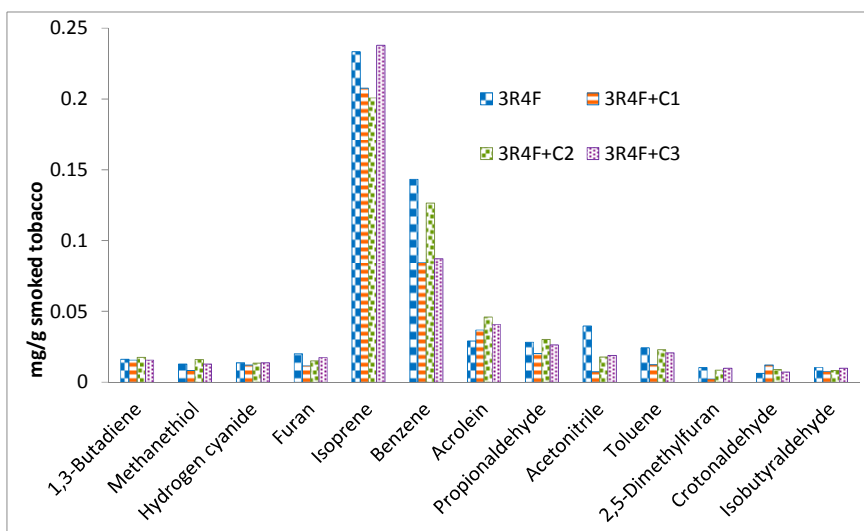
+ catalysts, and two reference tobaccos). Figures 1, 2 and 3 show the results corresponding to the major compounds.



**Figure 1.** Yield of CO from the reference tobaccos in the presence and in the absence of catalysts



**Figure 2.** Yield of some selected compounds of gaseous fraction for the reference tobacco 1R5F and its mixtures with different catalysts



**Figure 3.** Yield of some selected compounds of gaseous fraction for the reference tobacco 3R4F and its mixtures with different catalysts

According to Figure 1, C1 is the most effective catalyst for reducing the yield of CO from both reference tobaccos, with around 36% of reduction in the case of 1R5F and 46% in the case of 3R4F. The catalyst C2 causes a slight increase (around 18%) in the yield of CO obtained from 1R5F and a decrease (23%) in the yield from 3R4F, whereas C3 decreases the yield of CO from 3R4F by around 30%. These results are in good agreement with those shown in Table 3 for the TPM yields, that suggested that C1 is the best catalyst in order to globally reduce the yields of toxic and carcinogenic compounds, and that the effect of the studied catalyst is more noticeable on the American full flavour 3R4F than on the ultra-low tobacco 1R5F. The effect of the catalysts considered on the yield of CO obtained when cigarettes are smoked is an interesting issue because CO is one of the regulated products in order to control the adverse and harmful consequences of smoking tobacco.

As can be seen in Figures 2 and 3, generally, the presence of C1 significantly reduces the yield of all the compounds present in the gaseous fraction from both 1R5F and 3R4F, except acrolein, which seems to be increased in the presence of the studied catalysts, especially in the case of 1R5F. The yield of crotonaldehyde from 3R4F also shows a slight increase. The global decrease in the compounds analysed in the gases as a consequence of the C1 addition is around 27% and 40% for 1R5F and 3R4F, respectively. This catalyst significantly decreases the yields of benzene and toluene and, in the case of 1R5F, isobutyraldehyde. In the case of 3R4F, a noticeable decrease for acetonitrile can also be appreciated. The effect of C2 in the mainstream smoke from 1R5F is not very significant and produces only slight variations of all the compounds analysed, with an increase of around 13% in the global gases, which can be related with the increase in methanethiol, benzene, acrolein, propionaldehyde and acetonitrile. Nevertheless, the effect of C2 on the mainstream smoke from 3R4F is more significant, with a reduction of around 22% of the global gases, associated with reductions in most of the compounds, despite that some of them show almost no variation and others, such as acrolein, are increased. The effect of C3 on the mainstream smoke from 3R4F is worse than that of C1 and C2, with a global reduction of around 10%, which is dominated by the decrease of benzene and acetonitrile and the increase of isoprene and acrolein. The other compounds are affected to a very low extent. Also of great interest is the case of benzene, which shows noticeable reductions as a consequence of the presence of C1 (with 1R5F and 3R4F) and C3 (with 3R4F) but, in the presence of C2 this compound shows a small decrease for 3R4F or even an increase in the case of 1R5F.

According to the previous results, it seems apparent that the large pore size of the C1 catalyst and, consequently, the high pore volume are the more relevant characteristics for favouring the reduction of the yield of different compounds analysed in the gaseous fraction of the mainstream smoke. Thus, this catalyst is the most effective despite its lower surface area and null acidity in front of the other catalysts, which show higher surface areas, especially C3, and acidic

properties. These results are very interesting because previous studies showed that several materials with chemical and textural properties similar to that of C2 and C3 were able to reduce tobacco toxicity in a significant way (21). In this way, C1 would be an even more efficient additive for this purpose.

### 3.3. Particulate Matter

The main fraction of the smoke is formed by condensable products, which are the main constituents of the particulate matter. As explained in the "experimental" section, these condensable compounds are retained in the filters of the cigarettes and in a trap located before the Tedlar bag for the gas collection, yielding the total particulate matter retained in the filters (TPM-F), in the traps (TPM-T). The corresponding yields were presented and discussed in Table 3. In good agreement with the results obtained for the gaseous fraction, C1 produces the highest percentages of reduction, and the catalysts are more effective over 3R4F than over 1R5F. In this section, the results obtained when these condensable products -in the present work so-called liquids retained- have been extracted with isopropanol and analysed by GC/MS are presented and discussed.

84 compounds have been identified and quantified in these condensable products. The results corresponding to TPM-F and TPM-T from 1R5F and its mixtures with C1 and C2 are shown in Tables A3 and A4 of the Appendix. In order to facilitate the interpretation and comparison of the results, these compounds have been grouped by families, according to their chemical functionality, in the same manner as described elsewhere (21). Thus, the families considered are the following: nitrogenous, carbonyls, phenolics, epoxies, aromatics, aliphatics and others. Tables 5 and 6 show the yields obtained for such families, according to Tables A3 and A4. In order to simplify the tables, compounds which were below the detection limit of the analytical equipment have been omitted. The complete list of the 84 identified compounds is shown in Table A5, where the results for TPM-F from the systems including the 3R4F reference are presented. As seen, the first interesting observation is that the number of compounds retained in the filters is higher than that retained in the traps and, moreover the yields obtained in the filters are also higher. This behaviour can be observed for both types of systems, i.e., that involving 1R5F and 3R4F, respectively.

**Table 5.** Yield of different families of compounds analysed in the TPM-F of the mainstream smoke of systems involving 1R5F tobacco

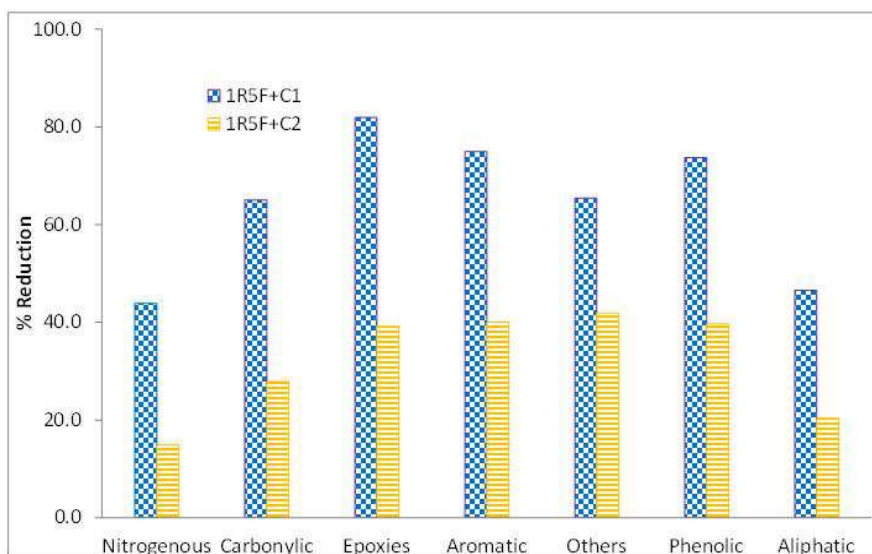
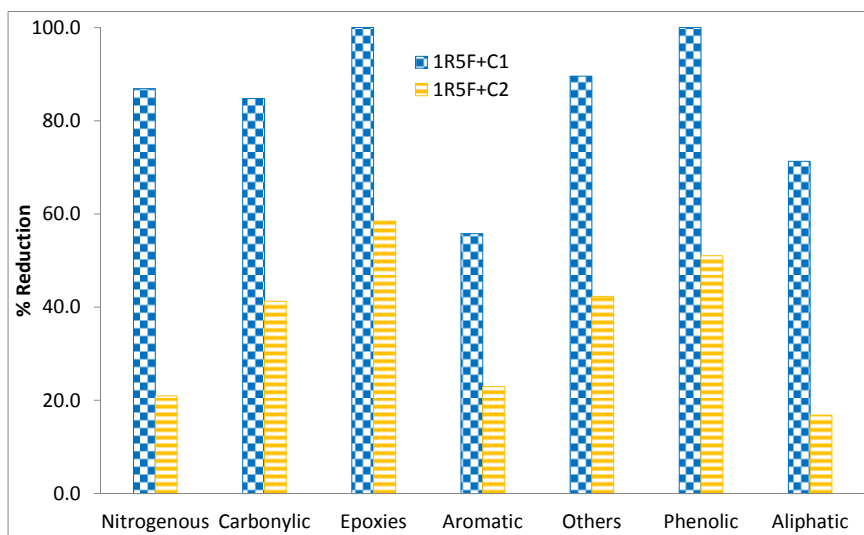
mg compound/g smoked tobacco	1R5F	1R5F+C1	1R5F+C2
Nitrogenous	1.91	1.07	1.63
Carbonylic	0.27	0.09	0.20
Epoxy	0.03	0.01	0.02
Aromatic	0.02	<0.01	0.01
Others	0.06	0.02	0.03
Phenolic	0.24	0.06	0.14
Aliphatic	0.25	0.13	0.20

**Table 6.** Yield of different families of compounds analysed in the TPM-T of the mainstream smoke of systems involving 1R5F tobacco

mg compound/g smoked tobacco	1R5F	1R5F+C1	1R5F+C2
Nitrogenous	1.91	1.07	1.63
Carbonylic	0.27	0.09	0.20
Epoxy	0.03	0.01	0.02
Aromatic	0.02	<0.01	0.01
Others	0.06	0.02	0.03
Phenolic	0.24	0.06	0.14
Aliphatic	0.25	0.13	0.20

Figures 4 and 5 show the percentages of reduction (calculated as previously described) obtained for the different

families of compounds considered, in the case TPM-F and TPM-T, respectively, when mixtures of C1 and C2 with the reference tobacco 1R5F were smoked. As can be seen, C1 permits to obtain higher reductions than C2 for all the considered families, both in TPM-F and TPM-T. Moreover, generally, the percentages de reductions obtained for each family are higher in TPM-T than in TPM-F. In fact, the average reduction obtained for the different families in TPM-F is around 63% in the presence of C1, and 32% in presence of C2, and the corresponding values for TPM-T are around 89% and 35%, respectively.

**Figure 4.** Percentages of reduction of several families of compounds appearing in TPM-F as consequence of the addition of C1 and C2 as catalysts**Figure 5.** Percentages of reduction of several families of compounds appearing in TPM-T as consequence of the addition of C1 and C2 as catalysts

The previous results indicate that, as was pointed out from the gaseous fraction, C1 is able to reduce the appearance of most of the compounds analysed in the condensable products of the mainstream smoke obtained from 1R5F cigarettes, and that it is better than C2 at reducing the yield of these compounds. In this case, it also seems that the main property that conducts the ability for the studied solid materials is the

size and volume of pores, which is much more significant than the acidity.

Tables A5 and A6 of the Appendix show the results corresponding to the yield of the different compounds analysed in TPM-F and TPM-T in the case of systems involving the 3R4F reference tobacco. As mentioned above, Table A5 contains the complete list of the 84 identified



compounds. The same grouping in families as in the previous case has been done, and the results obtained are presented in Tables 7 and 8. The percentages of reduction obtained for each family as a consequence of the addition of catalysts have been calculated and are graphically shown in Figures 6 and 7.

**Table 7.** Yield of different families of compounds analysed in the TPM-F of the mainstream smoke of systems involving 3R4F tobacco

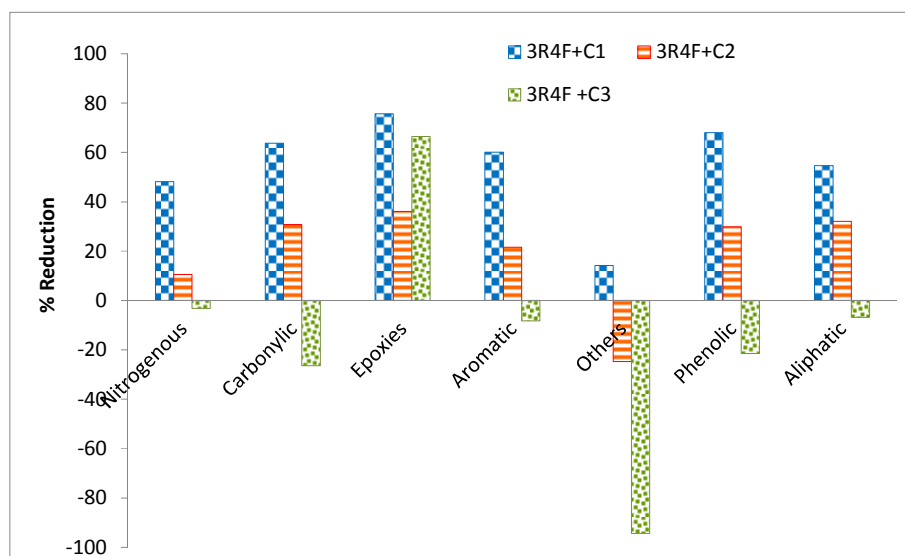
mg compound/g smoked tobacco	3R4F	3R4F+C1	3R4F+C2	3R4F+C3
Nitrogenated	1.372	0.711	1.226	1.415
Carbonylic	0.280	0.102	0.194	0.354
Epoxy	0.023	0.006	0.015	0.008
Aromatic	0.031	0.012	0.024	0.033
Others	0.039	0.033	0.048	0.075
Phenolic	0.228	0.073	0.160	0.277
Aliphatic	0.219	0.099	0.149	0.233

**Table 8.** Yield of different families of compounds analysed in the TPM-T of the mainstream smoke of systems involving 3R4F tobacco

mg compound/g smoked tobacco	3R4F	3R4F+C1	3R4F+C2	3R4F+C3
Nitrogenated	1.028	0.229	0.665	0.795
Carbonylic	0.046	0.003	0.012	0.023
Epoxy	0.004	0.001	0.002	0.003
Aromatic	0.016	0.000	0.001	0.000
Others	0.019	0.002	0.009	0.017
Phenolic	0.073	0.003	0.016	0.050
Aliphatic	0.146	0.018	0.058	0.103

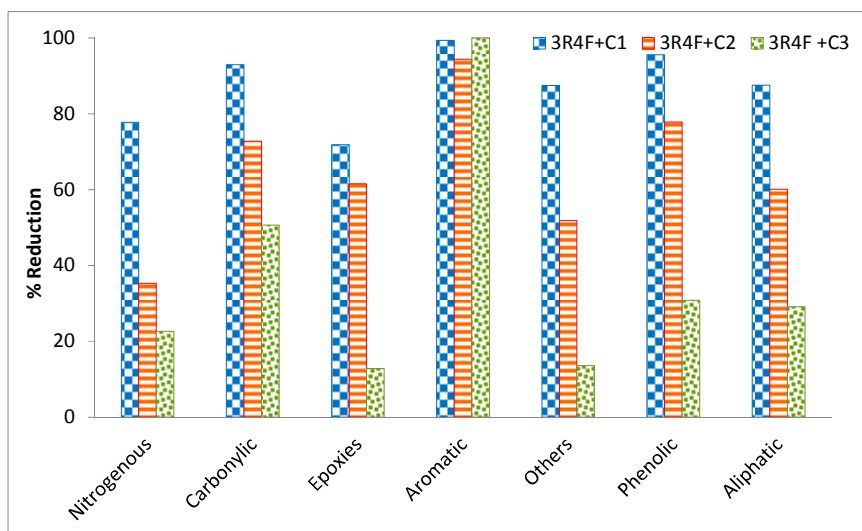
As observed for the reference 1R5F, the yields of the different compounds analysed in the condensable fraction of the mainstream smoke from 3R4F are higher in the filters than in the traps. As expected, the numbers of detected compounds as well as the corresponding yields are higher in the case of the 3R4F full-flavour tobacco than in the ultra-low 1R5F. The behaviour of the catalysts is also in agreement with the previous statements, and C1 produces higher reductions than C2, despite its absence of acidity. The global reductions obtained in the case of TPM-F are 52% and 17%, in the presence of C1 and C2, whereas in the presence of C3 a slight increase of 9% is observed. In the case of the TMF-T, these reductions are at around 81%, 43% and 26% (values calculated from Tables A5 and A6) respectively.

With respect to TPM-F, if the behaviour of the catalyst from the point of view of the different families of compounds (Figure 6 and Table 13) is analysed, it can be seen that, with the only exception of the group of "Others", the reductions provided by C1 are in the range of 48-74%, and for C2 in the range of 11-35%. Moreover, the effect of each catalyst is quite different depending on the family considered. Thus, C1 mainly reduces the group of epoxy compounds (at around 74%), followed by carbonyl, aromatic and phenolic (61-68%), whereas the reductions obtained with C2 are ordered as follows: epoxies (35%), carbonylic, aliphatic and phenolic (30-32%), aromatics (23%) and nitrogenous (11%). The group of "Other" compounds shows a decrease of 15% in the presence of C1 and an increase of 23% in the presence of C2. With C3 and 3R4F all the families are increased in TPM-F, with the only exception of epoxies, which are reduced at around 65%.



**Figure 6.** Percentages of reduction of several families of compounds appearing in TPM-F as consequence of the addition of C1, C2 and C3 as catalysts





**Figure 7.** Percentages of reduction of several families of compounds appearing in TPM-T as consequence of the addition of C1, C2 and C3 as catalysts

Noticeable differences have been found between the effect of the studied catalyst on the yields of compounds obtained in TPM-F and in TPM-T. Effectively, according to Table 8 and Figure 7, different than the behaviour observed for TPM-F, the three considered catalysts contribute to decrease the yield of all the families of compounds appearing in the TPM-T. Moreover, the percentages of reduction obtained are very interesting for all the families (in the range of 75-100%, 35-94% and 11-100% for C1, C2 and C3, respectively). As in the previous cases, the best catalyst is C1, followed by C2 and by C3. Nevertheless, in this case, C3 is also capable of provide interesting reductions. The group of aromatics is the one showing the highest reductions in the presence of the three catalysts. As pointed out, very high reductions are also obtained for the other families when C1 is added, the lowest (75%) being for the group of epoxies. The reduction of aromatics by the effect of C2 is around 94%, and the reduction for the others families ranges between 50% and 78%, with the only exception of nitrogenous, which shows with this catalyst the lowest reduction (35%). The results obtained in the presence of C3 are quite different, with practically a 100% of reduction of aromatics, followed by carbonyl compounds (50%) The rest of families are in the range of 11-32% (in this case, then nitrogenous compounds are reduced by around 23%).

The reductions of nicotine as a consequence of the C1, C2 and C3 addition are, respectively, around 47%, 10% and -2% (i.e., increase of 2%) in TPM-F and 77%, 34% and 22% in TPM-T.

The results obtained agree with the previously commented great influence of the pore size. Effectively, in all the considered cases, the highest pore size SBA-15 (C1) is the catalyst providing the highest reductions. Moreover, when both mesoporous MCM-41 (C2 and C3) are compared, the one with higher pore size (C2) also seems to be better, despite its lower acidity. The great influence (i.e., the higher reductions) of the studied catalyst on TPM-T than on TPM-F is also very interesting because TPM-T is the most interesting fraction if we consider that it is the one that is inhaled by active smokers.

A remarkable aspect that can be observed in Tables A3, A4,

A5 and A6 is the way compounds are delivered between the filter and the trap according to their retention time, an aspect already observed in previous articles (4). Compounds with low retention time (i.e., compounds with relatively low molecular weight) are higher in the filters than in the traps, while the very opposite is true for the heaviest compounds.

## 4. Conclusions

In this work the ability of three mesoporous aluminosilicate solids to reduce the amount of the different compounds appearing in the mainstream smoke from two reference cigarettes has been studied. The results obtained reveal that these materials permit to decrease the yields of most of the analysed compounds, both in the gaseous and in the liquid fraction of the mainstream smoke. The material with the highest pore size (SBA-15 or C1 according with the employed nomenclature) seems to provide higher reductions than the MCM-41 samples, C2 and C3, with significant lower pore size. C2, with higher pore size and lower BET area and acidity than C3 also seems to be better than C3, thus enhancing the importance of the pore size role. In general, higher percentages of reduction have been obtained for the full-flavour reference cigarette 3R4F than for the ultra-low reference tobacco 1R5F. Higher reductions have also been obtained for TPM-T than for TPM-F. Thus, the most spectacular results correspond to the cigarettes prepared with a mixture of C1 and 3R4F tobacco. Thus, as an example, for this system, the following percentages of reduction have been obtained:

- Total TPM (TPM-F+TPM-T): 69%
- Global yield of gases: 40%
- CO: 47%
- Chemical families in TPM-F: nitrogenous (48%), carbonyls (64%), epoxies (74%), aromatics (61%), other compounds (15%), phenolics (68%) and aliphatics (55%)
- Chemical families in TPM-T: nitrogenous (78%), carbonyls (93%), epoxies (75%), aromatics (100%),

other compounds (89%), phenolics (96%) and aliphatics (88%)

- Nicotine: 77%

Reductions obtained in the yields of CO in the case of tobacco 3R4F, were 47% for the C1 catalyst, 24% for the C2 catalyst and 30% for the C3 catalyst. In the case of the ultra-light 1R5F tobacco, only the C1 catalyst was capable of reducing the evolution of this compound. The total amount of the gaseous fraction for 3R4F was reduced 40% when catalyst C1 was used, 22% in presence of C2 and 10% in presence of C3. When smoking 1R5F tobacco, the total amount of the gaseous fraction was 27% reduced in the presence of C1. The effect of C2 is not very significant and produces only slight variations of all the compounds analysed. Global gases are increased around 13 with the C2.

The total amount of TPM in the two tobaccos analysed, 1R5F and 3R4F, was reduced over 60% in the presence of C1. Others catalysts also reduce this fraction, though to a lesser extent. When tobacco 1R5F is smoked, all families in TPM-F and in TPM-T are reduced in the presence of the two catalysts, being the effect of C1 more remarkable. When tobacco 3R4F is smoked, the yields of all families in TPM-T are reduced in the presence of the three catalysts, all the families in TPM-F are reduced by C1 and C2, with the only exception of the group of others in the 3R4F+C2 system, and all the families are increased by C3, with the only exception of epoxies, which are decreased. It has been observed that in TPM-F, the compounds with lower molecular height are retained in higher proportion, contrarily to the effect observed in the traps, where

the compounds with higher molecular weight are retained in greater extent.

In conclusion, catalyst C1 (i.e., SBA-15) is the one providing a larger reduction of the yields of the majority of the compounds analysed, and for all the groups of compounds considered.

These results agree with the data reported by Lin *et al.* (20), that obtained that SBA-15 allows higher reduction of TPM than MCM-41 when these materials are used as cigarette additives, in spite of the yields obtained are different due to the differences between the tobacco rod characteristics and the experimental conditions for the smoking process simulation. These authors suggested that the main mechanism involved in the tobacco nitrosamines reduction by mesoporous silica is the filtration of the particles in smoke, due to the fiber-like morphology of the catalyst. The SBA-15 used in the present work has a similar fiber-like morphology as compared to the spherical one of the other catalysts tested. In addition, this catalyst is the one having the largest pore size and pore volume, both characteristics contributing to increase the reduction effect.

## Acknowledgements

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## Appendix

**Table A1.** Yield of different compounds analysed in the gaseous fraction of the mainstream smoke of systems involving 1R5F tobacco. Yields are expressed in mg of compound/g of smoked tobacco

Compound	1R5F	1R5F+C1	1R5F+C2
CO	10.4	6.62	12.3
CO <sub>2</sub>	34.4	26.2	38.4
Methane	0.61	0.39	0.66
Ethane	0.27	0.17	0.27
Ethylene	0.12	0.089	0.14
Ethyne	0.0092	0.0079	0.019
Propane	0.13	0.085	0.13
Propene	0.13	0.087	0.14
Iso-butane	0.013	0.0083	0.015
Chloromethane	0.024	0.015	0.024
Butane	0.043	0.026	0.039
1-Butene	0.032	0.020	0.031
1,2-Propadiene	0.0040	0.0030	0.0050
1,3-Butadiene	0.0063	0.0050	0.0070
Isobutene	0.035	0.021	0.031
cis-2-Butene	0.027	0.015	0.024
Pentane	0.012	0.0069	0.011
Methanethiol	0.0040	0.0026	0.011
Hydrogen cyanide	0.0099	0.0059	0.0080
1-Pentene	0.010	0.0059	0.0090

Compound	1R5F	1R5F+C1	1R5F+C2
Furan	0.012	0.012	0.010
Isoprene	0.11	0.10	0.088
Hexane	0.0029	0.0034	0.0020
1-Hexene	0.0076	0.0048	0.0075
Benzene	0.065	0.039	0.078
Acetaldehyde	0.36	0.17	0.35
Acrolein	0.012	0.019	0.038
Propionaldehyde	0.017	0.012	0.025
Acetonitrile	0.0075	0.0052	0.020
Toluene	0.016	0.0091	0.018
2,5-Dimethylfuran	0.0056	0.000	0.0020
Crotonaldehyde	0.0065	0.0038	0.0059
Isobutyraldehyde	0.040	0.018	0.044
Sum	86.6	52.0	67.4

**Table A2.** Yield of different compounds analysed in the gaseous fraction of the mainstream smoke of systems involving 3R4F tobacco. Yields are expressed in mg of compound/g of smoked tobacco

Compound	3R4F	3R4F+C1	3R4F+C2	3R4F+C3
CO	16.2	8.67	12.4	11.4
CO <sub>2</sub>	66.3	40.4	51.0	63.4
Methane	1.20	0.86	1.15	1.04
Ethane	0.49	0.37	0.47	0.43
Ethylene	0.25	0.19	0.26	0.24
Ethyne	0.027	0.025	0.040	0.032
Propane	0.23	0.17	0.21	0.19
Propene	0.24	0.19	0.24	0.22
Iso-butane	0.026	0.022	0.058	0.027
Chloromethane	0.060	0.045	0.055	0.056
Butane	0.067	0.055	0.066	0.059
1-Butene	0.056	0.043	0.067	0.052
1,2-Propadiene	0.010	0.0074	0.010	0.011
1,3-Butadiene	0.016	0.016	0.018	0.016
Isobutene	0.054	0.043	0.055	0.044
cis-2-Butene	0.039	0.033	0.043	0.038
Pentane	0.019	0.014	0.018	0.017
Methanethiol	0.013	0.0082	0.016	0.013
Hydrogen cyanide	0.014	0.012	0.014	0.014
1-Pentene	0.015	0.013	0.017	0.0089
Furan	0.020	0.012	0.015	0.017
Isoprene	0.23	0.21	0.20	0.24
Hexane	0.0070	0.0047	0.0061	0.0074
1-Hexene	0.013	0.010	0.014	0.013
Benzene	0.14	0.085	0.13	0.087
Acetaldehyde	0.61	0.44	0.74	0.36
Acrolein	0.029	0.037	0.046	0.041
Propionaldehyde	0.028	0.020	0.030	0.026
Acetonitrile	0.040	0.0073	0.018	0.019
Toluene	0.024	0.012	0.023	0.021
2,5-Dimethylfuran	0.010	0.0023	0.0086	0.010
Crotonaldehyde	0.006	0.012	0.0090	0.0072
Isobutyraldehyde	0.010	0.0075	0.0083	0.010
Sum	46.9	34.2	53.0	46.9

**Table A3.** Yield of different compounds analysed in TPM-F of the mainstream smoke of systems involving 1R5F tobacco. Yields are expressed in mg of compound/g of smoked tobacco (it is continued in the next page). nd = not detected compounds

Compound	Family	1R5F	1R5F+C1	1R5F+C2
Pyridine, 4-methyl-	nitrogenous	0.0060	0.0012	0.0033
Pyrazine, methyl-	nitrogenous	0.0076	0.0033	0.0041
Furfural	carbonylic	0.040	0.016	0.028
2-Pentanone, 4-hydroxy-4-methyl-	carbonylic	0.0097	0.0018	0.0045
Ethanol, 2-(1-methylethoxy)-	others	0.0058	0.0015	0.0015
2-Furanmethanol	epoxy	0.0083	0.0004	0.0041
Pyridine, 3-methyl-	nitrogenous	0.0050	nd	0.0027
2-Propanone, 1-(acetyloxy)-	carbonylic	0.014	0.0069	0.011
4-Cyclopentene-1,3-dione	carbonylic	0.017	0.0090	0.013
Styrene	aromatic	0.0075	0.0020	0.0018
2-Cyclopenten-1-one, 2-methyl-	carbonylic	0.023	0.0071	0.015
2-Acetylfuran	carbonylic	0.016	0.0023	0.010
2(5H)-furanone	carbonylic	0.0097	0.0008	0.0084
Pyrazine, 2,3-dimethyl-	nitrogenous	0.0010	0.0005	0.0006
2-Hydroxycyclopent-2-en-1-one	carbonylic	0.0065	0.0026	0.0051
Pyridine, 3,5-dimethyl-	nitrogenous	0.0008	nd	0.0007
2,5-Dimethyl-2-cyclopentenone	carbonylic	0.0054	0.0021	0.0031
2(3H)-furanone, 5-methyl-	carbonylic	0.0013	0.0008	0.0013
Butanoic acid, 3-methyl-	others	0.0040	0.0030	0.0018
Ethanol, 2-butoxy-	others	0.0029	0.0012	0.0015
Benzaldehyde	carbonylic	0.0067	0.0042	0.0055
Furfural, 5-methyl-	carbonylic	0.017	0.0020	0.0037
Pyridine, 3-ethenyl-	nitrogenous	0.0055	0.0004	0.0003
2(5H)-Furanone, 3-methyl-	carbonylic	0.0061	0.0019	0.0041
Phenol	phenolic	0.054	0.018	0.040
2-isopropylfuran	epoxy	0.014	nd	0.0035
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	carbonylic	0.027	0.0034	0.017
Limonene	others	0.031	0.0067	0.015
2,3-Dimethyl-2-cyclopenten-1-one	carbonylic	0.010	0.0029	0.0062
Indene	PAH	0.010	0.0014	0.0074
o-Cresol	phenolic	0.073	0.0088	0.020
nitrogenous	nitrogenous	0.011	0.0044	0.0061
p-Cresol	phenolic	0.0420	0.013	0.030
2 ethyl tiophene	others	0.0051	0.0023	0.0051
Phenol, 2-methoxy-	phenolic	0.016	0.0060	0.012
2-Propanamine	nitrogenous	0.0056	0.0017	0.0057
2,4-Dimethyl-4-cyclohexen-1,3-dione-one	carbonylic	0.0059	nd	0.0052
3-Ethyl-2-hydroxy-2-cyclopenten-1-one	carbonylic	0.0095	0.0027	0.0070
2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	carbonylic	0.014	0.0088	0.016
Phenol, 2,4-dimethyl-	phenolic	0.011	0.0055	0.0085
Naphthalene	PAH	0.0034	0.0019	0.0035
Ethanone, 1-(3-methylphenyl)-	carbonylic	0.0053	0.0025	0.0042
p-cresol 2 methoxy	phenolic	0.0032	nd	0.0016
2,3-Dihydro-benzofuran	epoxy	0.0072	0.0048	0.010
1H-Inden-1-one, 2,3-dihydro-	carbonylic	0.0071	0.0024	0.0067
Hydroquinone	phenolic	0.021	0.0074	0.020
1H-Indole	nitrogenous	0.021	0.0078	0.016
4-vinyl-2-methoxy-phenol	nitrogenous	0.011	0.0022	0.0072
Nicotine	nitrogenous	1.73	0.99	1.48
1H-Indole, 3-methyl-	nitrogenous	0.011	0.0045	0.012
Myosmine	nitrogenous	0.022	0.012	0.019
Nicotyrine	nitrogenous	0.026	0.017	0.022
Norsolanadiona	carbonylic	0.011	0.0036	0.01
2,3'-Bipyridine	nitrogenous	0.033	0.026	0.033
Megastigmatrienone	carbonylic	0.011	0.0096	0.010
Cotinine	nitrogenous	0.016	0.0052	0.012
N(b)-formylornicotine	nitrogenous	0.010	nd	0.0078

Compound	Family	1R5F	1R5F+C1	1R5F+C2
Neophytadiene	aliphatic	0.16	0.099	0.12
8-Quinolinemethanol	nitrogenous	0.0044	0.0047	0.0064
Hexadecanoic acid, ethyl ester	others	0.0062	0.0044	0.0073
Eicosane	aliphatic	0.0041	0.0028	0.0043
pentadecane	aliphatic	0.0026	0.0017	0.0032
Docosano	aliphatic	0.0017	0.0015	0.0013
Tricosane	aliphatic	0.013	0.0048	0.011
2,6,10,14,18,22-Tetracosahexaene, 2,6,10,15,19,23-hexamethyl-	aliphatic	0.0036	0.0016	0.0031
Heptacosane	aliphatic	0.012	0.0039	0.0095
Triacontane	aliphatic	0.016	0.0045	0.012
Octadecane	aliphatic	0.041	0.014	0.032
Tocopherol	phenolic	0.0075	0.0020	0.0042

**Table A4.** Yield of different compounds analysed in TPM-T of the mainstream smoke of systems involving 1R5F tobacco. Yields are expressed in mg of compound/g of smoked tobacco (it is continued in the next page). nd = not detected compounds

Compound	Family	1R5F	1R5F+C1	1R5F+C2
2-Pentanone, 4-hydroxy-4-methyl-	carbonylic	0.0003	nd	0.0002
Ethanol, 2-(1-methylethoxy)-	others	0.0007	0.0004	0.0006
4-Cyclopentene-1,3-dione	carbonylic	0.0002	nd	0.0002
Styrene	aromatic	0.0003	0.0001	0.0002
Butanoic acid, 3-methyl-	others	0.0002	nd	0.0000
Benzaldehyde	carbonylic	0.0002	0.0001	0.0001
Limonene	others	0.0005	nd	0.0000
o-Cresol	phenolic	0.0006	nd	0.0004
p-Cresol	phenolic	0.0009	nd	0.0006
2 ethyl tiophene	others	0.0004	nd	0.0000
2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	carbonylic	0.0019	0.0003	0.0010
Phenol, 2,4-dimethyl-	phenolic	0.0011	nd	0.0006
Phenol, 4-ethyl-	phenolic	0.0010	nd	0.0000
2,3-Dihydro-benzofuran	epoxy	0.0019	nd	0.0008
1H-Indole	nitrogenous	0.0011	nd	0.0006
4-vinyl-2-methoxy-phenol	phenolic	0.0004	nd	0.0000
Nicotine	nitrogenous	0.34	0.046	0.27
1H-Indole, 3-methyl-	nitrogenous	0.0011	nd	0.0008
Myosmine	nitrogenous	0.0022	nd	0.0019
Nicotyrine	nitrogenous	0.0040	nd	0.0022
2,3'-Bipyridine	nitrogenous	0.0018	nd	0.0014
Cotinine	nitrogenous	0.0017	nd	0.0009
5-Tetradecene	aliphatic	0.0010	nd	0.0010
N(b)-formylornicotine	nitrogenous	0.0025	0.0000	0.0037
Neophytadiene	aliphatic	0.012	0.0030	0.011
Farnesol	others	0.0010	nd	0.0009
Hexadecanoic acid, ethyl ester	others	0.0007	nd	0.0005
Eicosane	aliphatic	0.0006	nd	0.0003
Tricosane	aliphatic	0.0012	0.0005	0.0010
2,6,10,14,18,22-Tetracosahexaene, 2,6,10,15,19,23-hexamethyl-	aliphatic	0.0013	0.0007	0.0011
Heptacosane	aliphatic	0.0015	0.0006	0.0011
Triacontane	aliphatic	0.0017	0.0007	0.0010
Octadecane	aliphatic	0.0036	0.0012	0.0031
Tocopherol	phenolic	0.0010	nd	0.0009
2-Pentanone, 4-hydroxy-4-methyl-	carbonylic	0.0003	nd	0.0002
Ethanol, 2-(1-methylethoxy)-	others	0.0007	0.0004	0.0006
4-Cyclopentene-1,3-dione	carbonylic	0.0002	nd	0.0002
Styrene	aromatic	0.0003	0.0001	0.0002
Butanoic acid, 3-methyl-	others	0.0002	nd	0.0000
Benzaldehyde	carbonylic	0.0002	0.0001	0.0001
Limonene	others	0.0005	nd	0.0000
o-Cresol	phenolic	0.0006	nd	0.0004
p-Cresol	phenolic	0.0009	nd	0.0006
2 ethyl tiophene	others	0.0004	nd	0.0000
2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	carbonylic	0.0019	0.0003	0.0010
Phenol, 2,4-dimethyl-	phenolic	0.0011	nd	0.0006

Compound	Family	1R5F	1R5F+C1	1R5F+C2
Phenol, 4-ethyl-	phenolic	0.0010	nd	0.0000
2,3-Dihydro-benzofuran	epoxy	0.0019	nd	0.0008
1H-Indole	nitrogenous	0.0011	nd	0.0006
4-vinyl-2-methoxy-phenol	phenolic	0.0004	nd	0.0000
Nicotine	nitrogenous	0.34	0.046	0.27
1H-Indole, 3-methyl-	nitrogenous	0.0011	nd	0.0008
Myosmine	nitrogenous	0.0022	nd	0.0019
Nicotyrine	nitrogenous	0.0040	nd	0.0022
2,3'-Bipyridine	nitrogenous	0.0018	nd	0.0014
Cotinine	nitrogenous	0.0017	nd	0.0009
5-Tetradecene	aliphatic	0.0010	nd	0.0010
N(b)-formylornicotine	nitrogenous	0.0025	0.0000	0.0037
Neophytadiene	aliphatic	0.012	0.0030	0.011
Farnesol	others	0.0010	nd	0.0009
Hexadecanoic acid, ethyl ester	others	0.0007	nd	0.0005
Eicosane	aliphatic	0.0006	nd	0.0003
Tricosane	aliphatic	0.0012	0.0005	0.0010
2,6,10,14,18,22-Tetracosahexaene, 2,6,10,15,19,23-hexamethyl-	aliphatic	0.0013	0.0007	0.0011
Heptacosane	aliphatic	0.0015	0.0006	0.0011
Triacotane	aliphatic	0.0017	0.0007	0.0010
Octadecane	aliphatic	0.0036	0.0012	0.0031
Tocopherol	phenolic	0.0010	nd	0.0009

**Table A5.** Yield of different compounds analysed in the TPM-F of the mainstream smoke of systems involving 3R4F tobacco. Yields expressed in terms of mg of compound/g of smoked tobacco (it is continued in the next pages). nd = not detected compounds

Compound	Family	3R4F	3R4F+C1	3R4F+C2	3R4F+C3
Pyridine, 4-methyl-	nitrogenous	0.0081	0.0031	0.0054	0.0099
Pyrazine, methyl-	nitrogenous	0.0056	0.0027	0.0044	0.0052
Furfural	carbonylic	0.0508	0.0218	0.0387	0.0750
2-Pentanone, 4-hydroxy-4-methyl-	carbonylic	0.0023	nd	nd	0.0013
Ethanol, 2-(1-methylethoxy)-	others	0.0039	0.0010	0.0040	0.0079
2-Furanmethanol	epoxy	0.0096	0.0015	0.0057	0.0000
Pyridine, 3-methyl-	nitrogenous	0.0145	0.0011	0.0069	0.0169
2-Propanone, 1-(acetyloxy)-	carbonylic	0.0182	0.0065	0.0103	0.0188
4-Cyclopentene-1,3-dione	carbonylic	0.0145	0.0058	0.0102	0.0169
Styrene	aromatic	0.0028	0.0019	0.0036	0.0039
2-Cyclopenten-1-one, 2-methyl-	carbonylic	0.0218	0.0086	0.0169	0.0254
2-Acetylfuran	carbonylic	0.0133	0.0052	0.0104	0.0169
2(5H)-furanone	carbonylic	0.0097	0.0002	0.0011	0.0116
Pyrazine, 2,3-dimethyl-	nitrogenous	0.0018	0.0001	0.0013	nd
2-Hydroxycyclopent-2-en-1-one	carbonylic	0.0087	0.0018	0.0042	0.0022
Pyridine, 3,5-dimethyl-	nitrogenous	0.0040	0.0004	nd	0.0038
2,5-Dimethyl-2-cyclopentenone	carbonylic	0.0040	0.0025	0.0041	0.0045
2(3H)-furanone, 5-methyl-	carbonylic	0.0022	0.0006	0.0010	0.0025
Butanoic acid, 3-methyl-	others	0.0025	0.0008	0.0022	nd
Ethanol, 2-butoxy-	others	0.0021	0.0012	0.0025	0.0046
Benzaldehyde	carbonylic	0.0084	0.0035	0.0034	0.0146
Furfural, 5-methyl-	carbonylic	0.0266	0.0028	0.0169	0.0303
Pyridine, 3-ethenyl-	nitrogenous	0.0050	0.0053	0.0115	0.0053
2(5H)-Furanone, 3-methyl-	carbonylic	0.0064	0.0019	0.0041	0.0097
Phenol	phenolic	0.0508	0.0169	0.0387	0.0690
2-isopropylfuran	epoxy	0.0067	nd	nd	nd
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	carbonylic	0.0230	0.0082	0.0145	0.0363
Limonene	others	0.0133	0.0206	0.0206	0.0399
Benzenemethanol	aromatic	0.0022	0.0028	0.0034	nd
2,3-Dimethyl-2-cyclopenten-1-one	carbonylic	0.0133	0.0042	0.0092	0.0120
Indene	PAH	0.0056	0.0019	0.0069	0.0076
o-Cresol	phenolic	0.0266	0.0087	0.0303	0.0399
2-Acetylpyrrole	nitrogenous	0.0030	0.0021	0.0034	0.0019
Phenol, 4-methoxy-	phenolic	0.0038	0.0010	0.0034	0.0050
Ethanone, 1-phenyl-	carbonylic	0.0029	0.0010	0.0018	0.0045
p-Cresol	phenolic	0.0351	0.0133	0.0327	0.0508
2 ethyl tiophene	others	0.0018	0.0029	0.0035	0.0000
Phenol, 2-methoxy-	phenolic	0.0206	0.0077	0.0157	0.0218
2-Propanamine	nitrogenous	0.0070	0.0016	0.0044	0.0351

Compound	Family	3R4F	3R4F+C1	3R4F+C2	3R4F+C3
2,4-Dimethyl-4-cyclohexen-1,3-dione-one	carbonylic	nd	nd	nd	nd
3-Ethyl-2-hydroxy-2-cyclopenten-1-one	carbonylic	0.0121	0.0034	0.0085	0.0157
Benzeneacetonitrile	nitrogenous	0.0068	0.0025	0.0050	0.0068
2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	carbonylic	0.0038	0.0067	0.0034	0.0157
Phenol, 2,4-dimethyl-	phenolic	0.0074	0.0061	0.0042	0.0145
Phenol, 4-ethyl-	phenolic	0.0090	0.0028	0.0034	0.0133
Naphthalene	PAH	0.0051	0.0022	0.0050	0.0054
Ethanone, 1-(3-methylphenyl)-	carbonylic	0.0030	0.0024	0.0035	0.0021
p-cresol 2 methoxy	phenolic	0.0030	0.0008	0.0035	0.0036
2,3-Dihydro-benzofuran	epoxy	0.0067	0.0041	0.0090	0.0077
2-furancarboxaldehyde, 5-(hydroxymethyl)-	carbonylic	0.0070	0.0011	0.0053	nd
1H-Inden-1-one, 2,3-dihydro-	carbonylic	0.0104	0.0027	0.0069	0.0121
Hydroquinone	phenolic	0.0291	0.0054	0.0054	0.0218
1H-Indole	nitrogenous	0.0169	0.0157	0.0266	0.0145
4-vinyl-2-methoxy-phenol	phenolic	0.0105	0.0053	0.0076	0.0097
Nicotine	nitrogenous	1.2093	0.6428	1.0858	1.2299
1H-Indole, 3-methyl-	nitrogenous	0.0119	0.0041	0.0074	0.0133
Myosmine	nitrogenous	0.0145	0.0052	0.0116	0.0116
Phenol, 2-methoxy-4-(2-propenyl)-	phenolic	0.0114	0.0016	0.0080	0.0116
Nicotyrine	nitrogenous	0.0117	0.0069	0.0145	0.0117
Norsolanadiona	carbonylic	0.0047	0.0025	0.0051	0.0042
2,3'-Bipyridine	nitrogenous	0.0169	0.0075	0.0145	0.0242
1,4-dihydrophenanthrene	PAH	0.0075	nd	nd	0.0087
Diethyl phatolate	carbonylic	0.0069	0.0042	0.0084	0.0075
Megastigmatrienone	carbonylic	0.0063	0.0039	0.0062	0.0145
N-propyl- normicotine	nitrogenous	0.0045	nd	nd	0.0046
Cotinine	nitrogenous	0.0145	0.0077	0.0113	0.0121
1H-Indene, 2,3-dihydro-1,1,3-trimethyl-3-phenyl-	aromatic	0.0036	0.0023	0.0034	0.0075
5-Tetradecene	aliphatic	0.0092	nd	nd	0.0122
N(b)-formylnormicotine	nitrogenous	0.0022	0.0019	0.0039	0.0019
2,4-Diphenyl-4-methyl-penten-1-ene	aromatic	0.0038	0.0011	0.0017	nd
Neophytadiene	aliphatic	0.1017	0.0714	0.0980	0.1404
Farnesol	others	0.0062	0.0041	0.0059	0.0073
8-Quinolinemethanol	nitrogenous	0.0133	nd	0.0079	0.0063
DBP	carbonylic	nd	nd	nd	nd
Hexadecanoic acid, ethyl ester	others	0.0090	0.0027	0.0097	0.0157
Eicosane	aliphatic	0.0028	0.0017	0.0033	0.0016
pentadecane	aliphatic	0.0013	0.0008	0.0013	nd
Docosane	aliphatic	0.0012	nd	nd	nd
Tricosane	aliphatic	0.0133	0.0047	0.0061	nd
2,6,10,14,18,22-Tetracosahexaene, 2,6,10,15,19,23-hexamethyl-	aliphatic	0.0056	0.0018	0.0033	0.0053
Heptacosane	aliphatic	0.0169	0.0044	0.0074	0.0133
Triacotane	aliphatic	0.0206	0.0030	0.0050	0.0182
Octadecane	aliphatic	0.0460	0.0113	0.0242	0.0424
Tocopherol	phenolic	0.0206	0.0033	0.0070	0.0157

**Table A6.** Yield of different compounds analysed in the TPM-T of the mainstream smoke of systems involving 3R4F tobacco. Yields are expressed in mg of compound/g of smoked tobacco (it is continued in the next page). nd = not detected compounds

Compound	Family	3R4F	3R4F+C1	3R4F+C2	3R4F+C3
Pyridine, 4-methyl-	nitrogenous	0.0004	nd	nd	nd
Pyrazine, methyl-	nitrogenous	0.0006	nd	nd	nd
Furfural	carbonylic	0.0008	nd	0.0001	nd
2-Pentanone, 4-hydroxy-4-methyl-	carbonylic	0.0007	nd	0.0004	0.0006
Ethanol, 2-(1-methylethoxy)-	others	0.0016	0.0004	0.0008	0.0016
Pyridine, 3-methyl-	nitrogenous	0.0002	nd	nd	nd
2-Propanone, 1-(acetyloxy)-	carbonylic	0.0002	nd	nd	nd
4-Cyclopentene-1,3-dione	carbonylic	0.0004	0.0001	0.0001	nd
Styrene	aromatic	0.0001	0.0001	0.0001	nd
2-Cyclopenten-1-one, 2-methyl-	carbonylic	0.0013	nd	nd	0.0005
2-Acetyl furan	carbonylic	0.0004	nd	nd	nd
2(5H)-furanone	carbonylic	0.0001	nd	nd	nd
2-Hydroxycyclopent-2-en-1-one	carbonylic	0.0010	nd	nd	nd
Pyridine, 3,5-dimethyl-	nitrogenous	0.0002	nd	nd	nd
2,5-Dimethyl-2-cyclopentenone	carbonylic	0.0007	nd	nd	0.0002
Butanoic acid, 3-methyl-	others	0.0022	nd	0.0006	nd
Ethanol, 2-butoxy-	others	0.0007	nd	0.0004	0.0005



Compound	Family	3R4F	3R4F+C1	3R4F+C2	3R4F+C3
Benzaldehyde	carbonylic	0.0004	nd	0.0001	nd
Furfural, 5-methyl-	carbonylic	0.0002	nd	nd	nd
Phenol	phenolic	0.0050	nd	0.0005	0.0064
2-isopropylfuran	epoxy	0.0004	nd	nd	nd
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	carbonylic	0.0029	nd	nd	nd
Limonene	others	0.0028	nd	nd	0.0023
2,3-Dimethyl-2-cyclopenten-1-one	carbonylic	0.0004	nd	nd	nd
o-Cresol	phenolic	0.0044	0.0002	0.0008	0.0035
p-Cresol	phenolic	0.0070	0.0002	0.0017	0.0052
2 ethyl tiophene	others	0.0012	0.0004	0.0010	0.0008
Phenol, 2-methoxy-	phenolic	0.0022	nd	0.0002	0.0010
2-Propanamine	nitrogenous	0.0029	nd	0.0005	0.0019
3-Ethyl-2-hydroxy-2-cyclopenten-1-one	carbonylic	0.0048	nd	nd	0.0024
2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	carbonylic	0.0084	0.0013	0.0057	0.0052
Phenol, 2,4-dimethyl-	phenolic	0.0036	0.0005	0.0015	0.0041
Phenol, 4-ethyl-	phenolic	0.0033	0.0006	0.0008	0.0030
Naphthalene	PAH	0.0090	nd	nd	nd
p-cresol 2 methoxy	phenolic	0.0021	nd	0.0005	nd
2,3-Dihydro-benzofuran	epoxy	0.0035	0.0011	0.0015	0.0034
2-furancarboxaldehyde, 5-(hydroxymethyl)-	carbonylic	0.0028	0.0000	0.0010	nd
1H-Inden-1-one, 2,3-dihydro-	carbonylic	0.0018	nd	nd	0.0025
Hydroquinone	phenolic	0.0169	nd	0.0047	0.0090
1H-Indole	nitrogenous	0.0099	0.0008	0.0027	0.0030
4-vinyl-2-methoxy-phenol	phenolic	0.0058	0.0004	0.0015	0.0045
Nicotine	nitrogenous	0.9587	0.2203	0.6367	0.7481
1H-Indole, 3-methyl-	nitrogenous	0.0045	0.0006	0.0017	0.0047
Myosmine	nitrogenous	0.0075	0.0008	0.0030	0.0067
Phenol, 2-methoxy-4-(2-propenyl)-	phenolic	0.0041	nd	0.0016	0.0024
Nicotyrine	nitrogenous	0.0051	0.0021	0.0038	0.0052
Norsolanadiona	carbonylic	0.0038	nd	0.0016	0.0027
2,3'-Bipyridine	nitrogenous	0.0073	0.0012	0.0042	0.0065
1,4-dihydrophenanthrene	PAH	0.0070	nd	0.0008	nd
Diethyl phatalate	carbonylic	0.0085	0.0011	0.0011	0.0036
Megastigmatrienone	carbonylic	0.0039	0.0007	0.0023	0.0036
N-propyl- normicotine	nitrogenous	0.0035	nd	0.0008	0.0019
Cotinine	nitrogenous	0.0111	0.0010	0.0069	0.0109
5-Tetradecene	aliphatic	0.0035	nd	0.0019	nd
N(b)-formylnormicotine	nitrogenous	0.0103	0.0017	0.0046	0.0047
NEOPHYTADIENE	aliphatic	0.0602	0.0110	0.0369	0.0606
Farnesol	others	0.0047	0.0012	0.0030	0.0040
8-Quinolinemethanol	nitrogenous	0.0056	nd	nd	0.0012
DBP	carbonylic	0.0021	nd	nd	0.0012
Hexadecanoic acid, ethyl ester	others	0.0059	0.0004	0.0034	0.0073
Eicosane	aliphatic	0.0013	0.0002	0.0010	0.0012
pentadecane	aliphatic	0.0015	nd	0.0007	nd
Docosano	aliphatic	0.0021	nd	0.0000	nd
Tricosane	aliphatic	0.0082	0.0008	0.0027	nd
2,6,10,14,18,22-Tetracosahexaene, 2,6,10,15,19,23-hexamethyl-	aliphatic	0.0050	0.0006	0.0013	0.0025
Heptacosane	aliphatic	0.0157	0.0011	0.0036	0.0076
Triacontane	aliphatic	0.0145	0.0012	0.0025	0.0133
Octadecane	aliphatic	0.0339	0.0033	0.0076	0.0182
Tocopherol	phenolic	0.0182	0.0013	0.0023	0.0111
Pyridine, 4-methyl-	nitrogenous	0.0004	nd	nd	nd
Pyrazine, methyl-	nitrogenous	0.0006	nd	nd	nd
Furfural	carbonylic	0.0008	nd	0.0001	nd
2-Pentanone, 4-hydroxy-4-methyl-	carbonylic	0.0007	nd	0.0004	0.0006
Ethanol, 2-(1-methylethoxy)-	others	0.0016	0.0004	0.0008	0.0016
Pyridine, 3-methyl-	nitrogenous	0.0002	nd	nd	nd
2-Propanone, 1-(acetyloxy)-	carbonylic	0.0002	nd	nd	nd
4-Cyclopentene-1,3-dione	carbonylic	0.0004	0.0001	0.0001	nd
Styrene	aromatic	0.0001	0.0001	0.0001	nd
2-Cyclopenten-1-one, 2-methyl-	carbonylic	0.0013	nd	nd	0.0005
2-Acetylfuran	carbonylic	0.0004	nd	nd	nd
2(5H)-furanone	carbonylic	0.0001	nd	nd	nd
2-Hydroxycyclopent-2-en-1-one	carbonylic	0.0010	nd	nd	nd
Pyridine, 3,5-dimethyl-	nitrogenous	0.0002	nd	nd	nd
2,5-Dimethyl-2-cyclopentenone	carbonylic	0.0007	nd	nd	0.0002

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