ESTUDIO DEL EFECTO DE LA PRESENCIA DE DIFERENTES CATALIZADORES SOBRE LA COMPOSICIÓN DEL HUMO DEL TABACO. SÍNTESIS Y MODIFICACIÓN DE CATALIZADORES

Isabel Martínez Castellanos

UNIVERSIDAD DE ALICANTE

ESCUELA POLITÉCNICA SUPERIOR

Instituto Universitario de los Procesos Químicos

ESTUDIO DEL EFECTO DE LA PRESENCIA DE DIFERENTES CATALIZADORES SOBRE LA COMPOSICIÓN DEL HUMO DEL TABACO. SÍNTESIS Y MODIFICACIÓN DE CATALIZADORES.

Memoria para optar al Grado
de Doctor presentada por

Isabel Martínez Castellanos
2011

D. ANTONIO MARCILLA GOMIS, Catedrático del Departamento de Ingeniería Química de la Facultad de Ciencias de la Universidad de Alicante, y

Dña. AMPARO GÓMEZ SIURANA, Catedrática del Departamento de Ingeniería Química de la Facultad de Ciencias de la Universidad de Alicante, y

Dña. Mª ISABEL BELTRÁN RICO, Profesora Titular del Departamento de Ingeniería Química de la Facultad de Ciencias de la Universidad de Alicante.

CERTIFICAMOS:

Que Dña. ISABEL MARTÍNEZ CASTELLANOS, Ingeniera Química, ha realizado bajo nuestra dirección, en el Departamento de Ingeniería Química de la Escuela Politécnica Superior de la Universidad de Alicante, el trabajo que con el título "ESTUDIO DEL EFECTO DE LA PRESENCIA DE DIFERENTES CATALIZADORES SOBRE LA COMPOSICIÓN DEL HUMO DEL TABACO. SÍNTESIS Y MODIFICACIÓN DE CATALIZADORES" constituye su memoria para aspirar al Grado de Doctor, reuniendo a nuestro juicio, las condiciones necesarias para ser presentada y defendida ante el Tribunal correspondiente.

Y para que conste a los efectos oportunos, en cumplimiento de la legislación vigente, firmamos el presente certificado en Alicante, a 20 de Diciembre de 2011.

Fdo.Antonio Marcilla Gomis   Fdo.Amparo Gómez Siurana   Fdo.Mª Isabel Beltrán Rico

Amparo Gómez Siurana
Directora del Instituto U. Procesos Químicos

Debido a mi formación científica e ingenieril, he estado tentada de ser sintética y práctica, y sustituir diez al cubo palabras por una imagen de grupo y rematarla con un simple “gracias”. Sin embargo una vez finalizada mi Tesis Doctoral, creo conveniente resumir en unas breves palabras mi sentida y más sincera gratitud hacia todas las personas que me han ayudado y han compartido mi día a día durante todos estos años.

En primer lugar quiero dar las gracias a los que confiaron en mí desde el principio y me brindaron la oportunidad de llevar a cabo este trabajo, mis directores de Tesis, Antonio, Amparo y Maribel, si he llegado hasta aquí ha sido gracias a vosotros. Gracias por la dirección de este trabajo y el apoyo para la consecución del mismo. Trabajar con vosotros ha sido un placer y una fuente constante de aprendizaje.

También quiero darles las gracias a todos mis compañeros de “habitación”, Erika, Lucía, Mila, Vicky, Vero, como no a Miriam, que también estuvo por aquí, y no puedo olvidarme de los Manolos, Estefanía, Pilar, Ara, Ana y todos aquellos con los que he compartido estos años, por compartir el día a día, ratos de risas, dudas, ratos buenos y menos buenos, que han hecho del trabajo en la Universidad una experiencia muy agradable y divertida, y en especial, quiero agradecer su ayuda y compresión a Desi y Rosa, quienes a parte de ser unas grandes compañeras de trabajo son muy buenas amigas.

Gracias a mis padres y mi hermano, por lo valores que me han inculcado y por todo lo que he recibido de ellos, este trabajo va dedicado a vosotros.

Y como no a mi niño, que es el que más me ha apoyado y aguantado, que ha estado a mi lado en el día a día. Sin ti, cariño, nada de esto hubiera llegado.

Y por último quiero acordarme del 22 de abril de 2006 y del 26 de junio de 2010, gracias mi niño por todo lo que tú y yo solo sabemos.

Índice

RESUMEN

1

El tabaco es un producto tóxico y perjudicial, que implica un riesgo para la salud del fumador y para las personas que le rodean. En la combustión del tabaco se han identificado más de 4000 compuestos diferentes de entre los cuales, por lo menos sesenta se reconocen como tóxicos y cancerígenos. Debido a la presencia de estos compuestos, los gobiernos han establecido leyes con objeto de proteger la salud de los fumadores y no fumadores, que limitan el consumo de este producto en lugares públicos, parques, etc. Esta ley “Ley 42/2010, de 30 de diciembre, por la que se modifica la Ley 28/2005, de 26 de diciembre, de medidas sanitarias frente al tabaquismo y reguladora de la venta, el suministro, el consumo y la publicidad de los productos del tabaco” representa un paso más en la lucha contra el tabaco y los efectos perjudiciales que su consumo provoca.

Las restricciones y leyes impuestas no garantizan la disminución en el consumo del tabaco, ni reducen sus efectos perjudiciales en el fumador, por lo que se hace necesario desarrollar estudios e investigar diferentes vías, buscando la eliminación o reducción de algunos de los componentes más perjudiciales presentes en el humo del tabaco. Dentro de los principales compuestos en el humo del tabaco se encuentran alquitranes, monóxido de carbono, acetaldehído, fenoles, acetona, formaldehído, benceno, tolueno y nicotina, siendo este último el principal componente adictivo presente en el tabaco y, que en el cuerpo humano se transforma en un metabolito denominado cotinina, que, dado que se ha encontrado únicamente en personas fumadoras y en fumadores pasivos, se utiliza como un índice de referencia para medir el grado de exposición al humo del tabaco.

Por todo lo comentado anteriormente, resulta de gran interés llevar a cabo diferentes estudios, que engloben desde el proceso de fumado de un cigarrillo y el efecto que provoca en la composición del humo del tabaco la adición de determinados aditivos o catalizadores, hasta posibles alternativas en la síntesis de los diferentes catalizadores estudiados, viendo como estas variaciones en la síntesis afectan a posteriori cuando son utilizados como aditivos, mejorando o no su efectividad sobre el humo del tabaco.

En el presente trabajo se va a analizar el efecto que producen diferentes materiales adicionados al tabaco. Estos materiales son zeolitas comerciales, o bien materiales sintetizados en el propio laboratorio y posteriormente tratados de diferentes maneras para modificar sus propiedades.

Englobando los estudios llevados a cabo, se podría decir que los efectos analizados en el presente trabajo han sido:

1.- Estudio del empleo de un catalizador sintetizado en el Departamento de Ingeniería Química de la Universidad de Alicante como aditivo para reducir la presencia de algunos de los compuestos presentes en el humo del tabaco y efecto de la concentración de aluminio presente en el catalizador sintetizado.

2.- Estudio de dos vías de síntesis alternativas de un catalizador, en lo que respecta a la eliminación del tensioactivo, así como el comportamiento de estos dos nuevos materiales sobre la corriente principal del humo del tabaco en el proceso de fumado.

3.- Estudio de la adición de tres zeolitas comerciales y un material sintetizado a una marca comercial de tabaco. Efecto que producen sobre la corriente principal del humo del tabaco.

4.- Estudio del comportamiento de diez marcas comerciales, elegidas por el volumen de ventas que tienen en España.

2

INTRODUCCIÓN

2.1. El tabaco

El tabaco es un producto vegetal que se obtiene tras un extenso proceso de elaboración de las hojas de la planta denominada Nicotiana, perteneciente a la familia de las solanáceas. El género Nicotiana abarca más de 60 especies, clasificadas en 3 subgrupos; Nicotiana Petunoides que comprende 45 especies, aunque carentes de interés económico, Nicotiana Rústica que proporciona tabacos fuertes y abarca 9 especies y Nicotina Tabacum, que es la más importante pues comprende el 90% de los tabacos cultivados en el mundo.

La Nicotiana Tabacum es una planta perenne procedente de América y se encuentra emparentada con otro tipo de plantas cultivadas tales como el tomate (*Solanum lycopersicum*) y la papa (*Solanum tuberosum*). Se trata de una planta no muy alta, entre 5-12 cm, con hojas grandes y flores en racimo, que pueden presentarse en dos colores distintos, verde-amarillentas o rosadas (Figura 2.1). Presenta un olor fuerte y muy característico, con ciertas propiedades narcóticas que se atribuyen al alto contenido en las hojas de un alcaloide conocido como nicotina.

Figura 2.1.- Fotografía de un ejemplar de Nicotiana tabacum.
(http://www.lapshin.org/cultivar/N36/Pogany/Nicotiana-tabacum.jpg)

La especie Nicotiana Tabacum reúne un gran número de razas que pueden agruparse en cuatro variedades de tabaco (Snarkis, 1989).

-Nicotiana Tabacum Havanensis (modelo de planta elipsoidal), que se emplea para hacer los cigarros puros del tipo Habano y que comprende ciertas razas de tabaco de Oriente, Java y Sumatra.

-Nicotiana Tabacum Brasiliensis (modelo de la planta cónica) cuyas razas principales son el Brasil de Bahía, el Burley y el Paraguay.

-Nicotiana Tabacum Virginica (modelo de la planta formado por dos conos reunidos por su base) cuyas razas principales son el Kentucky y el Virginia.

-Nicotiana Tabacum Purpurea (modelo de planta cilíndrica) que comprende los tabacos orientales.

Los diferentes tipos de tabaco que se comercializan en el mercado surgen de las cuatro variedades distintas de Nicotiana tabacum, del modo de cultivo, clima y tipo de suelo, forma de cuidado y fermentación, y del proceso de fabricación. El tipo de curado o deshidratación de la hoja del tabaco determinará especialmente su aroma y sabor final.

La hoja de la Nicotiana tabacum contiene 3800 compuestos, tanto orgánicos como inorgánicos (Baker, 2006). Los compuestos orgánicos se pueden agrupar en nitrogenados, tales como proteínas, aminoácidos, amoniaco y alcaloides, entre los que se encuentra la nicotina, y no nitrogenados, como los hidratos de carbono (almidón, celulosa, lignina, entre otros), polifenoles, resinas, aceites, pectinas, etc. Los compuestos inorgánicos son básicamente sales y óxidos minerales, principalmente de calcio y potasio.

Los componentes mayoritarios de la hoja son el agua y la nicotina. El agua representa un 80% de total de peso de la hoja tras la recolección y en el caso de la nicotina los niveles en la hoja pueden presentar valores entre 1-12%.

El componente de mayor importancia es, sin duda, la **nicotina**, puesto que debido a su alto carácter narcótico, es la molécula a la cual se le atribuye la adicción que genera el consumo del tabaco. Fue identificada por primera vez a principios del siglo XIX por Jean Nicot (persona a quien debe su nombre) y, de los componentes del humo del tabaco, puede decirse que es uno de los más estudiados, dado que se ha demostrado que presenta numerosos efectos sobre la salud de los fumadores tanto activos como pasivos. Su nombre sistemático es *(L)-3-(1-metilpirrolidin-2-il) piridina* y su fórmula molecular es $C_{10}H_{14}N_2$. Sus propiedades son:

- Masa molar: 162,23 g/mol

- Densidad: 1,01 g/ml (a 4ºC)

- Punto de fusión: -7,9℃

- Punto de ebullición: 247℃.

Esta molécula, en pequeñas concentraciones, se comporta como un estimulante, que puede provocar en la persona que la consume un incremento de la actividad y del sentido de alerta. La nicotina es una amina terciaria compuesta por piridina y un anillo pirrólico al cual hay enlazado un grupo metilo (Figura 2.2). Se trata de una sustancia incolora, que al quemarse toma un tono marrón y genera el olor tan característico que da su identidad al tabaco. Esta molécula presenta dos estereoisómeros, siendo la forma activa y la presente en las hojas del tabaco la L-Nicotina.

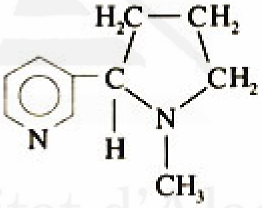


Figura 2.2 Estructura de la molécula de Nicotina

2.1.1.- Curado del tabaco y elaboración de cigarrillos

Cuando las hojas de tabaco se recolectan, tienen un alto contenido de humedad, cercano al 85%. El curado consiste en secar la hoja, a fin de que se conserve y sea adecuada para su manufactura posterior, dando lugar a una serie de cambios químicos. Básicamente existen cuatro tipos de curado. Al tabaco Virginia, que es el tabaco que tiene más aceptación para cigarrillos y ciertos tabacos de pipa, se le aplica el método de *curado en atmósfera controlada*. En este tipo de curado la temperatura del aire varía desde temperatura ambiente hasta unos 700ºC de forma controlada durante 60 horas aproximadamente, obteniéndose un tabaco color amarillo claro y altas tasas de nicotina y alquitranes. El *curado al aire* es el método más antiguo, y consiste en exponer las hojas (o a veces la planta completa) a una corriente de aire durante dos o tres meses, tomando precauciones para regular el contenido en humedad del aire. Los tabacos así curados suelen ser de tipo Burley, se emplean para cigarros y tienen un color pardo rojizo. También se emplean mezclados y son más fuertes que el tipo Virginia. El *curado al sol* también produce hojas de color pardo rojizo, y se emplea con tabaco Oriental. Las hojas marchitas se exponen al sol hasta que están totalmente secas y curadas, proceso que por lo general dura de cuatro a seis semanas. La mayoría del tabaco turco cultivado en Europa oriental se cura por este procedimiento. Por último el *curado al fuego*, en el que el humo entra en contacto directo con las hojas, no se usa en gran escala y se utiliza básicamente para obtener rapé, tabaco para mascar y pipa. El tiempo empleado depende del combustible utilizado (varios tipos de maderas) y de la cantidad de humo producido, obteniéndose un tabaco de color oscuro y fuerte aroma. Se emplea con el tabaco tipo Kentucky.

Las hojas secas se "despalillan" (eliminación del nervio de la hoja por métodos mecánicos), se ajusta su humedad al 10-12%, y se apilan en paquetes para su "añejamiento" (cigarrillos) o fermentación (cigarros puros). Estos procesos pueden durar entre 1 y 3 años. Durante el añejamiento del tabaco destinado a cigarrillos tienen lugar una serie de cambios físicos y químicos, algunos poco conocidos. En general las hojas se oscurecen lentamente, se produce una disminución del pH y del contenido en nitrógeno amínico, aumentan los compuestos volátiles como el ácido fórmico y disminuyen los azucares reductores. Después del añejamiento se procede a la elaboración de los cigarrillos que comprende todavía diversas etapas. En primer lugar se reajusta la humedad de las hojas mediante procesos de humidificación o desecación y se realiza el mezclado en tambores rotatorios antes y después del picado. La formulación empleada en el mezclado es un secreto de cada fabricante, está regida por el análisis que se realiza a las hojas, y por lo general se mezclan y pican hojas procedentes de un número muy elevado de barricas, se combinan tabacos procedentes de diferentes zonas y tipos, y curados en diferentes condiciones, para obtener el producto requerido.

En las últimas etapas de la elaboración de los cigarrillos se produce la impregnación, que consiste en la inmersión en una suspensión acuosa que contiene azúcar invertido como ingrediente principal y regaliz, chocolate y otros aditivos en menor proporción que dan el sabor característico de cada marca comercial, y humectantes como glicerina o sorbitol, que dan esponjosidad y flexibilidad al tabaco. El número total de ingredientes añadidos durante esta etapa puede ser muy elevado, como se explica más adelante y puede llegar a suponer un 25% del peso total del tabaco que se encuentra en los cigarrillos.

Durante todas las etapas de elaboración de los cigarrillos es importante operar en atmósfera acondicionada para tener un control efectivo de la humedad de los cigarrillos en todo momento.

2.1.2.- Producción en España

España es el tercer país productor de tabaco en la Unión Europea, sólo por detrás de Grecia e Italia. El cultivo de tabaco está muy repartido por la península principalmente en Extremadura, Andalucía, Canarias, Castilla y León, Castilla–La Mancha, Navarra y País Vasco, siendo el principal productor el territorio de Extremadura, sobre todo la provincia de Cáceres, donde se concentra el 85% de la producción nacional de tabaco (http://www.agronet.com). Dependiendo de la zona y del clima se cultiva una variedad diferente.

En la Figura 2.3 se muestran las zonas de producción de tabaco en España, figurando las cantidades contratadas en la cosecha 2007 por grupos de variedades, correspondiendo estas variedades a: (Datos FEGA-MAPA),

Grupo I (Virginia)

Grupo II (Burley E, utilizado para cigarrillos rubios)

Grupo III (Burley Fermentado, usado para cigarrillos negros, y Havana)

Grupo IV (Kentucky)

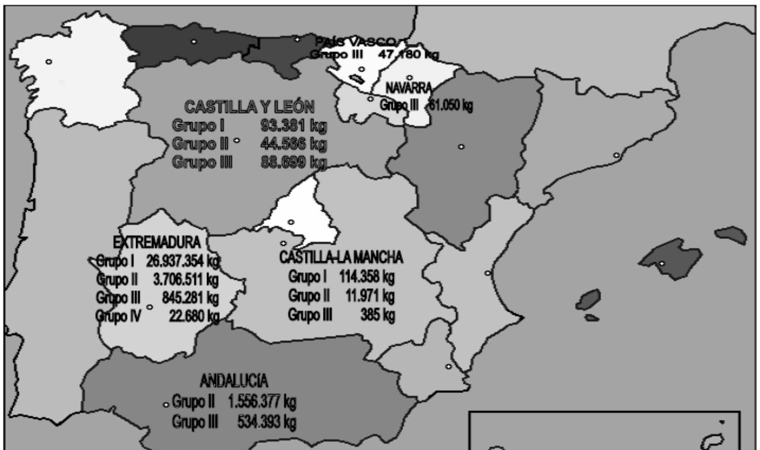


Figura 2.3.-Zonas de producción de tabaco en España

En la Unión Europea se cultiva alrededor del 4% de la producción mundial de tabaco, estando por detrás de países como China, Brasil, India y Estados Unidos.

El consumo de tabaco en el mundo está muy arraigado, sólo en España el consumo de cigarrillos contabilizados como cajetillas de 20 unidades, en enero de 2011 fue de 194.770.461, siendo Andalucía, Cataluña, Madrid y la Comunidad Valenciana las comunidades con mayor consumo, puesto que entre ellas cubren el 62% del consumo total en España. En el mismo mes del año anterior el consumo fue de 295.225.074 un 34% superior al de 2011, hecho debido probablemente a la entrada en vigor de la nueva ley sobre el tabaco *(Ley 42/2010, de 30 de diciembre, por la que se modifica la Ley 28/2005, de 26 de diciembre, de medidas sanitarias frente al tabaquismo y reguladora de la venta, el suministro, el consumo y la publicidad de los productos del tabaco).*

2.1.3.- Historia

El acto de fumar podría estar asociado al descubrimiento del fuego. Ya en la prehistoria los hombres primitivos se percataron de que ciertas plantas, al quemarse, generaban humos de un olor agradable y placentero, que provocaban en ellos estados de consciencia desconocidos hasta el momento y que les resultaban agradables. Fue por esto que poco a poco fueron descubriendo plantas de las cuales aspiraban el humo, naciendo de esta forma el acto de fumar, y convirtiéndolo en un rito.

Aunque se sospecha que mucho antes ya se fumaba, fueron los mayas, hace más de 1500 años, quienes comenzaron a quemar las hojas del tabaco para luego aspirar el humo. En esta época no sólo se fumaba, sino que el tabaco también se bebía, se mascaba y se aspiraba por la nariz. El uso de tabaco en la antigüedad viene íntimamente asociado a ritos religiosos, pero también se tiene constancia de su uso con fines curativos, como alucinógeno y como ofrenda a los espíritus a los que adoraban, puesto que se pensaba que el humo del tabaco ayudaba a expulsar la enfermedad del cuerpo, y como complemento dietético, aunque de este último uso no se tiene certeza. En la Figura 2.4 se muestra la imagen de un maya fumando.

Figura 2.4.- Imagen de un individuo de la civilización maya fumando.
(http://www.tabaqueria-martin.com/images/maya.jpg)

Como ya se ha dicho, durante la época de los mayas, fumar tenía connotaciones prácticamente religiosas, aunque como se ha indicado, también se utilizaba para otros fines, pero en menor medida. Son los aztecas, alrededor del siglo XII, quienes tras incorporar a sus costumbres el acto de fumar de los mayas, dan a éste un carácter mucho más social, ocurriendo posiblemente de esta forma el origen de fumar tabaco tal y como se conoce actualmente.

En Europa, hasta el descubrimiento de América no se tiene conocimiento de la existencia de la planta del tabaco. Durante las expediciones de Cristóbal Colón a este continente se observa que los nativos fuman cigarros descubriendo este nuevo acto que tanta repercusión tendrá en el mundo con el paso de los años.

Una vez descubierta América, y con ella la existencia de la planta Nicotiana Tabacum, ésta no tarda en llegar a España. La semilla del tabaco llega a España de la mano de Francisco Hernández de Toledo, médico elegido por Felipe II para dirigir una expedición científica a América en 1571; la costumbre de fumar fue introducida por Rodrigo de Jerez, marino que navegó hacia América en la Santa María en el primer viaje de Colón en 1492, y a quien se le atribuye ser el primer europeo en fumar. Es a partir de este momento que, gracias a los navegantes españoles y portugueses, el tabaco entra en Europa. Fueron los grandes viajes marítimos de los siglos XVI, XVII, XVIII los que expandieron el tabaco y su consumo por las costas de Asia, África y Oceanía.

Las connotaciones atribuibles al tabaco en los primeros años de su consumo en Europa son dos y además de carácter muy distinto. Por un lado, el tabaco representa para unos un elevado carácter medicinal. Así, en 1493 Nicolás Monardes incluyó al tabaco entre las plantas beneficiosas para la salud, ya que era considerada una planta curativa. En cambio, por otro lado, y sobre todo para la Iglesia, su uso no estaba bien visto, lo que trajo consigo prohibiciones a su uso. En 1642 el Papa Urbano VIII excomulgaba a todos aquellos que consumieran tabaco.

A finales del siglo XIX tiene lugar lo que podría considerarse como la epidemia del tabaquismo. El consumo del tabaco sufrió un elevado ascenso sobre todo en los países industrializados. Este ascenso en el consumo vino propiciado por la fabricación de cigarrillos a escala industrial, hecho que puso de moda el consumo de tabaco, sobre todo por razones económicas y de mercado; el consumo de cigarrillos resultaba muy rentable para los productores y además se trataba de un producto que se encontraba al alcance de todos. Todo esto junto provocó elevadas inversiones en técnica y publicidad para las empresas tabacaleras, sobre todo en una época en la que no existía ningún tipo de restricción sobre los productos del tabaco. Además, esta gran expansión hizo que los gobiernos vieran en este consumo un gran negocio, puesto que se creó un comercio internacional, con la consiguiente aplicación de impuestos sobre los productos del tabaco.

Todos los factores que acaban de ser comentados supusieron un gran impulso al consumo del tabaco, por lo que en muy poco tiempo el hábito de fumar se había extendido a más del 50% de la población de Europa.

Hasta este momento, el perjuicio del consumo del tabaco no era todavía conocido, pero poco a poco sus efectos fueron apareciendo en la sociedad, convirtiéndose en el origen de uno de los problemas sociales y de salud pública más graves que existen actualmente a nivel mundial, puesto que afecta a la salud tanto de fumadores, que se exponen al humo del tabaco de forma consciente y voluntaria, como de los no fumadores, expuestos al humo del tabaco por el simple hecho de encontrarse en un ambiente donde haya humo de tabaco.

El primer informe donde se indica la peligrosidad del tabaco data de 1851. En este año, la Academia de Medicina de Francia establece que el tabaco es un veneno. Diferentes estudios llevados a cabo, sobre todo a partir de la segunda mitad del siglo XX, muestran esta peligrosidad, y ponen de manifiesto que el tabaco supone un gran riesgo para la salud de los fumadores y de todos aquellos que se encuentran expuestos al humo, denominados también fumadores pasivos.

Actualmente en España fuman 3 de cada 10 personas mayores de 16 años, dato todavía a tener en cuenta debido al riesgo que su consumo supone.

2.2.- EL TABAQUISMO

La real academia española define el **tabaquismo** como *Intoxicación crónica producida por el abuso del tabaco*.

Según el Dr. José Javier Lorza Blasco (Neumólogo y Presidente del Comité Organizador del VI Congreso Nacional de Prevención y Tratamiento del Tabaquismo) una definición también muy válida para tabaquismo sería: *"tabaquismo es un fenómeno social de primera magnitud que se ha convertido en la primera causa de muerte y discapacidad en los países desarrollados. La elevada capacidad adictiva de la nicotina hace que el tabaquismo pueda considerarse como una auténtica drogadicción y también como una enfermedad crónica."*

La definición de tabaquismo permite agrupar la población en determinados grupos, según tengan contacto directo o no con el humo del tabaco:

1.- Fumadores: aquellos que consumen tabaco de forma habitual o de forma esporádica.

2.- Exfumadores: aquellos que fueron fumadores, pero llevan ya el plazo de un año de abstinencia.

3.- No fumadores: personas que nunca han fumado, no han tenido una exposición al tabaco activa.

4.- Fumadores pasivos: personas que respiran la corriente secundaria del humo del tabaco.

Según el Comité Nacional para la prevención del Tabaquismo (CNPT) se puede hablar de tabaquismo pasivo, el cual consiste en la inhalación involuntaria de la ETS (environmental tobacco smoke) también llamada ACHT (aire contaminado por humo de tabaco) lo que provoca que muchas personas no fumadoras se encuentren expuestas a los riesgos asociados al tabaco.

2.2.1.- Efectos sobre la salud

Las enfermedades asociadas al tabaquismo pueden agruparse en función del órgano o aparato principalmente afectado, de esta manera se pueden agrupar estas enfermedades en dos grupos, las que afectan al aparato respiratorio y aquellas que afectan al sistema cardiovascular:

ENFERMEDADES DEL APARATO RESPIRATORIO

Edema

Hiperplasia

Enfisema pulmonar

EPOC (enfermedad pulmonar obstructiva crónica)

Cáncer de pulmón

ENFERMEDADES ASOCIADAS AL SISTEMA CARDIOVASCULAR

Subida de tensión arterial

Cardiopatía isquémica

Enfermedad arterial periférica

Enfermedad cerebrovascular

Todas estas enfermedades, implican un gasto para los departamentos de salud de los diferentes países. Los datos proporcionados en España por la Agencia Estatal de la Administración Tributaria para el 2008 muestran que los gastos sanitarios directos atribuibles al consumo del tabaco son 14.170 millones de euros, los ingresos obtenidos por el Estado por la venta de tabaco que ese año fueron de 9.266 millones de euros, por lo que las pérdidas debidas al tabaquismo fueron de 5.444 millones de euros. Por este motivo se cree que la ampliación de la ley que ha entrado en vigor en enero de 2011 supondrá un gran ahorro en los costes de la sanidad pública. (SEPAR)

La Organización Mundial de la Salud (OMS) considera conveniente aplicar políticas con objeto de disminuir en la medida de lo posible los efectos tóxicos y perjudiciales del consumo del tabaco. Una política que pretende establecer la OMS es conocida como el programa MPOWER.

Para aplicar el plan de políticas MPOWER (OMS) los países deben establecer las actuaciones siguientes:

- Monitor-- vigilar el consumo de tabaco.

- Protect-- proteger a la población del humo de tabaco.

- Offer-- ofrecer ayuda para el abandono del tabaco.

- Warm-- advertir de los peligros del tabaco.

- Enforce-- hacer cumplir las prohibiciones sobre publicidad, promoción y patrocinio.

- Raise-- aumentar los impuestos al tabaco.

2.2.2.- Evolución de los estudios llevados a cabo sobre los efectos perjudiciales del tabaco

Diferentes estudios a lo largo de los años han ido profundizando en la toxicidad asociada al consumo del tabaco y paralelamente se han ido estableciendo, en consecuencia, diferentes leyes asociadas a dicho consumo. Una breve cronología de esta evolución sería:

- 1956, el tabaco es declarado como la primera causa de muerte previsible por la Organización Mundial de la salud (OMS).

- 1692, se publica un estudio por el Real Colegio de médicos de Londres donde se muestra la relación entre una mayor tasa de mortalidad debida a cáncer de pulmón en personas fumadoras.

- 1964, aparece el informe Ferry, el cual pone de manifiesto que el índice de mortalidad es mucho mayor en personas fumadoras que en aquellas que no lo son.

- 1965, el Congreso de los Estados Unidos publica una ley donde se obliga a los fabricantes de cigarrillos a imprimir en el paquete una advertencia sobre los efectos perjudiciales que estos presentan.

- 1967, primera Conferencia mundial sobre Tabaco y Salud en Nueva York.

- 1978, aparición en España de las primeras leyes restrictivas sobre el tabaco.

- 1988, El UK Independent Committee on Smoking and Health realiza un estudio donde se asegura que el tabaquismo pasivo provoca cáncer de pulmón en fumadores pasivos. Además se celebra por primera vez el Día Mundial sin Tabaco.

- 1992, la US Environmental Protection Agency concluye que la corriente secundaria del tabaco constituye un peligro para la salud puesto que contiene compuestos cancerígenos, por lo que ser fumador pasivo también puede provocar cáncer.

- 2006, entrada en Vigor en España de la Ley Antitabaco, en la que se prohíbe fumar en lugares públicos, en lugares de trabajo y en todas aquellas zonas públicas, bares, restaurantes, que no se encuentren habilitadas para ello.

-2011, entrada en vigor de la Ley 42/2010, de 30 de diciembre, por la que se modifica la Ley 28/2005, de 26 de diciembre, de medidas sanitarias frente al tabaquismo y reguladora de la venta, el suministro, el consumo y la publicidad de los productos del tabaco.

2.3.- EL CIGARRILLO

Las hojas de tabaco se emplean para fabricar picadura para cigarrillos, hebras para liar y para cigarros, rapé, tabaco de mascar y extracto de nicotina. La forma más común y más consumida de tabaco en la mayoría de los países desarrollados es el cigarrillo, como se pone claramente de manifiesto en los datos de ventas en 2010 en España:

Tabaco de pipa: 376.310 kg.

Tabaco de liar: 5.399.855 kg.

Cigarros: 1.535.600.067 unidades.

Cigarrillos: 3.621.537.558 cajetillas de 20 cigarrillos o 54 millones de toneladas de tabaco.

Como es más que evidente, en vista de los datos proporcionados, en España los cigarrillos son, con diferencia, el mayor producto consumido de tabaco, aunque se aprecia en los últimos años un ligero incremento en el tabaco de liar, aumentando en este último año el consumo alrededor de un 6%.

El cigarrillo consiste en una mezcla de tabacos picados introducidos en papel de liar, donde además se suele acoplar un filtro que se une con papel hidrofugado al cilindro formado por el tabaco y el papel. En la figura 2.5 se describe de forma muy esquemática la composición de un cigarrillo:

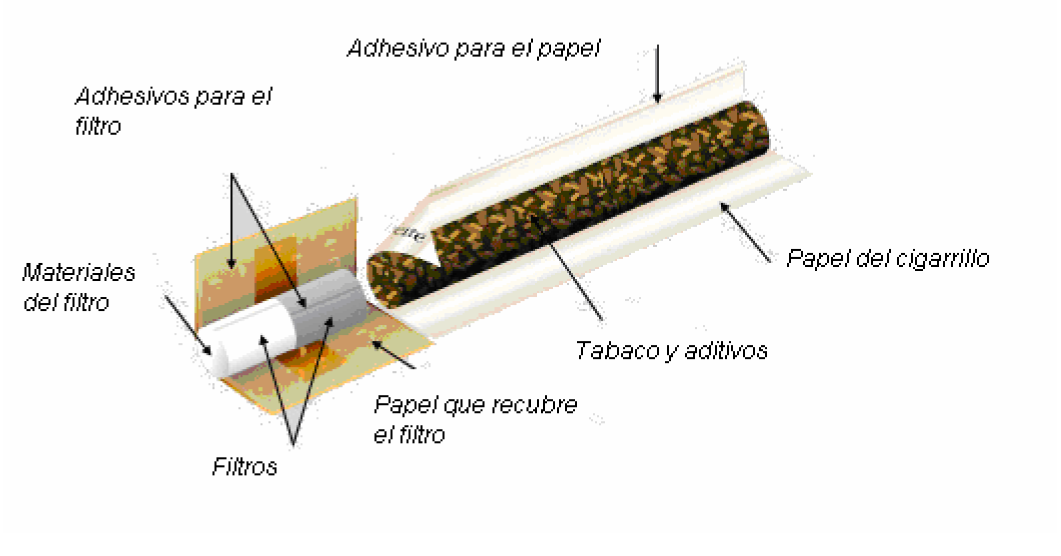


Figura 2.5.- Partes constituyentes de un cigarrillo. (Philip Morris Internacional)

Las partes principales de un cigarrillo son:

TABACO: mezcla de distintos tipos de tabacos junto con aditivos y aromas, que definirán el cigarrillo.

PAPEL DE LIAR: papel utilizado para recubrir el tabaco. Se obtiene a partir de pasta de celulosa procedente de fibras vegetales, en su fabricación no se utilizan ni blanqueadores ni cloro. Cuanto más poroso es el papel, más aire permite pasar para la combustión del cigarrillo, lo que diluye en mayor medida el humo.

FILTRO*:* Cilindro de acetato de celulosa anexado a uno de los extremos de un cigarrillo con el fin de reducir el nivel de compuestos tóxicos que inhala una persona al fumar. Suele unirse al cilindro formado por el tabaco y el papel mediante un papel hidrofugado, el cual presenta normalmente unas perforaciones que permiten el paso del aire. La ventilación que lleva el filtro se encarga de diluir el humo durante la calada (Borgerding y Klaus, 2005).

En la elaboración de un cigarrillo o de cualquier otro tipo de producto del tabaco, se adicionan gran cantidad de ingredientes. Se puede distinguir entre componente del tabaco e ingrediente o aditivo:

- Componente del tabaco: sustancia natural presente en el tabaco.

- Ingrediente (o aditivo) del tabaco: sustancia, sin contar el agua, que se adiciona al tabaco durante el proceso de producción.

La lista de aditivos proporcionada por Baker incluye 450 compuestos (Baker y col., 2004), y, de acuerdo con este autor, se pueden clasificar según la función que desempeñan en la mezcla de tabaco. Los aditivos más habituales son los siguientes:

Sabores o aromas: se encargan de dar determinadas características organolépticas al tabaco. Algunos de ellos son: fenilalanina, 5-metilfurfural, acetaldehído, alanina, butanol, cacao, caramelo, diversos aceites, extracto de malta, café, nerol, piridina, octanal.

Modificadores de la combustibilidad: como acetato de potasio, carbonato de calcio, citrato de sodio y de potasio.

Humectantes: azúcares, glicerol, propilenglicol, sorbitol.

Conservantes: benzoato de sodio, sorbato de potasio.

Aglomerantes: celulosa, goma guar (polisacárido soluble en agua).

"Casing" ingredientes o melazas: sustancias utilizadas para mejorar las propiedades sensoriales del tabaco. Rustemeier y col. (2002) los define como agentes higroscópicos aplicados al tabaco que permiten acondicionarlo para el proceso.

2.4.- COMBUSTIÓN Y PIRÓLISIS DEL TABACO

Durante el proceso de fumado de un cigarrillo tienen lugar varios mecanismos, los cuales provocan la generación del humo del tabaco. De entre todos estos mecanismos cabe destacar los siguientes: pirolisis/destilación, combustión, pirosíntesis, condensación y dilución, que contribuyen a la formación de la mezcla de compuestos que forman el humo del tabaco. (Baker, 2006 y Borgerding y col., 1998).

En la zona de incandescencia, zona formada al encenderse el cigarrillo y que va avanzando a lo largo de éste, es donde tienen lugar la combustión y pirólisis/destilación que son los dos mecanismos predominantes. Se distinguen dos zonas:

- Zona de combustión, rica en O_2, debida al aire que pasa a través del cigarrillo durante la calada, y donde tiene lugar la reacción del tabaco con el O_2 del aire. Se producen una serie de procesos exotérmicos y se generan principalmente CO_2, CO e H_2O. Esta zona está alrededor de unos 700-950ºC.

- Zona de pirólisis/destilación, situada a continuación de la zona de combustión. Aquí tienen lugar variedad de reacciones que dan lugar al resto de compuestos presentes en el humo del tabaco. Son principalmente procesos endotérmicos. Esta zona se encuentra entre 200-600ºC. Esta zona es deficiente en O_2 y rica en N_2.

En la Figura 2.6 se muestra el esquema del cigarrillo y las dos zonas principales que tienen lugar durante el consumo del cigarrillo.

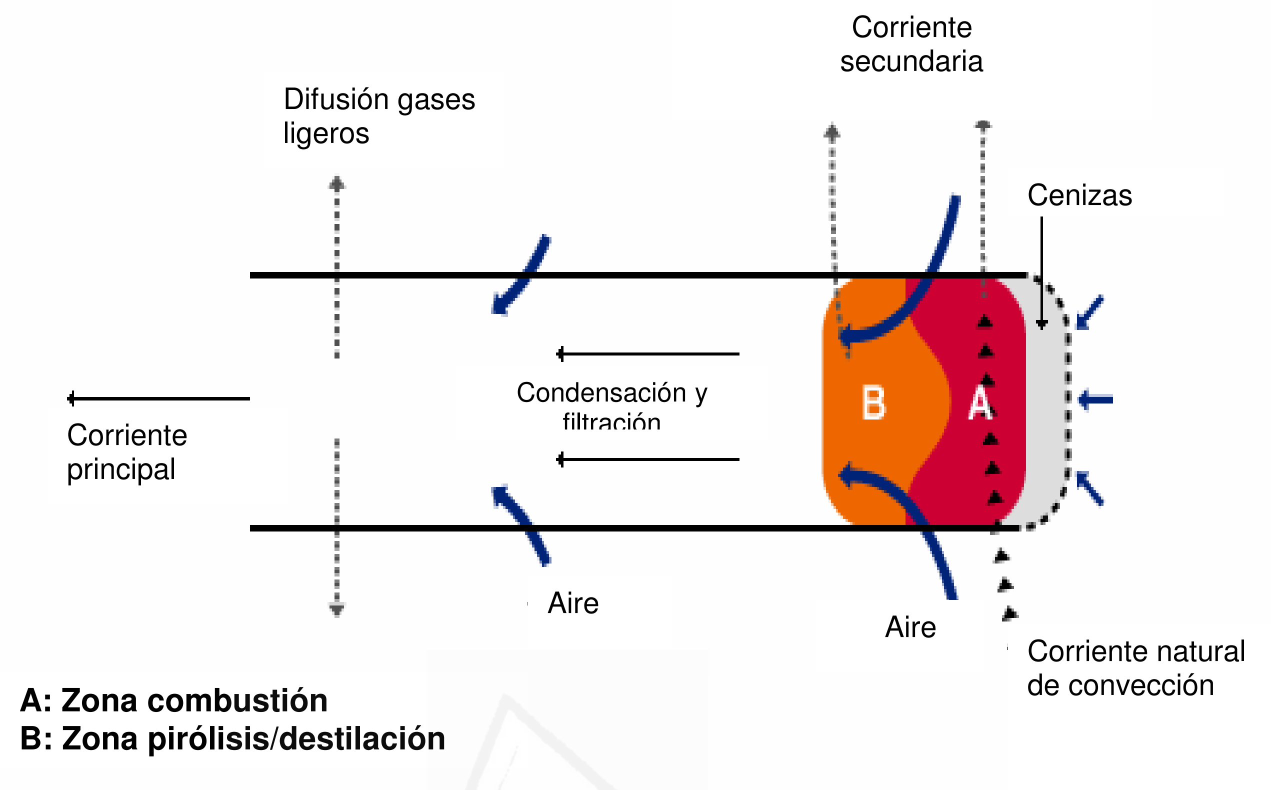


Figura 2.6.- Zonas presentes en el cigarrillo durante su proceso de fumado

Desde 1950 diversos investigadores han estudiado cómo modificar la combustión y formación del humo del tabaco con objeto de eliminar y reducir los constituyentes perjudiciales presentes.

La combustión y pirólisis/destilación del tabaco genera dos corrientes de humo, una denominada corriente principal (mainstream smoke*)* y otra denominada corriente secundaria (sidestream smoke). La primera supone un 25% del humo total generado y es la que atraviesa la longitud del cigarrillo y es inhalada directamente por el fumador y, por lo tanto, es la que recorre parte del sistema respiratorio hasta llegar a los pulmones. La corriente secundaria supone un 75% del humo total generado y se trata de la corriente procedente de la combustión pasiva del tabaco entre caladas que es diluida por el aire. Además se conoce como ETS (environmental tobacco smoke) (Connolly y col., 2000) a la mezcla del humo exhalado por el fumador y el humo de la corriente secundaria. Es un importante contaminante del aire de interiores y responsable del tabaquismo pasivo. Los factores que afectan a la composición y concentración de cada una de corrientes son:

<u>Corriente principal</u>: (Borgerding y Klus, 2005), en lo que respecta al diseño del cigarrillo, los factores que mayor influencia presentan sobre la cantidad y

composición de la corriente principal son la masa de tabaco presente en el cigarrillo, las dimensiones de este (longitud y diámetro), la mezcla de tabaco utilizada, el tipo de filtro, el tipo de papel, los ingredientes adicionados al tabaco en el proceso de fabricación de cigarrillos y el contenido en humedad que presenta la mezcla de tabaco utilizada. Otros factores que también afectan, propios del proceso de fumado, son el volumen de calada, la frecuencia de calada, la duración de la calada, la forma de la calada, el diseño del cigarrillo, la permeabilidad del papel, la presencia o no de agujeros de ventilación en el filtro, el flujo de aire alrededor del cigarrillo, el tipo de encendedor utilizado, el régimen de encendido y la longitud del extremo final.

Corriente secundaria: la mayor contribución a la corriente secundaria tiene lugar por el número de fumadores presentes en ese momento, la cantidad de cigarrillos que son fumados por hora, la ventilación del espacio considerado, el volumen de la estancia, así como la temperatura y la humedad relativa de esta y el número de fumadores pasivos presentes.

2.4.1.- Diferentes regímenes utilizados para simular el fumado de un cigarrillo

Dependiendo de las condiciones utilizadas en el proceso de fumado, volumen de calada, duración, frecuencia, etc. se han propuesto varios regímenes de fumado que intentan establecer condiciones comparables entre diferentes laboratorios, pero que en ningún caso pretenden simular el comportamiento del fumador. (Counts y col., 2005 y Hammond y col., 2006)

Los tres métodos más conocidos y utilizados son el ISO 3308, Massachusetts (MDPH) y el Canadiense (HC). Sus características se resumen el la Tabla 2.1:

Tabla 2.1.- Características de los principales regímenes de fumado

TEST STANDARD	Obstrucción agujeros de ventilación (%)	Intervalo entre caladas (s)	Velocidad media de flujo (mL/s)	Volumen de caladas (mL)
ISO	0	60	17.5	35
MASSACHUSETTS	50	30	22.5	45
CANADIENSE	100	30	27.5	55

La repetibilidad y reproducibilidad de estos métodos es mayor cuando se trata del método Canadiense (Borgerding y Klaus, 2005), siendo este también el que mejor podría representar de forma más aproximada al comportamiento de un fumador.

Si ordenamos de menor a mayor los diferentes métodos en función del rendimiento obtenido para los distintos componentes presentes en el humo del tabaco tendríamos que el método ISO es el que menores valores proporciona, puesto que presenta menor volumen de calada, mayor intervalo entre caladas y no se bloquean los agujeros de ventilación, y el método canadiense los mayores valores, puesto que presenta los valores más intensos para los parámetros que determinan las condiciones de fumado.

2.5.- COMPOSICIÓN Y TOXICIDAD DEL HUMO DEL TABACO

2.5.1.- Composición

En el humo del tabaco se han llegado a identificar 4800 compuestos de los cuales al menos 60 han sido identificados como tóxicos y cancerígenos (Baker y Bishop, 2005). Uno de los componentes generados durante la combustión y pirolisis del tabaco es el CO, compuesto de gran importancia debido a su elevada toxicidad. El análisis de la corriente principal del humo del tabaco ha sido abordada por diferentes autores (Rustemeier y col., 2002; Calafat y col., 2004; Borgerding and Klus, 2005). Como se ha comentado en apartados anteriores, la composición del humo del tabaco viene determinada por numerosos factores; por ello, aunque a lo largo de muchos años se han llevado a cabo multitud de estudios sobre la composición y toxicidad del tabaco, hay que tener en cuenta que todos ellos presentan limitaciones, puesto que los resultados obtenidos son específicos de las condiciones seleccionadas para llevar a cabo el experimento.

Durante el proceso de fumado de un cigarrillo, tabaco de pipa, tabaco de liar, etc., se generan dos fases bien diferenciadas cuya composición es bastante variada puesto que presentan un elevado número de compuestos. Estas dos fases son:

-Fase particulada, formada por partículas de 0,35-0,40 micras de diámetro, y compuesta principalmente por agua, hidrocarburos aromáticos polinucleares (PAH), nicotina, fenol, cresol, benzo[a]pireno, oligometales, indol, carbazol, catecol (orto-dihidroxibenceno).

Los compuestos más importantes presentes en esta fase son la nicotina y el alquitrán. Según la Real Academia Española el alquitrán es un “producto obtenido de la destilación de maderas resinosas, carbones, petróleo, pizarras y otros materiales vegetales y minerales. Es líquido, viscoso, de color oscuro y fuerte olor, y tiene distintas aplicaciones industriales”. Según la norma ISO 4387, la materia particulada libre de agua y nicotina (NFDPM: nicotine free dry particulate matter), más conocida como alquitrán del tabaco, es la porción de la corriente principal del humo del tabaco que condensa en la trampa de humo, menos el agua y la nicotina, expresada en mg/cigarrillo. Entre las sustancias que componen el **alquitrán** del tabaco, se encuentran los hidrocarburos aromáticos policíclicos (PAH), aminas aromáticas y compuestos inorgánicos.

-Fase gaseosa*,* donde los principales componentes son monóxido de carbono, cianuro de hidrógeno, acetaldehído, acroleína, amoníaco, formaldehído, óxidos de nitrógeno e hidracina.

El monóxido de carbono es un gas incoloro, muy venenoso y de elevado poder tóxico. Otras sustancias irritantes presentes en la fase gaseosa como acroleína, aldehídos, cianuro de hidrógeno y amoníaco afectan a la mucosa de las vías respiratorias, la pituitaria y la zona conjuntiva.

La IARC (Agencia Internacional de Investigación sobre el Cáncer) ha llegado a identificar más de sesenta compuestos potencialmente cancerígenos, entre ellos: (Ding y col., 2008)

- 10 PAH's, hidrocarburos policíclicos aromáticos
- 8 TSNA's, nitrosaminas específicas del tabaco
- 45 compuestos adicionados

Baker (2006) establece los compuestos mayoritarios obtenidos en el humo del tabaco en función de la temperatura a lo largo del cigarrillo:

300-550ºC→ C1-C3

400-700ºC → alcanos y alquenos

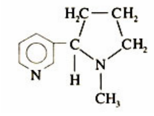
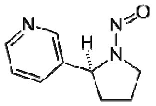
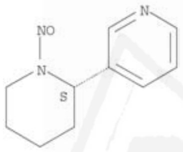
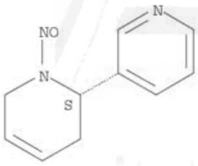
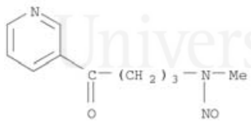
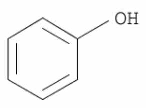
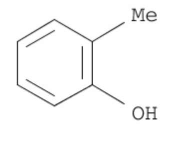
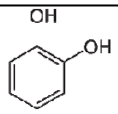
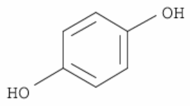
500ºC → benceno y alquilbencenos

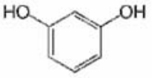
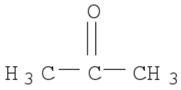
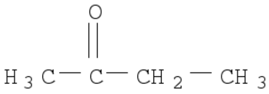
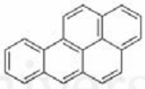
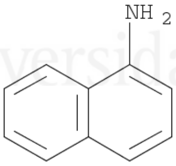
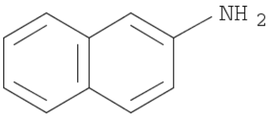
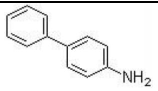
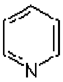
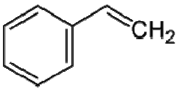
700ºC → naftalenos

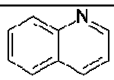
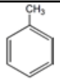
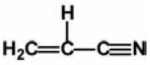
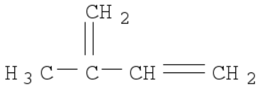
800ºC → PAH's

Aunque existen muchas otras clasificaciones, la mayoría de autores que trabajan en el estudio del humo del tabaco emplean la lista Hoffmann (Hoffmann and Hoffmann, 1997) que se muestra en la Tabla 2.1. La lista Hoffmann incluye los compuestos más tóxicos presentes en el humo del tabaco.

Tabla 2.2.- Compuestos, fórmula y clase de compuesto

COMPUESTO	**CLASE**
Alquitrán	Componente mayoritario
 Nicotina	Componente mayoritario
CO	Componente mayoritario
NH_3	Gas inorgánico
HCN	Gas inorgánico
NO_x	Gas inorgánico
NNN (N-Nitrosonornicotina) 	Nitrosaminas
NAB (N-Nitrosoanabasina) 	Nitrosaminas
NAT (N-Nitrosoanatabina) 	Nitrosaminas
NNK (4-(metilnitrosamino)-1-(3-piridil)-1-butanona) 	Nitrosaminas
Fenol 	Fenoles
o,m,p-cresol 	Fenoles
Catecol 	Fenoles
Hidroquinona 	Fenoles

COMPUESTO	CLASE
Resorcinol 	Fenoles
Formaldehído $H_2C{=}O$	Carbonilos
Acetaldehído $H_3C-CH{=}O$	Carbonilos
Acetona  $H_3C-C(=O)-CH_3$	Carbonilos
Propionaldehido $H_3C-CH_2-CH{=}O$	Carbonilos
Metil-etil-cetona  $H_3C-C(=O)-CH_2-CH_3$	Carbonilos
Acroleina $H_2C{=}CH-CH{=}O$	Carbonilos
Butiraldehido $H_3C-CH_2-CH_2-CH{=}O$	Carbonilos
Crotonaldehido $H_3C-CH{=}CH-CH{=}O$	Carbonilos
Benzo[a]pireno 	PAH's
1-Aminonaftaleno 	Aminas aromáticas
2-Aminonaftaleno 	Aminas aromáticas
3-Aminobifenilo	Aminas aromáticas
4-Aminobifenilo 	Aminas aromáticas
Piridina 	Semivolátiles
Estireno 	Semivolátiles

COMPUESTO	CLASE
Quinolina 	Semivolátiles
1,3-Butadieno $CH_2=CH-CH=CH_2$	Fase vapor
Benceno 	Fase vapor
Tolueno 	Fase vapor
Acrilonitrilo  $H_2C=C(H)-C\equiv N$	Fase vapor
Isopreno  $H_3C-C(=CH_2)-CH=CH_2$	Fase vapor
Pb	Metales
Cr	Metales
Ni	Metales
Hg	Metales
As	Metales
Cd	Metales
Se	Metales

2.5.2.- Toxicidad

Actualmente el consumo del tabaco produce la muerte a más de 3,5 millones de personas/año en el mundo, aunque si se mantiene la tendencia actual de incremento de consumo de tabaco, el número de muertes será el doble en unos 20 años. Es por este motivo que la adopción de medidas de prevención al respecto es una cuestión de una considerable importancia, puesto que de no ser así, el consumo del tabaco podría convertirse en la principal causa de muerte previsible en un futuro no muy lejano.

Calafat y col. (2004) establecen una pauta de consumo en función del país considerado, concluyendo que los tabacos oscuros son preferidos en Francia, en Grecia prefieren tabaco oriental, en Gran Bretaña tabaco Virginia y en Suiza tabaco Maryland. Todo esto, debido a las diferencias entre unos y otros tipos de tabaco, genera diferentes variedades de humo.

La toxicidad del tabaco está íntimamente relacionada con el producto en cuestión que se esté consumiendo, ya que no todos los tabacos y todos los productos del tabaco presentan la misma peligrosidad. Si se estableciera un orden en el grado de toxicidad se tendría, en orden de toxicidad decreciente:

1. Cigarrillo rubio sin filtro
2. Cigarrillo negro sin filtro
3. Cigarrillo rubio con filtro
4. Cigarrillo negro con filtro
5. Cigarro puro
6. Cigarrillo rubio con boquilla
7. Cigarrillo negro con boquilla
8. Pipa recta
9. Pipa curva
10. Cigarro puro con boquilla

↓ MENOR TOXICIDAD

Como puede verse, en general, los cigarrillos de tabaco rubio son más tóxicos que los de tabaco negro, y éstos a su vez más que los puros. Además, la mayor o menor toxicidad de cada producto está íntimamente ligada con las posibilidades que tienen los componentes del humo del tabaco de condensar o quedar retenidos antes de llegar a ser inhalados.

Una forma de cuantificar el nivel de toxicidad de los diferentes compuestos presentes en la corriente principal del humo del tabaco, es la dada por la Agencia Internacional de Investigación sobre el Cáncer (IARC), que establece cuatro grupos donde poder incluir el compuesto en particular en función del efecto que éste tenga sobre el ser humano. Esta clasificación es la siguiente:

<u>Grupo 1</u>: conocido como cancerígeno humano.

<u>Grupo 2A</u>: probable cancerígeno humano.

<u>Grupo 2B</u>: posible cancerígeno humano.

Grupo 3: no clasificado como cancerígeno humano.

Otros autores, como Fowles y Dybing (2003) han elaborado un estudio donde calculan un CRI (índice de riesgo de cáncer) teniendo en cuenta los rendimientos obtenidos de aquellos compuestos presentes en la corriente principal del humo del tabaco, que han sido clasificados por la IARC, utilizando una máquina de fumar que lleva a cabo los experimentos bajo la Norma ISO 3308, y un valor dado por la Agencia de protección Ambiental de California (Cal/EPA), denominado CPF (factor de potencia cancerígena) considerando una frecuencia respiratoria estándar de 20m^3/día. El CRI se define como:

$$CRI = {}^{R(\mu g / cigarrillo) x CPF(\mu g / m^3)^{-1}}\!\Big/_{20(m^3 / día)}$$

R es el rendimiento de cada compuesto determinado.

En la tabla 2.2 se muestra un listado de compuestos presentes en el humo del tabaco, junto con su clasificación según la IARC y el valor CRI obtenido de acuerdo con la expresión anterior.

En la primera columna de la tabla 2.2 el tipo de tóxico corresponde a la categoría de compuesto dada por Fowles y Dybing (2003), que establecen que el tipo 1 corresponde a compuestos como aldehídos y pequeños compuestos orgánicos, el tipo 2 indica metales, el tipo 3 incluye las nitrosaminas el tipo 4 engloba a otros compuestos y finalmente, el tipo 5 corresponde a PAH's (hidrocarburos polícíclicos aromáticos).

Tabla 2.3.- Clasificación de compuestos según el tipo de tóxico, el Grupo IARC y el CRI.

Tipo de tóxico	**Grupo IARC**	**Constituyente de la corriente principal del humo del tabaco**	**CRI (cigarrillo/día)**
1	2A	1,3–Butadieno	3,02E–04
1	2B	Acrilonitrilo	1,29E–04
2	1	Arsénico	1,16E–04
1	2B	Acetaldehído	9,18E–05
1	1	Benceno	6,71E–05
1	2B	Acetamida	4,70E–05
3	2B	N-Nitrosonornicotina (NNN)	3,80E–05
3	2B	N-Nitrosopirrolidina (NP)	3,39E–05
2	1	Cromo (hexavalente)	3,15E–05
2	1	Cadmio	2,16E–05

Tipo de tóxico	***Grupo IARC***	***Constituyente de la corriente principal del humo del tabaco***	***CRI (cigarrillo/día)***
1	2A	Formaldehído	9,90E–06
4	2B	Hidracina	8,33E–06
3	2B	4-N-Nitrosometilamino)-1-(3-piridil)-1-butanona (NNK)	7,80E–06
3	2A	N-Nitrosodimetilamina (NDMA)	5,58E–06
4	2B	DDT	4,61E–06
3	2A	N-Nitrosodietilamina (NDEA)	4,27E–06
5	2A	Benzo[a]pireno	1,93E–06
3	2B	N-Nitroso-N-dibutilamina	1,89E–06
3	2B	N-Nitrosoetil-metilamina	1,89E–06
5	2B	Dibenzo[a,i]pireno	1,38E–06
3	2B	N-Nitrosodietanolamina	1,20E–06
3	2B	N Nitrosopiperidina	6,04E–07
1	2B	Uretano	4,14E–07
4	1	4-Aminobifenilo	3,60E–07
5	2B	Benzo(j)fluoranteno	3,30E–07
5	2A	Benz[a]antraceno	2,48E–07
5	2A	Dibenz[a,h]antraceno	2,40E–07
5	1	2-Aminonaptaleno	1,80E–07
5	2B	Benzo[b]fluoranteno	1,65E–07
2	1	Niquel	1,43E–07
5	2B	Indeno[1,2,3-c,d]pireno	6,60E–08
3	2B	N-Nitroso-N-propyilamina	5,00E–08
5	2B	Benz[k]fluoranteno	4,95E–08
5	2B	7H-Dibenzo[c,g]-carbazol	3,85E–08
1	1	Cloroetileno o vinilcloruro	3,35E–08
5	2B	5-Metilcriseno	3,30E–08
2	1	Berilio	3,00E–08
5	2B	Criseno	2,75E–08
5	2B	Dibenz[a,j]acridina	1,49E–08
2	2B	Plomo	7,68E–09
5	2B	Dibenz[a,h]acridina	5,50E–10

2.6.- LEGISLACIÓN SOBRE EL TABACO Y SU CONSUMO

La toxicidad del tabaco así como sus efectos representa un grave problema para la mayoría de países. Por todo esto, y debido al elevado consumo de tabaco, los distintos países han considerado necesario la creación de leyes más estrictas, que sean capaces de concienciar a la población y disminuir en la medida de lo posible el consumo de tabaco.

En España la primera ley que entró en vigor, donde se empieza a regular en mayor medida el consumo del tabaco es la **DIRECTIVA 2001/37/CE DEL PARLAMENTO EUROPEO Y DEL CONSEJO de 5 de junio de 2001 relativa a la aproximación de las disposiciones legales, reglamentarias y administrativas de los Estados miembros en materia de fabricación, presentación y venta de los productos del tabaco**. En esta ley se establece cómo medir ciertas sustancias presentes en el humo del tabaco, se define producto de tabaco, alquitrán, nicotina, tabaco de uso oral e ingrediente. Además se establecen los contenidos máximos permitidos de alquitrán, nicotina y monóxido de carbono. También se establece que a partir de este momento las cajetillas del tabaco deben llevar impresos contenidos como advertencias, etc.

El 1 de enero de 2006 entró en vigor otra ley algo más restrictiva (**LEY 28/2005, de 26 de diciembre, de medidas sanitarias frente al tabaquismo y reguladora de la venta, el suministro, el consumo y la publicidad de los productos del tabaco**), que establece numerosas restricciones a la venta y consumo de tabaco en ciertos lugares. El artículo 7 de esta ley dice:

“Artículo 7. Prohibición total de fumar.

Se prohíbe totalmente fumar, además de en aquellos lugares o espacios definidos en la normativa de las Comunidades Autónomas, en:

a) Centros de trabajo públicos y privados, salvo en los espacios al aire libre.

b) Centros y dependencias de las Administraciones públicas y entidades de Derecho público.

c) Centros, servicios o establecimientos sanitarios.

d) Centros docentes y formativos, independientemente de la edad del alumnado y del tipo de enseñanza.

e) Instalaciones deportivas y lugares donde se desarrollen espectáculos públicos, siempre que no sean al aire libre………”

A pesar de esta ley, la Unión Europea instó al gobierno español a endurecer la normativa y a ampliar los impuestos existentes en la actualidad sobre el tabaco, encareciendo el precio de las cajetillas de cigarrillos, ya que según el estudio HELP-COmets (Carbon Monoxide Measure of Exposure to Tobacco Smoke), España se sitúa en el octavo puesto de países con mayor nivel de contaminación ambiental por CO entre sus ciudadanos debida al consumo del tabaco. Mientras que el nivel máximo de CO establecido para la calidad del aire ambiental es de 8,5 ppm, en España estas concentraciones alcanzan a 17,5 ppm en el aire espirado por fumadores, 3,9 ppm en el aire espirado por personas no expuestas al tabaco y 8 ppm entre los fumadores pasivos.

En 2011 entró en vigor la **Ley 42/2010, de 30 de diciembre, por la que se modifica la Ley 28/2005, de 26 de diciembre, de medidas sanitarias frente al tabaquismo y reguladora de la venta, el suministro, el consumo y la publicidad de los productos del tabaco.**

Esta ley restringe todavía más el consumo de tabaco en espacios cerrados a “Espacios de uso público: lugares accesibles al público en general o lugares de uso colectivo, con independencia de su titularidad pública o privada. En cualquier caso, se consideran espacios de uso público los vehículos de transporte público o colectivo. A efectos de esta Ley, en el ámbito de la hostelería, se entiende por espacio al aire libre todo espacio no cubierto o todo espacio que estando cubierto esté rodeado lateralmente por un máximo de dos paredes, muros o paramentos”.

Con esta ley se ha restringido todavía mucho más el consumo de tabaco, quedando totalmente prohibido en espacios cerrados.

2.7.- ESTUDIOS SOBRE LA REDUCCIÓN DE LA TOXICIDAD DEL TABACO

A lo largo de los años se han llevado a cabo gran cantidad de estudios con objeto de reducir la toxicidad del tabaco.(Baker, 2006; Seeofer, 1980; Meier, 2001). En los primeros estudios realizados, centrados todos ellos en diseñar un cigarrillo mucho menos perjudicial para la salud, se observó que al intentar eliminar benzo[a]pireno y PAH's mediante la adición de nitritos y nitratos a la mezcla de tabaco, se producía un incremento en el nivel de nitrosaminas en el humo del tabaco, efecto no deseado puesto que la eliminación de un grupo de compuestos incrementa los niveles de otro (Baker, 2006). Esto hizo pensar que los riesgos para la salud asociados al consumo del tabaco no debían relacionarse con los compuestos o clases de compuestos en particular, si no que el efecto adverso del consumo de tabaco se debía cuantificar con el humo en su totalidad.

Los primeros estudios de los que se tiene constancia datan de 1957 (Baker, 2006). En estos primeros estudios realizados buscando reducir la toxicidad del tabaco, se llevaban a cabo modificaciones sobre el cigarrillo en cuestión, bien mediante el uso de filtro, añadiendo ventilación a la zona del filtro, modificando el papel o bien modificando la mezcla de tabaco que es añadida al cigarrillo. Con la introducción de ventilación en el filtro, por ejemplo, el volumen de gas que pasa a través del cigarrillo disminuye, motivo por el cual la combustión en el tabaco es menor, y por lo tanto los rendimientos de los compuestos generados también decrecen.

Otros autores que también resumen de manera general los avances dados en la investigación sobre la reducción de la toxicidad del tabaco son Green y col. (2007). Estos autores describen cómo se han ido diseñando diferentes tecnologías para fabricar cigarrillos "menos perjudiciales". Todas estas tecnologías han evolucionado desde 1950 hasta nuestros días, y son las siguientes:

- Modificación de la mezcla de tabacos.
- Filtración eficiente y efectiva.
- Uso de tabaco reconstituido (restos de tabaco que son tratados para generar una lámina que luego se utiliza para la fabricación de cigarrillos).

- Dilución a través de la permeabilidad del papel.
- Uso de aditivos en el filtro.
- Uso de aditivos en el papel.
- Uso de tabaco expandido, tabaco que tras impregnarse con nitrógeno líquido o CO_2 se somete a elevadas temperaturas para que se produzca la expansión o dilatación de la estructura celular. (http://yesmoke.eu/brand/selected-tobaccos/expanded-tobacco/).
- Perforación del filtro para dilución del humo.

Se han propuesto distintos métodos y aditivos con el fin de reducir la toxicidad del humo del tabaco. En la mayoría de éstos se usan materiales de tipo zeolitas o aluminosilicatos. Los diferentes estudios de mayor relevancia se describen a continuación.

Entre las primeras patentes se encuentra la de Rosen (1974), en la que se propone el uso de un material adsorbente, con un contenido de humedad elevado, y en una proporción comprendida entre un 1 y un 50%, para reducir los productos no deseables generados en la combustión del tabaco. El material propuesto pertenece al grupo de tierra de diatomeas y silicatos de calcio o magnesio.

Otra de las primeras propuestas corresponde a Seeofer y Kausch (1980), que utilizan un compuesto de fórmula $M_2M'RuO_6$, donde M es un metal divalente, M' es a un metal trivalente lantanoide o actinoide, Ru actúa con valencia 5, y M y M' pueden formar una capa de perovskita con los iones de Ru. Este compuesto, una vez mezclado con el tabaco o incorporado al papel o al filtro, contribuye a la eliminación de NO y CO del humo del tabaco. En el mismo sentido, Rongved (1997) también describe un tipo de relleno que permite reducir las sustancias tóxicas, como el CO, de los gases de combustión del tabaco, por adición de catalizadores sólidos, inertes, estables y no contaminantes, junto con o cerca del tabaco. Entre estos catalizadores, propone el uso de pentóxido de vanadio, trióxido de molibdeno y óxidos de rodio.

Otras patentes, como la de Stanbridge (1990), centran su objetivo en el procedimiento utilizado para incorporar los aditivos al tabaco. En este caso, el aditivo se deposita en la corriente de tabaco durante el proceso de elaboración del cigarrillo, utilizando un dispositivo que permite depositar el material, en forma de polvo o en forma líquida, en suspensión o como espuma.

Meier y col. (1995) describen el uso de materiales zeolíticos, naturales y sintéticos, como aditivos para reducir los compuestos tóxicos en el humo del tabaco. En la patente que presentan se reivindica un artículo para fumar que está compuesto por un filtro, el tabaco y un envoltorio. Los aditivos, con caraterísticas diferentes según sea el destino del aditivo, se incorporan tanto al filtro como al tabaco. Así, mientras que el aditivo que se introduce en el filtro es hidrofóbico, para mezclar con el tabaco se prefieren materiales hidrofílicos. Estos aditivos hidrofílicos se utilizan saturados de agua y consisten en zeolitas X, Y, L, mordenita y HBeta, y se añaden al tabaco, utilizando o no agentes de adhesión, como por ejemplo gel de sílice. A temperaturas elevadas, estos materiales actúan como catalizadores y tienen efectos positivos de cara a la reducción de los compuestos tóxicos generados en la combustión del tabaco, sin afectar al sabor del mismo. Otra patente similar (Meier, 2001) se centra en el proceso de preparación de los cigarrillos utilizando los aditivos previamente citados, sin necesidad de utilizar agentes adherentes. El procedimiento consiste en 1) distribuir el material catalíticamente activo en el tabaco y 2) presionar dicho material sobre el tabaco.

Otra aplicación también descrita por Meier (Meier y Siegmann, 1999), hace referencia al uso de zeolitas tipo Y, con objeto de eliminar compuestos cancerígenos del humo del tabaco. Los compuestos que mayormente son eliminados son nitrosaminas y PAH's. En este estudio los cigarrillos se preparan de manera análoga a la forma utilizada en el presente estudio, mezclando el tabaco con el polvo del catalizador y luego rellenando el cigarrillo. En este estudio solo se habla de la preparación de las muestras, puesto que los análisis son realizados por un laboratorio externo.

Más recientemente, Li y Hajaligol (2003) han descrito el uso de nanopartículas de Fe_2O_3, CuO, TiO_2, CeO_2, Ce_2O_3, Al_2O_3, Y_2O_3 dopado con Zr, Mn_2O_3 dopado con Pb, así como de mezlas de éstos materiales, para aumentar el grado de conversión de CO a CO_2. En esta patente se describe también el procedimiento para la preparación de los cigarrillos, que incluye a) la adición del aditivo a base de nanopartículas a la picadura de tabaco, b) la introducción de la mezcla de picadura de tabaco más aditivo en una máquina de fabricación de cigarrillos para formar un cigarrillo y c) la colocación del envoltorio de papel alrededor del tabaco para dar forma al cigarrillo final. En una continuación de esta patente (Li y Hajaligol, 2003), los mismos autores ponen de manifiesto la capacidad de los aditivos descritos para reducir la cantidad generada de otros constituyentes del humo del tabaco como por ejemplo, aldehídos, 1,3-butadieno, isopreno, acroleína, acrilonitrilo, cianuro de hidrógeno, o-toluidina, 2-naftilamina, óxidos de nitrógeno, benceno, N-nitrosonornicotina, fenol, catecol o benzantraceno). En otra patente, Li y col. (2004.a) ponen de manifiesto que la coprecipitación de óxido de manganeso con alguna de las nanopartículas previamente estudiadas también contribuye a aumentar el grado de conversión de óxido nítrico a nitrógeno. En la misma línea que las patentes anteriores, Li y col. (2004.b) también describen un aditivo consistente en un catalizador que contiene nanopartículas de un metal y/o un óxido metálico soportadas sobre un material fibroso, que aumenta la conversión de monóxido de carbono en dióxido de carbono y de óxido nítrico en nitrógeno, mientras que en otra patente diferente (Rasouli y col., 2005), se propone el uso, con la misma finalidad, de aditivos a base de hidroperóxidos de metales de transición o de tierras raras o mezclas de estos materiales. En todas estas patentes también se describe el papel y los métodos utilizados para la preparación de los cigarrillos, así como las condiciones en que éstos fueron fumados.

En 2004, Li y col. (2004.c) describieron el uso de un aditivo formado por nanopartículas de óxido de hierro, que se genera in situ mientras se está quemando el cigarrillo, y que es capaz de aumentar el grado de conversión de CO y NO a CO_2 y N_2, respectivamente. Por otro lado, también pueden utilizarse como aditivos sales orgánicas de potasio, que permiten reducir el rendimiento de CO, nicotina y materia particulada seca libre de nicotina (NFDPM: nicotine free dry particulate matter) (Li y Parry, 2003).

Se ha encontrado otras patentes o publicaciones científicas en las que se describe el uso de zeolitas como aditivos del tabaco. Así, Cvetkovic y col. (2002) utilizan un catalizador basado en zeolita Cu-ZSM-5 con el fin de disminuir la cantidad de NO y NO_x en la corriente principal del humo del tabaco. Este aditivo puede incorporarse al filtro o mezclarse directamente con el tabaco y, de acuerdo con el mecanismo propuesto por estos autores, son las propiedades de adsorción del aditivo y la difusividad en el mismo las que determinan su actividad. Hay también otros autores que proponen el uso de ciertos aditivos, basándose en su capacidad de adsorción. Por ejemplo, Jianhua y col. (2003) describen el uso de un catalizador sólido alcalino y de un material funcional basado en un tamiz molecular mesoporoso a base de silicio (por ejemplo MCM-41 o zeolitas NaA, NaY y ZSM-5), que contiene un lantanoide, actinoide o metal de transición, para la reducción de nitrosaminas por adsorción selectiva. El uso de zeolitas para la reducción de la materia particulada seca y libre de nicotina, NFDPM (nicotine free dry particulate matter), que como ya se ha comentado es la porción de la corriente principal del humo del tabaco que condensa en la trampa de humo (TPM: total particulate matter); menos el contenido en agua y nicotina y de hidrocarburos aromáticos polinucleares (PAH) ha sido puesto de manifiesto también por Radojicic y col. (2004).

Otras aportaciones también relacionadas con las anteriores son, por ejemplo, la de Shahtyar y col. (2005), que describe el procedimiento para preparar aditivos a base de partículas que incluyen óxidos metálicos soportados.

Otros estudios en los que se describe el uso de aditivos, que bien se añaden al filtro o directamente al tabaco, proponen la utilización del material MCM-48, que se utiliza para reducir PAH’s de la corriente principal del humo del tabaco (Yong y col., 2006). También se han utilizado filtros con nanotubos de carbón, o carbón activado y zeolita NaY. (Chen y col., 2006). Xu y col. (2003) describen el uso en el filtro de materiales como zeolitas tipo NaY y ZSM5, además de SBA-15 y MCM-48. Estos materiales se utilizan como adsorbentes selectivos, puesto que favorecen la eliminación de las nitrosaminas específicas del tabaco. El uso de partículas de óxido de hierro para la eliminación de CO ha sido descrito por Li y Hajaligol (2003).

Estudios más recientes son los llevados a cabo por Gao y col. (2009) y Branton y col. (2009). Gao y col. en sus estudios utilizan materiales calco-silicatos para la eliminación de las nitrosaminas específicas del tabaco del aire contaminado por humo de tabaco. Branton y col. llevan a cabo estudios con carbón activo con objeto de maximizar la adsorción del humo del tabaco. Sus investigaciones se centran en analizar como afecta la estructura porosa del carbón activo a la adsorción de los compuestos generados al fumar un cigarrillo.

2.8.- ZEOLITAS Y OTROS TAMICES MOLECULARES MICRO Y MESOPOROSOS

Tal y como se ha indicado en la sección anterior, los materiales zeolíticos ocupan un lugar destacado dentro de las diferentes alternativas propuestas para la reducción de la toxicidad del tabaco. Las zeolitas son aluminosilicatos hidratados de elementos alcalinos o alcalinotérreos (Na, K, Mg, Ca), altamente cristalinos, que al deshidratarse desarrollan, en el cristal ideal, una estructura porosa con diámetros de poro mínimos de 3 a 10 Å. Una zeolita puede definirse como un alumino-silicato cuya estructura forma cavidades ocupadas por iones grandes y moléculas de agua con gran libertad de movimiento, que permiten el cambio iónico y la deshidratación reversible. El nombre de zeolita deriva del griego **ςζείυ**, hervir y **λίθος**, piedra, es decir, piedra que hierve. Se trata de materiales que presentan poros bien definidos, una alta superficie interna, una extraordinaria estabilidad térmica y una elevada capacidad de intercambio iónico.

La fórmula química que describe este tipo de materiales es (Breck, 1974):

$(SiO_2)_x(Al_2O_3)_y(Me_2O)_z \cdot nH_2O$ donde Me es un metal alcalino o alcalinotérreo.

Químicamente se caracterizan por la relación entre los contenidos de sílice y alúmina (SiO_2/Al_2O_3). La estructura de las zeolitas viene determinada por la organización espacial de sus unidades básicas, que son tetraedros $[SiO_4]^{4-}$, que se combinan formando anillos o unidades estructurales secundarias. Además estos anillos se unen formando celdas para determinar así la estructura completa de la zeolita (Figura 2.7).

Existen zeolitas tanto naturales como sintéticas. Las zeolitas naturales suelen encontrarse en rocas ígneas, bien como cristales individuales o como agregados policristalinos. Los principales constituyentes de las zeolitas son silicio, hidrógeno, oxígeno y aluminio, pudiendo presentar también en algunos casos otros elementos como sodio, hierro, etc.

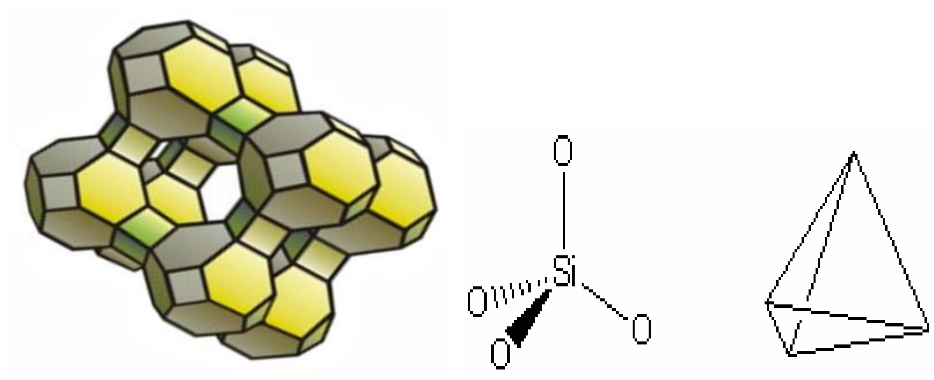


Figura 2.7.- Estructura cristalina de las zeolitas.

Las zeolitas presentan una alta relación Si/Al, donde la sustitución de un ión Si^{4+} por un ión Al^{3+} requiere la presencia adicional de un protón (H^+), siendo este el responsable del nivel de acidez de la zeolita.

Existe una amplia gama de zeolitas que se diferencian principalmente por las características de su celda unidad y por las dimensiones de su estructura porosa. La IUPAC clasifica los materiales en función de su porosidad en sólidos microporosos (<2nm), mesoporosos (2-50 nm) y macroporosos (>50nm). Las zeolitas estarían engobladas dentro de los sólidos microporosos, existiendo también algún material de este tipo dentro de los sólidos mesoporosos. En la tabla 2.3 se presenta un resumen de la clasificación de las zeolitas y otros tamices moleculares en función del tamaño de poro.

Tabla 2.4.- Clasificación de zeolitas y otros tamices moleculares en función del tamaño de poro.

Tamaño de poro (A)	**Definición**	**Material típico**	***CE**	**Ejemplo**	**Tamaño del anillo**	**Diámetro de poro (A)**
20-500	Mesoporoso	SBA-15				
		MCM-41				15-100
< 20	Microporoso	Arcillas naturales				
		Arcillas Apilaradas		7-9		
		Zeolitas		Cloverita	20	6,0x13,2
				VPI-5	18	12,1
				AlPO$_4$-8	14	7,9x8,7
			FAU	Faujasita	12	7,4
				AlPO$_4$-5	12	7,3
				ZSM-12	12	5,5x5,9
				ZSM-48	10	5,3x5,6
			MFI	ZSM-5	10	5,3x5,6 5,1x5,5
				CaA	8	4,2
			LTA	SAPO-42		4,1
			AFT	AlPO-52		2,8x4,4

**CE código estructural*

Las principales propiedades físicas y químicas de mayor interés de las zeolitas, que determinan el elevado número de aplicaciones de estos materiales, son:

- Gran estabilidad térmica.

- Existencia de canales y poros que les confieren unas características texturales peculiares.

- Posibilidad de adsorber gases y vapores, por lo que suelen utilizarse mucho en procesos de separación y purificación.

- Propiedades catalíticas, debidas a la presencia de centros ácidos de tipo Brönsted y Lewis.

- Uso como tamices moleculares, muy relacionado con sus propiedades de adsorción.

- Posibilidad de intercambio iónico con el medio, lo que permite modificar las propiedades y adaptar el uso de la zeolita a aplicaciones muy variadas.

Todas estas propiedades permiten el uso de zeolitas en multitud de aplicaciones, destacando la utilización como acondicionador y fertilizante de suelos, ablandador de aguas, catálisis y refino del petróleo, separación de gases y purificación del gas natural, producción de gasolina sintética a partir de metanol, isomerización en la industria de polímeros, control de la contaminación atmosférica y como catalizadores ultra selectivos, para fotocatálisis y electrocatálisis.

Las zeolitas A, X e Y fueron descubiertas entre 1949 y 1954 por Milton y Breck. Estas zeolitas sintéticas presentan un elevado valor comercial, puesto que poseían una composición rica en aluminio, motivo por el cual fueron las primeras que se introdujeron comercialmente como adsorbentes y catalizadores. También se estudió la posibilidad de incorporar metales a la red para mejorar las propiedades catalíticas de las zeolitas. Todo ello ha dado lugar a que en la actualidad exista una amplia gama de este tipo de materiales, con propiedades físicas, químicas y catalíticas de elevado interés.

Existen numerosos estudios sobre diferentes aspectos de las zeolitas, como posibles modificaciones químicas que permitan aumentar su estabilidad térmica e hidrotérmica. Los primeros estudios fueron llevados a cabo por investigadores de la compañía Grace (1969), y consistían en el tratamiento de la zeolita Y con vapor de agua a elevadas temperaturas. De esta forma la zeolita presentaba una mayor estabilidad térmica e hidrotérmica, por lo que se la denominó zeolita Y-ultra estable, (USY, Ultrastable Steaming Y). Otras modificaciones llevadas a cabo consistieron en un aumento del contenido en Si. Así, investigadores de la compañía Mobil Oil patentaron la síntesis de las zeolitas HBeta y HZSM-5, ambas con un elevado contenido en Si.

2.8.1. Zeolita HZSM-5

La zeolita HZSM-5 (Zeolita Socony Mobil-five) pertenece al grupo MFI (Tabla 2.3). Fue sintetizada por primera vez por la empresa Socony Mobil (Argauer y Landolt, 1972). El número 5 indica las dimensiones de la abertura de los poros de la zeolita, en Å.

La zeolita HZSM-5 es un material altamente poroso y presenta dos tipos de poros, ambos formados por anillos de oxígeno de 10 miembros. El primer tipo de poro es recto y con la sección transversal elíptica, mientras que en el segundo tipo los poros rectos se intersectan perpendicularmente, dando lugar un patrón en zigzag. Las dimensiones de las aberturas de los poros para esta zeolita son 5,3x5,6 Å en el plano [010] y 5,1x5,5 Å en el plano [100] como se puede observar en la Figura 2.8.

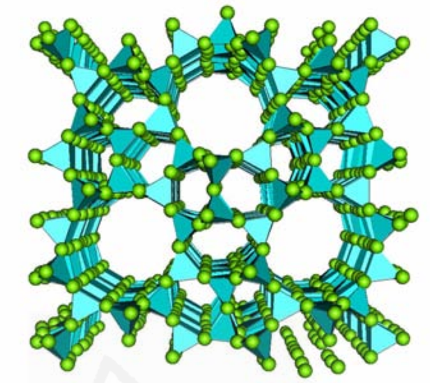


Figura 2.8.- Estructura y dimensiones de los poros de la zeolita HZSM-5.

Dada su alta acidez y selectividad suele emplearse en multitud de procesos. Estas propiedades derivan de su tamaño de poro, siendo una de sus aplicaciones más importantes para la obtención de gasolinas sintéticas a partir de metanol.

2.8.2. Zeolita HUSY

La zeolita HY presenta la estructura de la faujasita. Su célula unidad es cúbica, presentando una fracción de volumen hueco de 0,48. La relación Si/Al es de 2,43.

La zeolita ultraestable HUSY se consigue tras tratar con vapor de agua a elevada temperatura y presión la zeolita HY y es un tipo de zeolita que presenta una relación de Si/Al más baja y un tamaño de poro mayor que la zeolita HZSM-5. La estructura de la zeolita HUSY se caracteriza por presentar grandes cavidades (supercages), esencialmente esféricas, constituidas por anillos de 12 átomos de oxígeno, formando un sistema de poros tridimensionales, con un tamaño de poro de 7,4 Å en el plano [111], y una cavidad de 13 Å (ver Figura 2.9).

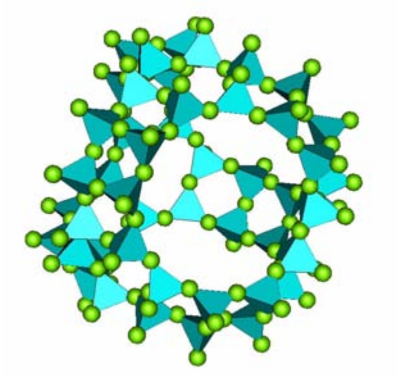


Figura 2.9.- Estructura y dimensiones de los poros de la zeolita HUSY

2.8.3. Zeolita Beta

La zeolita HBeta es un material con un alto contenido en silicio. Fue sintetizada por primera vez por Wadlinger en 1967. Treacy y col. (1988) la describieron como un híbrido entre dos estructuras similares que presentan simetría tetragonal y monoclínica.

Estas dos estructuras están constituidas por anillos de 12 átomos de oxígeno que dan lugar a canales tridimensionales interconectados que presentan tres direcciones cristalográficas; dos morfológicamente idénticas de canales lineales perpendiculares al plano [001] que corren en direcciones diferentes, a y b, y en otra dirección paralela al eje de c, de forma sinusoidal. Los canales sinusoidales presentan aberturas circulares (5,6 Å × 5,6 Å), y los canales rectos tienen aberturas elípticas. La única diferencia entre los dos organismos polimorfos está en la dimensión del poro de los canales rectos. En el sistema tetragonal, los canales rectos tienen aberturas de 6,0 x 7,3 Å (politipo A), mientras que en el sistema monoclínico tiene una abertura de 6,8 x 7,3 Å (politipo B) (Corma y col., 1996). En la Figura 2.10 se puede ver la estructura tridimensional de la zeolita beta así como un ejemplo de los poros en el plano [100] y en el plano [001], y la disposición de los dos politipos A y B.

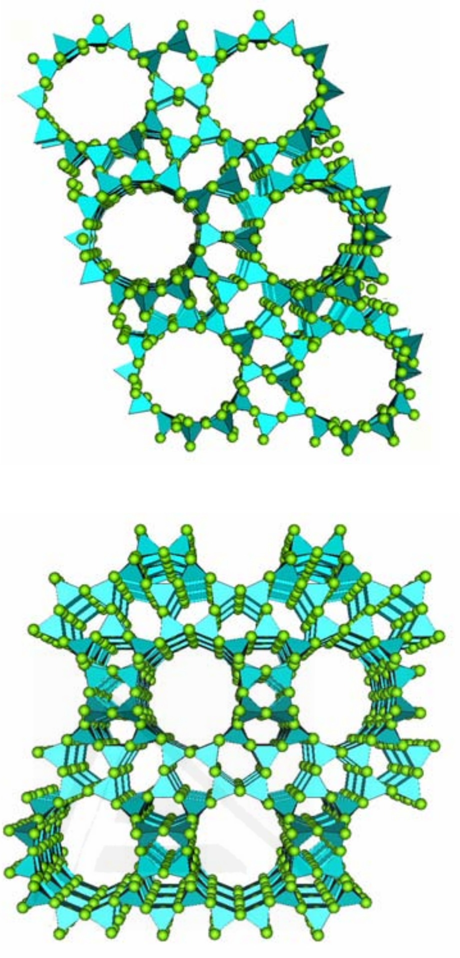


Figura 2.10.- Estructura y politipos de la zeolita HBeta

2.8.4. Material MCM-41

En 1992, investigadores de la empresa Mobil sintetizaron una familia de tamices moleculares mesoporosos, conocidos como M41S, en el cual la mesofase hexagonal (MCM-41) posee canales altamente regulares y cuyo tamaño de poro puede variar dentro de un intervalo que se extiende desde 1,5 hasta 10 nm y que, además, presenta un área superficial grande y una buena estabilidad térmica. Estos materiales suelen tener áreas BET superiores a 1000 m^2/g y un volumen de poro que puede variar entre 0,7-1,2 cm^3/g (Kresge y col., 1992).

Así pues, el material MCM-41 es un aluminosilicato de muy baja cristalinidad, formado por una estructura uniforme de canales hexagonales, cuyo diámetro se puede variar entre 12-100 Å mediante una adecuada selección de las condiciones de síntesis (temperatura, relación Si/Al, etc.). Presenta una estructura porosa unidimensional, sin interconexión entre los poros. En la Figura 2.11 se muestra la forma típica de un poro de MCM-41.

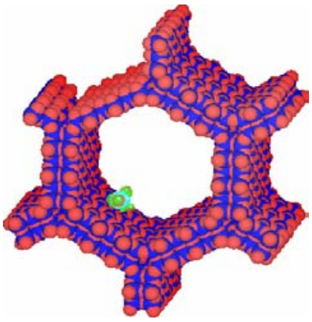


Figura 2.11. Poro hexagonal del material MCM-41

La primera vez que se sintetizó este material se utilizó un medio básico, temperaturas del orden de 150ºC, presiones autogeneradas y tiempos de síntesis del orden de 48 h. Sin embargo, hoy en día se ha conseguido sintetizar en condiciones mucho más suaves: temperatura ambiente, sin presión y en unas pocas horas (Aguado y col., 2000). Según Beck (1992), la fuerza impulsora de la síntesis del MCM-41 es la interacción electroestática entre las micelas cargadas del surfactante promotor de la estructura y las especies aniónicas de silicio y aluminio. Este mecanismo de síntesis es marcadamente diferente al de las zeolitas, donde la construcción ocurre a partir de iones individuales, que se combinan para dar una estructura cristalina. En la Figura 2.12 se presenta un esquema del proceso de obtención del MCM-41.

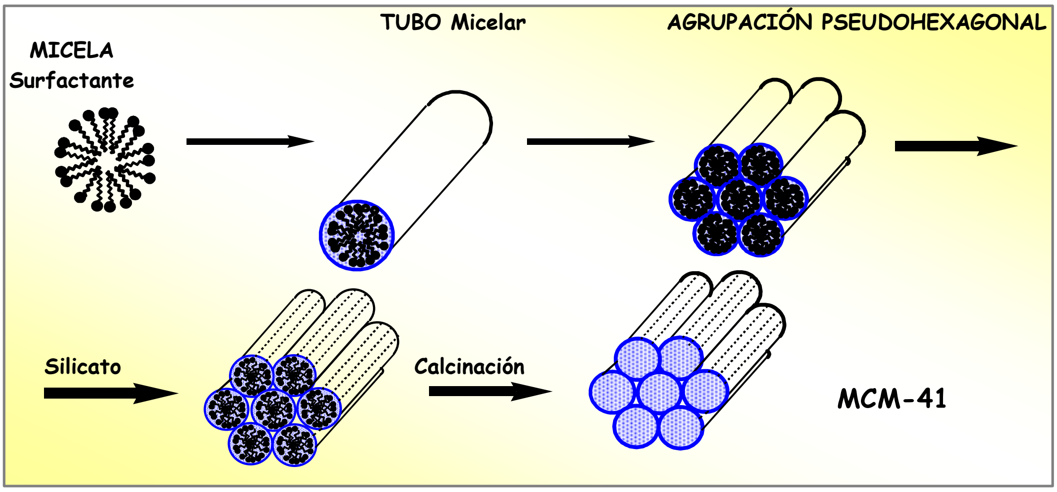


Figura 2.12.- Crecimiento del material MCM-41

La posibilidad de incorporar aluminio en la estructura del MCM-41 provocó un interés considerable, ya que permitía obtener un material con mayores propiedades ácidas que las zeolitas, puesto que se generan centros ácidos, que unido a su carácter mesoporoso, lo convertía en un catalizador sumamente interesante para reacciones que implicasen moléculas voluminosas. Este material puede ser preparado como sílice pura, alumino-silicato o silicato de titanio. Además resulta de interés puesto que se pueden adicionar otros metales, así como variar la cantidad de aluminio que se incorpora a la estructura (Aguado y col., 2000).

Con respecto al aluminio, según Chen y col. (1999) cabe destacar que éste puede ser adicionado post-síntesis cuando a partir de la MCM-41 de sílice pura. La adición de aluminio tras la síntesis mejora algunas de sus propiedades, como son la estabilidad térmica y la acidez, puesto que cuando es sintetizada como sílice pura no presenta centros ácidos de Brönsted, generándose estos cuando se adiciona el aluminio. Una de las formas de añadir el aluminio post-síntesis consiste en poner en contacto el material con una disolución 0,25M de $Al(NO_3)_3$ a 60ºC durante 3 horas. Cuando la adición se hace de esta forma, el material sigue siendo mesoporoso incluso después de incorporar una gran cantidad de aluminio, lo que permite crear diferentes materiales con distintas relaciones Si/Al.

3

OBJETIVOS

El objetivo del presente trabajo, realizado para optar al Grado de Doctor, se centra básicamente en el estudio de la composición de la corriente principal del humo del tabaco y en como la adición de diferentes catalizadores afectan a los componentes presentes en esta. Además se estudian diferentes catalizadores comerciales y uno sintetizado y se realiza una serie de modificaciones al material sintetizado.

El objetivo general se puede estructurar en los siguientes objetivos, correspondientes a las diferentes publicaciones que forman parte del presente trabajo:

- Determinación de la relación entre el contenido de aluminio del catalizador MCM-41y sus propiedades texturales y acidez y establecimiento de la proporción óptima de aluminio contenido en el catalizador MCM-41 para obtener las mayores reducciones en el rendimiento de los principales componentes de la corriente principal del humo del tabaco.

- Estudio del proceso de eliminación del tensioactivo retenido en la estructura del catalizador MCM-41 mediante extracción y/o calcinación y establecimiento de un método (TGA) para evaluar la eficiencia de los diferentes métodos de eliminación del tensioactivo.

- Estudio de la capacidad de cuatro catalizadores de propiedades físico-químicas diferentes para actuar como aditivos para reducir el rendimiento de los compuestos presentes en la corriente principal del humo del tabaco.

- Estudio de las características de diseño y de la composición de la corriente principal del humo del tabaco de marcas comerciales de cigarrillos entre las más vendidas en España.

MATERIALES
Y MÉTODOS

4

4.1.- MATERIALES Y SÍNTESIS DE CATALIZADORES

4.1.1.- Tabacos

El tabaco de referencia utilizado en todos los estudios realizados en el presente trabajo ha sido Fortuna, comprado directamente del estanco. El tabaco Fortuna es una marca de cigarrillos rubios fabricada por Imperial Tobacco Group PLC (conocida anteriormente como Altadis), perteneciente a la compañía británica Imperial Tobacco. Esta marca fue introducida en España en 1974. Se trata de un tabaco compuesto por mezcla americana, que suele llevar un promedio de 0,66 g de tabaco/cigarrillo. La longitud del filtro es de 20,8 mm y la longitud del cigarrillo es de 82,6 mm.

En uno de los artículos que componen el presente trabajo se ha realizado la comparación de diferentes marcas comerciales. Las diez marcas de tabaco rubio utilizadas han sido elegidas entre las doce marcas con mayor número de ventas en España en 2010. Las marcas seleccionadas han sido Malboro, Winston, Fortuna, Chesterfield, Ducados Rubio, Camel, L&M, Nobel, Lucky Strike and John Player. En la Tabla 4.1 se muestra la compañía a la que pertenece cada una de las marcas y el porcentaje total de ventas de cigarrillos que correspondió a cada una de ellas en el año 2010 en España.

Tabla 4.1.- Principales marcas de tabaco consumidas en España

	COMPAÑÍA DE TABACO	***% € EN ESPAÑA***
Marlboro	Philip Morris International	15,78
Fortuna	Imperial Tobacco	9,90
Winston	R.J. Reynolds	10,69
Chesterfield	Philip Morris International	8,80
Camel	R.J. Reynolds	6,20
Ducados Rubio	Imperial Tobacco	5,35
L&M	Philip Morris International	5,69
Nobel	Imperial Tobacco	4,90
Lucky Strike	BAT	5,25
John Player	BAT	2,06

Las principales características de estas diez marcas comerciales se muestran en la Tabla 4.2

Tabla 4.2. Información disponible de las marcas seleccionadas

	COMPAÑÍA DE TABACO	***TIPO DE MEZCLA***	***TABACO POR CIGARRILLO (mg/cigarrillo)***	***LONGITUD DEL FILTRO (mm)***
Malboro	Philip Morris	Mezcla americana	690	21,1
Winston	R.J. Reynolds	Mezcla americana	684	21,2
Fortuna	Imperial Tobacco	Mezcla americana	660	20,8
Chesterfield	Philip Morris	Mezcla americana	677	20,9
Ducados Rubio	Imperial Tobacco		673	20,3
Camel	R.J. Reynolds	Virginia y turco	696	21,1
L&M	Philip Morris	Mezcla americana	698	20,6
Nobel	Imperial Tobacco		605	27,0
Lucky Strike	BAT	Mezcla europea	718	22,6
John Player	BAT	Mezcla americana	605	21,8

4.1.2. Catalizadores

En el presente trabajo se han sintetizado y posteriormente modificado diferentes muestras de Si-MCM-41. También se han realizado estudios con diferentes zeolitas comerciales. En los siguientes apartados se presenta una breve descripción de todas ellas.

4.1.2.1.- Catalizadores sintetizados

En esta sección se describen los métodos de síntesis utilizados para el MCM-41(SMc, M ó MCM-41 según al nomenclatura usada en los artículos incluidos en este trabajo) y las modificaciones llevadas a cabo durante la síntesis y la post-síntesis. Las técnicas de caracterización y las propiedades fisicoquímicas y texturales de los materiales sintetizados y de los catalizadores comerciales empleados se describen en los apartados posteriores.

El método de síntesis utilizado para la obtención del material MCM-41 ha sido el descrito por Gaydhankar y col. (2007). El proceso de síntesis consiste en disolver 2,04 g de CTMACl (cloruro de cetriltrimetilamonio) en 114 mL de agua destilada con agitación continua a temperatura ambiente. A esta disolución se añaden 16,33 g de amoniaco y se agita durante 10 minutos. Finalmente, se añaden 7,0 g de TEOS (ortosilicato de tetraetilo). La disolución formada se agita durante 4 h. Pasado este tiempo, el sólido formado se filtra, se lava con agua destilada y se seca en una estufa a 373 K, durante al menos 4 h, obteniendo el material denominado SM en las publicaciones incluidas en este trabajo. La eliminación del tensioactivo tiene lugar durante la etapa de calcinación del sólido en aire a 813 K, durante un periodo de 6 h. El material obtenido se denomina **MCM-41** (SMc o M en las diferentes publicaciones incluidas en este trabajo). Todas las modificaciones en la síntesis y las variaciones en los procesos posteriores que se describen a continuación se han hecho siempre, antes de llevar a cabo el proceso de calcinación, sobre el material **SM**.

El material obtenido por el procedimiento descrito no posee aluminio, por lo que tal y como describen Chen y col. (1999) este puede adicionarse a la estructura en un proceso post-síntesis. La adición del aluminio tiene lugar mediante intercambio iónico y consiste en añadir 4,69 g de $Al(NO_3)_3.9H_2O$ y 50 g de agua por gramo de SMc (Disolución ≅ 0,25 M de $Al(NO_3)_3.9H_2O$). Dicha disolución se introduce en un baño a 60ºC y se agita durante 3 horas. A continuación el sólido se filtra y se lava con agua destilada para posteriormente secarlo a 100ºC durante 12 horas. El material obtenido de esta manera se ha designado como Al-MCM-41 (también llamado Al-SMc o AM según la publicación considerada).

MODIFICACIONES

- ESTUDIO DE LA CONCENTRACIÓN DE ALUMINIO

El proceso de aluminización post-síntesis permite la adición de aluminio en grandes cantidades sin que el material pierda la estructura mesoporosa, sin mas que modificar la concentración de la disolución de $Al(NO_3)_3$ utilizada en el intercambio. Las concentraciones utilizadas han sido 0,5M (obteniendo el material 2AM), y 2M (obteniendo el material 4AM). El material AM (también llamado Al-SMc) será considerado como referencia.

Tabla 4.3. Materiales sintetizados

MATERIAL	***CONCENTRACIÓN DE LA DISOLUCIÓN DE ALUMINIO(M)***
AM	0,25 M
2AM	0,50 M
4AM	2M

- ELIMINACIÓN DEL TENSIOACTIVO

Tal y como se ha puesto de manifiesto en la descripción de la síntesis del MCM-41, en la última etapa del proceso de síntesis es necesario calcinar el material para eliminar el tensioactivo que ha quedado retenido en los poros, por tratamiento con aire a 873 K durante un período de 6 h. La utilización de altas temperaturas favorece la eliminación del tensioactivo, aunque se debe tener cuidado de que la estructura del material no sea destruida (Souza y col. 2004).

Sin embargo, otra posibilidad que también se ha estudiado es la extracción del tensioactivo con disolventes, seguida de una etapa de calcinación. Se trata de una buena alternativa, no sólo porque es una técnica que contamina menos, puesto que disminuye los gases que se generan durante el proceso de calcinación, sino porque también permite que una parte del tensioactivo pueda ser reciclado. Además, la estructura mesoporosa se mantiene después del tratamiento. Puesto que el tensioactivo no es eliminado por completo en el proceso de extracción, el paso de la calcinación sigue siendo necesario.

Se han empleado las técnicas de extracción del tensioactivo descritas por Hua y col. (2001) y Xiao y col. (2006), que utilizan diferentes agentes de extracción:

Extracción del tensioactivo con HCl/etanol (Hua y col., 2001):

Se pone en contacto el material MCM-41 sin calcinar (SM) con una disolución 1M de HCl/EtOH. Los lavados se llevan a cabo por etapas. Se han comparado los resultados obtenidos en las siguientes condiciones:

1.- contacto de 1 g de material SM con 20 g de HCl 1M en etanol durante 1 h a 70ºC. Se llevan a cabo 3 lavados consecutivos, renovando el disolvente en cada una de las etapas. El material obtenido se ha designado como SMEC20-3.

2.- contacto de 1 g de SM con 10 g de HCl 1M en etanol durante 15 min a 70ºC. Se lleva a cabo una extracción en 5 etapas, renovando el disolvente cada vez. El material obtenido se ha designado como SMEC10-5.

Extracción con H_2O_2 (Xiao y col. 2006):

3.- El extractante utilizado en el lavado es una disolución acuosa de H_2O_2 al 2% en peso. El lavado se hace por etapas, poniendo en contacto 0,5 g de material con 50 g H_2O_2 durante 1 h a temperatura ambiente. El pH de la disolución debe ajustarse a

3,5 utilizando HCl. Se realizan 5 lavados consecutivos, renovando el disolvente tras cada lavado. El material final obtenido se designa como SMPO-5.

Una vez extraído el tensioactivo, mediante alguno de los procesos descritos anteriormente, el material resultante se calcina a 873 K durante 6 horas.

A continuación se incorpora el aluminio según el procedimiento descrito por Chen y col. (1999) por intercambio iónico con $Al(NO_3)_3$ en disolución acuosa, tal y como se ha expuesto con anterioridad.

La nomenclatura de los materiales finales obtenidos tras los lavados y la calcinación, se muestra en la tabla siguiente:

Tabla 4.4.- Nomenclatura de los materiales obtenidos

MATERIAL	***MÉTODO DE ELIMINACIÓN DE TENSIOACTIVO***
Al-SMc	*Calcinación*
Al-SMEC-20-3c	*Lavado 1+Calcinación*
Al-SMEC-10-5c	*Lavado 2+Calcinación*
Al-SMPO-5c	*Lavado 3+Calcinación*

4.1.2.2. Zeolitas comerciales

Además de los materiales sintetizados y modificados según los procedimientos descritos en la sección anterior, se han empleado varios catalizadores comerciales: zeolitas HUSY y HZSM-5, que fueron suministradas por Grace Davison y zeolita HBeta, suministrada por Süd-Chemie Inc. (HBeta 25).

4.1.3.- Reactivos para síntesis, disolventes y patrones utilizados en el análisis del humo

Para llevar a cabo la síntesis de MCM-41 se han utilizado los reactivos comerciales que se muestran en la tabla 4.5.

Tabla 4.5. Reactivos empleados para la síntesis de los materiales Si-MCM-41

MATERIAL	CARACTERÍSTICAS	CASA COMERCIAL
Ortosilicato de Tetraetilo	Líquido, pureza min 99%	Merck
Nitrato de aluminio	Polvo, pureza 98%	VWR
Cloruro de Hexadecitrimetilamonio	Disolución 25%w	Kao Corporation, S.A.
Amoniaco	Disolución 25% w	Merck

Para la extracción de los líquidos condensados se ha hecho uso de un disolvente orgánico, en este caso el 2-Propanol. Se han utilizado dos marcas diferentes, 2-Propanol para análisis EMSURE® ACS, ISO, Reag.Ph.Eur. Merck. y 2-Propanol LC-MS CHROMASOLV®, ≥99.9%. Fluka

Para llevar a cabo la cuantificación de los diferentes compuestos analizados, tanto en la corriente gaseosa, como en los líquidos condensados, es necesaria la utilización de patrones para calcular los factores de respuesta, valores que posteriormente permitirán la cuantificación de los diferentes compuestos o familias de compuestos.

Los patrones utilizados para la cuantificación de la corriente gaseosa han sido:

C_1-C_6 (Referencia 501816) Análisis estándar de parafinas, concentración 1000 ppm de cada componente en helio (aerosol de 4 L), proporcionado por Supelco (Sigma Aldrich).

Monóxido de carbono, dióxido de carbono, hidrógeno, metano y oxígeno, (Referencia 501970) 1% (w/w) de cada componente en Nitrógeno (aerosol de 4 L), proporcionado por Supelco (Sigma Aldrich).

Butanos, butenos y butinos (Referencia 22567), 15 ppm de cada componente en Nitrógeno (aerosol de 4 L), proporcionado por Supelco (Sigma Aldrich).

Monóxido de carbono, dióxido de carbono, metano, etano, etileno y acetileno (Referencia 501662) 1% (w/w) de cada componente en Nitrógeno (aerosol de 4 L), proporcionado por Supelco (Sigma Aldrich).

Otros compuestos empleados como patrones para identificar y cuantificar los gases generados por el humo del tabaco han sido:

Benceno AnalaR NORMAPUR para análisis botella de vidrio 1L , Min. 99,7 % (VWR BDH Prolabo (BDH Prolabo))

Acetonitrilo LC-MS CHROMASOLV®, ≥99.9%. Fluka

Acetaldehído pureza ≥ 99.0% (GC). Fluka

Tolueno para análisis EMSURE® ACS, ISO,Reag. Ph Eur 1L purísimo (Merck)

Acetona para análisis EMSURE® ACS, ISO, Reag.Ph.Eur. Merck

Furano pureza ≥ 99% (Aldrich)

Para la cuantificación de la nicotina y otros líquidos condensados se ha utilizado un patrón de nicotina:

(-)-Nicotina para síntesis 1 * 100 ml. Merck

4.2.- EQUIPOS Y TÉCNICAS DE CARACTERIZACIÓN DE CATALIZADORES

Para determinar las propiedades fisicoquímicas y estructurales, de los diferentes materiales sintetizados, y posteriormente modificados, así como de las zeolitas comerciales empleadas se utilizaron las siguientes técnicas:

- Isotermas de adsorción de Nitrógeno

- Fluorescencia de rayos X

- Desorción térmica programada de amoníaco

- Difracción de rayos X

- Resonancia magnética nuclear

- Ensayos de termogravimetría (TGA)

- Estudio de estabilidad hidrotérmica

4.2.1. Isotermas de adsorción de Nitrógeno

La adsorción de nitrógeno es muy utilizada para la caracterización de la textura porosa de sólidos y permite determinar el área superficial (o superficie específica), el volumen y la distribución de tamaño de poro.

Para la determinación de estos parámetros se puede recurrir, entre otros, a la adsorción de un gas (N_2, CO_2, hidrocarburos, etc.) a temperatura constante (para N_2 77K, para CO_2 273K, etc.), obteniéndose así la isoterma de adsorción. Dicha isoterma puede determinarse gravimétricamente (se mide la ganancia de peso experimentada por la muestra, como consecuencia de la adsorción, a cada presión relativa de gas) y/o volumétricamente.

En las isotermas de adsorción se representa la cantidad de nitrógeno adsorbido, V, frente a la presión relativa, P/P_0, siendo P la presión del nitrógeno y P_0 la presión de saturación del nitrógeno a la temperatura a la que se obtiene la isoterma.

Tras la determinación de la isoterma de adsorción, es posible calcular algunos parámetros, entre los que se destacan:

- el cálculo del tamaño de poro mediante el método BJH (Barret y col., 1951)

- el cálculo del área BET (Brunauer y col., 1938), usando el método BET

- el cálculo del área externa, mediante el método t (Marcilla y col., 2006).

- el volumen de poro, a partir de la adsorción de N_2 a P/P_0=0,995

Para el análisis se ha utilizado un equipo volumétrico automático de adsorción física de gases AUTOSORB-6 y desgasificador AUTOSORB DEGASSER, ambos de la marca Quantachrome. Los gases disponibles son N_2 y CO_2, por lo que es posible realizar adsorciones de N_2 a 77K y CO_2 a 273K. El equipo está indicado para la caracterización de la textura porosa (área superficial y porosidad) de muestras sólidas.

En la Figura 4.1 se muestra, a título de ejemplo, la isoterma de adsorción obtenida para el catalizador Al-MCM41:

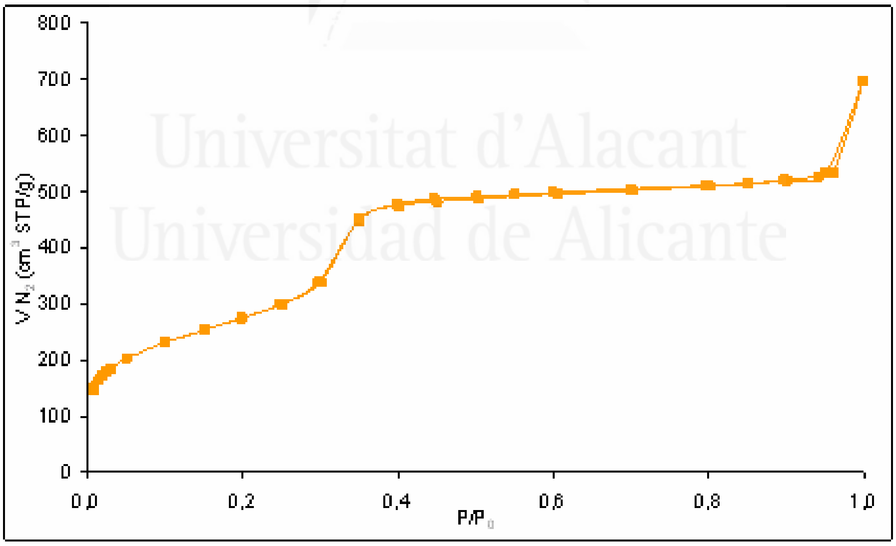


Figura 4.1.- Isoterma de adsorción de N_2 para la Al-MCM-41.

4.2.2. Fluorescencia de Rayos X

La fluorescencia de rayos X (FRX) se basa en la emisión secundaria o fluorescente de radiación X que se produce al excitar una muestra con una fuente de radiación X. La radiación X incidente o primaria expulsa electrones de capas interiores del átomo, provocando que los electrones de capas más externas ocupen los lugares vacantes, y el exceso energético resultante de esta transición se disipe en forma de fotones, radiación X fluorescente o secundaria. La energía disipada presentará una longitud de onda característica que dependerá del gradiente energético entre los orbitales electrónicos implicados y una intensidad directamente relacionada con la concentración del elemento en la muestra.

La FRX se utiliza principalmente en el análisis químico elemental, tanto cualitativo como cuantitativo, de los elementos comprendidos entre el fluor (F) y el uranio (U) de muestras sólidas y líquidas. En este estudio se ha empleado FRX para establecer la relación Si/Al de los catalizadores empleados. El equipo utilizado es un espectrómetro PHILIPS MAGIX PRO dotado de software analítico SuperQ.

4.2.3. Desorción térmica programada de amoniaco

La desorción térmica programada (DTP) de amoniaco se utiliza para la determinación de la acidez de materiales sólidos ácidos. Esta técnica consiste en el tratamiento del material con una corriente de amoniaco que se adsorbe en los centros ácidos accesibles, sometiendo posteriormente al material a un programa de calefacción controlada. La desorción del amoniaco que se produce al calentar la muestra tiene lugar a mayor o menor temperatura en función de la fuerza ácida de los centros sobre los que ha sido adsorbido. La selección del amoniaco como adsorbato se debe a sus características básicas, que permiten su adsorción en prácticamente todos los centros ácidos, aun siendo débiles, y a su reducido tamaño, que le permite alcanzar los centros del interior de los poros de gran multitud de materiales, como zeolitas o sólidos mesoporosos. Los catalizadores analizados deben encontrarse en su forma ácida.

El proceso de DTP de amoníaco consta de 4 etapas:

- Desgasificación, para eliminar todas las sustancias que pueda haber presentes en sus centros ácidos.
- Adsorción de amoniaco.
- Desorción del gas fisisorbido, con ayuda de un gas inerte.

- Desorción térmica programada o DTP, proceso en el cual mediante un programa de temperatura y un gas inerte, se produce el fenómeno de deserción del amoniaco adsorbido en los centros ácidos del material.

El equipo utilizado para llevar a cabo la desorción térmica programada de amoniaco es una termobalanza Netzsch TG 209. Las condiciones utilizadas en el programa de DTP se describen a continuación:

Desgasificación:

Caudal de 45 mL/min de N_2.

Rampa de calentamiento de 20ºC a 500ºC a 10 ºC/min.

Isoterma a 500ºC durante 30 min.

Enfriamiento hasta 100ºC a una velocidad de 10ºC/min.

Tratamiento con NH_3*:*

Caudal de 35 mL/min de NH_3.

Isoterma a 100ºC durante 30 min.

Fisidesorción de NH_3*:*

Caudal de 45 mL/min de N_2.

Desorción: isoterma a 100ºC durante 60 min.

Desorción térmica programada de amoniaco:

Caudal de 45 mL/min de N_2.

Calentamiento de 100ºC a 900ºC a una velocidad de 10ºC/min.

La acidez del material, expresada en milimoles de amoniaco por gramo de sólido ácido, se calcula mediante la expresión siguiente:

$$Acidez = \frac{PM}{100} * \frac{1}{PM\ \mathrm{NH}_3} * \frac{1000 mmol}{1 mol} = mmol / g$$

siendo "PM" la perdida de masa registrada por la termobalanza, en porcentaje, en la etapa de desorción térmica programada de amoniaco (DTP). La curva de TGA y su derivada, DTG, obtenidas durante la DTP permiten, además, obtener más información sobre la acidez del material. Si el material estudiado presenta diferentes tipos de centros ácidos, la curva DTG presentará diferentes picos de desorción. La temperatura correspondiente al máximo de desorción de cada pico se encuentra estrechamente relacionada con la fuerza ácida de los centros y se considera habitualmente como una medida directa de dicha fuerza con fines comparativos. Esta técnica, no obstante, presenta la limitación de no poder diferenciar entre lo centros ácidos de Brönsted y los de Lewis. En la figura 4.2, se representan las curvas de TG y DTG obtenidas para uno de los catalizadores comerciales.

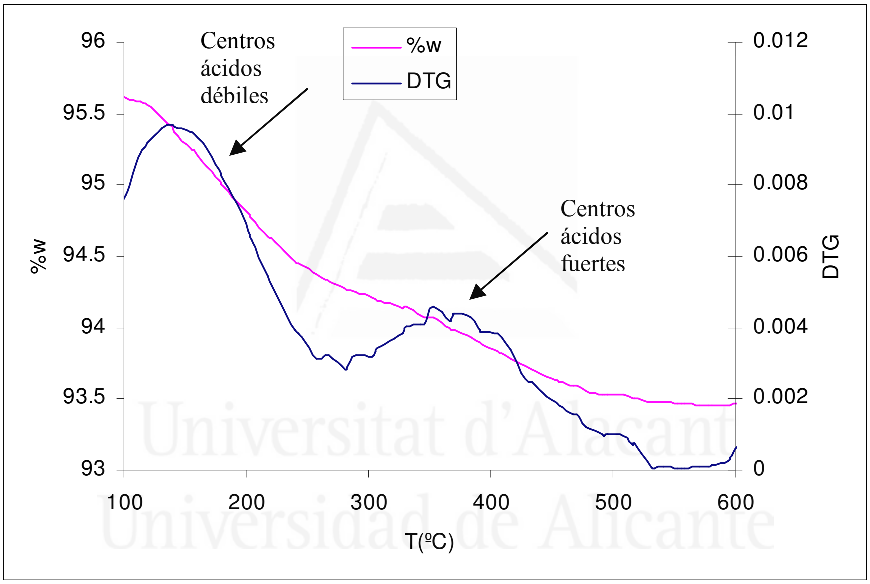


Figura 4.2.- Curvas de pérdidas de peso y DTG obtenidas a partir de la DTP de NH_3 para la zeolita HZSM-5

4.2.4 Difracción de rayos X (DRX)

La difracción es un fenómeno característico de las ondas, que consiste en su dispersión cuando interaccionan con un objeto ordenado. Ocurre en todo tipo de ondas, desde las sonoras, hasta las ondas electromagnéticas como la luz, y también los rayos X. Los rayos X tienen longitudes de onda similares a las distancias interatómicas en los materiales cristalinos, por lo que podemos utilizar la difracción de rayos X como método para explorar la naturaleza de la estructura molecular.

Cuando un haz de rayos X incide en un material sólido, parte de este haz se dispersa en todas direcciones a causa de los electrones asociados a los átomos o iones que encuentra en el trayecto, pero el resto del haz puede dar lugar al fenómeno de difracción, que tiene lugar si existe una disposición ordenada de átomos y si se cumplen las condiciones que vienen dadas por la **Ley de Bragg** que relaciona la longitud de onda de los rayos X y la distancia interatómica (d) con el ángulo de incidencia del haz difractado (θ), **$n\lambda = 2d \cdot sen\theta$**. Si no se cumple la ley de Bragg, la interferencia es de naturaleza no constructiva y el campo del haz difractado es de muy baja intensidad.

La difracción de rayos X se utiliza principalmente para la identificación cualitativa de la composición mineralógica de muestras cristalinas, aunque también permite la identificación de compuestos sólidos cristalinos, tamaño de cristales, cambios de fase y cristalinidad. Esta técnica se puede utilizar para compuestos sólidos cristalinos, además de para una amplia gama de materiales, incluso fluidos, metales, minerales, polímeros, catalizadores, plásticos, productos farmacéuticos, recubrimientos de capa fina, cerámicas y semiconductores.

En el presente trabajo se ha utilizado la DRX para caracterizar los materiales que se han sintetizado y posteriormente han sido utilizados como aditivos del tabaco. Se ha utilizado un equipo Bruker D8-Advance con espejo Göebel (muestras no planas) con cámara de alta temperatura (hasta 900ºC), que dispone de un generador de Rayos-X KRISTALLOFLEX K 760-80F (Potencia: 3000W, Tensión: 20-60KV y Corriente: 5-80mA) y un Seifert modelo JSO-DEBYEFLEX 2002 que está provisto de un cátodo de cobre y un filtro de níquel.

4.2.5.- Resonancia magnética nuclear de Al^{27} y Si^{29} (RMN)

La resonancia magnética nuclear (RMN) es una técnica que fue descubierta durante los años 30 por Isidor Isaac Rabi y su grupo de investigación de la Universidad de Columbia. Estos desarrollaron la resonancia magnética nuclear de haces moleculares como técnica para estudiar las propiedades magnéticas y la estructura interna de las moléculas, los átomos y los núcleos.

Esta técnica se basa en la absorción de energía de una frecuencia determinada, en un intervalo de radiofrecuencias asociada a los cambios de orientación del spin nuclear en presencia de un campo magnético fuerte. Esta interacción se ve influenciada por los núcleos vecinos, por lo que esta técnica permite obtener información sobre la estructura y geometría de la molécula.

La resonancia magnética nuclear utiliza propiedades fundamentales de los núcleos atómicos como son los momentos magnéticos. Cuando se colocan en un campo magnético externo potente, la dirección del momento magnético oscila o cambia según la dirección del campo, con una frecuencia proporcional a la fuerza del campo externo. La resonancia magnética se produce cuando la fuerza del campo magnético se manipula hasta que la frecuencia de la partícula coincide con la de la frecuencia aplicada. Esto hace que el momento magnético de la partícula cambie de orientación en relación al campo magnético externo, dando lugar a una señal detectable que revela la estructura interna y la actividad de la especie que genera la señal.

Para el caso de zeolitas (silicatos y alumino-silicatos) y de zeotipos (alumino-fosfatos y silicoalumino-fosfatos), la RMN de Al^{27} y Si^{29} da información sobre el entorno local de los átomos en la red. Esta información complementa los datos de difracción de rayos X y permite la elucidación estructural de nuevos materiales.

En el presente trabajo se ha utilizado un espectrómetro de RMN de Transformada de Fourier de la marca Bruker modelo AC-300. En el equipo, el imán es una bobina superconductora que produce 300 MHz. En la Figura 4.3 se muestra a modo de ejemplo un espectro típico de Al^{27} de una zeolita HZSM-5. Como puede verse, presenta dos picos, resultado de los dos entornos en que puede encontrarse el Al en la estructura de la zeolita, tetraédrico y octaédrico. En general, el aluminio hexacoordinado presenta un pico alrededor de 0 ppm, mientras que el aluminio tetraédrico aparece a unas 54 ppm (Corma y col., 2000).

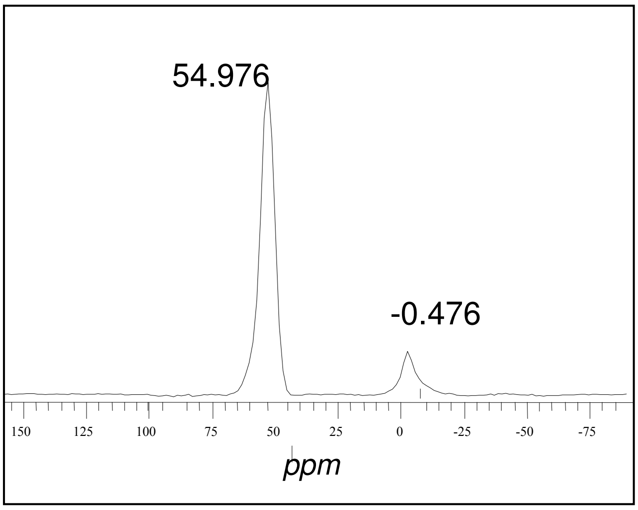


Figura 4.3. RMN Al^{27} de HZSM-5

4.2.6. Análisis termogravimétrico

La termogravimetría (TGA) consiste en la medida de la variación de la masa de una muestra, ya sea pérdida o ganancia de masa, en una atmósfera controlada, en función de un programa de temperaturas. Esta técnica es ampliamente utilizada en estudios de descomposición y estabilidad térmica, composición, contenido en humedad, materia volátil, cenizas y estudios cinéticos.

El equipo utilizado en este trabajo ha sido una Termobalanza Netzsch, modelo TG 209. La balanza y el termopar fueron calibrados siguiendo las instrucciones del fabricante, y las condiciones experimentales fueron controladas mediante un ordenador que opera bajo entorno Windows. Se trabajó en una atmósfera de oxígeno y con un caudal de 0,5 cm^3 STP s^{-1}. El programa de temperatura utilizado fue de 25 a 550ºC, con una rampa de calefacción de 10ºC/min. En el portamuestras se colocaron aproximademente 8 mg de muestra para cada uno de los materiales estudiados.

4.2.7. Tratamiento hidrotérmico

El estudio de estabilidad hidrotérmica de algunos de los materiales sintetizados se ha llevado a cabo tratando el material con agua a 100ºC durante 4 días a reflujo. Los cambios estructurales después del tratamiento fueron analizados mediante la isoterma de adsorción de nitrógeno a 77K, para posteriormente comparar el material inicial con el tratado a reflujo con agua a 100ºC.

4.3. CARACTERIZACIÓN DE CATALIZADORES

A continuación se muestra la caracterización de los catalizadores utilizados en cada caso, resultante de la aplicación de las técnicas anteriormente descritas en el apartado 4.2.

En la Tabla 4.6 se muestran los resultados obtenidos mediante adsorción de nitrógeno, FRX y desorción térmica programada de amoniaco de las muestras empleadas en el estudio del efecto de la concentración de aluminio del material MCM-41 sobre su actividad catalítica en los procesos de pirólisis y combustión del tabaco.

Tabla 4.6.- Características de los materiales sintetizados en este trabajo

MATERIAL	***BET(m^2/g)***	***VOLUMEN TOTAL DE POROS (cm^3/g)***	***TAMAÑO DE PORO (Å), BJH***	***ACIDEZ (mmol/g)***	***Si/Al***
SMc o M	964	0,78	29	0,10	157
Al-SMc o AM	923	0,74	29	0,26	119
2AM	869	0,69	27	0,28	48
4AM	877	0,74	27	0,35	23

En la Tabla 4.7 se muestran los resultados correspondientes a los materiales utilizados en el estudio de la actividad del MCM-41 obtenido tras la eliminación del tensioactivo mediante extracción con disolventes, tras su caracterización mediante adsorción de nitrógeno y desorción térmica programada de amoniaco.

Tabla 4.7.- Características de los materiales modificados en este trabajo

MATERIAL	***BET(m^2/g)***	***VOLUMEN TOTAL DE POROS (cm^3/g)***	***TAMAÑO DE PORO (Å), BJH***	***ACIDEZ (mmol/g)***
Al-SMc	1007	0,825	27,3	0,31
Al-SMEC-20-3c	849	0,610	24,5	--
Al-SMEC-10-5c	835	0,707	27,3	0,20
Al-SMPO-5c	916	0,768	27,4	0,30

Hay que hacer notar que los materiales Al-SMc que figuran en las Tablas 4.6 y 4.7 se obtienen en etapas de síntesis diferentes y, por tanto, sus parámetros estructurales no coinciden exactamente. Estos resultados demuestran la importancia de llevar a cabo la caracterización de todos los materiales sintetizados.

Los materiales obtenidos tras la eliminación del tensioactivo por extracción con disolventes fueron sometidos a un estudio de estabilidad hidrotérmica. Las variaciones producidas en las propiedades texturales tras dicho estudio se analizaron a través de sus respectivas isotermas de adsorción de nitrógeno. Los resultados obtenidos se muestran en la tabla 4.8.

Tabla 4.8.- Características de los materiales modificados en este trabajo tras el estudio de estabilidad realizado

MATERIAL	***BET(m^2/g)***	***VOLUMEN TOTAL DE POROS (cm^3/g)***	***TAMAÑO DE PORO (Å), BJH***
Al-SMc-s	935	0,744	24,6
Al-SMEC-20-3c-s	222	0,341	24,3
Al-SMEC-10-5c-s	778	0,684	24,5
Al-SMPO-5c-s	823	0,671	24,5

Los resultados obtenidos para la caracterización de las tres zeolitas comerciales utilizadas en el presente trabajo se muestran en la tabla 4.9. Las técnicas de caracterización utilizadas han sido adsorción de nitrógeno, FRX y desorción térmica programada de amoniaco.

Tabla 4.9.- Características de las zeolitas comerciales utilizadas

MATERIAL	***BET(m^2/g)***	***VOLUMEN TOTAL DE POROS (cm^3/g)***	***TAMAÑO DE PORO (Å), BJH***	***ACIDEZ (mmol/g)***	***Si/Al***
HUSY	624,5	0,32	7,4	2,1	4,8
HZSM-5	330,4	0,18	0,51x0,55	2,0	22
H-Beta	519,2	0,17	0,66x0,67 0,56x0,56	2,1	25

El análisis de los resultados correspondientes a la caracterización de materiales se presenta en el apartado de discusión de resultados.

4.4.- MÁQUINA DE FUMAR Y REALIZACIÓN DE LOS EXPERIMENTOS

4.4.1.- Diseño de la máquina

Los experimentos de fumado se llevan a cabo en máquinas de fumar ideadas para realizar los experimentos de manera precisa, reproducible y automática.

Por este motivo, se ha construido en el departamento de Ingeniería Química una máquina de fumar diseñada para trabajar en las condiciones establecidas en la norma ISO 3308 que se detallan en la sección 4.4.2 de esta memoria. Dicha máquina de fumar consta de cinco puertos paralelos, donde se colocan cinco cigarrillos. La conexión cigarrillo-puerto se realiza mediante unos tubos de vidrio donde se colocan las trampas de humo que retienen la materia particulada para su posterior análisis. Tras cada una de las trampas hay una válvula de 2 vías donde se conectan unas jeringuillas de 50mL (6% Luer, Marca Terumo) y una bolsa Tedlar de recogida de gases de 2L de capacidad (bolsa recomendada por la EPA (Agencia de Protección Ambiental), de la casa Supelco y proporcionada por Sigma Aldrich. Las jeringuillas están unidas a un émbolo que es actuado por aire a presión (2 bar). Durante una calada retrocede el émbolo y se realiza la aspiración del humo que queda recogido en las jeringuillas, tras lo cual cambia la posición de las válvulas y el émbolo avanza de modo que el humo es enviado a la bolsa de recogida de gases.

En la Figura 4.4 se puede observar una fotografía que muestra una vista frontal de la máquina de fumar y en la Figura 4.5 se muestra la parte posterior.

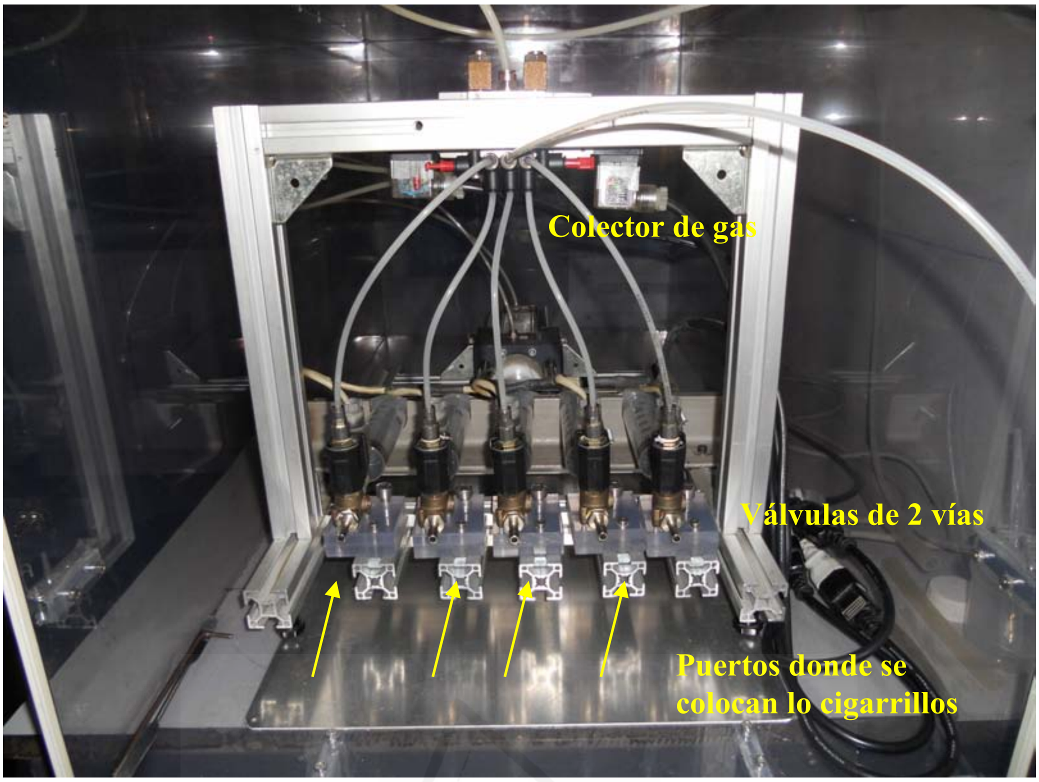


Figura 4.4.- Vista frontal de la máquina de fumar.

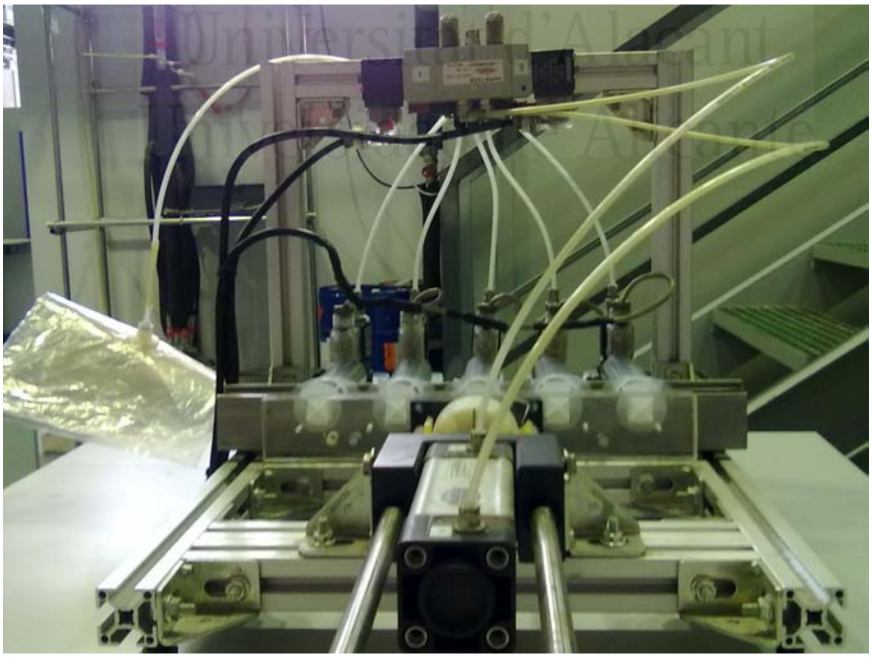


Figura 4.5.- Vista posterior de la máquina de fumar.

En la Figura 4.6 se muestra la bolsa Tedlar de recogida de gases, así como el sistema de apertura-cierre que llevan este tipo de bolsas.

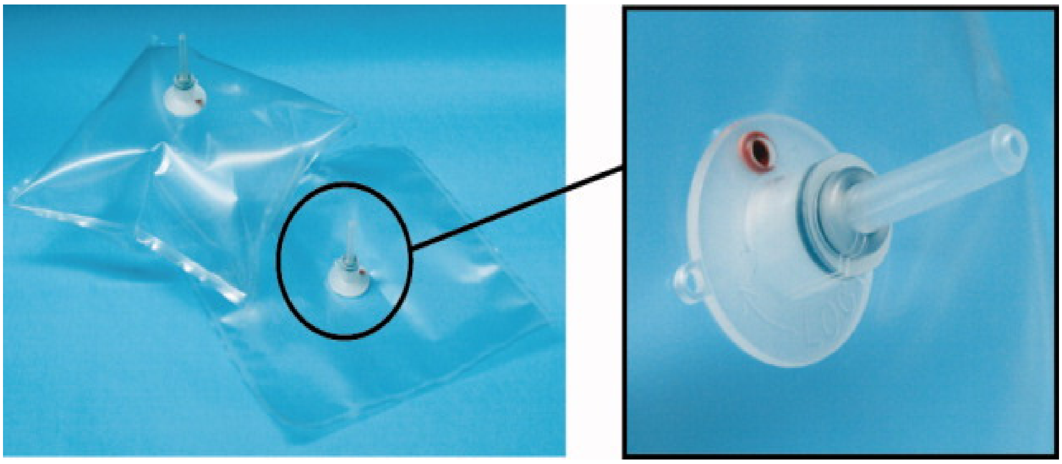


Figura 4.6.- Bolsa Tedlar de recogida de gases. Ampliación del sistema de apertura y cierre de la bolsa.

Un controlador conectado a la máquina, se encarga de controlar el tiempo entre caladas y el número de caladas que va a realizar la máquina en un experimento. La presión del aire de aspiración se fija en 2 bar, porque de esta forma se consigue el valor determinado por la norma ISO 3308 para el tiempo de calada, $2{,}00 \pm 0{,}02$ s. En la Figura 4.7 se muestra el controlador del proceso.

Figura 4.7.- Controlador del tiempo entre caladas y número de caladas.

El volumen de calada se consigue colocando un tope al pistón de aspiración de la máquina. El volumen total aspirado es proporcional al número de cigarrillos fumados y al número de caladas realizadas durante el experimento. En las Figuras 4.8, 4.9 y 4.10 se muestran tres fotografías de la máquina de fumar durante la realización de un experimento, donde se puede observar el pistón y las jeringuillas durante la aspiración del humo (Fig 4.8) y tras el vaciado de las jeringuillas (Fig 4.9).

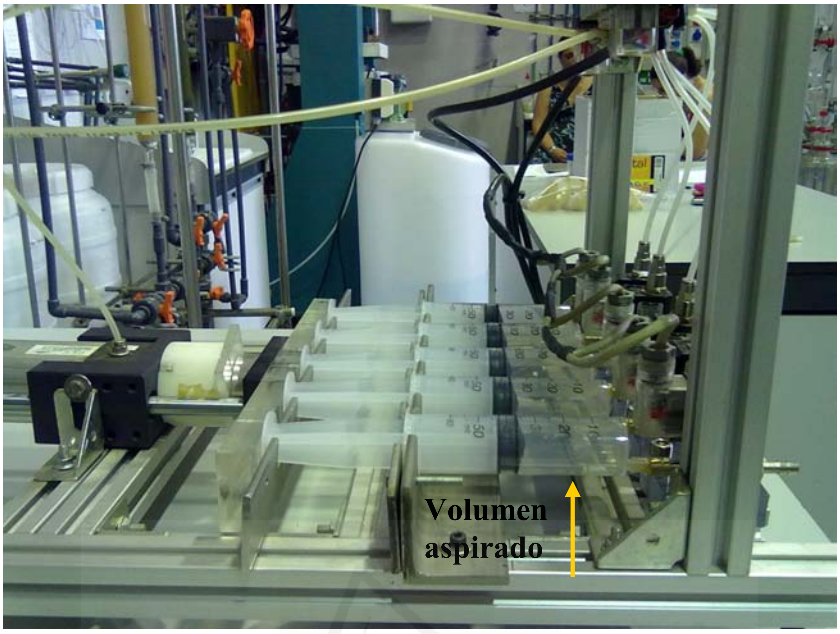


Figura 4.8.- Vista lateral de la máquina de fumar, en posición de aspiración, cuando toma la calada

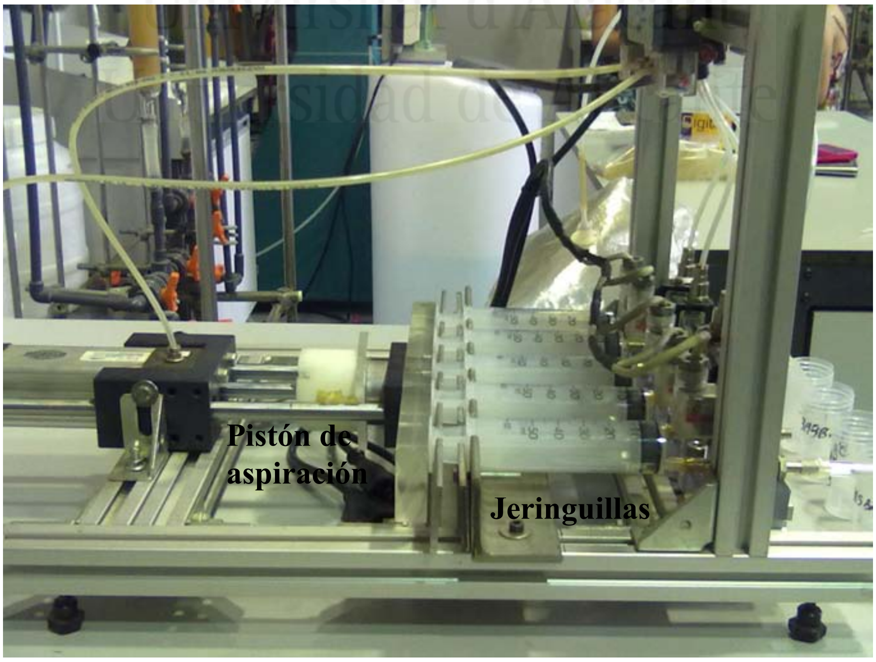


Figura 4.9.- Vista lateral de la máquina de fumar, en posición de reposo, o bien tras vaciado de la calada

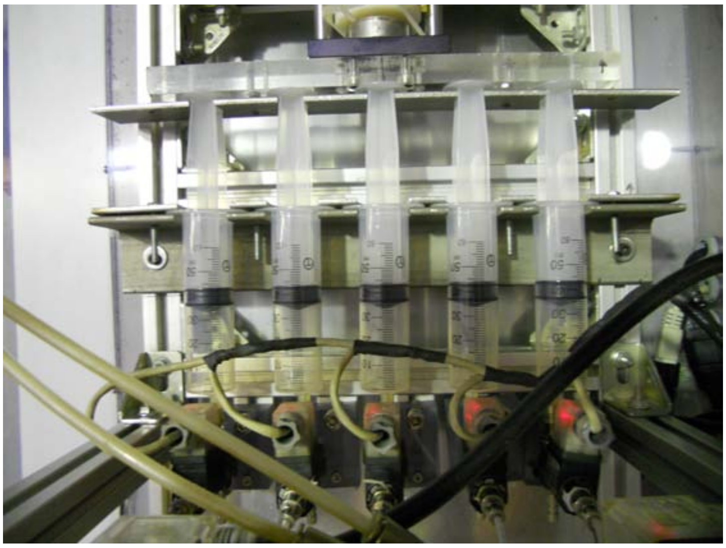


Figura 4.10.- Vista superior de la Máquina de fumar, en posición de aspiración.

4.4.2.- Condiciones de fumado

El régimen de fumado que establece la norma ISO 3308 es el siguiente:

1.- Duración de la calada: $2{,}00 \pm 0{,}02$ s.

2.- Volumen de calada: $35{,}0 \pm 0{,}3$ mL.

3.- Frecuencia de caladas: $60 \pm 0{,}5$ s.

4.- Pérdida de presión en la máquina: no debe exceder en ningún caso de 300Pa.

El número de caladas se estableció en 8 caladas para todos los experimentos. En este punto la norma ISO 4387 establece que las dimensiones de la colilla una vez acabado el experimento de fumado debe ser de 23 mm, la longitud del filtro + 8 mm o la longitud de la envoltura + 3 mm. Sin embargo se decidió fijar el número de caladas en todos los experimentos dado que las dimensiones y contenido de tabaco de todos los cigarrillos empleados era muy similar.

En cuanto al tipo de trampas de humo que se emplean para recoger los productos condensables de la corriente principal del humo del tabaco, la norma ISO 3308 establece que deben ser de fibra de vidrio, en caso de fumar cinco cigarrillos tener un diámetro de 44 mm, y retener al menos el 99.9% de las partículas de tamaño mayor o igual a 0.3 μm. En este estudio a modo de trampa de humo se emplearon 3 filtros consecutivos de acetato similares a los empleados en los cigarrillos (marca OCB regular filtres, los filtros son de 7 mm y masa media de 0,07g). Se añadió un cuarto filtro delante de la bolsa de recogida de gases y se comprobó mediante pesada que este filtro permaneció limpio tras la realización del experimento.

Para asegurarse que los agujeros de ventilación no se bloquean, se introdujeron los cigarrillos en el puerto hasta un longitud de aproximadamente 3 mm, se aseguraron los cigarrillos al puerto mediante parafilm y se comprobó que los agujeros de ventilación no se encontraban tapados. Para el encendido de los cigarrillos se empleó un mechero electrónico de llama. Los cigarrillos fueron encendidos uno por uno, tomándose la primera calada en el instante en el que se enciende el último cigarrillo.

4.4.3.- Realización de un experimento

Para llevar a cabo un experimento en primer lugar deben prepararse las muestras con las que se llevará a cabo el estudio.

El tabaco seleccionado para llevar a cabo los experimentos corresponde a la marca Fortuna. Para la preparación de las muestras se vacían 200 cigarrillos de la marca seleccionada y se mezcla el tabaco contenido en todos ellos y luego los tubos vacíos de los cigarrillos son rellenados de nuevo con la muestra en estudio (bien tabaco o tabaco+catalizador). Esto se hace con el objeto de que la muestra de tabaco sea más homogénea, pues se ha comprobado que para esta marca existen diferencias considerables entre cajetillas y así se mejora la reproducibilidad. Las mezclas tabaco+catalizador fueron preparadas manualmente, mezclando 0,70 g de tabaco (cantidad de tabaco contenida en un cigarrillo estándar) con 0,028 g de catalizador en polvo, usando aproximadamente 0,1 g de etanol para facilitar la adherencia entre el catalizador y el tabaco. Así el contenido nominal de catalizador en el cigarrillo es de alrededor del 4% (w/w). El contenido real de catalizador se determina por pesada del catalizador que no se ha adicionado al tabaco durante la mezcla.

La norma ISO 3308 establece que los cigarrillos con los que se van a llevar a cabo los experimentos deben permanecer al menos durante 48 horas en una atmósfera controlada, a una temperatura de $22 \pm 2^{\circ} C$ y una humedad relativa de $60 \pm 5\%$, condiciones que se consiguen colocando las muestras en un recipiente cerrado que contiene una disolución saturada de nitrito sódico y que se mantuvo a temperatura adecuada. Los experimentos se llevaron a cabo a temperatura y humedad ambiental.

En cada experimento se fumaron cinco cigarrillos de manera simultánea.

Los pasos previos a la realización del experimento de fumado consisten en la preparación y pesada de todo el material que se va a utilizar durante el experimento, como son los recipientes donde se recogerán las cenizas, cada uno de los cigarrillos que se introducirán en la máquina de fumar así como todos y cada uno de sus partes integrantes por separado (filtro, papel y tabaco) y las trampas de humo. A continuación se prepara la máquina de fumar colocando trampas de humo en los puertos, la bolsa de gases con su trampa correspondiente, los cigarrillos en sus puertos y los recipientes de recogida de cenizas.

El experimento comienza cuando se encienden los cigarrillos con un mechero electrónico de llama, de la marca Varila y la máquina de manera automática realiza las caladas correspondientes. La máquina aspira moviendo el pistón hacia atrás, y conduce el gas recogido en las jeringuillas hacia la bolsa de gases volviendo el pistón a la posición inicial. Este proceso se repite ocho veces. Terminadas las caladas, los cigarrillos se apagan y se introducen en sus recipientes, se retiran las trampas de humo, los recipientes de las cenizas y la bolsa de recogida de gases, para posteriormente llevar a cabo las pesadas de los mismos componentes que se pesaron previamente al experimento, la extracción de los materiales condensados y el análisis correspondiente de líquidos y gases.

Los rendimientos globales de las distintas fracciones generadas se obtienen por diferencia de pesada de filtros y trampas antes y después del experimento así como por pesada directa de las cenizas obtenidas. La cantidad de tabaco fumado se calcula como diferencia entre el tabaco inicial añadido y el tabaco que ha quedado sin fumar en cada cigarrillo tras el experimento.

El gas recogido en la bolsa Tedlar es analizado mediante cromatografía de gases con detector de conductividad térmica (GC/TCD) e ionización de llama (GC/FID).

Para llevar a cabo la determinación de la nicotina y otros compuestos condensados tras el experimento tanto en filtros como en trampas de humo se realiza el proceso descrito en la norma ISO 4387. En esta norma se describe el procedimiento para el análisis de TPM (total particulate matter), de nicotina y de agua. TPM se define como la fracción de la corriente principal del humo del tabaco que queda retenida en las trampas de humo expresada en mg/cigarrillo.

Para llevar a cabo la extracción de la TPM se utiliza un disolvente orgánico, en este estudio 2-propanol. Tanto los filtros del cigarrillo como las trampas de humo se ponen en contacto alrededor de 25-30 g de disolvente, de modo que queden totalmente recubiertos por el disolvente. El tiempo de contacto es de 20 minutos con agitación vigorosa. Los líquidos extraídos se secan con sulfato de sodio, para eliminar el agua, se filtran y se analizan por cromatografía de gases, en este caso acoplado a un equipo de espectrometría de masas (GC/MS) para llevar a cabo la identificación de los diferentes componentes de las mezclas analizadas.

4.5.- ANÁLISIS DEL HUMO DEL TABACO

Las diferentes fracciones generadas durante un proceso de fumado son gases, líquidos condensados y cenizas. En apartado se describen las técnicas utilizadas para el análisis de los gases y líquidos condensados.

4.5.1.- Análisis de compuestos gaseosos

La cromatografía de gases (GC) es una técnica ampliamente utilizada para el análisis de mezclas de compuestos. Una de sus aplicaciones principales es el análisis cuantitativo de mezclas multicomponentes. En esta técnica la muestra es inyectada en la cabeza de una columna cromatográfica. La elución se produce por el flujo de una fase móvil de un gas inerte que suele ser nitrógeno o helio. Existen dos tipos de cromatografía, la cromatografía gas-sólido (GSC) y la cromatografía gas-líquido (GLC). La diferencia entre estos dos tipos de técnicas es principalmente la fase estacionaria, puesto que en el primer caso se trata de un sólido inerte y en el segundo es un líquido inmovilizado sobre la superficie de un sólido. Para el análisis de las muestras generadas en los experimentos de fumado realizados en el presente trabajo se han utilizado dos detectores diferentes, el detector de conductividad térmica (TCD) para el análisis de CO_2 y CO, y el detector de ionización de llama (FID) para el análisis del resto de componentes gaseosos.

4.5.1.1.- Detector de conductividad térmica (TCD)

El detector de conductividad térmica (TCD) se basa en los cambios producidos en la conductividad térmica de la corriente de gas provocados por la presencia del analito.

El cromatógrafo utilizado es un Shimadzu GC-14A. La columna utilizada para el análisis es una CTRI, una columna concéntrica utilizada para el análisis de O_2, N_2, CH_4, CO_2 y CO.

El programa de temperatura utilizado es:

- Temperatura del inyector: 28ºC

- Temperatura del detector: 110ºC

- Gas portador: Helio

- Volumen de muestra inyectada: 2,5 mL

- Flujo de columna constante: 40 mL/min

- Programa de temperatura del horno: isotermo a 110ºC

- Tiempo análisis 20 min

Mediante esta técnica se han detectado CO_2 y CO. La cuantificación ha sido realizada calculando el factor de respuesta (gramos de compuesto/área de pico) de estos compuestos mediante la inyección de diferentes volúmenes (entre 0,5 y 2,5 mL) del patrón correspondiente (Monóxido de carbono, Dióxido de carbono, Hidrógeno, Metano y Oxígeno). A partir de la pendiente de la recta de regresión obtenida de la representación gráfica de la cantidad de compuesto inyectado frente al área de pico se obtuvo el valor del factor de respuesta (FR) correspondiente. Los tiempos de retención y los factores de respuesta obtenidos han sido:

CO_2, tiempo de retención 1,47 min, FR = $9{,}03^{-10}$ g/ área

CO, tiempo de retención 11,03 min, FR = $3{,}15^{-10}$ g/ área

La asignación de los picos cromatográficos obtenidos en los gases producidos se realizó mediante la comparación de los tiempos de retención con los patrones, mientras que la determinación cuantitativa de los gases se efectuó mediante la aplicación de los factores de respuesta calculados. Los gramos de cada compuesto presentes en la mezcla se han calculado multiplicando el área correspondiente por el factor de respuesta y la cantidad total de dicho compuesto en la mezcla de gases recogida tras el experimento de fumado, a través de la siguiente expresión:

$$m_i = {}^{m_{i.inyectado}}\!\big/_{V_{inyectado}} \times V_{total}$$

donde m_i es la cantidad de compuesto generado en el experimento de fumado, $m_{i,inyectado}$ el valor obtenido a partir del cromatograma (área*FR), $V_{inyectado}$ el volumen de muestra inyectado en el cromatógrafo y V_{total} el volumen total de gases recogido tras el experimento.

4.5.1.2.- Detector de ionización de llama (FID).

El detector de ionización de llama (FID) es uno de los detectores más ampliamente utilizados para el análisis cromatográfico. Consiste en la entrada del efluente de la columna en un quemador, donde se mezcla con hidrógeno y con aire y donde se produce la combustión por acción de chispa eléctrica.

Multitud de compuestos sufren modificaciones a la temperatura de la llama hidrógeno/aire, produciéndose iones y electrones que conducen la electricidad a través de la llama. Aplicando una diferencia de potencial entre un electrodo colector y el extremo del quemador se genera una corriente cuya intensidad se mide utilizando un amplificador operacional de alta impedancia. El detector de ionización es un detector que responde al número de átomos de carbono que entran en el detector por unidad de tiempo, por lo que se trata de un detector sensible a la masa, más que un sistema sensible a la concentración.

El equipo utilizado para el análisis es un Cromatógrafo de gases Agilent 6890N. La columna utilizada es una columna capilar **GAS-PRO**. El programa de temperaturas utilizado para los análisis realizados en este trabajo es:

- Temperatura del inyector: 150ºC

- Temperatura del detector: 210ºC

- Gas portador: Helio

- Volumen de muestra inyectada: 150 μL

- Flujo de columna constante: 2 mL/min

- Programa de temperatura del horno:

    - Temperatura inicial de la columna 35ºC durante 10 min

    - Calentamiento hasta 100 ºC con una rampa de 5ºC/min

    - Calentamiento hasta 200 ºC con una rampa de 15ºC/min

    - Tiempo final: 10 min

La cuantificación de los compuestos analizados ha sido realizada de la misma manera que se indica en el apartado 4.5.1.1 inyectando diferentes volúmenes (entre 50 y 205 μL) de los patrones siguientes de la casa Supelco, Ref. 501816, Ref. 501670, Ref. 22567 y Ref. 501662. El cálculo del factor de respuesta de algunos compuestos presentes en la fase vapor, pero que son líquidos a temperatura ambiente y presión atmosférica, tales como benceno, acetonitrilo, acetaldehído, tolueno, acetona y furano, se realizó introduciendo una cantidad de líquido en un vial y se inyectó en el cromatrógrafo un determinado volumen del vapor en equilibrio con el líquido a 8ºC. Los volúmenes inyectados fueron 20, 30, 40, 50 y 60μL. Los compuestos analizados de esta forma fueron benceno, acetonitrilo, acetaldehído, tolueno, acetona y furano. El cálculo del factor de respuesta y la cuantificación se llevó a cabo de forma análoga al resto de componentes comentados anteriormente. Para aquellos que no se disponía de patrón, se ha utilizado el factor de respuesta medio calculado con los obtenidos a partir de las mezclas de gases utilizadas.

Para la asignación de los picos cromatográficos obtenidos, además de la comparación de los tiempos de retención con los patrones, se utilizó la ayuda de los datos obtenidos en un análisis del gas mediante GC/MS, donde se asignaron los picos con ayuda de la librería Wiley.

4.5.2.- Análisis de líquidos condensados

4.5.2.1.- Espectrometría de masas.

Para el análisis de la fracción líquida obtenida tras la extracción de los filtros de los cigarrillos y de las trampas de humo, se utilizó cromatografía de gases con detector de espectrometría de masas.

La espectrometría de masas es una técnica de alta sensibilidad que permite la determinación de la estructura e identidad de compuestos. Consiste en la ruptura e ionización en fragmentos de las moléculas presentes. Los espectros de masas se obtienen por conversión de los componentes de una muestra en iones gaseosos que se mueven rápidamente y se separan en función de su relación masa/carga. Esta técnica es capaz de proporcionar elevada información sobre una muestra como su composición cualitativa y cuantitativa, la estructura de especies complejas, las relaciones isotópicas de los átomos de una muestra así como su estructura y composición.

El equipo en el cual se han realizado los experimentos es un espectrómetro de masas Agilent 5973N de baja resolución con analizador de cuádruplo acoplado a un cromatógrafo de gases (Agilent 6890N) para columnas capilares con dos inyectores, uno split/splitless y otro PTV (inyector de temperatura variable). La ionización de las muestras se puede realizar tanto en impacto electrónico como en ionización química positiva o negativa. El equipo incorpora un inyector automático (Agilent 7683) con bandeja muestreadora con capacidad para 100 viales. Para la identificación de compuestos se dispone de una librería Wiley. La columna utilizada para el análisis de la fracción condensada es una HP-5/MS. El programa de temperaturas utilizado para todos los análisis llevados a cabo es el siguiente:

- Temperatura del inyector: 250ºC

- Gas portador: Helio

- Volumen de muestra inyectada: 1 µL

- Flujo de columna constante: 2 mL/min

- Programa de temperatura del horno:

    - Temperatura inicial de la columna 40ºC durante 5 min

    - Calentamiento hasta 320ºC con una rampa de 12ºC/min

    - Tiempo final: 25 min

Para la cuantificación de los compuestos presentes en la fase condensada del humo del tabaco se ha empleado un patrón de nicotina. Se prepararon patrones de nicotina de diferentes concentraciones (entre 5 y 100 ppm). Se inyectaron en el equipo y a partir de la pendiente de la recta obtenida de la representación gráfica de la cantidad de compuesto inyectado frente al área de pico se obtuvo el valor del factor de respuesta correspondiente. La cuantificación se llevó a cabo de forma análoga a los gases, utilizando el factor de respuesta obtenido para la nicotina para el resto de compuestos analizados.

4.6. ANÁLISIS ESTADÍSTICO MULTIVARIANTE

El análisis estadístico multivariante es una herramienta que permite analizar y estructurar conjuntos de datos correspondientes a la evaluación de un número considerablemente elevado de variables en uno o varios conjuntos de muestras. El objetivo es proporcionar métodos que permiten describir, estimar, comparar y relacionar variables. El desarrollo espectacular de las técnicas y herramientas para el procesado automático de datos ha permitido el desarrollo de una serie de programas específicos de ordenador que, a una gran capacidad de manejo de la información, unen una elevada velocidad de cálculo y una relativa facilidad de uso que permite la aplicación de los métodos sin necesidad de que el investigador usuario sea experto matemático o informático.

En este trabajo se han aplicado métodos de análisis multivariante con el objetivo de facilitar la interpretación de los resultados correspondientes a los rendimientos obtenidos en los compuestos presentes en la corriente principal del humo del tabaco, las principales características de diseño del cigarrillo y la cantidad de tabaco fumado y, especialmente, para buscar las similitudes y diferencias entre las marcas comerciales más vendidas en España. Con esta finalidad, se han utilizado el análisis de clusters, para establecer agrupaciones de las muestras (cigarrillos) en función de los valores de las variables analizadas (rendimientos de productos y/o características del cigarrillo) en cada una de ellas y el análisis de componentes principales para reducir las dimensiones del problema y encontrar interpretaciones para las causas que explican la formación de los grupos generados por el análisis de clusters.

ANALISIS DE CLUSTERS

El análisis de clusters trata de encontrar grupos de muestras similares dentro de una población. En la bibliografía se describen diferentes algoritmos para obtener la agrupación buscada (Varmuza y Filzmoser, 2009), que no sólo desarrollan esquemas de cálculo diferente, sino que también obedecen a principios de agrupación diferentes. En el caso de los métodos jerárquicos, los objetos y las particiones entre estos se ordenan de manera jerárquica, de forma que en el primer nivel de la jerarquía cada objeto forma un cluster separado, en el segundo nivel se agrupan los objetos más próximos, y así sucesivamente hasta que se tiene a todos los objetos agrupados en un único cluster.

La matriz inicial de datos es una tabla de muestras-variables (Nxn) que debe ser transformada en una tabla de “distancias”, (NxN) que recoge las disimilaridades entre todos los individuos. Pueden definirse diferentes tipos de distancias multivariantes, que dependen de las unidades y de los valores de las variables. La heterogeneidad entre éstas se resuelve estandarizando las variables, para evitar el mayor peso en los cálculos de aquellas de valores más grandes.

La metodología de este tipo de análisis consiste en calcular todas las distancias entre pares de variables. A continuación selecciona los dos más próximos, definiendo un grupo para estos dos, calcula un centroide para este grupo y vuelve a calcular distancias entre pares de resultados. En definitiva el método consiste en calcular distancias entre muestras o clusters, para posteriormente generar un dendograma (árbol) que muestra el orden en que se van uniendo las muestras (según distancias) hasta tenerlos todos en un grupo.

ANÁLISIS DE COMPONENTES PRINCIPALES

El análisis de componentes principales es un método que permite la reducción de las dimensiones de un problema, es decir, permite pasar de un sistema que está definido y caracterizado por un número elevado de variables, a otro, más sencillo, con menor número de variables, con una pérdida de información mínima.

Si cada muestra, caso u objeto estudiado se define como un punto en un espacio definido por tantos ejes coordenados como variables analizadas, el análisis de componentes principales permite calcular “variables latentes” o “componentes” de forma que la primera componente principal se elige como la variable latente que corresponde a la dirección en el espacio que mejor conserva las distancias relativas entre los objetos, es decir, la dirección a través de la cual la varianza de las muestras es máxima. La segunda componente principal se define como una dirección ortogonal a la primera, a lo largo de la cual la varianza se sigue maximizando, y así sucesivamente.

De esta manera, con solo unas pocas componentes principales se consigue obtener una representación en la que se incluye un porcentaje elevado de la varianza de las muestras, es decir, que suponen una pérdida de información pequeña y que, por tanto, permiten reducir las dimensiones del problema.

Las componentes principales se obtienen como combinación lineal de las variables originales y, aunque el conocimiento de los fundamentos matemáticos de este método no son necesarios para poderlo aplicar mediante los programas de cálculo y paquetes estadísticos comerciales disponibles en la actualidad, cabe decir que las componentes principales se obtienen diagonalizando la matriz de covarianzas entre las muestras:

$C = T\,D_{\lambda}T'$ (donde $T \times T' = T' \times T = I$)

Donde D_{λ} es la matriz diagonal que contiene los valores propios de la matriz de covarianzas, C. Las componentes son las combinaciones lineales cuyos coeficientes son las columnas de la matriz ortogonal T. El % de la varianza explicada por cada componente principal se calcula como el cociente entre el valor propio correspondiente a dicha componente por la suma de todos los valores propios.

PUBLICACIONES

5

I.- Catalytic Effect of MCM-41 in the Pyrolysis and Combustion Processes of Tobacco. Effect of the Aluminium Content, A. Marcilla, A. Gómez-Siurana, M.I. Beltrán, I. Martínez and D. Berenguer. Thermochimica Acta, 518, Issue 1-2 (2011), Pages 47-52.

II.- Evaluation of the efficiency of solvent extraction for template removal in the synthesis of MCM-41 type materials to be used as tobacco additives for smoke toxicity reduction. A. Marcilla, M. Beltran, A. Gómez-Siurana, I. Martínez, D. Berenguer, Applied Catalysis A: General, 378, Issue 1 (2010), Pages 107-113.

III.- Template removal in MCM-41 type materials by solvent extraction. Influence of the treatment on the textural properties of the material and the effect on its behaviour as catalyst for reducing tobacco smoking toxicity, A. Marcilla, M. Beltran, A. Gómez-Siurana, I. Martínez, D. Berenguer. Chemical Engineering Research and Design, 89, (2011), Pages 2330-2343.

IV.- Reduction of tobacco smoke components yields by zeolites and synthetysed Al-MCM-41. A. Marcilla, A. Gómez-Siurana, D. Berenguer, I. Martínez-Castellanos, M.I. Beltrán En revisión, Microporous and mesoporous materials

V.- Comparative study of the main characteristics and composition of the mainstream smoke of ten cigarettes brands sold in Spain I. Martínez, D. Berenguer, A. Gómez-Siurana, M.I.Beltrán and A. Marcilla. En revisión, Food and Chemical Toxicology.

A continuación se muestra el listado de las publicaciones de las que consta la presente tesis doctoral.

I.- Catalytic Effect of MCM-41 in the Pyrolysis and Combustion Processes of Tobacco. Effect of the Aluminium Content, A. Marcilla, A. Gómez-Siurana, M.I. Beltrán, I. Martínez and D. Berenguer. Thermochimica Acta, 518, Issue 1-2 (2011), 47-52.

II.- Evaluation of the efficiency of solvent extraction for template removal in the synthesis of MCM-41 type materials to be used as tobacco additives for smoke toxicity reduction. A. Marcilla, M. Beltran, A. Gómez-Siurana, I. Martínez, D. Berenguer, Applied Catalysis A: General, 378, Issue 1 (2010), 107-113.

III.- Template removal in MCM-41 type materials by solvent extraction. Influence of the treatment on the textural properties of the material and the effect on its behaviour as catalyst for reducing tobacco smoking toxicity. A. Marcilla, M. Beltran, A. Gómez-Siurana, I. Martínez, D. Berenguer. Chemical Engineering Research and Design, 89 (2011), 2330-2343.

IV.- Reduction of tobacco smoke components yields by zeolites and synthetysed Al-MCM41. A. Marcilla, A. Gómez-Siurana, D. Berenguer, I. Martínez-Castellanos and M.I. Beltrán. En revisión, Microporous and mesoporous materials.

V.- Comparative study of the main characteristics and composition of the mainstream smoke of ten cigarettes brands sold in Spain. I. Martínez, D. Berenguer, A. Gómez-Siurana, M.I. Beltrán and A. Marcilla. En revisión, Food and Chemical Toxicology.

Otras publicaciones

I.- “Mezclas tabaco-catalizador para la reducción de los compuestos tóxicos presentes en el humo del tabaco”, A. Marcilla Gomis, M.I. Beltrán Rico, A. Gómez Siurana, R. Navarro Martínez, D. Berenguer Muñoz, I. Martínez Castellanos, P200602816, España 07.11.2006.

I.a).- ”Tobacco-catalyst mixtures for reducing the toxic compounds present in tobacco smoke”. A. Marcilla Gomis, M.I. Beltrán Rico, A. Gómez Siurana, R. Navarro Martínez, D. Berenguer Muñoz, I. Martínez Castellanos, EURO-PCT078230349 (ES LA EXTENSIÓN DE LA PATENTE ANTERIOR A EUROPA).

II.- Thermogravimetric study of the pyrolysis of tobacco and several ingredients used in the fabrication of commercial cigarettes. Effect of the presence of MCM-41. A. Gómez-Siurana, A. Marcilla, M. Beltran I. Martínez, D. Berenguer, R. García-Martínez, T. Hernández-Selva, Thermochimica Acta. 523, Issues 1-2 (2011), 161-169.

IV.- Study of the oxidative pyrolysis of tobacco-sorbitol-saccharose mixtures in the presence of MCM-41. Gómez-Siurana,A., A. Marcilla, A., Beltran, M., Martinez-Castellanos, I., Berenguer, D. and García-Martínez, R. and T. Hernández-Selva, T. En revisión, Thermochimica Acta.

Publicación I. *Catalytic effect of MCM-41 in th pyrolysis and combustion processes of tobacco. Effect of the aluminium content. A. Marcilla, A. Gómez-Siurana, M.I. Beltrán, I. Martínez and D. Berenguer. Thermochimica Acta, 518, Issue 1-2 (2011), Pages 47-52.*

En este trabajo se ha estudiado la influencia de la cantidad de aluminio contenido en la estructura del catalizador MCM-41 sobre sus propiedades texturales y acidez y se ha comprobado su capacidad para reducir la cantidad de compuestos tóxicos presentes en la corriente principal del humo del tabaco.

Para ello, se ha sintetizado el catalizador MCM-41 (llamado M en este trabajo), al que se le ha realizado un intercambio iónico con disoluciones de diferente concentración de aluminio, obteniendo finalmente los materiales AM, 2AM y 4AM, que se han caracterizado mediante isotermas de adsorción de nitrógeno a 77K, desorción térmica programada de amoniaco, y fluorescencia de rayos X.

Para realizar el análisis del comportamiento de los catalizadores sintetizados como aditivos del tabaco se han llevado a cabo experimentos de fumado en una máquina de fumar. Los cigarrillos conteniendo un 4% de aditivo, se acondicionaron durante al menos 48 h a temperatura ambiente y una humedad del 60% y se fumaron de acuerdo con las especificaciones de la norma ISO 3308.

Se determinó la cantidad de gases y materia particulada condensada en los filtros y en las trampas situadas tras los cigarrillos y se analizó el CO y CO_2 de la fracción gaseosa generada mediante CG/TCD y diferentes compuestos que componen los alquitranes condensados en los filtros y en las trampas situadas tras los cigarrillos mediante CG/MS.

Los resultados obtenidos en este trabajo han permitido cubrir los siguientes objetivos específicos:

- Determinación de la relación entre el contenido de aluminio del catalizador MCM-41 y sus propiedades texturales y acidez.

- Establecimiento de la proporción óptima de aluminio contenido en el catalizador MCM-41 para obtener las mayores reducciones en el rendimiento de los principales componentes de la corriente principal del humo del tabaco.

Thermochimica Acta 518 (2011) 47–52

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Catalytic effect of MCM-41 on the pyrolysis and combustion processes of tobacco. Effect of the aluminium content

A. Marcilla, M. Beltran, A. Gómez-Siurana, I. Martinez, D. Berenguer*

Dpto. Ingeniería Química, Universidad de Alicante, Apdo. 99, 03080 Alicante, Spain

ARTICLE INFO

Article history:
Received 22 December 2010
Received in revised form 28 January 2011
Accepted 3 February 2011
Available online 3 March 2011

Keywords:
MCM-41
Aluminium content
Additive
Tobacco
Smoke

ABSTRACT

The hydrothermal stability and the acidity of mesoporous MCM-41 materials are strongly related with their aluminium content. In this work, the influence of the concentration of Al on the textural and acidic properties of MCM-41, as well as on its role as tobacco additive for reducing the toxicity of the smoke generated in the smoking process has been studied. The results obtained show that the material with an intermediate content of aluminium presents acceptable hydrothermal stability, and higher values for the decrease of the yields of CO, CO_2, and the condensed and non-condensed products, thus showing the best results from the point of view of reducing the toxicity associated with the generation of toxic and carcinogenic compounds in tobacco smoke.

1. Introduction

Tobacco smoking is the largest preventable cause of disease and death in the world, causing about five million deaths annually, a toll projected to rise to 10 million by the 2020s, 70% of which will be in developing countries [1].

The health hazard caused by smoking cigarettes has been well established [2]. Besides nicotine, the major inducer of tobacco dependence, cigarette smoke also contains various toxic compounds and noticeably carcinogenic agents such as nitrosamines and polycyclic aromatic hydrocarbons (PAHs). Zeolites and molecular sieves such as MCM-41 have been employed as additives in cigarettes in order to remove such dangerous products [3–9].

Since the disclosure by Mobil [10], in the early 1990s, of the synthesis of mesoporous materials with regular structure, the so-called MCM-41 series has drawn considerable attention. These materials present a long range ordered structure with a regular hexagonal array of one-dimensional mesopores, whose diameters can be adjusted in the range of 2–10 nm, depending on the surfactant agent, on various additives and on the synthesis conditions. This set of characteristics makes them attractive for fundamental studies, as well as for applications in the fields of adsorption and catalysis, especially when bulky molecules, which do not fit into the pores of usual adsorbents and catalysts such as zeolites, are involved. However, this material has as a disadvantage its sensitivity to moisture at ambient temperature, which can limit its use in some applications.

The hydrothermal stability of MCM-41 in boiling water or steam at high temperatures has been studied in several publications [11], and it seems to be dependent on the synthesis conditions [12] and, in particular, on the aluminium content.

It has been reported that structural degradation of pure silica MCM-41 materials can occur even at 298 K if the material is exposed to water vapour for long periods [13]. Improvement of stability can be achieved by modification of the surface with organosilanes [14], by pyrolytic carbon deposition [15] or by post-synthesis treatment such as silanization, using tetraethoxysilane in hexane [16].

Therefore, the low hydrothermal stability of MCM-41 is a factor which must be considered, and if it is possible be improved, in a parallel way to the studies focused on its catalytic role in the tobacco pyrolysis and combustion processes, before trying to exploit its use as a tobacco additive for reducing toxicity at an industrial scale. In this work, the behaviour of several samples of MCM-41with different contents of aluminium, obtained by a post-synthesis Al-ion exchange treatment has been studied. The structure and acidity of these materials, as well as their role as tobacco additives for reducing the toxicity of the smoking process have been studied.

2. Experimental

2.1. Synthesis of materials

MCM-41 not including aluminium (so-called “M” in the nomenclature used in this work) was prepared according to the procedure

---

* Corresponding author. Tel.: +34 96 590 2953; fax: +34 96 590 3826.
E-mail addresses: desi.bm@ua.es, antonio.marcilla@ua.es (D. Berenguer).

0040-6031/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2011.02.005

Table 1
Characterization of the different catalysts studied in this work.

Material	BET (m^2/g)	Vol. total pore (cm^3/g, 0.995)	Pore size (Å), BJH	Acidity (mmol/g)	Si/Al
M	964	0.78	29	0.10	157
AM	923	0.74	29	0.26	119
2AM	869	0.69	27	0.28	48
4AM	877	0.74	27	0.35	23

reported in literature [17]: CTMACl (25 wt% aqueous solution, Aldrich) and dissolved in distilled water under constant stirring. An aqueous ammonia solution was added to this solution, which was stirred for 10 min. Finally, the silica source (TEOS, Aldrich, 99 wt%) was added dropwise with vigorous stirring to obtain the final gel. The stirring was continued for a period of 4 h. The product was recovered by filtration, washed thoroughly with distilled water and then dried at 100 °C for 4 h. The removal of the template was accomplished by calcination in air at 550 °C for 6 h.

Additionally, aluminium containing MCM-41 materials (so-called "AM" in the nomenclature used in this work) were prepared by stirring the M sample prepared according to the previous procedure in aqueous solutions of $Al(NO_3)_3·9H_2O$ of different concentrations at 60 °C, for 3 h. The exchanged solid product was recovered by filtration, washed with distilled water, and dried at 100 °C. Three concentrations of Aluminium were checked, and materials AM, 2AM and 4AM were prepared, respectively, from 0.25 mol/L, 0.5 mol/L and 2 mol/L aqueous $Al(NO_3)_3·9H_2O$ solutions in order to obtain materials with the Si/Al ratios shown in Table 1.

2.2. *Catalyst characterization*

The textural characteristics of the different samples studied were established from the measurement of the N_2 adsorption isotherms at 77 K. The equipment used was an automatic Quantachrome AUTOSORB-6. The surface area measurements were done according to the BET method. The pore size distributions were obtained applying the BJH model with cylindrical geometry of the pores and using the Harkins and Jura equation for determining the adsorbed layer thickness (t) and the external surface area.

The acidity of the materials was measured by temperature-programmed desorption (TPD) of ammonia, performed in a Netzsch TG 209 thermobalance, following the procedure described elsewhere [18].

The Si/Al ratio was measured by X-ray fluorescence (XRF) in a sequential spectrometer of V rays PHILIPS MAGIX PRO, model PW2400.

2.3. *Smoking experiments*

In order to check the influence of the aluminium content on the activity of the aluminium containing MCM41 materials for reducing tobacco toxicity, cigarettes were prepared with mixtures of tobacco and the different samples of catalysts. Such cigarettes have been smoked in a smoking machine described elsewhere [9]. Then, the results obtained for the chemical composition of the gaseous and condensed products were compared with those corresponding to a reference cigarette, where the same tobacco was used, but without the catalyst. The smoking machine permits five cigarettes to be smoked simultaneously under some specifications of the ISO 3308 conditions [19]. During the smoking process, the mainstream smoke crosses the filter of the cigarette as well as a trap placed after the cigarette, for the purpose of retaining the condensable products, and finally, the non-condensable products in these conditions are collected in a Tedlar bag. It is interesting to point out that the trap located after the cigarette captures the condensable products which could condensate in the mouth and the lungs of active smokers.

The cigarettes, with a nominal percentage of catalyst of around 4% (wt), were prepared and then kept at 25 °C and 60% relative humidity for at least 48 h before the smoking process (i.e., in a drier provided with a saturated sodium nitrite solution). The pressure of aspiration of the machine is of the order of 1.5 kPa.

The condensable products retained in the filter of the cigarette and in the trap were extracted with 2-propanol as solvent and analyzed by GC/MS using a HP-5MS column.

The measurement of the content of CO and CO_2 in the gaseous product was carried out by GC-TCD using a CTR I column. Finally, the rest of non-condensable products were analyzed by GC-FID using a GAS-PRO column.

3. Results and discussion

The results of the characterization of the catalysts prepared (M sample) and modified in the post-synthesis ion exchange procedure (AM, 2AM and 4AM) are shown in Table 1. The stabilizing role of aluminium in the structure, and the corresponding improvement of the hydrothermal resistance have been pointed out elsewhere [9,20]. As expected, when the aluminium concentration in the solution used to carry out the ion exchange increases, the aluminium content in the structure also increases, and the Si/Al ratio decreases. However, some kind of saturating effect seems to appear, and the highest incorporation of aluminium in the structure occurs in the presence of low concentrations of aluminium. In fact, above 0.5 mol/L of Al^{3+}, the increase in the aluminium content is relatively low. The acidity of the samples increases as its aluminium content also increases, and a near linear relationship between Si/Al and acidity can be observed. However, the textural properties are hardly modified by the introduction of aluminium in the structure, despite some apparent worsening.

The catalytic role of the samples prepared in this work in the pyrolysis and combustion processes of tobacco has been analyzed through smoking experiments performed following the procedure described in Section 2. Table 2 shows the yields of CO, CO_2 and other

Table 2
Yields (mg comp./g tobacco fumed) of CO, CO_2 and other gases and liquids condensed in filters and traps obtained when smoking the reference tobacco in the absence of (R) and in the presence of catalysts with different Al contents (R + M, R + AM, R + 2AM and R + 4AM).

Compound	R	R + M	R + AM	R + 2AM	R + 4AM
CO	5.47	3.88	4.08	2.27	4.89
CO_2	39.8	31.0	32.5	22.0	37.6
Non-condensed	2.51	2.00	1.82	1.37	2.18
Condensed in traps	959	411	539	327	599
Condensed in filters	962	512	663	475	693

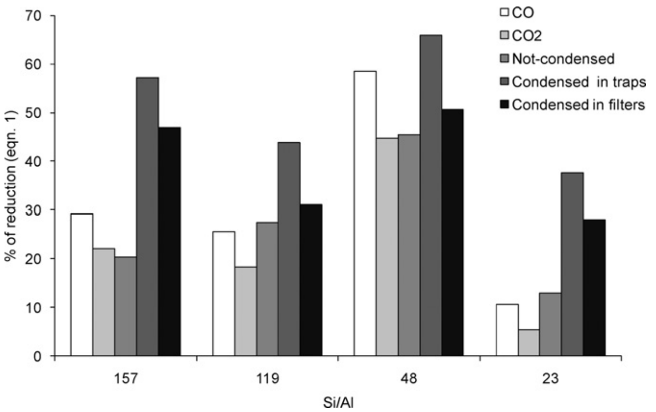


Fig. 1. Percentages of reduction (calculated with Eq. (1)) of the yields of CO, CO_2, liquids and gases achieved with the catalysts studied in this work.

non-condensed compounds as well as of the condensed materials collected in the traps placed after the cigarettes and in the filters of the cigarettes. It is interesting to point out that the amount of CO, nicotine and tar generated when cigarettes are smoked is restricted by law. Nicotine is enclosed in the condensed products, and tar is defined as the condensed products, after the water and nicotine content have been discounted. As can be seen, all the catalysts checked have the ability to reduce the yields of the products evolved from the smoking process. Fig. 1 shows the percentages of reduction achieved with each catalyst, calculated as follows:

$$\%\,\text{reduction} = \frac{\text{yield in the reference tobacco} - \text{yield in the presence of catalyst}}{\text{yield in the reference tobacco}} \times 100 \qquad (1)$$

As can be seen, in all the cases the best results correspond to the sample 2AM, followed by M, AM and 4AM which act in a relatively similar way, with the only exception of M, which is slightly better at reducing the liquids (but worse than 2AM). From the point of view of the reduction of toxic compound generation in a smoking tobacco process, when the MCM-41 catalysts have relatively similar textural properties, these results suggest that the best catalyst is that having a Si/Al ratio of around 50. Thus, the results obtained indicate that the relationship between the percentages of reduction of the yields of different compounds evolved in the smoking process and the acidity of the catalysts shows a maximum corresponding to an intermediate value of acidity. It must be considered that, according to [20] the incorporation of high levels of Al may destroy the porous structure, and consequently a maximum of the activity with the Al content would be expectable.

Fig. 2 presents the yields for the main components of the non-condensed fraction of the mainstream smoke obtained in different smoking experiments. The 10 compounds shown represent 80% of this fraction. As can be seen, in good agreement with the previous statements, 2AM could be considered as the best additive, and is the catalyst which reduces in higher extent the yields of all the compounds, with the only exception of isobutene and acetone. On the other hand, other minor components (around 20 compounds) also appear, and 2M is also the catalyst providing the highest reductions with respect to the reference tobacco.

The analysis of the particulate matter retained (i.e., liquids or condensed fraction) in the filters of cigarettes and in the traps located after the cigarettes in the smoking experiments is a complex task due to the appearance of more than 100 peaks, i.e., more than 100 different compounds, most of them at very low levels. Tables 3 and 4 show the yields obtained for some compounds which have been identified with a matching factor higher than 80% with the aid of the library of the GC/MS equipment, in the traps and in the filters, respectively. As can be expected, there are compounds appearing in the filters which have not been detected in the traps, thus indicating that these materials have been retained almost completely. In good agreement with the results previously presented and commented on, 2AM seems to be the best catalyst from the point of view of the reduction of tobacco toxicity. Similar behaviour can be observed for the rest of compounds (not identified by the library used) of the liquid fraction. At this point, it is worth mentioning that, in accordance with Ref. [21], the complexity of the mainstream smoke suggests that the toxicity of the condensed products evolved from tobacco in the smoking process, and the effect of additives for reducing its toxicity, could be evaluated through the overall yield of particulate matter. In this way, it is interesting to consider the effect of the additives studied in this work on all the compounds appearing in the chromatograms, even those where the identification of peaks is doubtful. Figs. 3 and 4 show the percentages of reduction, calculated with Eq. (1), for all

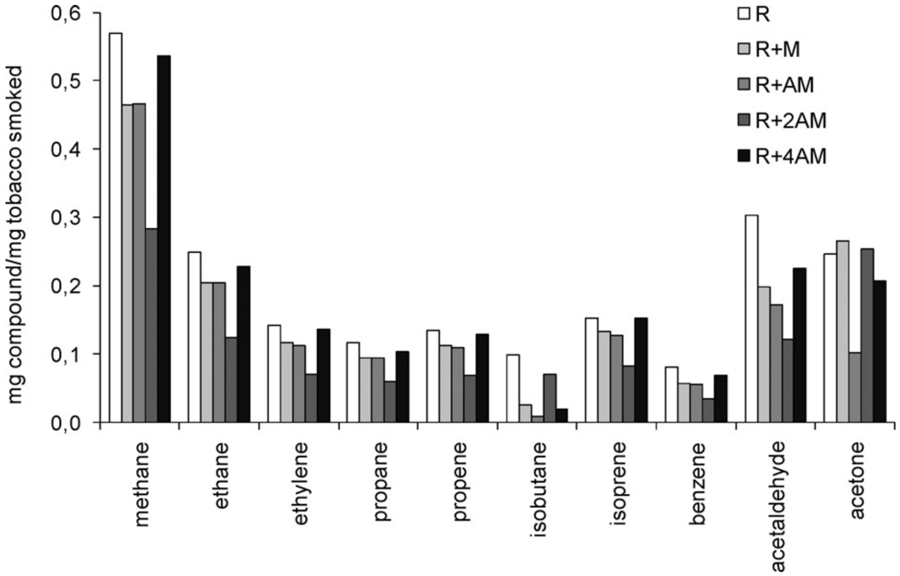


Fig. 2. Yields corresponding to the major compounds of the non-condensed fraction of the mainstream smoke.

Table 3
Yields of the different compounds identified and analyzed in the condensed fraction retained in the traps located after the cigarettes in a smoking experiment in the absence (R) and in the presence of catalysts with different Al contents (R + M, R + AM, R + 2AM and R + 4AM).

Residence time (min)	Compound	mg/g tobacco smoked				
		R	R + M	R + AM	R + 2AM	R + 4AM
8.62	Furfural	3.29	4.95	4.56	4.31	4.19
9.66	2-Furanmethanol	1.01	7.02	3.51	7.77	1.74
10.09	4-Cyclopentene-1,3-dione	2.02	1.17	0.66	1.54	1.11
10.77	2-Methyl-2-cyclopenten-1-one	0.60	0.38	0.01	0.20	0.39
11.00	2(5H)-furanone	1.32	0.55	0.97	0.86	1.04
11.30	2-Hydroxycyclopent-2-en-1-one	1.53	0.32	0.38	0.27	0.43
12.55	5-Methyl-2-furfural	0.82	0.34	0.52	0.37	0.38
13.39	Phenol	8.87	0.37	4.47	2.55	4.91
14.50	2-Hydroxy-3-methyl-2-cyclopenten-1-one	2.27	0.43	0.70	0.33	0.79
14.57	Limonene	2.07	0.86	0.76	0.78	1.15
14.90	2,3-Dimethyl-2-cyclopenten-1-one	1.11	0.38	0.18	0.24	0.72
15.41	o-Cresol	3.79	1.25	2.05	0.24	3.25
15.55	2-Acetylpyrrole	0.75	0.43	0.62	0.27	0.65
16.03	p-Cresol	8.21	2.36	3.79	2.28	5.68
17.96	Benzeneacetonitrile	0.98	0.44	0.54	0.39	0.86
18.11	2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	2.08	0.52	1.71	0.62	4.85
18.26	3,5-Dimethyl-phenol	3.10	2.05	3.34	1.11	3.61
18.83	4-Ethyl-phenol	4.06	0.30	0.89	0.69	1.24
19.27	Naphthalene	0.86	0.35	0.26	0.28	0.61
22.10	Hydroquinone	10.7	1.41	5.63	1.54	1.21
23.00	4-Vinyl-2-methoxy-phenol	4.10	1.70	2.86	1.42	3.57
23.87	Nicotine	654	256	335	196	370
24.97	3-Methyl-1H-indole	3.91	2.32	2.34	1.48	3.36
32.55	Cotinine	6.14	2.45	3.65	1.94	4.81
34.13	N(b)-formylnornicotine	4.44	2.22	2.96	1.86	2.91
35.29	Neophytadiene	37.0	16.5	22.9	13.2	25.5
55.92	Vitamin E	3.35	3.07	3.17	1.92	3.80

Table 4
Yields of the different compounds identified and analyzed in the condensed fraction retained in the filters of the cigarettes in a smoking experiment.

Residence time (min)	Compound	mg/g tobacco smoked				
		R	R + M	R + AM	R + 2AM	R + 4AM
8.08	3-Furaldehyde	1.70	1.19	1.17	1.26	1.70
8.24	2-Methyl-pyridine	2.80	0.84	1.36	0.95	1.82
8.37	Methyl-pyrazine	3.19	1.34	1.27	1.11	2.55
8.62	Furfural	26.5	10.5	17.3	10.9	20.9
9.66	2-Furanmethanol	3.80	1.04	1.38	0.85	3.18
10.09	4-Cyclopentene-1,3-dione	7.08	3.48	6.23	5.52	8.98
10.25	Styrene	1.00	0.51	0.83	0.91	1.28
10.77	2-Methyl-2-cyclopenten-1-one	9.95	4.63	7.22	4.68	9.42
10.91	2(5H)-furanone	10.77	4.56	6.31	4.74	9.35
11.30	2-Hydroxycyclopent-2-en-1-one	3.07	1.49	2.42	1.89	3.53
11.48	3,5-Dimethyl-pyridine	0.94	0.37	0.65	0.45	0.60
11.61	2,5-Dimethyl-2-cyclopentenone	0.34	0.32	0.32	0.31	0.29
12.55	5-Methyl-2-furfural	15.88	5.38	9.44	6.21	12.39
13.39	Phenol	23.8	10.0	16.7	12.1	19.2
14.50	2-Hydroxy-3-methyl-2-cyclopenten-1-one	7.87	4.03	6.04	3.47	6.67
14.57	Limonene	6.31	4.34	6.15	2.27	5.12
14.83	Benzenemethanol	0.73	0.37	0.58	0.44	0.69
14.90	2,3-Dimethyl-2-cyclopenten-1-one	7.32	3.01	4.45	2.97	5.78
15.42	o-Cresol	8.39	4.27	6.38	4.47	7.09
15.55	2-Acetylpyrrole	2.67	1.31	2.00	1.34	1.74
16.03	p-Cresol	12.7	6.20	11.3	7.87	13.4
17.96	Benzeneacetonitrile	2.69	1.48	2.06	1.56	2.66
18.11	2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	0.83	0.57	0.61	0.61	0.95
18.26	3,5-dimethyl-Phenol	3.49	2.83	4.74	3.14	4.55
18.83	4-Ethyl-phenol	1.81	1.00	0.73	1.15	1.68
19.27	Naphthalene	1.58	1.34	1.53	0.88	1.52
22.10	Hydroquinone	3.61	2.03	3.41	1.84	2.33
23.00	4-Vinyl-2-methoxy-phenol	3.41	2.22	2.73	2.09	2.01
23.87	Nicotine	537	262	331	244	341
24.97	3-Methyl-1H-indole	4.01	2.42	3.12	2.33	2.59
32.55	Cotinine	2.97	1.40	2.40	2.04	2.88
34.13	N(b)-formylnornicotine	2.42	1.39	1.79	0.90	1.57
35.29	Neophytadiene	27.5	19.5	22.9	18.7	25.6
55.92	Vitamin E	1.66	3.28	1.24	0.68	0.94

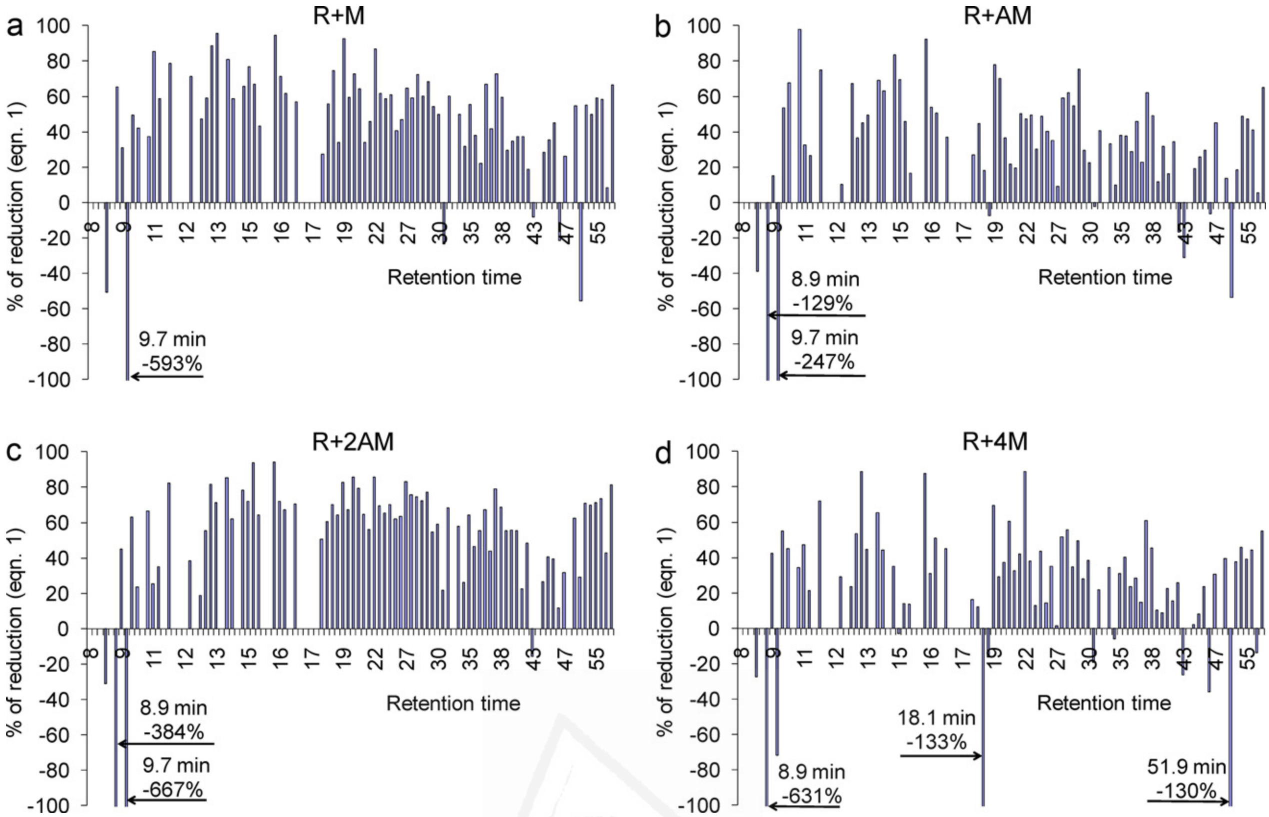


Fig. 3. Percentages of reduction of the yields of the different compounds obtained in the condensed fraction retained in the traps after cigarettes when (a) M, (b) AM, (c) 2AM, and (d) 4AM were used as tobacco additives. Components out of scale are marked, and the corresponding retention times in the chromatograms are shown. The equivalence for the identified compounds can be seen in Table 3.

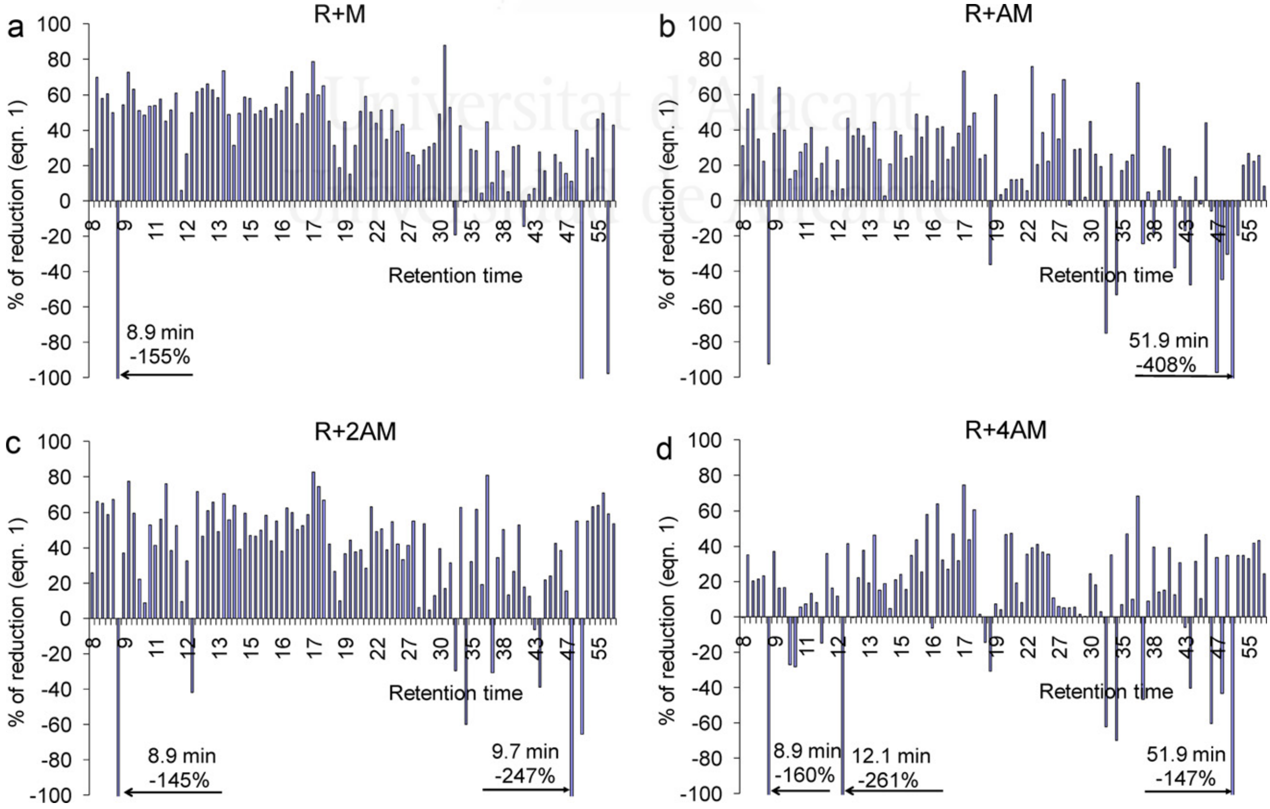


Fig. 4. Percentages of reduction of the yields of the different compounds obtained in the condensed fraction retained in the filters after cigarettes when (a) M, (b) AM, (c) 2AM, and (d) 4AM were used as tobacco additives. Components out of scale are marked, and the corresponding retention times in the chromatograms are shown. The equivalence for the identified compounds can be seen in Table 4.

the compounds appearing in the condensed products retained by the traps and by the filters, respectively. In these figures the *X* axis represents the retention time corresponding to each peak. The negative values in the *Y* axis indicate an increase occurring as a consequence of the presence of the catalyst, whereas the positive values correspond to the percentage of reduction obtained. As can be seen, an overview of Figs. 3 and 4 indicates that, in general, as expected from the previous results, 2AM is the catalyst showing the best properties for reducing tobacco toxicity, followed by M and by AM and 4AM.

4. Conclusions

In this work, the ability of MCM-41 materials with different aluminium contents, prepared by aluminium ion exchange, to act as catalysts in order to reduce tobacco toxicity has been studied. The results obtained indicate that the catalytic activity of such materials in the processes of pyrolysis and combustion of tobacco not only depends on the textural properties of the samples, but also on the acidity, and the material with acceptable catalytic properties should show good textural properties and an intermediate value of acidity (Si/Al ratio around 50 and acidity around 0.28 mmol/g).

Acknowledgement

Financial support for this investigation has been provided by the Spanish “Secretaría de Estado de Investigación” del Ministerio de Ciencia e Innovación (CTQ2008-01023).

References

[1] D. Bettcher, C. Sbramaniam, E. Guindon, A.-M. Perucic, L. Soll, G. Grabman, Confronting the Previous Tobacco Epidemic in an Era of Trade Liberalization, WHO-previous Tobacco Free Initiative, Geneva, Switzerland, 2001.
[2] K. Warner, The economics of previous tobacco: myths and realities, Tob. Control 9 (2000) 78–89.
[3] D. Hoffmann, I. Hoffmann, The changing cigarette, 1950–1995, J. Toxicol. Environ. Health 50 (1997) 307–364.
[4] P.C.H. Mitchell, Zeolite-encapsulated metal complexes: biomimetic catalysts, Chem. Ind. (1991) 308–311.
[5] H.C. Weiner, Oral tolerance: immune mechanisms and treatment of autoimmune diseases, Immunol. Today 18 (1997) 335–343.
[6] M.W. Meier, K. Siegmann, Significant reduction of carcinogenic compounds in tobacco smoke by the use of zeolite catalysts, Chem. Ind. 33 (1999) 307–310.
[7] Y. Xu, Y. Wang, J.H. Zhu, L.L. Ma, L. Liu, Progress in the application of zeolite in the life science: novel additive for cigarette to remove N-nitrosamines in smoke, Stud. Surf. Sci. Catal. 142 (2002) 1489–1496.
[8] Y. Xu, Z.-Y. Yun, J.H. Zhu, J.-H. Xu, H.-D. Liu, Y.-L. Wei, K.-J. Hui, Trapping volatile nitrosamines with the copper incorporated zeolites, Chem. Commun. (2003) 1894–1895.
[9] A. Marcilla, A. Gómez-Siurana, M. Beltrán, I. Martínez, D. Berenguer, Evaluation of the efficiency of solvent extraction for template removal in the synthesis of MCM41 type materials to be used as tobacco additives for smoke toxicity reduction, Appl. Catal. A: Gen. 378 (1) (2010) 107–113.
[10] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism, Nature 359 (1992) 710–712.
[11] T.R. Pauly, V. Petkov, Y. Liu, S.J.L. Billinge, T.J. Pinnavaia, Role of framework sodium versus local framework structure in determining the hydrothermal stability of MCM-41 mesostructures, J. Am. Chem. Soc. 124 (2002) 97–103.
[12] A. Davidson, Modifying the walls of mesoporous silicas prepared by supramolecular-templating, Curr. Opin. Colloid Interface Sci. 7 (2002) 92–106.
[13] K.A. Koyano, T. Tatsumi, Y. Tanaka, S. Nakata, Stabilization of mesoporous molecular sieves by trimethylsilylation, J. Phys. Chem. B 101 (1997) 9436–9440.
[14] X.S. Zhao, G.-Q. Lu, X. Hu, Characterization of the structural and surface properties of chemically modified MCM-41 material, Microporous Mesoporous Mater. 41 (2000) 37–47.
[15] M.M.L. Ribeiro Carrott, A.J.E. Candeias, P.J.M. Carrott, K.S.W. Sing, K.K. Unger, Stabilization of MCM-41 by pyrolytic carbon deposition, Langmuir 16 (2000) 9103–9105.
[16] A.E. Candeias, M.M.L. Ribeiro Carrott, P.J.M. Carrott, K. Schumacher, M. Grun, K.K. Unger, Characterisation of porous solids VI, Stud. Surf. Sci. Catal. 144 (2002) 363–370.
[17] T.R. Gaydhankar, V. Samuel, R.K. Jha, R. Kumar, P.N. Joshi, Room temperature synthesis of Si-MCM-41 using polymeric version of ethyl silicate as a source of silica, Mater. Res. Bull. 42 (8) (2007) 1473–1484.
[18] A. Marcilla, A. Gómez-Siurana, D. Berenguer, Study of the influence of the characteristics of different acid solids in the catalytic pyrolysis of different polymers, Appl. Catal. A: Gen. 301 (2) (2006) 222–231.
[19] SO 3308:2000, Routine analytical cigarette-smoking machine – definitions and standard conditions.
[20] L.Y. Chen, Z. Ping, G.K. Chuah, S. Jaenicke, G. Simon, A comparison of post-synthesis alumination and sol–gel synthesis of MCM-41 with high framework aluminum content, Microporous Mesoporous Mater. 27 (2–3) (1999) 231–242.
[21] R.R. Baker, Smoke generation inside a burning cigarette: modifying combustion to develop cigarettes that may be less hazardous to health, Prog. Energy Combust. Sci. 32 (2006) 373–385.

Publicación II. *Evaluation of the efficiency of solvent extraction for template removal in the synthesis of MCM-41 type materials to be used as tobacco additives for smoke toxicity reduction. A. Marcilla, M. Beltran, A. Gómez-Siurana, I. Martínez, D. Berenguer, Applied Catalysis A: General, 378, Issue 1 (2010), Pages 107-113.*

Para sintetizar el material MCM-41 se emplean tensioactivos orgánicos que quedan retenidos en su estructura y deben ser eliminados antes de que pueda ser empleado como catalizador o adsorbente. Por lo general, los tensioactivos se eliminan mediante calcinación a elevadas temperaturas, pero este proceso podría alterar la estructura del material, por lo que en la bibliografía se proponen otros métodos de eliminación del tensioactivo.

En este trabajo se estudia la posibilidad de eliminar el tensioactivo mediante calcinación y mediante extracción con disoluciones de HCl/Etanol y de H_2O_2 seguida en algunos casos de calcinación. El proceso de extracción se realiza en varias etapas sucesivas, con diferentes cantidades de extractante y tiempos de contacto. Tras la extracción y a efectos comparativos, en algunas muestras se procede a la calcinación y a la adición de aluminio mediante intercambio iónico. La caracterización de los diferentes materiales obtenidos, tras los lavados sucesivos, calcinación y adición de aluminio, se ha realizado mediante isotermas de adsorción de nitrógeno y desorción térmica programada de amoniaco. La estabilidad hidrotérmica de los catalizadores se ha estudiado mediante tratamiento a reflujo en agua seguida de la caracterización de las propiedades texturales del material.

La cantidad de tensioactivo eliminado tras cada etapa de extracción y tras los tratamientos realizados se ha analizado mediante TGA. Se ha comprobado que el TGA es una excelente herramienta para evaluar la eficiencia de los diferentes métodos de eliminación del tensioactivo.

Por último, para evaluar la influencia de los diferentes tratamientos realizados sobre la capacidad del catalizador para reducir la toxicidad del humo del tabaco, se han llevado a cabo experimentos de fumado en las condiciones descritas en las normas ISO 3308 (sobre el proceso de fumado) e ISO 4387 (sobre acondicionamiento previo de los cigarrillos). En este trabajo se ha analizado el rendimiento global de líquidos condensados en los filtros de los cigarrillos y en las trampas y el rendimiento en CO y CO_2 CG con un detector TCD.

Los resultados obtenidos en este trabajo han permitido cubrir los siguientes objetivos específicos:

-Estudio del proceso de eliminación del tensioactivo retenido en la estructura del catalizador MCM-41 mediante extracción y/o calcinación.

-Establecimiento de un método (TGA) para evaluar la eficiencia de los diferentes métodos de eliminación del tensioactivo.

Applied Catalysis A: General 378 (2010) 107–113

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Evaluation of the efficiency of solvent extraction for template removal in the synthesis of MCM-41 type materials to be used as tobacco additives for smoke toxicity reduction

A. Marcilla, M. Beltran, A. Gómez-Siurana, I. Martínez, D. Berenguer *

Dpto. Ingeniería Química, Universidad de Alicante, Apdo. 99, 03080 Alicante, Spain

ARTICLE INFO

Article history:
Received 17 December 2009
Received in revised form 1 February 2010
Accepted 3 February 2010
Available online 10 February 2010

Keywords:
MCM-41
Template elimination
Tensioactive
Extraction
Additive
Tobacco
Smoke

ABSTRACT

In this work different methods of elimination of the organic template remaining in a piece of as-synthesized Si-MCM-41 material have been studied: calcination, and two different extraction processes, with ethanol and with hydrogen peroxide. TGA has been applied in order to analyze and to compare the characteristics of the materials obtained by the three different treatments studied. The textural properties of the samples resulting after the extraction of the template, as well as the resulting hydrothermal stability of the materials, have been evaluated. Finally, the ability of the different samples as tobacco additives in order to reduce tobacco toxicity has been studied.

The results show that TGA is an excellent tool for the evaluation of the efficiency of the different treatments applied. It can be concluded that the samples treated with a mixture of HCl/EtOH and with hydrogen peroxide, respectively, are able to be used as tobacco additives. Depending of the experimental conditions for the leaching process, the samples can have hydrothermal stability and activity similar to that of the conventional MCM-41, where the template has been removed by calcination.

1. Introduction

Tobacco smoking is the largest preventable cause of disease and death in the world, causing about five million deaths annually, a toll projected to rise to 10 million by the 2020s, 70% of which will be in developing countries [1]. This epidemic is promoted by an industry that has argued that efforts to reduce tobacco use would have direct economic implications, especially in developing countries, and that efforts to regulate the production and marketing violate international trade laws [2].

The health hazard caused by smoking cigarettes has been well established [3–5]. Besides nicotine, the major inducer of tobacco dependence, cigarette smoke also contains various toxic compounds, notably carcinogenic agents such as nitrosamines and polycyclic aromatic hydrocarbons (PAHs). In the past 40 years or so great efforts have been expended in the development of filter tips [5], which bind considerable amounts of unwanted components in the mainstream inhaled by smokers. However, filter tips are inherently without avail in removing harmful constituents in the sidestream, i.e., the tobacco smoke emitted in between puffs.

Zeolites and molecular sieves such as MCM-41 have been employed in slow release drugs, enzyme mimetic drugs [6], antitumour drugs [7], and additive in cigarettes to remove carcinogenic agents such as nitrosamines [8–11]. The MCM-41 type silicates are generally synthesized using surfactant-type organic templates, which should be removed before utilization, especially before applying them as an adsorbent or catalyst. In most cases the as-synthesized samples are heat-treated to remove the template in the presence of oxygen or air above 550 °C. Moreover, partial collapse of the structure may occur during the usual high-temperature treatment in oxidative atmosphere. Alternative methods used in removing the template are extraction techniques (by conventional solvents or by supercritical fluids) [12], ozone treatment [13] and microwave methods (by digestion and calcination) [14]. These methods may alleviate the adverse effects associated with the removal of the template, mainly resulting from its rapid decomposition due to shrinkage of the structure [15].

In this work, an MCM-41 sample was prepared, and three methods of elimination of the organic template have been studied: calcination, and two different extraction processes, with ethanol and with hydrogen peroxide. Information related to the effect of the treatment with solvents as well as the possible mechanisms

---

* Corresponding author. Tel.: +34 96 590 2953; fax: +34 96 590 3826.
E-mail addresses: antonio.marcilla@ua.es (A. Marcilla), Desi.BM@ua.es (D. Berenguer).

0926-860X/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2010.02.006

Table 1
Materials synthesised in this work.

Material	Aluminium treated	Template elimination	4 days under water reflux
SM	No	No	No
SMc	No	Calcination	No
Al-SMc	Yes	Calcination	No
Al-SMc-s	Yes	Calcination	Yes
SMEC20-1	No	One wash-20 g HCl/EtOH-1 h	No
SMEC20-2	No	Two washes-20 g HCl/EtOH-1 h	No
SMEC20-3	No	Three washes-20 g HCl/EtOH-1 h	No
SMEC20-3c	No	Three washes-20 g HCl/EtOH-1 h + calcination	No
Al-SMEC20-3c	Yes	Three washes- 20 g HCl/EtOH-1 h + calcination	No
Al-SMEC20-3c-s	Yes	Three washes-20 g HCl/EtOH-1 h + calcination	Yes
SMEC10-1	No	One wash-10 g HCl/EtOH-15 min	No
SMEC10-2	No	Two washes-10 g HCl/EtOH-15 min	No
SMEC10-3	No	Three washes-10 g HCl/EtOH-15 min	No
SMEC10-4	No	Four washes-10 g HCl/EtOH-15 min	No
SMEC10-5	No	Five washes-10 g HCl/EtOH-15 min	No
SMEC10-5c	No	Five washes-10 g HCl/EtOH-15 min + calcination	No
Al-SMEC10-5c	Yes	Five washes-10 g HCl/EtOH-15 min + calcination	No
Al-SMEC10-5c-s	Yes	Five washes-10 g HCl/EtOH-15 min + calcination	Yes
SMPO-1	No	One wash-H_2O_2-1 h	No
SMPO-2	No	Two washes-H_2O_2-1 h	No
SMPO-3	No	Three washes-H_2O_2-1 h	No
SMPO-4	No	Four washes-H_2O_2-1 h	No
SMPO-5	No	Five washes-H_2O_2-1 h	No
SMPO-5c	No	Five washes-H_2O_2-1 h + calcination	No
Al-SMPO-5c	Yes	Five washes-H_2O_2-1h + calcination	No
Al-SMPO-5c-s	Yes	Five washes-H_2O_2-1 h + calcination	Yes

involved in the template elimination was obtained by thermogravimetric analysis (TGA). This technique has been successfully applied by several authors [16,17], and four mass loss steps have been observed, related, respectively, with thermodesorption of physically adsorbed water, surfactant decomposition, residual surfactant decomposition and silanol condensation, at temperatures depending on the corresponding heating rate applied.

The hydrothermal stability of the materials obtained was tested, and finally, the role of these materials as tobacco additives for reducing the toxicity of the smoking process was checked.

2. Experimental

2.1. Synthesis of materials

A sample of MCM-41 not including aluminium (SM, in the nomenclature used in this work) was prepared according the method reported in literature [18], where CTMACl (25 wt% aqueous solution of cetyltrimethyl ammonium chloride, Aldrich) was dissolved in distilled water under constant stirring. Aqueous ammonia solution was added to this solution, which was stirred for 10 min. Finally, the silica source, TEOS (tetraethyl orthosilicate 99%, Aldrich) was added drop wise with vigorous stirring to obtain the final gel. The stirring was continued for a period of 4 h. The product was recovered by filtration, washed thoroughly with distilled water and then dried at 100 °C for 4 h. The removal of the template was accomplished by calcination in air at 550 °C for 6 h (SMc sample) or by extraction with an HCl/ethanol mixture (SMEC sample) or with hydrogen peroxide (SMPO sample). Two different ways for template elimination with ethanol were tested, i.e., by repeatedly treating 1 g of sample with 20 g of HCl 1 M in ethanol for 1 h at 70 °C (SMCE20 sample), and applying the same procedure with 10 g of the same solution for 15 min (SMCE10 sample). The samples obtained after each successive washing process have been identified by the corresponding code (i.e., SMEC20-1, SMEC20-2, ...), indicating the number of solvent contacts. The samples obtained after the last extraction step were calcined in order to remove the remaining amounts of template.

Additionally, aluminium containing MCM-41 materials (Al-SM samples) were prepared by using the above described procedure, by stirring the MCM-41 sample (SM) before template elimination in a 0.25 M solution of $Al(NO_3)_3 \cdot 9H_2O$ at 60 °C, for 3 h. The product was recovered by filtration, washed with distilled water and dried at 100 °C. Some portion of this material was calcined in air at 550 °C for 6 h in order to eliminate the template and to obtain the material of reference (Al-SMc sample) for comparison with the samples treated with solvents. The incorporation of Al in the samples permits their stabilization, since the materials are very unstable in contact with water [19]. On the other hand, the aluminium containing materials were treated with the same solvent extraction processes as the Si-MCM-41 samples, and after the last extraction step, they were calcined in order to remove the last traces of template and to obtain a catalyst to be used for reducing tobacco toxicity (Al-SMEC20-3c, Al-SMEC10-5c and Al-SMPO-5c samples).

Table 1 shows the samples prepared in this work and the corresponding notation.

2.2. Catalyst characterization

The textural characteristics of the different samples studied were determined by the corresponding N_2 adsorption isotherms at 77 K, measured in an automatic AUTOSORB-6 supplied by Quantachrome. The adsorption curves of the isotherms were recorded and the surface area measurements were done according to the BET method. The pore size distributions were obtained applying the BJH model with cylindrical geometry of the pores and using the de Boer equation for determining the adsorbed layer thickness (t) and the external surface area.

The acidity of the materials was measured by temperature-programmed desorption (TPD) of ammonia, performed in a Netzsch TG 209 thermobalance, following the procedure described elsewhere [20].

2.3. Extraction of the tensioactive

The ability of two different solvents to remove the template was tested, and the results obtained were compared with those corresponding to the material obtained by the conventional method, i.e., removing the template by calcination. Two extraction processes have been tested. The first one is based on the work of Zi-Le et al. [21], and uses a mixture of HCl and ethanol as a solvent. The experiments were carried out by stirring 1 g of SM in 20 g of a solution 1 M of HCl in ethanol at 70 °C for 1 h. The extracted samples were filtered and washed with ethanol. This procedure was repeated successive times, mixing the sample previously extracted with fresh solvent solution. A similar process was performed using 1 g of SM and stirring in 10 g of the HCl/Ethanol mixture at 70 °C for 15 min.

The second extraction method is based on the work of Xiao et al. [22]. 0.5 g of SM was stirred in 50 g of H_2O_2 (2%, w/w) at room temperature for 1 h, and the pH solution was adjusted at 3.5 with diluted HCl. Then the sample was filtered and washed with ethanol. The extraction step was successively repeated, mixing the extracted sample with fresh solvent solution.

2.4. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was applied in order to evaluate the amount of template removed in each extraction step. For this purpose, TGA runs were performed at a heating rate of 10 °C min^{-1} under oxygen atmosphere (0.5 cm^3 $STPs^{-1}$), thus emulating the conditions in the calcination process. In each run, around 8 mg of sample were placed in open Al_2O_3 pans.

A calibration of the temperature was performed using the curie-point transition temperatures of some standards. The metals as standards used, Nickel (D), iron (F) and several nickel/iron (A, B, C, E) alloys lose their magnetic properties at a specific temperature (74, 160, 266, 358, 497 and 770 °C, respectively).

2.5. Hydrothermal stability test

The study of the hydrothermal stability of the different catalysts studied in this work was performed by boiling the samples in distilled water for 4 days under reflux. The structural changes were analyzed after each treatment by comparing the textural characteristics of the samples, from the corresponding N_2 adsorption isotherms at 77 K.

2.6. Smoking experiments

In order to check the influence of the procedure for template extraction in the activity of the catalyst for reducing tobacco toxicity, cigarettes prepared with mixtures of tobacco and catalyst were smoked in a smoking machine, and the results obtained for the composition of the gaseous and condensed products were compared with those corresponding to a reference cigarette, where the same tobacco with no catalyst added was smoked. The smoking machine permits five cigarettes to be smoked simultaneously and follows most of the specifications of the ISO 3308 [23]. Tobacco from commercial cigarettes of the selected brand was removed from the tubes. This tobacco was mixed with the selected amount of the catalyst under study and mixed thoroughly. This mixture (tobacco plus catalyst) was used to refill the emptied tube. During the smoking process, the mainstream smoke crosses the filter of the cigarette as well as a trap placed after the cigarette, with the purpose of retaining the condensable products, and finally, the non-condensable products are collected in a Tedlar bag. It is interesting to point out that the trap located after the cigarette captures the condensable products which could condensate in the mouth and the lungs of active smokers.

The cigarettes were prepared and then kept at 23 °C and 60% relative humidity for at least 48 h before the smoking process (i.e., in a drier provided with a saturated solution of sodium nitrite). The pressure of aspiration of the machine must be of the order of 1.5 kPa.

The yield of liquids was obtained by weighing the traps and the filters before and after each experiment and the measurement of the content of CO and CO_2 in the gaseous product was carried out by GC-TCD using a CTR I column.

3. Results and discussion

The elimination of the template, after the MCM-41 synthesis process, liberates the typical porous structure of this type of material [12,24]. Therefore this is a necessary process in order to provide the activity desired in these catalysts. Moreover, a consolidation of the structure also occurs as a consequence of the calcination process [12,24].

Unfortunately, after calcination, small amounts of template remain which could generate dangerous toxic products when the catalyst is used as a tobacco additive or in other applications [12]. Therefore, the study of other procedures for template elimination, and the knowledge of the properties of the catalyst at the end of the process are of great interest.

On the other hand, template elimination procedures not based on heating processes could be interesting if the synthesis of MCM-41 is to be performed at an industrial scale because, although an economic study must be performed in order to compare the cost involved in the energy consumption and in the solvent supply, the gas step treatment, necessary if calcination is applied, would be alleviated.

Fig. 1 shows the TGA and DTG curves corresponding to the different samples prepared in this work, by using different procedures for template elimination. Fig. 1a shows the samples obtained by successive extractions of 1 g of a SM sample with 20 g of HCl/Ethanol for 1 h. Fig. 1b shows the samples obtained by successive extractions of 1 g of an SM sample with 10 g of HCl/Ethanol for 15 min, and finally, Fig. 1c shows the samples obtained by successive extractions with H_2O_2. In all the cases, the curves obtained for the material before the template elimination (SM) and for the sample where the template was removed by calcination (SMc), have also been included for comparison purposes.

According to the bibliography [16,17], at 10 °C min^{-1}, the weight loss shown by an unwashed MCM-41 sample involves four steps, in the following temperature ranges: (i) from 25 to 170 °C, corresponding to thermodesorption of physically adsorbed water; (ii) from 170 to 270 °C, related with the surfactant decomposition; (iii) from 270 to 530 °C, when residual surfactant decomposition and silanol condensation occurs, and (iv) from 530 to 740 °C, related with residual silanol condensation. As the results shown in Fig. 1 for the SM sample reflect, in this case, the temperatures of maximum decomposition rate for each step are 140 °C, 260 °C and 310 °C for the first, second and third step, respectively, whilst the fourth step is out of the range of temperature studied in this work. The non-volatile residue at 450 °C represents around 66% of the material, thus indicating a total weight loss of 34%. This percentage is representative of the total amount of template removed in the TGA, and can be considered as representative of the content of template in the original sample. As can be seen by comparison with the corresponding calcined sample (SMc), the heating program applied in the TGA removes practically all the template.

The TGA and DTG curves corresponding to the SMEC20-1 sample (Fig. 1a) indicate a 15% of weight loss at 450 °C. The comparison with the template content of the SM sample indicates that around 65% of the template has been removed in the first extraction step. The values of weight loss at 450 °C corresponding to the SMEC20-2 and SMEC20-3 samples are around 10% and 6%, respectively, which indicates that the percentage of the initial content of template which has been removed in each successive step is around 14% and 8%, respectively. As can be seen, the percentage of extraction in each successive step decreases, as

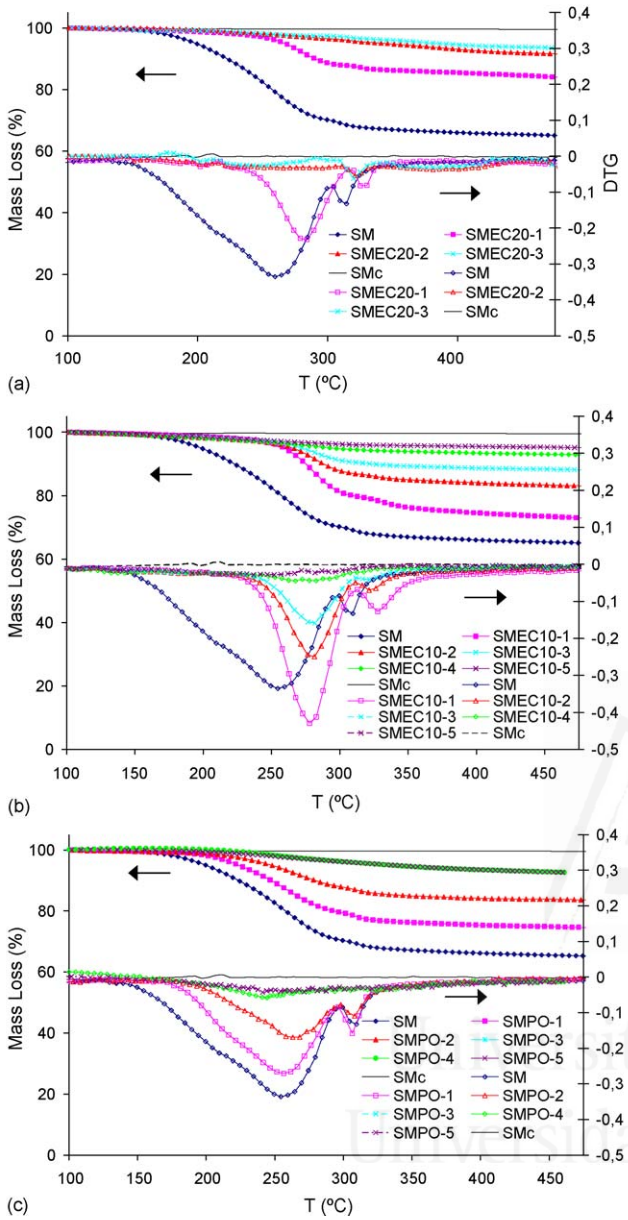


Fig. 1. (a) TG and DTG curves obtained by the successive solvent extraction of template with 20 g of HCl/EtOH for 1 h at 70 °C. (b) TG and DTG curves obtained by the successive solvent extraction of template with 10 g of HCl/EtOH for 15 min at 70 °C. (c) TG and DTG curves obtained by the successive solvent extraction of template with H_2O_2 for 1 h at 25 °C.

expected, and it seems that a residual template which cannot be removed by this procedure remains in the sample. In fact, after the three extraction steps, 13% of the weight of the initial template still remains unremoved, representing around 6% of the total weight of sample SMEC20-3.

The comparison of the TGA curves of the samples SM and SMEC20-1 clearly shows that a noticeable amount of the template (which evolves from the sample SM in the first broad peak, at around 260 °C) has been removed by the first extraction treatment. In good agreement, the weight loss corresponding to the equivalent degradation step shown by TGA for the sample SMEC20-1 is noticeably lowered. This step appears as a sharper peak centred at around 280 °C in the DTG curve of the SMEC20-1 sample, reflecting a displacement towards higher temperatures with respect to the SM sample. Moreover, a shift towards higher temperatures in this sample is also observed for the third peak that appears at 325 °C. This behaviour suggests that the solvent removes first those portions of the surfactant weakly interacting with the solid structure (which are decomposed at lower temperatures in the SM sample). It also seems that the remaining portions of the surfactant, as well as those compounds resulting form the surfactant decomposition, probably responsible for the last observed peak, increment the strength of the interaction with the solid matrix, and therefore are removed at higher temperatures in the SMEC20-1 sample.

The surfactant decomposition could involve different chemical processes: the simplest would be the elimination of the tertiary amine from the quaternary ammonium salt, but the secondary and primary amines formation could also be possible. Moreover, these primary decomposition products could also be cracked. Finally, all these products could be retained in the pores of MCM-41, thus favouring their decomposition, and the volatile products removed at different temperatures depending on the strength they are adsorbed.

The differences found in the DTG-peaks temperatures in the SM and SMEC20-1 sample seem to indicate that some alterations could take place as a result of the interaction with the solvent, which causes the stronger retention of these compounds. As will be discussed later, these alterations could probably cause some changes in the solid structure of the catalyst.

The TGA and DTG curves of the SMEC20-2 and SMEC20-3 samples reflect the disappearance of the main weight loss step observed in the previous SM and SMEC20-1 samples, in good agreement with the fact that the main part of the template has been already removed. In these cases, a DTG-peak at around 320 °C appears, corresponding to the DTG-peak at 310 °C in the case of the SM sample and at 325 °C for the SMEC20-1 sample. If this peak corresponds to the residual decomposition of surfactant or of its decomposition products [17], it can be concluded that the same displacement above-commented on for the SMEC20-1 sample appears, despite the fact that in these cases, the temperature is slightly lower, perhaps due to the presence of a lower amount of reacting material.

Fig. 1b shows the TGA and the DTG curves corresponding to the thermal treatment of the samples successively extracted with 10 g of HCl/Ethanol for 15 min. As can be seen, the same shift of the DTG-peaks commented on for the previous case occurs. However, the amount of template removed in the first extraction step is noticeably lower than that of the SMEC20-1 sample, as corresponds with the lower amount of solvent used and the shorter contact time employed in this second procedure (sample SMEC20-1). In this case, the process of template removal is milder than in the previous case, where the surfactant was mainly removed in the first extraction step. Another aspect that is worth mentioning is the fact that the long tail of the first peak observed in the SM sample has also been completely removed by the first treatment with 10 g of HCl/Ethanol for 15 min. Nevertheless the more strongly linked part of the template requires successive treatments to be removed. Moreover, the third peak at around 320 °C is only observed up to the third treatment with 10 g of HCl/Ethanol for 15 min, thus revealing that in these conditions the solvent is capable of a deeper elimination of the template. In this case it also seems that the rapid removal of the template in the first treatment may produce changes in the structure of the matrix increasing the links with the last portions of the template or of its products of decomposition. The percentages of the initial template content removed in each successive extraction step are, respectively: 31.6%, 30.9%, 12.7%, 10.9% and 4.7%, thus yielding 9.2% of unremoved template, which represents 4.6% of the total weight of the SMEC10-5 sample (all the values measured at 450 °C). It seems that the slower elimination of template is less aggressive with the sample. This behaviour could be in good agreement with the textural properties shown by the different samples, which will be discussed in the following paragraphs.

The TGA and DTG curves corresponding to the samples extracted with H_2O_2 are shown in Fig. 1c. As can be seen, these samples exhibit a completely different behaviour to that of the SMEC samples. A gradual decrease of the amount of template is obtained after each extraction step, but no shift in the temperatures can be observed. It seems that the oxygen peroxide equally removes all the portions of the surfactant and has no effect on the tail of the first peak, and only reduces the amount evolved, almost in a parallel way. It can be concluded in this case that this treatment does not alter the structure of the matrix, at least from the point of view of the strength of the interactions with the remaining template. As can be seen, in this case, the maximum accumulated extraction of template has been attained in the fourth step, and in the fifth step practically any additional elimination of template occurs. The successive percentages of template removed in each step, referred to the initial amount of surfactant are 36.3%, 27.4%, 10.0%, 11.5% and 0%, and the residual surfactant content in the SMPO5 sample is 7.2%, which is higher than in the previous cases.

Fig. 2 shows the percentage of the initial amount of template which is removed in each extraction step by using each one of the three procedures studied. As can be seen, in the SMEC20 samples, the first contact removes the highest amount of template, and in the successive washes, the elimination of template gradually decreases arriving at a situation where an additional extraction step does not eliminate a significant amount of template. On the other hand, for the SMEC10 and SMPO samples, the elimination of surfactant is more gradual. The comparison between the two extraction processes with different amounts of HCl/Ethanol shows that in the first extraction step, the amount of template removed is noticeably higher when 20 ml solvent were used and, therefore, the same extraction results can be obtained with fewer steps. Nevertheless, and as expected, the amount of solvent used for the same template removal is lower when using lower amounts of solvent in each step (60 g = 20 g/step × 3 steps, and 50 g = 10 g/step × 5 steps). A counter-current extraction process would be the most efficient process from this point of view. The comparison between the results obtained when HCl/ethanol and H_2O_2 are used as solvents, indicates that, after the successive extraction steps, H_2O_2 removes slightly lower amounts of template. However, the use of such a solvent could have an additional advantage since it would spontaneously decompose into H_2O and O_2 after the treatment, thus avoiding further washes to remove the remaining extractant.

According to Fig. 1, none of the extraction processes tested yields results as good as the calcination process (SMc sample), and in all the cases, the final material contains significant amounts of unremoved substances (i.e., 6.2% after three extractions with 20 ml of HCl/EtOH, 4.6% after five extractions with 10 g of HCl/EtOH, and 7.2% after five extractions with 50 g of H_2O_2, as obtained from the weight loss at 450 °C). However, the complete elimination of template is necessary if the catalyst is to be used as tobacco additive, because in this case, when the tobacco–catalyst mixture was smoked, the rests of the template join the mainstream and the secondary smoke and eventually participate in the combustion reactions taking place in the tip of the cigarette. Thus, such products or derivatives will be inhaled by active or passive smokers. Therefore, a hydrothermal stabilization of the samples through ionic exchange with aluminium [25], as well as the complete elimination of template through a last calcination step after the leaching processes, is necessary treatment in order to use these materials as tobacco additives.

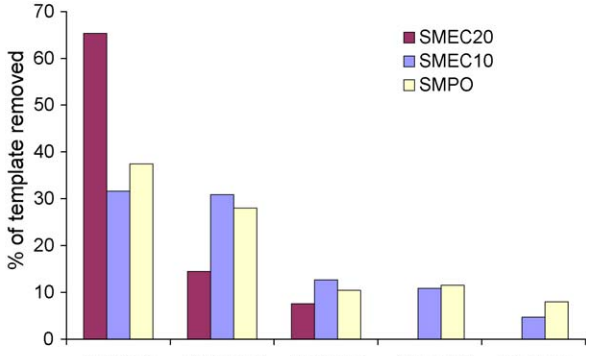


Fig. 2. Percentage of template removed in each extraction step by using each one of the three procedures studied.

Accordingly to the previous comments, samples containing aluminium were prepared and calcined, and the textural properties of the samples, as well as the ability of the resulting materials (Al-SMEC20-3c, Al-SMEC10-5c and Al-SMPO-5c) for reducing tobacco toxicity were checked. Moreover, the hydrothermal stability test described in the previous section was applied to these samples, and the properties of the resulting materials (Al-SMEC20-3c-s, Al-SMEC10-5c-s and Al-SMPO-5c-s) were also analyzed.

Fig. 3 shows the N_2 adsorption isotherms of the samples before (Fig. 3a) and after (Fig. 3b) the hydrothermal treatment and Table 2 shows the corresponding textural parameters. The BET area has been calculated considering values in the 0.04–0.25 range of relative pressure. The micropore volume has been calculated by the Dubinin-Radushkevich method, for relative pressures under 0.02. The total volume of pores corresponds to the amount of N_2 adsorbed at relative pressure under 0.99, and the pore diameter shown is the more abundant diameter found by applying the BJH method [26,27]. As can be seen, comparing the samples before

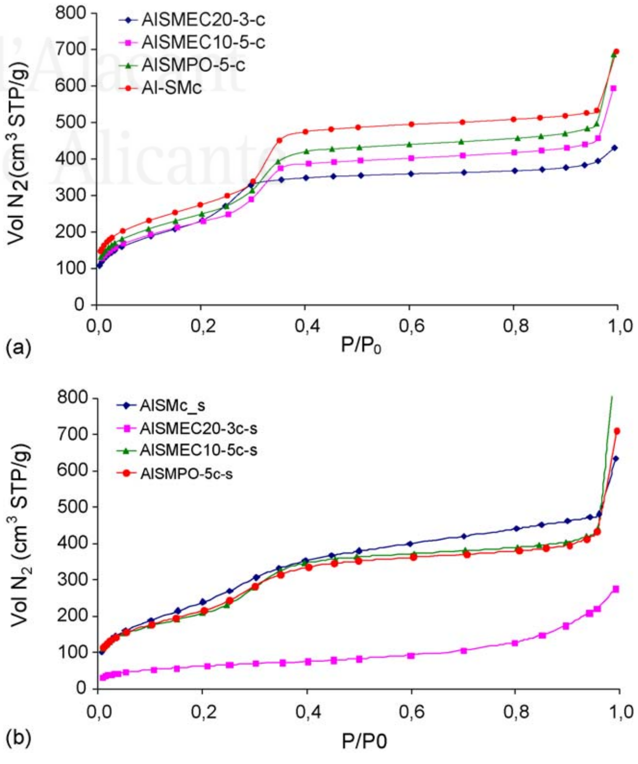


Fig. 3. (a) N_2 adsorption isotherms corresponding to the samples Al-SMc, Al-SMEC20-3c, Al-SMEC10-5c and Al-SMPO-5c. (b) N_2 adsorption isotherms corresponding to the samples Al-SMc-s, Al-SMEC20-3c-s, Al-SMEC10-5c-s and Al-SMPO-5c-s.

Table 2
Textural parameters of the samples shown in Fig. 3.

Sample	BET area (m^2/g)	Micropore volume (cm^3/g)	Volume total of pores (cm^3/g)	Pore diameter (Å)	Acidity (mol/g)
Al-SMc	1007	0.366	0.825	27.3	0.31
Al-SMEC20-3c	849	0.297	0.610	24.5	0.00
Al-SMEC10-5c	835	0.314	0.707	27.3	0.20
Al-SMPO-5c	916	0.335	0.768	27.4	0.30
Al-SMc-s	935	0.293	0.744	24.6	–
Al-SMEC20-3c-s	222	0.085	0.341	24.3[a]	–
Al-SMEC10-5c-s	778	0.279	0.684	24.5	–
Al-SMPO-5c-s	823	0.288	0.671	24.5	–

[a] Three maxima at 61.3A, 38.0A and 24.3A, the second is the most abundant.

hydrothermal treatment, the Al-SMEC20-3c has the lower micropore volume and almost the lowest BET area, only slightly higher than that corresponding to the Al-SMEC10-5c. These results seem to be in good agreement with the TGA results, which, as previously commented on, suggest that some specific solvent-solid interaction occurs that results in the template remaining more strongly retained by the porous structure. The N_2 adsorption results indicate that the treatment undergone by these samples (SMEC20-i) is perhaps aggressive enough to deteriorate the structure, causing poorer textural properties. This behaviour seems to be especially noticeable in the effect on the step observed in the isotherms due to the mesopores. As can be seen in Fig. 3a, the tendency shown by the samples Al-SMc, Al-SMEC10-5c and Al-SMPO-5c is broken by the sample Al-SMEC20-3c, which shows a much lower intensity step appearing at lower relative pressures than the other samples, this behaviour being reflected by the lower value of the more abundant pore diameter shown by the distribution calculated by the BJH method (see Table 2).

With respect to the other samples, the treatment undergone by the SMEC10 samples seems to be less aggressive, but also causes some damage in the structure, as the low values of BET area and volume of pores reflect; despite the fact that the pores size distribution is less affected. As in the previous case, these changes in the textural properties could be responsible for the higher temperatures needed for template elimination in TGA: the difficulty in removing the template, which is already retained in the inner part of the porous structure, increases as the volume of pores decreases.

Finally, the treatment with H_2O_2 is the less aggressive one, and the differences with the textural properties of the calcined samples are minima, in good agreement with the absence of temperature shifts observed in the TGA study. It can be seen that this sample maintains textural properties close to the calcined sample (Al-SMc-s), thus indicating that the extraction with the H_2O_2 process is the less damaging for the structure of the material.

Fig. 3b shows the N_2 adsorption isotherms corresponding to the samples after the hydrothermal treatment has been applied, and Table 2 shows the corresponding parameters, calculated as has been indicated for the previous samples. As can be seen, the aluminization of the samples process achieves the proposed objective, and the Al-SMc-s, Al-SMEC10-5c-s and Al-SMPO-5c-s samples maintain textural properties good enough to be used as catalysts. However, and as expected, some worsening with respect to the corresponding untreated samples appears. Nevertheless, the situation is dramatically different in the case of the Al-SMEC20-3c-s sample, which loses practically its textural properties at all. This behaviour seems to be in good agreement with the higher damage of the structure caused by the treatment with 20 g of HCl/Ethanol for 1 h, previously discussed, and clearly indicates that this treatment must be rejected.

Table 2 also shows the acidity of the Al-SMc, Al-SMEC20-3c, Al-SMEC10-5c Al-SMPO-5c samples. As can be seen, the treatment with H_2O_2 permits acidic properties to be obtained very close to calcined material (i.e., the material is not treated with any solvent to remove the template). The samples treated with HCl seem to lose some of the aluminium interchange ability, depending on the intensity of the treatment, and again, the Al-SMEC20-3c sample is the one showing the worse results, thus proving serious damage to the structure of the material.

The results shown in the previous paragraphs suggest that, if the solvent and the conditions for extraction are carefully selected, the elimination of template can be carried out by a leaching process. Moreover, both, the extraction with 10 g of HCl/Ethanol for 15 min, and the extraction with H_2O_2 seem to be capable for this purpose, although the former is better to some extent. However, the definitive proof for checking the ability of the materials to act as catalysts is their use in each specific application. In this way, Table 3 shows, as an example, some results obtained when the Al-SMEC20-3c, Al-SMEC10-5c and Al-SMPO-5c samples, respectively, are used as additives for reducing tobacco toxicity. The results corresponding to the reference tobacco, without additives, and to the cigarettes prepared with the Al-SMc sample, as a catalyst reference, are also shown. As can be seen, the percentages of reduction obtained in the presence of catalyst, with respect to the reference tobacco, calculated as 100 × (yield in the absence of catalyst − yield in the absence of catalyst)/(yield in the absence of catalyst), show that the amount of CO is decreased in the range 46–54%, thus revealing significant reductions for all the materials studied in this work. From this point of view, the samples extracted with HCl/ethanol seem to be better. It must be taken into account that the thermal stability of the Al-SMEC20-3c sample is very poor. Therefore, it could not be considered as an adequate additive despite the fact that it causes a marked reduction of the CO yield. With respect to the yields of liquids, the percentages of the reduction obtained are in the range 5–29%, corresponding to the best results for the catalyst of reference, Al-SMc. The three samples

Table 3
Results corresponding to the smoking experiments performed with cigarettes prepared by using the materials studied in this work as additives.

Sample: reference tobacco virginia + additive (the weight percentage of additive is shown)	g CO_2/cigarette	g CO/cigarette	g liquids/cigarette
Additive: none	0.1214	0.0319	0.0481
Additive: Al-SMc (3.64%)	0.1066	0.0259	0.0343
Additive: Al-SMEC20-3c (3.64%)	0.1106	0.0222	0.0457
Additive: Al-SMEC10-5c (3.70%)	0.0986	0.0224	0.0372
Additive: Al-SMPO-5c (3.65%)	0.0915	0.0240	0.0362

where the template was removed by leaching show worse results than the catalyst of reference (in the range 5–25%), but still maintain a noticeable reduction with respect to the reference tobacco, without additives, especially in the case of the materials of interest, i.e., Al-SMEC10-5c and Al-SMPO-5c, thus reflecting the ability of these materials to be used as tobacco additives. It is important to point out that the reported yield of liquids includes the yield of tars, which are restricted by laws, and water. Part of these liquids condense in the mouth and in the lungs of active smokers and are to a great extent responsible for the risks associated to tobacco consumption.

Obviously, despite the good results obtained with these materials in order to reduce tobacco toxicity, additional studies are needed in order to ensure that the catalyst do not pass trough the filters when a cigarette is smoked and to prevent eventual health risks related with this possibility, before the commercial exploitation of the material.

4. Conclusion

The results obtained in this work show that the extraction with solvent processes checked in this work is capable of template elimination in as-synthesized MCM-41 samples, yielding materials with enough activity to act as additives in order to reduce tobacco toxicity. It is interesting to emphasize the fact that the noticeable reduction of the amount of surfactant in the as-synthesized MCM-41 achieved by the use of the extraction process decreases the energy requirements in the last calcination step. In fact, when calcination is applied after extraction, according to the results obtained in this work, only about 5% of the weight of catalyst corresponds to the remainder surfactant, whereas when the as-synthesized sample is calcined, around 35% of the weight of the sample corresponds to the surfactant. This fact would be especially interesting if the process is being used for a commercial application of these catalysts. Moreover, the requirements for treating the gases evolving from the oven would also be noticeably reduced or even eliminated. Obviously, the overall economic balance would mark the selection of the final procedure.

As expected, the higher amount of template is removed in the first extraction step, and decreases in the successive extraction steps, thus suggesting that a counter-current leaching process would be the must efficient. However, an ultimate calcination step is needed in order to remove the residual content of surfactant.

The selection of the adequate experimental conditions for carrying out the extraction process is a very important task, and noticeable differences have been found when a mixture HCl/Ethanol has been used with ratios solid:solvent of 1:20 and 1:10 and contact time of 1 h and 15 min, respectively, both at 70 °C. In both cases, the removal of template in the first step seems to produce changes in the structure of the solid matrix, increasing the links with the last portions of template or of its products of decomposition. Moreover, when the elimination of template is faster (i.e., in the more aggressive treatment), these changes are deeper and seem to destroy the thermal stability of the resulting material. However, when H_2O_2 is used as a solvent, a gradual elimination of template, without structural changes, seems to occur, and the amount of surfactant removed is slightly lower. This solvent could have advantages because it decomposes spontaneously, thus avoiding further washes to remove the remaining extractant. Moreover, the acidity properties of the final catalyst are very close to those corresponding to the original calcined sample when this solvent is used.

Acknowledgements

Financial support for this investigation has been provided by the Spanish “Secretaría de Estado de Investigación” del Ministerio de Ciencia e Innovación (CTQ2008-01023).

References

[1] D. Bettcher, C. Sbramaniam, E. Guindon, A.-M. Perucic, L. Soll, G. Grabman, World Health Organization (WHO)-Tobacco Free Initiative, Geneva, Switzerland, 2001.
[2] K. Warner, Tob. Control 9 (2000) 78–79.
[3] The World Health Report 1995 World Health Organization, Geneva, 1995.
[4] Tobacco, Smoking International Agency for Research on Cancer, Monograph 38 World Health Organizations, 1986.
[5] D. Hoffmann, I. Hoffmann, J. Toxicol. Environ. Health 50 (1997) 307–364.
[6] P.C.H. Mitchell, Chem. Ind. 9 (1991) 308–311.
[7] H.C. Weiner, Immunol. Today 18 (1997) 335–343.
[8] M.W. Meier, K. Siegmann, Microporous Mesoporous Mater. 33 (1999) 307–310.
[9] Y. Xu, Y. Wang, J.H. Zhu, L.L. Ma, L. Liu, Stud. Surf. Sci. Catal. 142 (2002) 1489–1496.
[10] Y. Xu, Z.-Y. Yun, J.H. Zhu, J.-H. Xu, H.-D. Liu, Y.-L. Wei, K.-J. Hui, Chem. Commun. (2003) 1894–1895.
[11] Y. Xu, J. H-Zhu, L.L. Ma, A. Ji, Y.L. Wei, X.Y. Shang, Microporous Mesoporous Mater. 60 (2003) 125–137.
[12] F. Kleitz, W. Schmidt, F. Schüth, Microporous Mesoporous Mater. 65 (2003) 1–29.
[13] M.T.J. Keene, R. Denoyel, P.L. Llewellyn, Chem. Commun. 20 (1998) 2203–2204.
[14] T. Bozhi, L. Xiaoying, Y. Chengzhong, G. Feng, L. Qian, X. Songhai, Chem. Commun. 11 (2002) 1186–1187.
[15] S.A. Bagshaw, I. Brucea, J. Microporous Mesoporous Mater. 109 (1–3) (2008) 199–209.
[16] M.J.B. Souza, A.O.S. Silva, J.M.F.B. Aquino, V.J. Feernandes Jr., A.S. Araújo, J. Therm. Anal. Calorim. 75 (2004) 693–698.
[17] S.A. Araujo, M. Ionashiro, V.J. Fernandes Jr., A.S. Araujo, J. Therm. Anal. Calorim. 64 (2001) 801–805.
[18] T.R. Gaydhankar, V. Samuel, R.K. Jha, R. Kumar, P.N. Joshi, Mater. Res. Bull. 42 (8) (2007) 1473–1484.
[19] K.A. Koyano, T. Tatsumi, Y. Tanaka, S. Nakata, J. Phys. Chem. B 101 (1997) 9436–9440.
[20] A. Marcilla, A. Gómez-Siurana, D. Berenguer, Appl. Catal. A: Gen. 301 (2) (2006) 222–231.
[21] H. Zi-Le, S. Jian-Lin, L. Wang, Z. Wen-Hua, J. Non-cryst. Solids 292 (1–3) (2001) 177–183.
[22] L. Xiao, J. Li, H. Jin, R. Xu, Microporous Mesoporous Mater. 96 (1–3) (2006) 413–418.
[23] ISO 3308:2000, Routine analytical cigarette-smoking machine—definitions and standard conditions.
[24] W.A. Gomes Jr., L.A.M. Cardoso, A.R.E. Gonzaga, L.G. Aguiar, H.M.C. Andrade, Mater. Chem. Phys. 93 (1) (2005) 133–137.
[25] L.Y. Chen, Z. Ping, G.K. Chuah, S. Jaenicke, G. Simon, Microporous Mesoporous Mater. 27 (2–3) (1999) 231–242.
[26] Manual of Autosorb-6, Surface Area and Pore Size Analyzer.
[27] E.P. Barrett, L.G. Joyner, P.P. Halenda, J. Am. Chem. Soc. 73 (1951) 373–380.

Publicación III. *Template removal in MCM-41 type materials by solvent extraction. Influence of the treatment on the textural properties of the material and the effect on its behaviour as catalyst for reducing tobacco smoking toxicity, A. Marcilla, M. Beltran, A. Gómez-Siurana, I. Martínez, D. Berenguer. Chemical Engineering Research and Design, 89, (2011), Pages 2330-2343.*

En este trabajo, que es continuación del anterior, se profundiza en la caracterización de los catalizadores sintetizados a los que se aplica diferentes métodos de eliminación del tensioactivo mediante calcinación y/o extracciones sucesivas. A una parte de los materiales tratados se les incorpora aluminio mediante intercambio iónico y son sometidos a un tratamiento hidrotérmico para comprobar su estabilidad. La caracterización se ha realizado mediante fluorescencia de rayos X, difracción de rayos X, RMN Al^{27}, además de las isotermas de adsorción de N_2 a 77K, desorción térmica programada de amoniaco, y TGA que se había empleado previamente.

Se han realizado experimentos de fumado para comprobar la efectividad de estos materiales en la corriente principal del humo del tabaco de acuerdo con las condiciones experimentales descritas anteriormente. Se ha realizado el análisis de los gases mediante CG y detector TCD, para CO_2 y CO, y FID para el análisis de 34 compuestos presentes en la corriente gaseosa. Se ha obtenido el rendimiento global de líquidos condensados en filtros y trampas y el análisis de los mismos se ha realizado por GC/MS. En el caso de los líquidos se presenta el rendimiento para 24 compuestos. En este trabajo también se ha llevado a cabo el análisis de la cenizas obtenidas del proceso de fumado de tabaco mediante análisis termogravimétrico.

Los resultados obtenidos en este trabajo han permitido cubrir los siguientes objetivos específicos:

-Caracterización completa del catalizador MCM-41 tras someterse a diferentes métodos propuestos previamente de eliminación del tensioactivo y efecto sobre la estabilidad del catalizador.

- Establecimientos de métodos alternativos a la calcinación para la eliminación del tensioactivo que permitan obtener catalizadores con propiedades adecuadas para ser empleados como aditivos para reducir los compuestos presentes en la corriente principal del humo del tabaco.

CHEMICAL ENGINEERING RESEARCH AND DESIGN 89 (2011) 2330–2343

Contents lists available at ScienceDirect

Chemical Engineering Research and Design

journal homepage: www.elsevier.com/locate/cherd

Template removal in MCM-41 type materials by solvent extraction

Influence of the treatment on the textural properties of the material and the effect on its behaviour as catalyst for reducing tobacco smoking toxicity

*A. Marcilla**, *M. Beltran, A. Gómez-Siurana, I. Martinez, D. Berenguer*

Dpto. Ingeniería Química, Universidad de Alicante, Apdo. 99, 03080 Alicante, Spain

ABSTRACT

In this work a series of MCM-41 catalysts have been prepared by eliminating the template by calcination and by different extraction treatments. The extracted samples were also calcined and aluminium ion exchanged. A hydrothermal stability test of the final materials has also been performed. N_2 adsorption isotherms, NH_3 thermal desorption, X-ray fluorescence, X-ray diffraction, ^{27}Al NMR and thermogravimetry of each material have been determined in order to establish the influence of the procedure used for template elimination on the physicochemical and textural properties of the material. Moreover, the ability of the different catalysts prepared for reducing the toxicity of the mainstream smoke evolved when cigarettes are smoked has been checked too. The results obtained show that the final properties of the catalyst depend noticeably on the experimental conditions used in the template extraction process (i.e., the solvent selected, the solvent:catalyst ratio, the temperature, the contact time and the number of successive extraction steps). Thus, the adequate selection of such conditions permits a material to be obtained with properties very similar to that of the calcined MCM-41 material. As a conclusion, the material showing the best properties, among the catalysts studied in this work, produces a mean reduction of the yield of the different compounds analyzed in the gases and in the condensed products retained in the filters and in the traps of around 35%, 75% and 45%, respectively, which are slightly higher than the values corresponding to the calcined MCM-41 used as reference (i.e., 25%, 56% and 40%, respectively). These reductions results in an increase of the amount of ashes of around 2 mg/cigarette due to the presence of the catalyst.

Keywords: MCM-41; Template removal; Solvent extraction; Tobacco; Additive; Toxicity

Contents

---

* Corresponding author. Tel.: +34 96 590 2953; fax: +34 96 590 3826.
E-mail address: antonio.marcilla@ua.es (A. Marcilla).

Received 10 December 2010; Received in revised form 6 April 2011; Accepted 19 April 2011

doi:10.1016/j.cherd.2011.04.015

1. Introduction

The discovery in 1992 of MCM-41 silicates by Mobil opened the way to new zeotype molecular sieves with ordered mesoporous channels system (Beck et al., 1994). MCM-41 possesses highly regular arrays of uniform-size pore channels ranging from 1.5 to 10 nm in size and large surface area. Nevertheless, the utilization of MCM-41 in catalysis is now to some extent restricted by its relative low acidity and low hydrothermal stability, in comparison with those of microporous zeolites, such as HZSM-5 and USY.

Besides the known applications of zeolites and molecular sieves as MCM-41 as catalysts, these compounds have been also employed in a very wide range of processes, as for instance in the slow release of compounds for medical purposes (Mitchell, 1991; Weiner, 1997) and as additives in cigarettes to remove carcinogenic agents such as nitrosamines (Meier and Siegmann, 1999; Xu et al., 2002, 2003a,b). The synthesis of MCM-41 type silicates requires the use of surfactant-type organic templates, which should be removed before utilization, especially before applying them as an adsorbent or catalyst. In most cases the as-synthesized samples are heat-treated for the template removal in the presence of oxygen or air above 550 °C, for template removal. However, other alternatives, such as extraction techniques (Kleitz et al., 2003), ozone treatment (Keene et al., 1998) and microwave methods (Tian et al., 2002) have been also suggested.

The elimination of template, after the MCM-41 synthesis, is a necessary process in order to generate the porous structure and to provide the adequate catalytic properties. Moreover, a consolidation of the structure also occurs as a consequence of the calcination process (Kleitz et al., 2003; Gomes et al., 2005). However, several authors (Chen et al., 1999; Hitz and Prins, 1997; Shen and Kawi, 2002; Xiao et al., 2006) indicate that to burn out the organic templates may provoke the appearance of local defects and the structure shrinkage or collapse, specially if the inorganic framework is temperature sensitive and recognize that the use of alternative methods as solvent extraction, can non-destructively remove the organic template, yielding a material with a more perfect structure and allowing the recovery and reuse of expensive organic agents. Nevertheless, according with the bibliography, (Xiao et al., 2006), the templates cannot be removed completely by this method, and a calcination step is still necessary after the extraction, despite some authors indicate that increasing the contact time between the solid samples and the solvent (Hua et al., 2001) or repeating the extraction process (Zhao and Lu, 1998) could permit to completely remove the surfactant, thus providing a method environmentally friendly which provides a good support for the next processes. Thus, the possibility of eliminating the template through extraction with solvent processes (i.e., leaching) could be considered as an interesting alternative which would permit the recovery of the surfactant, which interact with the silicate species through coulombic interactions (Das et al., 1999; Zhao et al., 1996), avoiding the necessity of using heating processes which need high energy supply and imply the evolution of large amount of gases to be treated before disposal. This would be especially interesting if the synthesis of MCM-41 has to be performed at an industrial scale, when an economic study should be performed in order to compare the cost involved in both processes (i.e., calcination and leaching). In this way, the cost related with the amount of surfactant recovered and with the energy or solvent supply must be considered, as well as the cost involved in the treatment of the evolving gases treatment, which is needed after the calcination step, and which would be avoided or alleviated if a lixiviation process is previously used.

In this work, different samples of MCM41 have been prepared, and three methods of elimination of the organic template have been studied: calcination, and two different extraction processes, one with ethanol and another with hydrogen peroxide. The textural properties of all the samples obtained have been analyzed by measuring the N_2 adsorption isotherms and the influence of each solvent treatment on the solid characteristics has been studied. Moreover, the different samples have been also characterized by thermal desorption of NH_3 (NH_3 DTP) in order to show their acidic properties, which are related with the aluminium content, by X-ray fluorescence (XRF) for the semiquantitative estimation of the Al content, by X-ray diffraction for checking the crystalline structure of the materials, by ^{27}Al nuclear magnetic resonance (NMR) for to obtain information related to the environment of aluminium atoms, and by thermogravimentic analysis (TGA) for measuring the amount of template unremoved.

One potential use of MCM-41 materials, which is being studied by our research group (Marcilla et al., 2006a,b), is as additives for reducing tobacco toxicity. In this way, previous studies carried out by thermogravimetric analysis (Marcilla et al., 2010) demonstrate that both solvents are able to remove the template yielding a catalyst with enough activity to be used as a tobacco additive, despite the fact that temperature and the contact time in each extraction step have a noticeable influence on the final properties of the material. In this work, the composition of the gases and liquids obtained in smoking experiments have been analyzed in order to establish the effect of the treatment with solvents on the MCM-41 to be used as catalyst for reducing the toxicity of the mainstream tobacco smoke. The objective of the present work is not only to present alternative treatments for removing the template after the synthesis of MCM-41, but also to study the stability of the catalysts obtained and their effect as potential additives for reducing the smoke tobacco toxicity.

2. Experimental

2.1. Synthesis of materials

A sample of MCM-41 not including aluminium (SM, in the nomenclature used in this work) was prepared according the method reported in literature (Bagshaw and Brucea, 2008), where CTMACl (25 wt% aqueous solution of cetyl trimethyl

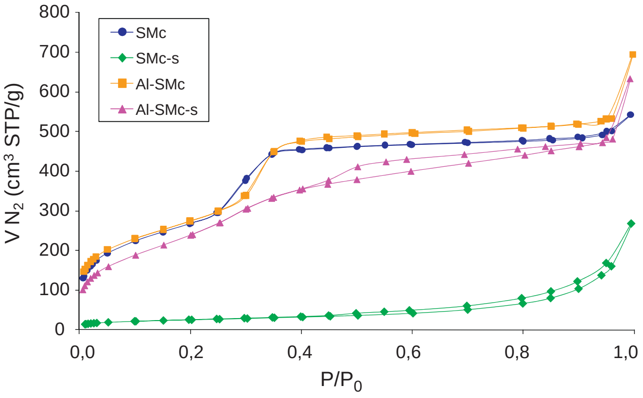


Fig. 1 – N_2 adsorption isotherms corresponding to the un-extracted samples SMc, Al-SMc, SMc-s and Al-SMc-s.

ammonium chloryde, Aldrich) was dissolved in distilled water under constant stirring. Aqueous ammonia solution was added to this solution, which was stirred for 10 min. Finally, the silica source, TEOS (tetraethyl ortosilicate 99%, Aldrich) was added drop wise with vigorous stirring to obtain the final gel. The stirring was continued for a period of 4 h. The product was recovered by filtration, washed thoroughly with distilled water and then dried at 100 °C over night. The removal of the template was accomplished by calcination in air at 550 °C for 6 h (SMc) or by extraction with an HCl/ethanol mixture (SMEC) or with hydrogen peroxide (SMPO). The procedures for the template elimination are described in the following section.

Additionally, aluminium containing MCM-41 materials (Al-SM) were prepared from samples obtained by using the above described procedure, by stirring the different solid samples after template elimination (SMc, SMEC20-3c, SMEC10-5c and SMPO-5c) in a 0.25 M solution of $Al(NO_3)_3{\cdot}9H_2O$ at 60 °C, for 3 h (Chen et al., 1999). The product (Al-SMc, Al-SMEC20-3c, Al-SMEC10-5c and Al-SMPO-5c) was recovered by filtration, washed with distilled water and dried at 100 °C. The incorporation of Al in the samples permits their stabilization, since the materials are very unstable in contact with water (Chen et al., 1999). Table 1 shows the samples prepared in this work and the corresponding notation.

2.2. *Elimination of tensioactive by extraction with solvents*

The ability of two different solvents to remove the template has been tested, and the results obtained have been compared with those corresponding to the material prepared by the conventional method, i.e., removing the template by calcination. Two extraction processes have been tested. The first one is based on the work of Hua et al. (2001), and uses a mixture of HCl and ethanol as a solvent. The experiments were carried out by stirring 1 g of SM in 20 g of a solution 1 M of HCl in ethanol at 70 °C for 1 h. The extracted samples were filtered and washed with ethanol. This procedure was repeated successive times, mixing the sample previously extracted with a fresh solvent solution. A similar process was performed using 1 g of SM and stirring in 10 g of the HCl/Ethanol mixture at 70 °C for 15 min.

The second extraction method is based in the work of Xiao et al. (2006). 0.5 g of SM were stirred in 50 g of H_2O_2 0.6 M at room temperature for 1 h, and the pH solution was adjusted at 3.5 with diluted HCl. Then the sample was filtered and washed with ethanol. The extraction step was successively repeated, mixing the extracted sample with fresh solvent solution.

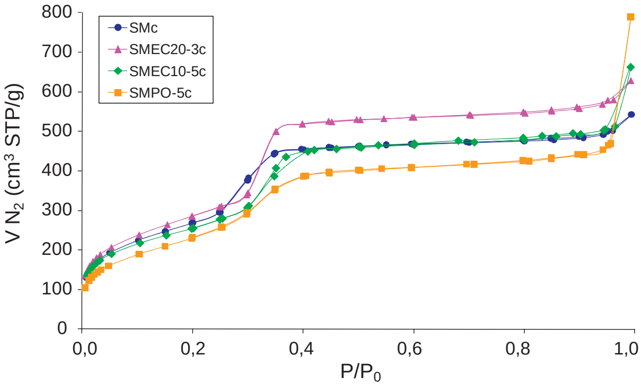


Fig. 2 – N_2 adsorption isotherms corresponding to the extracted samples SMEC20-3, SMEC10-5 and SMPO-5.

The materials resulting from the different steps of the extraction process (SMEC20-3, SMEC10-5 and SMPO-5) were studied by thermogravimetric analysis, in a Netzsch TG 209 thermobalance, in order to determine the amount of template removed. In this way, dynamic heating (25–550 °C, at 10 °C/min) was applied under an oxygen atmosphere, thus emulating the conditions in the calcination process The results obtained in this study have been shown elsewhere (Marcilla et al., 2010), and reveal that small quantities of template still remain retained in the structure. Therefore, the samples have been calcined, as is described in Section 2.1, in order to obtain the materials without template (SMEC20-3c, SMEC10-5c and SMPO-5c). Afterwards, as pointed out previously, the aluminium has been incorporated in order to improve the stability (samples Al-SMEC20-3c, Al-SMEC10-5c and Al-SMPO-5c).

2.3. *Hydrothermal stability test*

The study of the hydrothermal stability of the different catalysts studied in this work has been performed by boiling the samples in distilled water for four days under reflux. The resulting materials are identified, according to the nomenclature used in this work, as Al-SMEC20-3c-s, Al-SMEC10-5c-s and Al-SMPO5c-s. The structural changes were analyzed after each treatment by comparing the textural characteristics of the samples before and after applying the hydrothermal test, from the corresponding N_2 adsorption isotherms at 77 K.

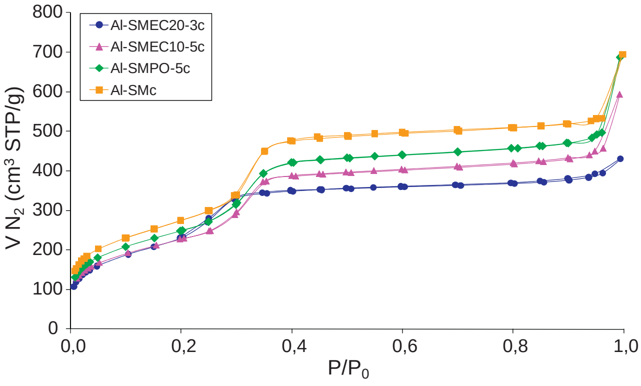


Fig. 3 – N_2 adsorption isotherms corresponding to the samples containing aluminium, after calcinations, Al-SMEC20-3c, Al-SMEC10-5c and Al-SMPO-5c.

Table 1 – Materials synthesized in this work.

Material	Aluminium reacted	Template removal	4 days under water reflux
SM	No	No	No
SMc	No	Calcination	No
SMc-s	No	Calcination	Yes
Al-SMc	Yes	Calcination	No
Al-SMc-s	Yes	Calcination	Yes
SMEC20-1	No	1 wash-20 g HCl/EtOH-1 h	No
SMEC20-2	No	2 washes-20 g HCl/EtOH-1 h	No
SMEC20-3	No	3 washes-20 g HCl/EtOH-1 h	No
SMEC20-3c	No	3 washes-20 g HCl/EtOH-1h + calcination	No
Al-SMEC20-3c	Yes	3 washes-20 g HCl/EtOH-1h + calcination	No
Al-SMEC20-3c-s	Yes	3 washes-20 g HCl/EtOH-1h + calcination	Yes
SMEC10-1	No	1 wash-10 g HCl/EtOH-15 min	No
SMEC10-2	No	2 washes-10 g HCl/EtOH-15 min	No
SMEC10-3	No	3 washes-10 g HCl/EtOH-15 min	No
SMEC10-4	No	4 washes-10 g HCl/EtOH-15 min	No
SMEC10-5	No	5 washes-10 g HCl/EtOH-15 min	No
SMEC10-5c	No	5 washes-10 g HCl/EtOH-15 min + calcination	No
Al-SMEC10-5c	Yes	5 washes-10 g HCl/EtOH-15 min + calcination	No
Al-SMEC10-5c-s	Yes	5 washes-10 g HCl/EtOH-15 min + calcination	Yes
SMPO-1	No	1 wash-H_2O_2-1 h	No
SMPO-2	No	2 washes-H_2O_2-1 h	No
SMPO-3	No	3 washes-H_2O_2-1 h	No
SMPO-4	No	4 washes-H_2O_2-1 h	No
SMPO-5	No	5 washes-H_2O_2-1 h	No
SMPO-5c	No	5 washes-H_2O_2-1h + calcination	No
Al-SMPO-5c	Yes	5 washes-H_2O_2-1h + calcination	No
Al-SMPO-5c-s	Yes	5 washes-H_2O_2-1h + calcination	Yes

2.4. *Catalysts characterization*

The textural characteristics of the different samples obtained after calcination (SMc, SMEC20-3c, SMEC10-5c and SMPO-5c) as well as of the materials containing aluminium (Al-SMc, Al-SMEC20-3c, Al-SMEC10-5c and Al-SMPO-5c) and the hydrothermally treated materials (SMc-s, Al-SMc-s, Al-SMEC20-3c-s, Al-SMEC10-5c-s and Al-SMPO-5c-s) were

Table 2 – Textural parameters of the samples of catalysts studied in this work.

Sample	BET area (m^2/g)	DR Micropores volume (cm^3/g)	BJH ore diameter (Å)
SMc	1003	0.35	25
Al-SMc	1007	0.37	27
SMc-s	90	0.04	24[a]
Al-SMc-s	935	0.29	25[a]
SM20-3c	1053	0.37	27
Al-SM20-3c	797	0.29	27
Al-SM20-3c-s	222	0.09	24[a]
SM10-5c	937	0.36	28
Al-SM10-5c	835	0.31	27
Al-SM10-5c-s	778	0.28	25
SMPO-5c	871	0.30	27
Al-SMPO-5c	916	0.34	27
Al-SMPO-5c-s	823	0.29	25[a]

[a] More than 1 maximum in the BJH plot.

determined by the corresponding N_2 adsorption isotherms at 77 K, measured in an automatic AUTOSORB-6 supplied by Quantachrome. The adsorption curves of the isotherms were recorded (Fig. 1–3 and 6) and the results of applying the BET model, considering values in the 0.04-0.25 range of relative pressure, and the Dubinin-Radushkevich method, for relative pressures under 0.02, are shown in Table 2, despite the true nature of the porous structure of MCM-41 (Berenguer-Murcia et al., 2002) as well as the validity of such conventional methods for the interpretation of the textural properties from the experimental adsorption isotherms (Marcilla et al., 2009) is a controversial topic.

The acidity of the materials was measured by temperature-programmed desorption (TPD) of ammonia, performed in a Netzsch TG 209 thermobalance, following the procedure described elsewhere (Marcilla et al., 2006a,b). The Si/Al ratio was measured by X-ray fluorescence in a Philips equipment, model PW1480. In addition, the ^{27}Al solid state nuclear magnetic resonance spectra were recorded on a Fourier Transform Bruker model AC-300, in the condition reported by Marcilla et al. (2006a,b) in order to obtain information about the coordination of the aluminium atoms in the structure. The X-ray diffraction (XRD) pattern was recorded by using a Seifert JSO-DEBYEFLEX 2002 X-ray difractometer. The amount of template which remains unremoved after the extraction with solvents treatment has been measured by thermogravimetric analysis, in a Netzsch TG 209 thermobalance, and using a dynamic heating (25–550 °C, at 10 °C/min) under oxygen atmosphere, thus emulating the conditions in the calcinations process.

2.5. *Smoking experiments*

In order to check the influence of the procedure for template extraction in the activity of the catalyst for reducing tobacco toxicity, cigarettes prepared with mixtures of tobacco and catalyst were smoked in a smoking machine, and the results obtained for the composition of the gaseous and condensed products have been compared with those corresponding to a reference cigarette, where the same tobacco with no catalyst added was smoked. The smoking machine permits five cigarettes to be smoked simultaneously and follows most of the specifications of the ISO 3308. Tobacco from commercial cigarettes of the selected brand was removed from the tubes. This tobacco was mixed thoroughly with around 4% (w/w) of catalyst under study. This mixture (tobacco plus catalyst) was used to refill the emptied tube. During the smoking process, the mainstream smoke crosses the filter of the cigarette as well as a trap placed after the cigarette, with the purpose of retaining the condensed products, and finally, the non-condensed products are collected in a Tedlar bag. It is interesting to point out that the trap located after the cigarette captures the condensable products which could condensate in the mouth and the lungs of active smokers.

The cigarettes were prepared and then kept at 25 °C and 60% relative humidity for at least 48 h before the smoking process (i.e., in a drier provided with a saturated solution sodium nitrite). The pressure of aspiration of the machine must be of the order of 1.5 kPa.

The yield of liquids was obtained by weighing the traps and the filters before and after each experiment and the measurement of the content of CO and CO_2 in the gaseous product was carried out by GC-TCD using a CTR I column. The condensable products retained in the filter of the cigarette and in the trap were extracted with 2-propanol as solvent and analyzed by GC/MS using a HP-5MS column. Finally, the rest of non-condensed products were analyzed by GC-FID using a GAS-PRO column. The percentage of reduction with respect to the reference tobacco achieved in the presence of each catalyst has been calculated as follows:

$$\%\,\text{reduction} = \frac{\text{yield in the reference tobacco} - \text{yield in the presense of catalyst}}{\text{yield in the reference tobacco}} \times 100.$$

3. Results and discussion

Fig. 1 shows the N_2 adsorption isotherms corresponding to the un-extracted samples SMc, Al-SMc, SMc-s and Al-SMc-s. The sample SMc corresponds to the MCM-41 material prepared by conventional methods Bagshaw and Brucea (2008), and is the reference for the comparison with the extracted samples. The sample Al-SMc shows the influence of the ionic exchange with aluminium on the textural characteristics of the material. As commented above, the introduction of aluminium in the structure is a necessary step in order to improve the thermal stability of the material. Finally, the comparison between the samples SMc-s and Al-SMc-s permits us to test if the introduction of aluminium results, as expected, in an increase of the thermal stability of the material. The textural parameters obtained from the isotherms shown in Fig. 1 by application of conventional BET and DR methods are presented in Table 2.

As can be seen in Fig. 1 (and Table 2), the comparison between the SMc and Al-SMc samples shows the existence of few differences in the textural properties. Both materials exhibit similar values of the BET area and the DR micropore volume, but the sample containing aluminium shows a slight shift of the maximum of the distribution of pore size towards higher values (i.e., the gap in the adsorption isotherm is displaced towards higher relative pressure values). Moreover, the stabilizing role of aluminium is clearly observed, and Fig. 1 shows that the sample not containing aluminium loses practically all its textural properties after the hydrothermal treatment (sample SMc-s), thus demonstrating the need for applying some stabilizing treatment, in order to ensure that the material retains its activity. On the other hand, the sample that contains aluminium (Al-SMc-s) maintains acceptable values of the textural parameters, thus suggesting that to some extent this sample also maintains its catalytic and adsorbent properties.

Fig. 1 also shows that the shift between the adsorption and desorption branches increases to some extent after the hydrothermal treatment (samples SMc-s and Al-SMc-s). This shift is not observed in the untreated samples (samples SMc and Al-SMc). As can be seen, these curves suggest that after the aggressive hydrothermal treatment applied, the structure of the solids results damaged, and the number of mesopores decreases at the expense of the formation of greater pores and, as a consequence, a widening of the mesopores step occurs. In the case of the non-stabilized sample (SMc-s), the hydrothermal treatment seems to destroy the porous structure completely.

As pointed out in Section 2.1, the extracted samples have been obtained by leaching with a HCl/ethanol mixture (SMEC samples) or with hydrogen peroxide (SMPO samples). In the first case, two different experimental conditions have been checked (1 g sample:20 g solvent for 1 h at 70 °C in three successive extraction steps, and 1 g sample:10 g solvent for 15 min at 70 °C in five successive extraction steps). In the case of the samples treated with hydrogen peroxide, a ratio of 1 g sample:50 g H_2O_2 were used and five extraction steps for 1 h at 25 °C were performed. The samples obtained after the last extraction step were calcined in order to remove the remaining amounts of template. In a previous work (Marcilla et al., 2010), where the solvent elimination was studied by thermogravimetric analysis, we discovered the possibility that the extraction with HCl/Ethanol causes changes in the solid matrix which contributes to a damage of the structure, this damage is more noticeable in the case where the removal of the template is faster (i.e., in the case of the SMEC20-3 sample). The N_2 adsorption results corresponding to the samples obtained after the extraction with solvents, where the remaining amounts of template (around 5–7% according to Marcilla et al., 2010) were removed by a final calcination step before the aluminium exchange process (samples SMEC20-3c, SMEC10-5c and SMPO-3c), are shown in Fig. 2 and Table 2. This is a necessary step because the results obtained by TGA indicate that, for the samples SMEC20-3, SMEC10-5 and SMPO-5, respectively, the 12.6%, 9.2% and 14.7% (weight percentages) of template remains unremoved after the extraction with solvents, thus reflecting the need of apply an additional calcination step after the leaching process. As can be seen, the shape of the adsorption isotherm curves is very similar in all the cases, despite the fact that some displacement towards higher size mesopores appears in the case of the extracted samples. The three extracted samples exhibit acceptable textural properties, but the sample SMEC20-3c shows a higher BET area, and the SMPO-5c has slightly poorer properties than the other samples. The sample SMEC10-5c has very similar textural parameters to the reference sample SMc. The comparison between the samples SMEC20-3c and SMEC10-5c reflects that the textural properties of the material are dependent of the ratio solvent:solid, the number of extraction steps, and the procedure used to contact the solvent with the solid. Therefore, a careful optimization of the experimental conditions for the extraction process is needed, simultaneously considering the activity of the material for each particular application in question.

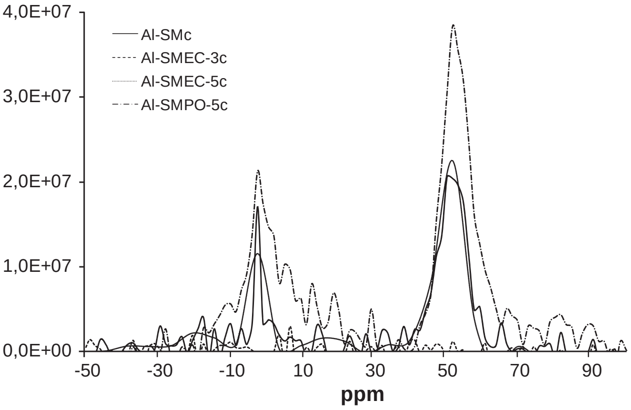


Fig. 4 – ^{27}Al NMR spectra of the aluminium containing catalysts studied in this work.

The need to incorporate aluminium in order to improve the hydrothermal stability of the materials has been pointed out previously (see Fig. 1). Moreover, the presence of aluminium in the structure is necessary in order to provide the acidic properties responsible for part of the catalytic properties of the material. Fig. 3 shows the adsorption isotherms of the samples containing aluminium, and Table 2 contains the corresponding textural parameters. As can be seen, the samples treated with Etanol/HCl present some worsening of the textural properties. Different than the case of the samples not containing aluminium, Al-SMEC20-3c and Al-SMEC10-5c samples show poorer properties than the reference calcined sample, Al-SMc. The opposite is the case of the Al-SMPO-5c sample, which shows better textural properties than the original SMPO-5c material, closer to the reference Al-SMc sample. These results are in good agreement with the observations previously reported (Marcilla et al., 2010) and also agree with the values of the acidity of the samples, measured by NH_3 DTP, i.e.: 0.31 mg NH_3/g sample for the catalyst of reference, Al-SMc, and 0, 0.20 and 0.30 mg NH_3/g sample for Al-SMEC20-5c, Al-SMEC10-5c and Al-SMPO-5, respectively. Therefore, we expect that the sample Al-SMEC20-5c should accordingly exhibit the poorer catalytic activity, not only due to its worse textural properties but also to the practical absence of acid properties. The values of the Si/Al mass ratio obtained by XRF also agree with these results, showing that no aluminium has been incorporated into the structure of the Al-SMEC20-3c sample, whereas for the other samples the corresponding semiquantitative values are 88.2, 70.5 and 43.3, for Al-SMc, Al-SMEC10-5c and Al-SMPO-5c, respectively. Once the use of H_2O_2 has been recognized as the best option, among those studied in the present work, we have checked the absence of any significant oxidizing oxidizing effect of H_2O_2 on the surfactant molecules, which could prevent its reuse as template.

Fig. 4 shows the ^{27}Al NMR spectra of the aluminium containing samples. With the only exception of the Al-SMEC-3c, these spectra are very similar to that corresponding to conventional Al-MCM-41 samples obtained by direct synthesis in the presence of aluminium and silicon sources (i.e., aluminium isopropoxide and TEOS) (Marcilla et al., 2006a,b), and contain two peaks: one around 54 ppm, corresponding to Al tetrahedrally coordinated, and another near 0 ppm, corresponding to octahedral Al species. These results are in good agreement with the bibliography (Chen et al., 1999), and reveal the effectiveness of the treatment by aluminium ion exchange (except for Al-SMEC-3c). The NMR results also corroborate the absence

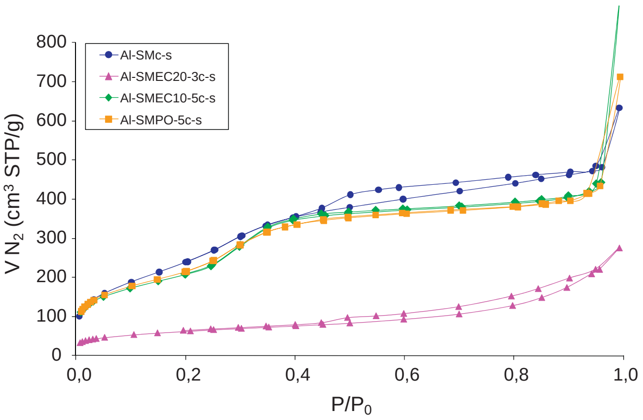


Fig. 5 – N_2 adsorption isotherms corresponding to the samples containing aluminium, after the hydrothermal treatment, Al-SMEC20-3c-s, Al-SMEC10-5c-s and Al-SMPO-5c-s.

of aluminium in the Al-SMEC-3c sample shown by XRF. On the other hand, the observed XRD patterns of the catalysts studied in this work confirm the typical (1 0 0), (1 1 0) and (2 0 0) peaks at around 2.0°, 3.6° and 4.1°, respectively, of the MCM-41 materials (Chen et al., 1999; Luan et al., 1995; Marcilla et al., 2006a,b), and indicate that impregnating SMc with aqueous $Al(NO_3)_3$ did not affect the mesoporous structure (Chen et al., 1999).

Fig. 5 shows the comparison of the behaviour of the samples containing aluminium after the hydrothermal treatment, and Table 2 shows the calculated values of the textural parameters. As can be seen, all the samples lose some textural properties after the treatment (see Table 2), and the values of the reported parameters are lowered with respect the original samples. The Al-SMc-s sample, where the template was removed by calcination shows higher stability. Nevertheless, the extracted samples maintain an acceptable stability, with the only exception of the Al-SMEC20-3c-s sample, thus indicating the effectiveness of the role of aluminium in the structure. It seems that the Al-SMEC20-3c-s sample loses its properties completely, probably as a consequence of the above-commented on damage of the solid matrix caused by the aggressive treatment with high amount of solvent and high time contact.

The gap between the adsorption and desorption branches in the isotherms previously commented on for samples SMc-s and Al-SMc-s in Fig. 1 also seems to appear after the hydrothermal treatment of the extracted samples, despite the fact that in the case of the more stable samples, which yield Al-SMPO-5c-s and Al-SMEC10-5c-s, it is almost negligible and can only be observed in the final zone of the curves, at relative pressures higher than 0.9. The widening of the mesopores step already discussed for the samples SMc-s and Al-SMc-s after the long contact time with hot water also appears. The case of the sample Al-SMEC20-3c-s is especially noticeable, and the porous structure seems to be destroyed, thus showing the very unstable nature of the Al-SMEC20-3c sample, with values very close to those corresponding to the SMc-s sample, obtained from the non-stabilized SMc sample (see Table 2).

As it has been stated in the introduction section, the ability of the catalysts studied in this work for reducing the toxicity associated to the process of tobacco smoking has been also checked. With this purpose, Fig. 6 shows the results obtained for the composition of the non-condensed products of the mainstream smoke obtained when cigarettes prepared with a reference Virginia tobacco and with mixtures of this tobacco with samples of the three catalysts Al-SMEC20-3c, Al-SMEC10-5c and Al-SMPO-5c were smoked under the conditions specified in the experimental procedures section. The results corresponding to the reference tobacco mixed with the reference Al-SMc catalyst are also shown. Fig. 6a shows compounds with yields higher than 0.05 mg/cigarette. As can be seen, the three samples prepared with materials where the template was removed by extraction exhibit similar behaviour to that of the samples prepared with the reference catalyst, Al-SMc. In fact, the yields obtained in the presence of Al-SMEC20-3c are slightly higher or approximately equal, whereas in the case of Al-SMEC10-5c and Al-SMPO-5c they are slightly lower than that corresponding to Al-SMc. In all the cases the yields are lower than those obtained in the absence of catalyst. With respect to the checked samples, it seems that the order for its ability to decrease the yields of the different compounds evolved is: Al-SMEC-3c < Al-SMEC-5c < Al-SMPO-5c (i.e., Al-SMPO-5 is the best catalyst from this point of view). Al-SMc is between Al-SMEC20-3c and Al-SMEC10-5c, except for acetone and acetaldehyde, which shows the worst results. It is interesting to point out the case of acetone, where the yields obtained when the extracted samples were used as catalysts are noticeably lower than those for the Al-SMc sample. The case of isoprene is also interesting because whereas the conventional Al-SMc catalyst produces practically no reduction (in fact some slight increase seems to appear), the isoprene formation decreases in the presence of the extracted Al-SMEC10-5c and Al-SMPO-5. Fig. 6b shows compounds with yields in the range of 0.01–0.05 mg/cigarette. In this case, the observed behaviour is very similar to that previously commented on for Fig. 6a. It is worth pointing out the case of ethyne, whose behaviour resembles to that of isoprene, and cis-2-butene, where the yield obtained in the presence of Al-SMEC20-3c is noticeably higher than in the presence of the other catalysts, and closest to the reference tobacco. It is also interesting to point out the case of furane, where Al-SMEC20-3c and Al-SMEC10-5c show yields higher than Al-SMc, but Al-SMPO-5c practically eliminates this compound completely, and acroleine, where the three samples show yields lower than Al-SMc, but are higher for the Al-SMEC10-5c sample. Additionally, this graph highlights the noticeable reduction of toluene caused by all the tested catalysts. Finally, Fig. 6c shows the results corresponding to minor compounds (<0.01 mg/cigarette). In this case, the differences with respect to the general tendency observed in Fig. 6a correspond to 1,2-propanediene, where the yield in the presence of Al-SMc is slightly higher than for the reference tobacco, and lower in the presence of the extracted samples (in decreasing order: Al-SMc > Al-SMPO-5c > Al-SME10-5c > Al-SMEC20-3c) and methanethiol, where the order of reduction is the same. However, the yield of methanethiol is lower than the reference tobacco in the presence of the four catalysts studied in this work, whereas in the case of 1,2-propanediene the yields are very close in all the cases, and are slightly higher than the reference tobacco in the presence of Al-SMc and slightly lower in the presence of the other catalysts. It is interesting the case of hexane and isobutiraldehyde, where the presence of Al-SMc increases the yields with respect to the reference tobacco, whereas in the cases of the Al-SMEC10-5c and Al-SMPO-5c samples some reduction takes place, especially noticeable for isobutiraldehyde in the presence of Al-SM10-5c and Al-SMPO-5c. Different than for the rest of the compounds,

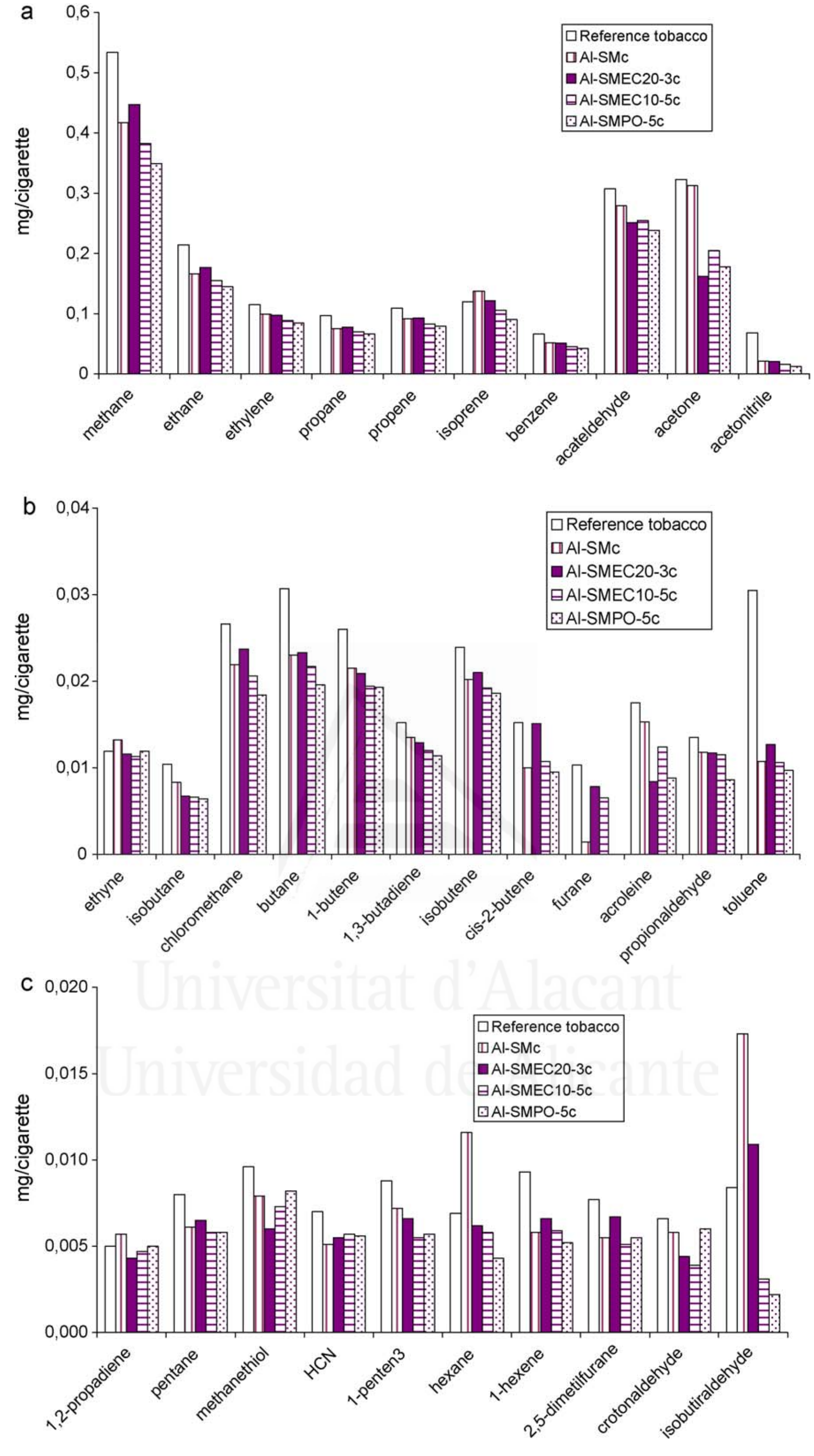


Fig. 6 – Yields corresponding to the different compounds analyzed in the non-condensed fraction of the mainstream smoke. (a) Maximum yield > 0.05 mg/cigarette, (b) 0.05 mg cigarette > maximum yield > 0.01 mg/cigarette and (c) 0.01 mg/cigarette > maximum yield.

the yields of crotonaldehyde are higher for Al-SMPO-5c than for the other catalyst, but lower than for the reference tobacco.

It is difficult to obtain definitive conclusions related to the order of activity of the four materials studied in this work. In fact, with the only exception of the sample Al-SMEC20-3c, which shows the worst results, the other three materials exhibit relatively similar behaviour, in good agreement with the similarity in their textural and acidic properties. On the other hand, the lower catalytic properties of Al-SMEC20-3c also agrees with its lower textural properties and its null acidic properties. However, it is interesting to point out that, despite the practical absence of acid sites in the case of Al-SMEC20-3c sample, it even maintains some capacity for reducing the yields of some compounds. This is especially noticeable in the case of the condensed fraction, whose results will be presented in the following paragraphs. This behaviour indicates

Table 3 – Yields corresponding to different compounds analyzed in the not-condensed fraction of the mainstream smoke retained in the traps located after the smoked cigarettes.

Compound	µg/cigarette				
	Reference tobacco	Reference tobacco + Al-SMc	Reference tobacco + Al-SMEC20-3c	Reference tobacco + Al-SMEC10-5c	Reference tobacco + AlSMPO-5c
Furfural	2.56	2.43	2.79	2.12	1.95
4-Cyclopentene-1,3-dione	0.70	0.57	0.63	0.61	0.52
2-Methyl-2-cyclopentenone	0.76	0.60	0.99	0.71	0.55
Acid 3-methyl-pentanoic	1.45	0.76	0.99	0.59	0.63
Phenol	4.22	1.89	1.94	1.15	1.10
Corylon (2-Hydroxy-1-methylcyclopenten-3-one)	1.90	0.66	0.98	0.43	0.34
Limonene	0.66	0.36	0.57	0.45	0.41
o-Cresol	3.51	1.38	1.58	0.97	0.86
p-Cresol	4.04	1.70	1.88	1.00	0.94
Guaiacol (o-Methoxyphenol)	0.94	0.45	0.57	0.31	0.38
2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	7.46	3.04	4.29	2.88	2.37
2,4-Dimethyl-phenol	3.10	0.26	1.03	1.32	0.95
4-Ethylphenol	3.72	0.63	1.23	2.04	2.05
Hydroquinone	5.98	1.50	3.23	5.15	1.74
Indole	4.59	1.84	3.60	2.87	1.66
4-Vinyl-2-methoxy-phenol	3.40	1.63	2.45	1.67	0.97
Nicotine	335.05	206.43	220.78	182.79	178.58
Skatol (3-Methylindole)	3.38	1.25	1.65	1.19	1.55
Myosmine	2.84	1.57	2.45	1.49	1.12
4-Methyl-2,6-di-tert-butylphenol	2.51	3.04	3.91	3.45	3.42
Megastigmatrienone 4	1.29	0.57	1.28	0.98	0.56
Diethyl phthalate	1.61	0.82	1.28	1.00	1.22
Cotinine	5.19	3.49	3.95	2.87	2.68
Neophytadiene	21.67	15.55	17.31	13.27	12.76

that some adsorption on the mesopores could occur. In this way, the complexity of the process, where the combustion, pyrolysis and oxidative pyrolysis of a very complex mixture of materials (i.e., tobacco and products evolved from tobacco) makes difficult the assessment of the relationship between the activity of the catalysts and their physicochemical and textural properties.

The previous results show the benefits of the use of the studied catalysts for reducing the yields of non-condensed organic compounds in the mainstream smoke when these materials are used as tobacco additives. However, their effect on the condensed products must be also checked. This is an important issue considering that these compounds are able of condensate in the mouth and in the respiratory system of smokers. In fact, laws restrict the yields of CO and tars evolved from cigarettes. In a previous work, the ability of the studied samples Al-SMEC20-3c, Al-SMEC10-5c and Al-SMPO-5c for reducing both CO and tars was pointed out (Marcilla et al., 2010). In the present work, the effect of these catalysts in the quantitative composition of the liquid fraction of the mainstream smoke, i.e., the liquids retained in the filters and in the traps located after the cigarettes in the smoking machine, is shown.

Table 3 shows the results corresponding to the composition of the condensed fraction retained in the traps located after the cigarettes in the smoking machine. This liquid fraction is

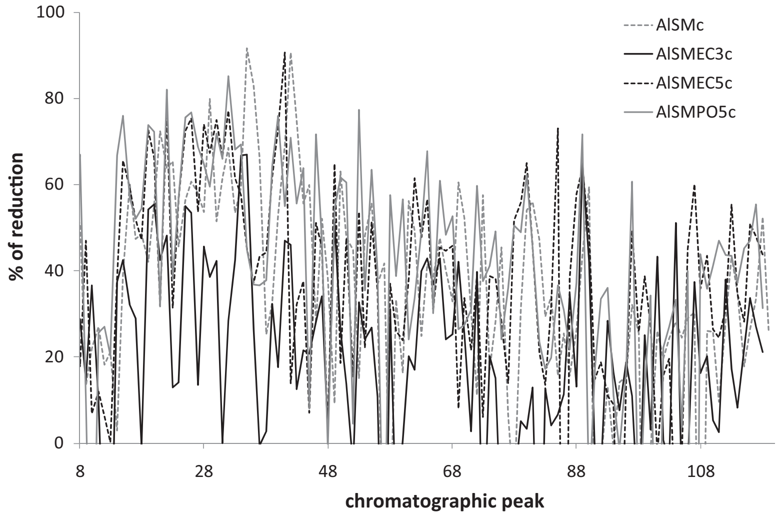


Fig. 7 – Percentages of reduction of the yields of the different compounds obtained in the condensed fraction retained in the traps after cigarettes when Al-SMc, Al-SMEC20-3c, Al-SM10-5c and Al-SMPO-5c were used as tobacco additives.

a very complex mixture, showing more than 120 compounds observable in the corresponding GC/MS chromatograms. In Table 3, only compounds whose identification by mass spectrometry was established are shown (i.e., >80% probability in all the samples and duplicated analysis). However, it is important to note that despite the probability of the assignment by mass spectrometry of the rest of components of the analyzed mixtures being relatively low, the same peaks, with the same assignments, appeared in all the chromatograms corresponding to the different mixtures analyzed and therefore, they should considered as integrants of the condensable fraction of the mainstream smoke. Another consideration that must be taken into account is the fact that despite the complexity of the composition of the samples analyzed by GC/MS, the existence of isomers and compounds with very similar chemical structures reduces the importance of the lack of clear assignment of certain chromatographic peaks, and permits us to draw conclusions about the comparative effect of the use of the catalysts studied in this work as tobacco additives. Compounds appearing at retention time higher than 35 min in the chromatograms have not been included in Table 3.

The main component of the liquid fraction of the mainstream smoke is triacetin (1,2,3-propanetriol triacetate), which has not been included in Table 3 because it saturates the chromatograms. Moreover, triacetin comes from the cigarette filters and, therefore, it is not susceptible to being reduced by the catalysts studied in this work. As can be seen, in general, the yields of all the compounds are reduced as a consequence of the presence of the catalyst. The only exceptions are furfural and 2-Methyl-2-cyclopentenone, which show values slightly higher in the presence of Al-SMEC20-3c than in the reference tobacco, and 4-methyl-2,6-di-tert-butylphenol, which is increased in the presence of the four catalysts considered in this work.

Very interesting is the case of Al-SMPO-5c, which reduces the yields of all the compounds included in Table 3 (with the exception of 4-methyl-2,6-di-tert-butylphenol), thus corroborating the previous consideration that, from the point of view of its application as tobacco additive, Al-SMPO-5c is the best catalyst, among the four materials studied in this work. This conclusion is in good agreement with the results shown in Fig. 7, where the results corresponding to all the compounds appearing in the chromatograms (i.e, all the detected chromatographic peaks) are shown. It must be considered that, actually, the toxicity of tobacco smoke it is not evaluated from the knowledge of its content of each individual chemical component. In fact, tobacco smoke contains around 5000 compounds and, according with the bibliography (Baker, 2006), tars are good as representative of tobacco toxicity because all the components are evaluated simultaneously. Therefore, the results shown in Fig. 7, despite a lot of peaks have not been completely identified, are useful to evaluate the overall decrease in tobacco toxicity. Moreover, once the best additive will be found, the identification of the eventual compounds which could increase must be performed in order to ensure that none of such compounds is recognized as toxic. Table 4 shows the retention times corresponding to the GC-peaks represented in Fig. 7 as well as the assignment of peaks, when it has been clearly established (i.e., compounds shown in Table 3). In Fig. 7, the percentage of reduction with respect to the reference tobacco has been calculated as has been described in the “Smoking experiments” section. Negative values of the percentage of reduction indicate that some increase occurs as a consequence of the presence of the catalyst. In Fig. 7, the lines represent the positive values of the % Reduction (i.e., compounds which are decreased as consequence of the presence of catalyst), and compounds which are increased in the presence of the studied catalysts (i.e., those showing negative values of the % reduction) have not been represented. As can be seen:

- When Al-SMc is used as catalyst, there are 11 compounds which are increased with respect to the reference tobacco (peaks 1, 2, 4, 57, 77, 90, 91, 93, 98, 99 and 107), whereas the other 107 compounds are decreased.
- The worst results are obtained in the presence Al-SMEC20-3c. However, even in this case, only a relatively low number of compounds are increased (21 compounds increased and 97 are decreased).
- In the presence of Al-SMEC10-5c, 9 compounds are increased (peaks 1, 2, 4, 57, 86, 95, 101, 104 and 105) and 109 are decreased.
- In the presence of Al-SMPO-5c, 10 compounds are increased (peaks 2, 4, 10, 48, 57, 90, 95, 98, 101, 107) and 108 are decreased.

Moreover, the increase shown by some of these compounds is very low, thus indicating that the presence of the catalyst does not affect the yield of such compounds. However, if we consider, in a general way, that each compound, i, is characterized by an associated toxicity, T_i, the overall toxicity, T, of a cigarette would be calculated as $T = \Sigma x_i \cdot T_i$, where x_i is the weight fraction of the different components of the condensed fraction of the mainstream smoke. Therefore, in good agreement with the results shown in Fig. 7, it can be concluded that the materials studied in this work contribute to a decrease of the overall toxicity, and the best material is Al-SMPO-5c.

From the point of view of the health of active and passive smokers, the composition of the liquids retained in the filters of the cigarettes it is not as interesting as that of the liquids retained in the traps after the cigarettes because the materials remaining the filters do not pass into the human respiratory system. However, these liquids should be taken into account in order to completely establish the behaviour of the catalysts studied in this work as tobacco additives. In this way, Table 5 shows the yields corresponding to the different compounds found in the liquid fraction extracted from the filters of cigarettes with GC/MS assignment probability higher than 80%. As can be seen, significant reductions have been obtained as a consequence of the presence of the catalyst. The Al-SMPO-5c sample, which according to the results obtained for the gases and for liquids retained in the traps was the best catalyst among the samples studied in this work, it is also the best considering the liquids retained in the filters. The diagram corresponding to the reductions observed in all the chromatographic peaks obtained in the chromatograms of the liquids retained in the filters as a consequence of the presence of catalysts is similar to that of Fig. 7, and reflects that the results associated with the presence of the catalysts used as tobacco additives practically reduce the yield of all the compounds. As was observed for the traps, in spite of all the additives studied showing interesting properties, Al-SMEC20-3c seems to be the worst and Al-SMPO-5c the best. Thus, the catalyst of reference, Al-SMc, reduces the yield of 165 compounds and increases the yield of 19 compounds; the increase is lower than 5% for 4 compounds, and lower than 10% for 7 compounds. In the presence of Al-SMPO-5c, only 12 compounds are increased, 2 of them

Table 4 – Retention times of the chromatographic peaks represented in Fig. 6.

Retention time (min)	Peak or compound	Retention time (min)	Peak or compound
8.22	peak 1	24.86	peak 49 (Skatol)
8.38	peak 2	25.14	peak 50
8.64	peak 3 (furfural)	25.74	peak 51 (Myosmine)
8.89	peak 4	26.21	peak 52
8.94	peak 5	26.50	peak 53
9.09	peak 6	27.28	peak 54
9.22	peak 7	27.36	peak 55
9.50	peak 8	27.69	peak 56
9.63	peak 9	28.00	peak 57 (4-Methyl-2,6-di-tert-butylphenol)
10.01	peak 10	28.42	peak 58
10.08	peak 11 (4-Cyclopentene-1,3-dione)	29.22	peak 59
10.71	peak 12 (2-Methyl-2-cyclopentenone)	29.58	peak 60 (Megastigmatrienone 4)
10.87	peak 13	29.93	peak 61 (Diethyl phthalate)
10.97	peak 14	30.64	peak 62
11.26	peak 15	30.85	peak 63
11.98	peak 13 (3-methyl-pentanoic acid)	31.27	peak 64
12.11	peak 17	31.87	peak 65
12.49	peak 18	32.22	peak 66
13.13	peak 19 (Phenol)	32.43	peak 67 (Cotinine)
13.54	peak 20	32.89	peak 68
13.70	peak 21	33.62	peak 69
14.42	peak 22 (Corylon)	34.04	peak 70
14.50	peak 23 (Limonene)	34.31	peak 71
14.80	peak 24	34.53	peak 72
15.36	peak 25 (o-Cresol)	34.90	peak 73
15.98	peak 26 (p-Cresol)	35.17	peak 74 (Neophytadiene)
16.11	peak 27	35.30	peak 75
16.22	peak 28	36.79	peak 76
16.37	peak 29 (Guaiacol)	36.81	peak 77
16.45	peak 30	36.91	peak 78
17.06	peak 31	37.12	peak 79
17.34	peak 32	37.66	peak 80
17.95	peak 33 (2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one)	38.23	peak 81
18.15	peak 34 (2,6-Dimethyl-phenol)	38.31	peak 82
18.72	peak 35 (4-Ethylphenol)	39.45	peak 83
19.20	peak 36	39.76	peak 84
19.44	peak 37	39.90	peak 85
19.94	peak 38	39.97	peak 86
20.30	peak 39	40.18	peak 87
20.63	peak 40	40.52	peak 88
21.02	peak 41	41.15	peak 89
22.06	peak 42 (Hydroquinone)	41.54	peak 90
22.15	peak 43	41.95	peak 91
22.32	peak 44 (Indole)	42.08	peak 92
22.68	peak 45	42.18	peak 93
22.88	peak 46 (4-vinyl-2-methoxy-phenol)	42.58	peak 94
23.75	peak 47	43.13	peak 95
24.07	peak48 (Nicotine)	44.31	peak 96
44.76	peak 97	51.93	peak 108
44.85	peak 98	52.64	peak 109
44.92	peak 99	53.62	peak 110
45.08	peak 100	53.95	peak 111
45.25	peak 101	54.54	peak 112
45.58	peak 102	54.77	peak 113
46.64	peak103	55.24	peak 114
46.87	peak 104	55.52	peak 115
49.24	peak 105	55.79	peak 116
49.86	peak 107	56.18	peak 117
51.72	peak 108	56.48	peak 118

show an increase lower than 5%, and 7, lower than 10%. These results, besides corroborating the conclusions obtained from the study of the liquids retained in the traps, indicate that the reductions observed in the compounds appearing in the mainstream smoke are not a consequence of the role of filters, but are directly related with the ability of the materials studied as modifiers of the pyrolysis and combustion processes involved in the smoking tobacco processes.

The comparison among the reductions obtained in the presence of each catalyst in the filters and in the traps shows

Table 5 – Yields corresponding to different compounds analyzed in the not-condensed fraction of the mainstream smoke retained in the filters of the smoked cigarettes.

Compound	μg/cigarette				
	Reference tobacco	Reference tobacco + Al-SMc	Reference tobacco + Al-SMEC20-3c	Reference tobacco + Al-SMEC10-5c	Reference tobacco + AlSMPO-5c
4-methylpyridine	1.92	0.71	0.77	0.67	0.54
Methylpyrazine	1.67	0.76	0.74	0.77	0.45
Furfural	17.59	8.39	7.92	7.10	5.43
3-Methylpyridine	3.89	1.79	1.64	0.85	0.48
Isopropenylacetylene	1.16	0.58	0.52	0.44	0.41
4-Cyclopentene-1,3-dione	6.79	3.40	3.20	3.72	2.192
2-Methyl-2-cyclopentenone	7.12	3.50	3.36	2.95	1.99
2(5H)-furanone	4.39	1.98	2.05	1.71	1.03
2-Hydroxycyclopent-2-en-1-one	4.14	2.13	2.38	1.67	1.11
3,5-Dimethylpyridine	2.35	0.47	1.16	0.37	0.50
2,5-Dimethyl-2-cyclopentenone	1.36	0.61	1.08	0.48	0.45
Acid 3-methyl-pentanoic	2.62	1.71	1.84	1.49	1.00
5-Methyl-2-furfural	13.27	6.05	6.05	4.93	3.36
Phenol	20.45	11.25	13.64	9.81	8.01
2,5-Dimethyl-2,4-hexadiene	3.18	1.55	1.76	0.93	0.70
Corylon (2-Hydroxy-1-methylcyclopenten-3-one)	8.19	3.98	4.79	3.29	2.77
Limonene	2.93	1.58	1.34	1.10	1.01
Phenylmethanol	4.47	3.57	4.12	4.19	3.49
2,3-dimethyl-2-cyclopenten-1-one	10.54	6.11	7.00	4.71	4.77
o-Cresol	9.58	4.97	6.60	3.99	3.76
2-Acetylpyrrole	1.78	0.91	1.17	0.61	0.71
3-ethyl-2-cyclopenten-1-one	2.11	1.07	1.40	0.95	0.56
p-Cresol	11.69	6.66	8.82	6.21	5.20
Guaiacol (o-Methoxyphenol)	6.64	3.37	4.24	3.05	2.31
3-Ethyl-2-hydroxy-2-cyclopenten-1-one	4.59	2.04	2.53	1.34	1.31
Phenylacetonitrile	3.39	1.44	2.53	1.21	1.32
2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	9.53	4.35	6.55	4.56	3.57
2,4-Dimethylphenol	3.16	1.54	2.48	1.60	2.07
2,3-Dimethylphenol	3.40	1.64	2.47	1.06	1.15
4-Ethylphenol	4.84	1.96	2.62	1.98	1.87
Naphthalene	0.95	0.78	0.79	0.55	0.70
2,3-Dihydro-benzofuran	6.01	3.33	4.76	3.92	2.98
Hydroquinone	6.71	4.60	3.57	4.04	3.19
Indole	7.73	4.67	5.79	4.43	4.97
4-vinyl-2-methoxy-phenol	4.23	2.44	3.27	2.82	1.49
Nicotine	310.02	189.44	190.01	194.70	174.95
Solanone	2.31	1.85	1.05	2.07	1.68
Skatol	2.93	1.49	1.67	1.69	1.46
Vanillline (4-hydroxy-3-methoxy-Benzaldehyde)	1.44	0.98	0.93	0.79	0.65
Myosmine	3.24	2.51	3.29	2.02	1.69
4-Methyl-2,6-di-tert-butylphenol	0.60	1.36	1.02	1.59	1.555
Megastigmatrienone 4	1.95	1.50	1.40	1.36	1.15
Diethyl phthalate	0.92	0.64	0.71	0.71	0.63
4-(3-hydroxy-1-butenyl)-3,5,5-trimethyl-2-Cyclohexen-1-one	0.86	0.70	0.97	1.00	0.49
Cotinine	3.54	2.35	2.83	2.00	1.74
2,4-Diphenyl-4-methyl-1(E)-pentene	2.80	2.72	3.47	3.16	2.93
Neophytadiene	20.58	16.01	17.64	18.24	14.82

that, in general, the effect of the additive is more noticeable in the case of liquids retained in the filters, thus indicating that the overall decrease of the yields obtained in the condensed products is high, and more significant than the analysis of the fraction retained in the traps (i.e., compounds inhaled by smokers) reflects. These results may be also interesting from the point of view of passive smokers exposed to side stream smoke not passing through any filter. In accordance with the previous comments, we can conclude that the use of extraction with solvent processes for the elimination of template in MCM-41 samples permits us to obtain materials showing an acceptable behaviour as additives in order to reduce tobacco toxicity. In fact, Al-SMEC10-5c and Al-SMPO-5c seem to be better than the reference catalyst, Al-SMc, especially Al-SMPO-5c. On the other hand, the behaviour of Al-SMEC-3c is relatively similar to Al-SMc, in spite of the fact that this material should be rejected due to its poor hydrothermal stability.

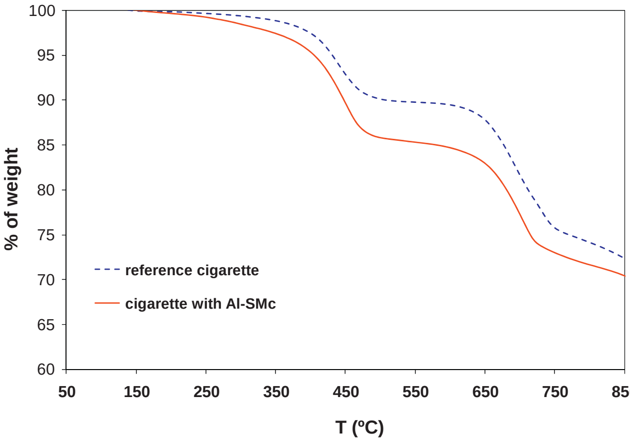


Fig. 8 – TGA curves obtained for the decomposition in air atmosphere of the ashes obtained in the smoking experiments of the cigarette of reference and a cigarette prepared with the same commercial tobacco + Al-SMc.

In order to emphasize on the role of the solid additives studied in this work, Fig. 8 shows the TGA curves corresponding to the thermal treatment of the ashes obtained in a smoking experiment in the absence of additive (i.e., ashes from the cigarette of reference) and in the presence of Al-SMc. The samples have been heated at 10 °C/min under air atmosphere from room temperature from 900 °C, and after an isothermal step of 1 h at 900 °C has been applied. As it can be seen, the weight loss is around 35% in the presence of catalyst and 38% in the case of the ashes from the reference cigarette. Considering the amount of ashes obtained in each case (around 78 mg/cigarette for the reference and 90 mg/cigarette in the presence of catalyst), it can be concluded the content of coke in the ashes containing catalyst are around 2 mg/cigarette higher than in the absence of catalyst. The curves shown in Fig. 8 indicates that there are three reaction steps, the first one corresponds to the oxidation of the more light coke, which appears in higher extent in the presence of catalyst. The amount of material oxidized in the second reaction step is similar in both cases, whereas the loss of weight involved in the third step is higher in the absence of catalyst. Moreover, the corresponding temperaures of maximum reaction rate also seem to be slightly lower in the presence of catalyst (i.e., around 418 °C, 674 °C and 867 °C for each consecutive reaction step in the presence of Al-SMc versus 429 °C, 679 °C and 871 °C in the absence of catalyst).

4. Conclusions

In this work, the ability of MCM-41 materials prepared by using leaching processes for template elimination for act as catalysts in order to reduce tobacco toxicity has been studied. The influence of the extraction with solvent processes on the textural properties of the material has been checked analyzing the corresponding N_2 adsorption isotherms. By this procedure, the stabilizing role of aluminium in the structure has been clearly observed, as well as the effect of a hydrothermal treatment applied in order to check the stability of the materials, and the changes in the textural properties related with the structural changes undergone by the materials. The results obtained suggest that the three samples prepared by elimination of the template by extraction with solvents exhibit acceptable textural properties, but the treatment with a mixture of HCl/Ethanol seems to cause some structural damage which is very dependent of the experimental conditions, thus suggesting that treatment with H_2O_2 is a better way for template elimination. The physicochemical characteristics of these samples have been also studied by TGA, XRF, XRD and ^{27}Al NMR. Moreover, the analysis of the mainstream smoke reveals that the catalysts studied in this work maintain the good properties shown by MCM-41 materials in order to reduce tobacco toxicity, and that the sample showing the best textural properties and the best hydrothermal stability (i.e., the sample treated with H_2O_2) is also the best as tobacco additive.

Acknowledgements

Financial support for this investigation has been provided by the Spanish “Secretaría de Estado de Investigación” del Ministerio de Ciencia e Innovación (CTQ2008-01023).

References

Bagshaw, S.A., Brucea, I.J., 2008. Rapid calcination of high quality mesostructured MCM-41 MSU-X, and SBA-15 silicate materials: a step towards continuous processing? Microp. Mesop. Mater. 109 (1–3), 199–209.

Baker, R.R., 2006. Smoke generation inside a burning cigarette: modifying combustion to develop cigarettes that may be less hazardous to health. Prog. Energy Combust. Sci. 32, 373–385.

Beck, J.S., Vartuli, J.C., Kennedy, G.J., Kresge, C.T., Schramm, S.E., 1994. Molecular or supramolecular templating: defining the role of surfactant chemistry in the formation of microporous and mesoporous molecular sieves. Chem. Mater. 6, 1816–1821.

Berenguer-Murcia, A., García-Martínez, J., Cazorla-Amorós, D., Martínez-Alonso, A., Tascón, J.M.D., Linares-Solano, A., 2002. About the exclusive mesoporous character of MCM-41. Stud. Surf. Sci. Catalysis 144, 83–90.

Chen, L.Y., Ping, Z., Chuah, G.K., Jaenicke, S., Simon, G., 1999. A comparison of post synthesis alumniation and sol-gel synthesis of MCM-41 with high framework aluminium content. Microp. Mesop. Mater. 27 (2–3), 231–242.

Das, D., Tsai, C.M., Cheng, S., 1999. Improvement of hydrothermal stability of MCM-41 mesoporous molecular sieve. Chem. Commun. 5, 473–474.

Gomes Jr., W.A., Cardoso, L.A.M., Gonzaga, A.R.E., Aguiar, L.G., Andrade, H.M.C., 2005. Influence of the extraction methods to remove organic templates from Al-MCM-41 molecular sieves. Mater. Chem. Phys. 93 (1), 133–137.

Hua, Z.L., Shi, J.L., Wang, L., Zhang, W.H., 2001. Preparation of mesoporous silicafilms on a glass slide: surfactant template removal by solvent extraction. J. Non-Cryst. Solids 292 (1–3), 177–183.

Hitz, S., Prins, R., 1997. Influence of template extraction on structure, activity, and stability of MCM-41 catalysts. J. Catal. 168, 194–206.

ISO 3308:2000, 2000. Routine analytical cigarette-smoking machine—definitions and standard conditions.

Keene, M.T.J., Denoyel, R., Llewellyn, P.L., 1998. Ozone treatment for the removal of surfactant to form MCM-41 type materials. Chem. Commun. 20, 2203–2204.

Kleitz, F., Schmidt, W., Schüth, F., 2003. Calcination behavior of different surfactant-templated mesostructured silica materials. Microp. Mesop. Mater. 65, 1–29.

Luan, Z., Chen, C.W., Zhou, W., Klinowski, J., 1995. Mesopore molecular sieve MCM-41 containing framework aluminum. J. Phys. Chem. 99 (3), 1018–1024.

Marcilla, A., Beltrán, I., Gómez, A., Navarro, R., Berenguer, D., Martínez, I., 2006a. Tobacco-catalyst mixtures for reducing the toxic compounds present in tobacco smoke. Patent Number(s): WO2008056011-A1; ES2301392-A1; ES2301392-B1;

EP2092838-A1P200602816. Priority Application Information and Date: ES002816, 07 Nov 2006.

Marcilla, A., Gómez-Siurana, A., Berenguer, D., 2006b. Study of the influence of the characteristics of different acid solids in the catalytic pyrolysisn of different polymers. Appl. Catal. A: Gen. 301 (2), 222–231.

Marcilla, A., Gómez-Siurana, A., Muñoz, A., Valdés, M.J.F.J., 2009. A new Dubinin-modified BET combined equation to correlate the full relative pressure range of 77 K N_2 isotherms of solids with different textural properties. Adsorp. Sci. Technol. 27 (1), 69–84.

Marcilla, A., Gómez-Siurana, A., Beltrán, M., Martínez, I., Berenguer, D., 2010. Evaluation of the efficiency of solvent extraction for template removal in the synthesis of MCM-41 type materials to be used as tobacco additives for smoke toxicity. Appl. Catal. A: Gen. 378 (1), 107–113.

Meier, M.W., Siegmann, K., 1999. Significant reduction of carcinogenic compounds in tobacco smoke by the use of zeolite catalysts. Microp. Mesop. Mater. 33, 307–310.

Mitchell, P.C.H., 1991. Zeolite-encapsulated metal complexes: biomimetic catalysts. Chem. Ind. 9, 308–311.

Shen, S.C., Kawi, S., 2002. MCM-41 with improved hydrothermal stability: formation and prevention of Al content dependent structural defects. Langmuir 18, 4720–4728.

Tian, B., Liu, X., Yu, C., Gao, F., Luo, Q., Xie, S., Tu, B., Zhao, D., 2002. Microwave assisted template removal of siliceous porous materials. Chem. Commun. 11, 1186–1187.

Weiner, H.C., 1997. Oral tolerance: immune mechanisms and treatment of autoimmune diseases. Immunol. Today 18, 335–343.

Xiao, L., Li, J., Jin, H., Xu, R., 2006. Removal of organic templates from mesopourous SBA-15 at room temperature using UV/dilute H_2O_2. Micropor. Mesopor. Mater. 96, 413–418.

Xu, Y., Wang, Y., Zhu, J.H., Ma, L.L., Liu, L., Xue, J., 2002. Application of zeolite in the health science: novel additive for cigarette to remove N-nitrosamines in smoke. Stud. Surf. Sci. Cat. 142, 1489–1496.

Xu, Y., Yun, Z.-Y., Zhu, J.H., Xu, J.-H., Liu, H.-D., Wei, Y.-L., Hui, K.-J., 2003a. Trapping volatile nitrosamines with the copper incorporated zeolite. Chem. Commun., 1894–1895.

Xu, Y., Zhu, J.H., Ma, L.L., Ji, A., Wei, Y.L., Shang, X.Y., 2003b. Removing nitrosamines from mainstream smoke of cigarettes by zeolites. Microp. Mesop. Mater. 60, 125–137.

Zhao, X.S., Lu, G.Q., Millaer, G.C., 1996. Advances in mesoporous molecular sieve MCM-41. Ind. Eng. Chem. Res. 35, 2075–2090.

Zhao, X.S., Lu, G.Q., 1998. Modification of MCM41 by surface silylation with trimethylchlorosilane and adsorption study. J. Phys. Chem. B 102, 1556–1561.

Publicación IV. *Reduction of tobacco smoke components yields by zeolites and synthetysed Al-MCM-41. A. Marcilla, A. Gómez-Siurana, D. Berenguer, I. Martínez-Castellanos, M.I. Beltrán. En revisión.*

En este trabajo se decidió comparar la capacidad para reducir el rendimiento de los compuestos presentes en el humo del tabaco del catalizador sintetizado Al-MCM-41 con el de otros catalizadores comerciales, más estables hidrotérmicamente y de fácil obtención.

Se han empleado las zeolitas comerciales HUSY, HZSM5 y Hβ, y el catalizador sintetizado Al-MCM-41. Se ha realizado la caracterización físico-química de los catalizadores empleados mediante isotermas de adsorción de nitrógeno, fluorescencia de rayos X y desorción térmica programada de amoniaco.

Los catalizadores se han mezclado con el tabaco en una proporción del 4% y los cigarrillos obtenidos se han acondicionado y fumado en las condiciones descritas en trabajos previos. La corriente principal del humo del tabaco se ha dividido en gases, líquidos retenidos en el filtro y en las trampas de humo. Se ha obtenido el rendimiento global de cada una de las corrientes, y se han analizado los compuestos más frecuentes presentes en cada una, mediante las técnicas descritas en trabajos previos. En este caso se han analizado 29 compuestos presentes en los gases y 87 en la fracción condensada. Para simplificar el análisis, estos compuestos se han agrupado en derivados nitrogenados, compuestos carbonilos, fenólicos, epoxis, aromáticos, alifáticos, PAH's y "otros" y se ha tratado de correlacionar la capacidad de los aditivos utilizados para reducir el rendimiento de cada una de las familias de compuestos con sus propiedades texturales y acidez.

Los resultados obtenidos en este trabajo han permitido cubrir los siguientes objetivos específicos:

-Estudio de la capacidad de cuatro catalizadores de propiedades físico-químicas diferentes para actuar como aditivos para reducir el rendimiento de los compuestos presentes en la corriente principal del humo del tabaco.

REDUCTION OF TOBACCO SMOKE COMPONENTS YIELDS BY ZEOLITES AND SYNTHETYSED Al-MCM41

A. Marcilla, A. Gómez-Siurana, D. Berenguer, I. Martínez-Castellanos, M.I. Beltrán*

Dpto. Ingeniería Química, Univ. Alicante, Apdo. 99, 03080 Alicante, Spain.

Tel.: +34 96 590 3400 ext. 2526; fax: +34 96 590 3826. e-mail address: maribel.beltran@ua.es

Keywords
Tobacco, catalyst, yields reduction

Abstract

Three commercial zeolites (HUSY, Hβ and HZSM-5) and a synthesized Al-MCM41 catalyst have been mixed with a commercial tobacco brand of cigarettes in order to study the modifications in the components of the tobacco smoke. Cigarettes with different tobacco-catalyst mixtures were prepared and smoked in a smoking machine, and the mainstream smoke was collected and analyzed. The mainstream smoke was divided in three fractions; the gaseous compounds, and the total particulate matter condensed in the filter tip (TPM-F), and in the traps (TPM-T). The same compounds were found in TPM-F and TPM-T but a differential distribution was observed. The lowest molecular weight products were preferably retained in the cigarette filter while the heaviest (and less polar) appeared in the trap in a higher concentration than in the filter. The results obtained show that the studied catalysts directly mixed with tobacco are capable of reducing the yields of most of the compounds which could be inhaled by active smokers, with Al-MCM41 being the most efficient from this point of view. CO and most of gaseous compounds generated are also reduced in the presence of catalysts. In the case of the condensable matter, the compounds were classified by their chemical nature and it was found that carbonyls and phenolics were markedly reduced by HZSM-5 and Al-MCM41, and the last one shows a remarkable ability to reduce nitrogenated compounds. As an example, the Al-MCM41 catalyst reduces the nicotine condensed in the traps by 41%.

1. INTRODUCTION

Tobacco smoking is a dangerous habit which is deeply rooted in modern society. The smoke obtained from a burning cigarette contains more than 4800 compounds, some of them toxic and carcinogenic [1]. Tobacco smoking represents an important issue for the Departments of Health, which are responsible for the laws recently developed in many countries limiting the places and circumstances where smoking is not forbidden [2]. In this way, the WHO (World Health Organization) has suggested that countries take certain actions such as imposing restrictions on advertising and promotion of tobacco, adopting a new packaging and labelling system, establishing controls to ensure clean air in indoor environments and strengthening legislation to combat illegal tobacco sales. Furthermore, information about the maximum nicotine, tar and carbon monoxide content in cigarettes is shown and regulated in the labelling of tobacco products. Moreover, measures concerning the ingredients and description of tobacco products have been also adopted. These laws can protect passive smokers and aid to prevent or reduce the number of still smokers and new smokers, but they cannot reduce tobacco toxicity.

In order to reduce tobacco toxicity, different proposals have been made. Borgerding et al. [3] for example proposed a new burning system and some researchers have added catalysts to tobacco or the tobacco filter tip. Most of them involve materials different from zeolites or aluminosilicates. Among the first attempts, Seeofer and Kausch [4] used a compound with the formula $M_2M'RuO_6$, where M is a divalent metal, M' is a trivalent rare earth metal, Ru has a valence of 5, and M and M' are capable of forming a perovskite lattice with the Ru ions. The authors claim that this compound, when mixed with tobacco or incorporated into the cigarette paper or filter, contributes to reduce NO and CO from tobacco smoke. In the same way, Rongved [5] also described a tobacco filled article adapted to produce less toxic substances such as CO in the combustion gases, by adding solid inert, stable non-polluting catalysts in or near tobacco, i.e., a metallic catalyst such as vanadium pentoxide, molybdenum trioxide or rhodium oxides. More recently, Li and Hajaligol [6] and [7] described the use of nanoparticles of Fe_2O_3, CuO, TiO_2, CeO_2, Ce_2O_3, Al_2O_3, Y_2O_3 doped with Zr, Mn_2O_3 doped with Pb, and mixtures thereof to increase the conversion of CO to CO_2. In 2004, Li et al. [8] described the use of a single oxidant/catalyst based on iron oxide nanoparticles, which is generated in situ when the cigarette is burning, and is capable of increasing the conversion of CO and NO to CO_2 and N_2, respectively. On the other hand, potassium organic salts can be used as burning additives in cigarettes, with capacity for the reduction of the yields of CO, nicotine and nicotine free dry particulate matter (NFDPM) [9].

The use of zeolites and other aluminosilicates as additives has been described by several authors. As an example, Cvetkovic et al. [10] used a catalyst based on a Cu-ZSM-5 zeolite in order to reduce the amount of NO and NO_x in mainstream tobacco smoke. This catalyst can be added to the cigarette filter or directly mixed with tobacco, and the mechanism proposed is based on the properties of adsorption or diffusivity of the material. Meier [11] and [12] also describes the use of zeolitic materials as additives, and Xu and Zhu [13] relates the use of different zeolites and two mesoporous materials (i.e., MCM-48, zeolite NaA, NaY, KA and NaZSM-5, SBA-15 and MCM-48) as cigarette additives capable of reducing the nitrosoamine content in the cigarettes smoke by selective adsorption. More recently other authors [14] also described the use of CAS-1 in the filter tip to selectively adsorb nitrosamines. Yong et al. [15] proposed the use of MCM-48 and Ce-MCM48 to reduce the content of polycyclic aromatic compounds in mainstream smoke. Chen et al. [16] introduced NaY zeolite, activated carbon and oxidized carbon nanotubes in the filter tips and found important reductions of tar and nicotine specialty in the case of the nanotubes catalyst. Branton et al. [17] also found important reductions in the composition of volatile species when active carbons where introduced in the filter tip.

Our research group has studied the synthesis of MCM41 for different purposes [18]. In a previous work [19], it was demonstrated that removing the template by solvent extraction prior to calcination gave a catalyst with the adequate properties to be used as tobacco additive and subsequently [20] the composition of the gases and liquids obtained in smoking experiments were analyzed in order to establish the effect of the treatment with solvents on the MCM41. The effect of aluminium content of different synthesised MCM41 catalyst on the pyrolysis and combustion processes of tobacco has also been studied more recently [21].

In this work, the effect of three commercial zeolites (HUSY, Hβ, HZSM-5) and a synthesized Al-MCM41 catalyst, on the composition of the mainstream smoke obtained from commercial tobacco cigarettes has been studied. Catalysts have been directly mixed with tobacco. The three commercial catalysts show at least some ability to reduce the yield of some toxic compounds present in the smoke, while the synthesized Al-MCM41 could reduce drastically the concentration of most toxic and carcinogenic compounds in the mainstream smoke.

2. MATERIALS AND EXPERIMENTAL METHODS

2.1. Materials

Commercial HUSY, HZSM-5 (both supplied by GRACE Davison) and Hβ (supplied by Süd-Chemie) zeolites were selected. Al-MCM41 was synthesized in the following way: MCM41 was prepared according to the method reported in literature [22], where CTMACl (25 wt% aqueous solution of cetyltrimethyl ammonium chloryde, Aldrich) was dissolved in distilled water under constant stirring. Aqueous ammonia solution was added while stirring for 10 min. Then, the silica source, TEOS (Tetraethyl ortosilicate 99%, Aldrich) was added dropwise with vigorous stirring to obtain the final gel. The stirring was continued for a period of 4 h. The product was recovered by filtration, washed thoroughly with distilled water and dried at 100ºC for 4 h. The removal of the template was accomplished by calcination in air at 550ºC for 6 h. Al-MCM41 was prepared by stirring the MCM41 obtained as described above in a 0,25 M solution of $Al(NO_3)_3.9H_2O$ at 60 ºC, for 3h. The product was recovered by filtration, washed with distilled water and dried at 100 ºC.

Typical physicochemical properties of the four catalysts are shown in Table 1.

Table 1.- Properties of the catalysts used.

Properties	HZSM-5	HUSY	Hβ	Al-MCM41
Pore size (nm)	0.51 x 0.55 0.53 x 0.56	0.74	0.55 x 0.65 0.64 x 0.76	2.73[a]
Area BET (m^2/g)[b]	330	625	519	1007
External surface (m^2/g)[c]	38	27	183	85
Pore Volume (cm^3/g)[d]	0.18	0.32	0.17	0.83
Si/Al ratio [e]	22	4.8	25	119
Acidity (mmol/g)[f]	2.0	2.1	2.1	0.3
Acidity (weak acid sites) (mmol/g)[f]	1.2	2.1	1.1	0.3
Acidity (strong acid sites) (mmol/g)[f]	0.8	0.0	1.0	0.0

[a] N_2 adsorption isotherms; BJH
[b] N_2 adsorption isotherms; BET method
[c] N_2 adsorption isotherms; t method
[d] N_2 adsorption isotherms; measured at $P/P_0=0.995$
[e] XRF
[f] TPD of NH_3

The textural properties of the catalysts studied were established from the measurement of the N_2 adsorption isotherms at 77K. The equipment used was an automatic AUTOSORB-6 supplied by Quantachrome. The pore size distributions were obtained applying the BJH model with cylindrical geometry of the pores and using the Harkins and Jura equation for determining the adsorbed layer thickness (t) and the external surface area. The surface area measurements were obtained applying the BET model, considering values in the 0.04-0.25 range of relative pressure. The Si/Al ratio was measured by X-ray fluorescence (XRF) in a sequential spectrometer of X rays PHILIPS MAGIX PRO, model PW2400. The acidity of the materials was measured by temperature programmed desorption (TPD) of ammonia, performed in a Netzsch TG 209 thermobalance. The calculation of the materials acidity and the differentiation among weak and strong acid sites has been performed following the procedure described elsewhere [18]. HZSM-5, HUSY and Hβ zeolites are microporous materials with very different properties. HZSM-5 is a porous material and poses two types of small channels (Table 1), zig-zag channels (0.51 x 0.55 nm) and linear channels (0.53 x 0.56 nm). HUSY has higher aluminium content (lower Si/Al ratio as seen in Table 1) and higher pore size (0.74 nm of diameter) than HZSM-5. The Hβ zeolite has a low aluminium content and as HZSM-5 two types of channels with a pore size between HZSM-5 and HUSY, and a higher external surface area. Al-MCM41 is a mesoporous material with a pore size of 2.7 nm and a very high BET surface area. The acidity of these materials increases in the order Al-MCM41<HUSY<HZSM-5<Hβ (Table 1) which, as expected, is in accordance with the Aluminium content. All catalysts employed were sieved to have particle sizes lower than 70 μm.

A commercial brand of cigarettes sold in Spain, Fortuna from Imperial Tobacco was selected for the preparation of the mixtures with the catalysts and as a reference for comparison of results. Fortuna is an American blend composed mainly by Virgina tobacco. The Fortuna cigarettes length is 82.6 mm and they use ventilated acetate filters 20.6 mm large.

In order to allow the adequate comparisons, 200 cigarettes were emptied and re-filled with the samples under study (tobacco or tobacco+catalyst). The mixtures tobacco+catalyst were prepared mixing manually around 0,028 g of powdered catalyst with 0,700 g of tobacco (i.e., the tobacco contained in a standard cigarette), using approximately 0,1 g of ethanol (99.9%. AnalaR NORMAPUR, from Prolabo) in order to facilitate the adherence between catalyst and tobacco. The actual content of catalyst was determined by weighing the amount of zeolite segregated from the mixture. All the experiments were triplicated and Table 2 shows the average catalyst weight (%) for the studied mixtures.

The obtained cigarettes were kept at 23ºC and 60% relative humidity for at least 48 h. Five cigarettes were simultaneously smoked in each run and at least three runs were carried out for each material. The results presented in the experimental section are the average of the three runs. Standard deviations lower than 20% were always obtained.

2.2. Experimental procedure

The smoking machine employed allows five cigarettes to be smoked simultaneously. The operating conditions have been selected according to most of specifications of the ISO 3308 standard. The smoking regimen was the following: 35 mL of puff volume, drawn over 2 s, once per minute. The pressure of aspiration of the machine was never higher than 1.5kPa. In each smoking experiment 8 puffs were done. A condensing trap was located after the mouth end of each cigarette, and the condensed products retained in these traps, as well as those in the filter of the cigarettes were extracted separately with isopropanol (99.9% purity from Fluka) and analyzed by GC/MS. The trap consisted in a series of three filters, of the same type as those used in the commercial cigarettes, which were placed at the entry of each line connecting the mouth end of the cigarette with the smoking machine. Therefore, the less volatile compounds may condense in two points, i.e., in the filter of the smoking cigarette and in the trap, while the rest of the smoke was collected in a Tedlar bag. To ensure that all condensable products had been collected and that any of them reached the Tedlar bag another trap was situated immediately before it. This trap was clean in all cases, but it was also weighed, extracted and analysed together to the other traps located after the cigarettes.

The products obtained from the smoking process have been classified as follows: the gases, i.e. those compounds collected in the Tedlar bag; this fraction includes the non-condensed and the more volatile products evolved in the pyrolysis and combustion of tobacco, together to the rest of the air crossing the burning cigarette (i.e., N_2 and the O_2 not consumed in the combustion process); and the particulate matter, which includes the total amount of products condensed in the filter of the cigarettes (TPM-F) and in the traps after the cigarettes (TPM-T). TPM-F and TPM-T were calculated as the difference in the mass of the filters and the traps after and before each experiment. The amount of smoked tobacco was calculated as the difference between the mass of tobacco contained in the cigarettes before and after smoking. The yields obtained for the different compounds are shown as mass of compound per mass of smoked tobacco.

2.3. Analytical procedure

The content of CO and CO_2 in the smoke collected has been analyzed by GC with a TCD detector (GC/TCD) in a Shimadzu GC-14A, with a CTRI column. The temperature of the injector was 28ºC and the temperature of the detector was 110ºC. Helium was used as carrier gas, with a flow rate of 40 mL/min. The volume of sample injected was 2.5 mL. The GC oven was maintained at 110ºC for 25 min. Standard gaseous mixtures of CO_2, CO and other gases (from Scott Speciality Gases) were used to identify and quantify these compounds.

The other non-condensed compounds collected in the Tedlar bag have been analyzed by GC with MS and FID detectors (GC/MS/FID) in an Agilent 6890N gas chromatograph, with a GS-GASPRO column. The temperature of the injector was 150ºC, and the GC oven temperature program was: initial temperature: 35ºC for 5 min, ramp of 6 ºC/min up to 200ºC and 10 min at the final temperature. As carrier gas 2 mL/min of Helium were used and the volume of sample injected was 150 µL. Standard gaseous hydrocarbons (from Scott Speciality Gases) were used to identify and quantify the hydrocarbons. To obtain the calibration curves for other compounds present in the gases fraction such as benzene, toluene, acetonitrile, acetone, furan or acetaldehyde, the calibration curves were obtained injecting different amounts of the vapour in equilibrium with the pure liquid at 8ºC. The vapour pressures of these compounds obtained from Perry and Green [23] have been employed to calculate the molar fraction, and assuming ideal gases law, the corresponding response factors were obtained.

The condensable products extracted from the cigarette filters and the traps, were analysed by GC/MS in an Agilent 6890N gas chromatograph, with a HP5-MS column. The injector temperature was 250ºC, and the GC oven program used in this case was: initial temperature column of 40ºC for 5 min, ramp of 12ºC/min up to 320ºC, and 25 min at final temperature: 25 min. The carrier gas was Helium with a flow rate of 2 mL/min, and the volume of sample injected was 1µL. A calibration curve with standards of nicotine was used to obtain the response factor. The assignation of peaks to compounds was done by comparison with the Wiley MS library. Most of peaks were assigned with probability close to or higher than 90% (the probability is shown in the tables corresponding to the particulate matter). As will be shown, few peaks presented lower probabilities, but despite the doubts in the assignation of these peaks, they have been included in the tables. The response factor of the nicotine has been employed for these compounds and consequently the values presented for the condensable products must be considered as semi-quantitative at best, but this analysis is very useful to compare the reduction in yields when catalysts are included and when they are not.

3. RESULTS AND DISCUSSION

Table 2 shows the average values of the actual weight percentage of catalyst mixed with the tobacco, the amount of tobacco introduced initially in each cigarette and the weight of smoked tobacco per cigarette in the smoking runs. The total particulate matter extracted from the traps (TPM-T) is also shown together with the total particulate matter retained in the filter of the cigarettes (TPM-F), both expressed as mg per gram of smoked tobacco.

Table 2. Actual catalyst content expressed in weight per cent, mean amount of tobacco introduced in the cigarettes, mean amount of smoked tobacco per cigarette and total particulate matter in the filter of the cigarettes (TPM-F) (mg/g smoked tobacco) and in the traps (TPM-T) (mg/g smoked tobacco).

	CATALYST wt.(%)	TOBACCO AMOUNT mg/cigarette	SMOKED TOBACCO mg/cigarette	TPM-F mg/g smoked tobacco	TPM-T mg/g smoked tobacco
Reference tobacco		684	505	10.4	8.9
HUSY	3.85	700	541	9.9	9.7
Hβ	3.82	704	454	10.1	9.9
HZSM-5	3.86	701	464	11.1	9.4
Al-MCM41	3.90	650	480	10.6	5.5

It has been demonstrated that smoking machine conditions do not reflect the behaviour of smokers neither in volume, frequency nor aspiration rate, and that the smoke yields obtained by smokers during real world use may be much higher than those obtained under the ISO conditions [24]. The rate of aspiration may vary for any particular smoker and it affects the combustion, pyrolysis, condensation and filtration processes that are taken place during smoking. Despite the total and relative amounts of TPM-F and TPM-T may vary with the smoking conditions, the particulate matter retained in the filter of the cigarettes would never reach the smoker and consequently it is not frequently reported. Nevertheless, as it will be shown below, an interesting behaviour of the composition of both, TPM-T and TPM-F, can be observed when individually analysed. Moreover, to evaluate adequately the activity of the catalyst it is necessary to know the actual change in quantity and composition of the total smoke generated.

The amount of tobacco smoked when HUSY was used was always much higher than in the other cases, thus producing an increase in the yields obtained if they are expressed in a "per cigarette" basis as is common in the tobacco industry. The addition of solid particles in the cigarette rod can modify the physical properties of the tobacco blend affecting the combustion behaviour of the cigarettes [25] and this may be the case of the

HUSY zeolite. If results are expressed in a “per mass of smoked tobacco” basis the results obtained with HUSY does not differ substantially from those obtained with HZSM-5 or Hβ.

The total amount of condensable matter retained in the filter of the cigarette (TPM-F) is higher (or very similar) to that retained in the traps (TPM-T), showing the importance of the filter in reducing the smoke leaving the end mouth of the cigarette. TPM-T from the reference tobacco is 8.9 mg/g of smoked tobacco and does not change significantly when HUSY, Hβ or HZSM-5 are introduced. These zeolites show a low activity for reducing TPM-T. The case of the Al-MCM41 catalyst is much encouraging since TPM-T is reduced by 38% if the values of mg/g of smoked tobacco are considered, and 42% in a per cigarette basis. The percentage of reduction has been calculated as the difference of the yields obtained in the reference tobacco and in the system tobacco+catalyst, divided by the yield corresponding to the reference tobacco. Recently, Baker [25] suggested that the health risks of smoking are not actually associated with individual compounds, or classes of compounds in the smoke, but with the total smoke yield, that would be indicative of health effects. Accordingly, the Al-MCM41 catalyst seems to exhibit a very interesting behaviour.

CO_2, CO and nicotine, together with water, are the major compounds in cigarette smoke. Carbon monoxide is a well known poison and it is considered among the more toxic products of tobacco smoke [26] while nicotine is the more addictive one [27]. Table 3 shows the yield of CO_2, CO and the corresponding ratio CO/CO_2. This ratio can be considered as an indicator of the extent of incomplete combustion reactions (i.e., the ratio increases as the extent of incomplete combustion increases).

Table 3. CO_2, CO and CO/CO_2 ratio, and nicotine retained in the filter and in the trap (Nicotine-F and Nicotine-T, respectively) in mg/g of smoked tobacco.

	CO_2 mg/g smoked tobacco	CO mg/g smoked tobacco	RATIO CO/CO_2 mg/mg	NICOTINE-F mg/g smoked tobacco	NICOTINE-T mg/g smoked tobacco
Reference tobacco	46.51	10.49	0.23	0.62	0.66
HUSY	44.53	10.53	0.24	0.46	0.64
Hβ	49.62	10.58	0.21	0.54	0.68
HZSM-5	45.87	9.91	0.22	0.54	0.67
Al-MCM41	40.24	8.13	0.20	0.41	0.39

From the point of view of reduction in tobacco toxicity, low values are desirable. As can be seen, all catalysts except HUSY reduce the ratio CO/CO_2 generated when the prepared cigarettes are smoked, and the highest reductions are shown by the sample containing the Al-MCM41 catalyst. This catalyst also reduces CO and CO_2 yields (reductions of 23% and 13% for CO and CO_2, respectively). In this way, as previous results indicate, the Al-MCM41 catalyst seems to be more active than the other catalysts.

Table 3 also shows results for nicotine retained in the filters and in the traps (nicotine-F and nicotine-T, respectively). Nicotine and water are, by far, the major compounds contained in the particulate matter of the cigarette smoke. HUSY, HZSM-5 and Hβ do not produce any reduction in the nicotine-T content while when the Al-MCM41 catalyst is used, nicotine-T is reduced by 41%. Contrarily to that observed for other compounds (i.e. the lowest molecular weight ones, as will be shown later), the nicotine is more or less uniformly delivered between the filter and the traps. All the catalysts reduce the content of nicotine in the filter, the major reduction is again for the Al-MCM41 catalyst (34%).

For the analysis of other compounds in the mainstream smoke, three fractions have been considered; non-condensed products collected in the Tedlar bag, and the condensed products extracted from the cigarette filter and the traps. Tables 4 to 6 show the yield (μg/g of smoked tobacco) of each compound for the reference tobacco and for the different mixtures studied.

Table 4 shows the results of the non-condensed products analysed by GC/MS/FID.

Table 4. Yield of the different compounds (μg/g of smoked tobacco) identified in the gases for the reference tobacco and tobacco plus catalyst systems.

	Reference tobacco	**HUSY**	**Hβ**	**HZSM-5**	**Al-MCM41**
Methane	896.5	883.4	985.4	907.4	739.2
Ethane	382.3	346.8	399.7	373.2	312.3
Ethylene	218.7	206.7	234.5	219.8	177.9
Ethyne	28.0	28.0	27.0	27.5	22.3
Propane	175.2	155.7	185.3	173.8	145.0
Propene	204.4	191.6	223.6	207.9	160.5
Chloromethane	53.2	51.4	52.9	53.2	39.5
Butane	52.4	49.1	54.6	50.2	36.4
1-butene	50.7	45.3	53.5	47.1	39.9
1,2-propadiene	12.6	9.4	12.6	10.6	8.9
1,3-butadiene	30.9	25.7	32.6	28.9	24.3
Isobutene	45.8	42.2	53.5	48.0	35.7
cis-2-butene	26.1	22.2	36.4	27.9	13.9
Pentane	14.2	12.6	14.8	13.9	11.8
HCN	11.6	10.7	13.3	12.8	9.9
1-pentene	13.3	13.4	16.5	15.4	11.4
Furan	15.7	14.0	19.2	15.2	15.8
Isoprene	358.4	233.2	292.7	237.4	254.9
Hexane	22.9	9.9	15.0	11.4	21.3
1-hexene	12.8	10.9	15.0	11.7	10.5
Benzene	127.0	104.7	128.7	111.3	96.4
Acetaldehyde	525.9	467.6	643.8	550.8	505.8
Acrolein	28.0	20.1	31.0	18.9	25.0
Propionaldehyde	26.5	22.6	27.2	31.2	26.9
Acetonitrile	56.2	41.2	46.6	40.4	39.7
Toluene	26.5	26.8	30.1	27.3	19.4
2,5-dimethylfuran	13.3	--	15.6	12.6	8.9
Crotonaldehyde	5.9	5.7	6.4	7.1	4.4

Isobutyraldehyde	14.5	6.1	15.8	6.6	6.3
Total	3449.6	3057.0	3683.2	3299.7	2824.2

Some gaseous compounds are present such as methane, ethane, propane, etc., but also condensable products with low vapour pressure which, in the conditions that they were collected, are vapours or vapours in equilibrium with the generated particulate matter.
The major compounds of tobacco smoke shown in Table 4 are by far methane, acetaldehyde, ethane and isoprene, followed by ethylene, propene and propane. Among these acetaldehyde and isoprene are included in the Hoffmann list and are among the highest toxic constituents of smoke. Other notable compounds included in the Hoffmann lists by their toxicity [27] and [28] and which appear in Table 4 are benzene, toluene, acrolein and propionaldehyde. Very important reductions in the yield of most of compounds are attained with the Al-MCM41 catalyst, while no reductions are obtained with Hβ or even the yield of some compounds increases. With HZSM-5 and HUSY most compounds reduce their yields up to some extent. The yields of the major hydrocarbons are reduced with Al-MCM41 by around 17 to 25%. Isoprene, benzene, toluene and 2,5-Dimethyl furan are reduced around 25%. The aldehydes suffer very variable reductions from 3% of acetaldehyde to 57% of isobutyraldehyde. The global yield for these compounds calculated as the sum of the yield of the individual compounds is 3450 μg/g of smoked tobacco for the reference tobacco and is reduced by 4.3%, 11.4% and 18.1% with HZSM-5, HUSY and Al-MCM41, respectively.

Tables 5 and 6 show the yield obtained for the compounds identified and quantified in the reference cigarettes and in the tobacco+catalyst systems, in the filters of the cigarettes and in the traps, respectively. Compounds have been ordered according to their retention time and, in order to facilitate the comparison, both tables show the same compounds despite there are 16 compounds which were not found in the traps.

Table 5. Yield of the different compounds (μg/g of smoked tobacco) identified in the TPM-F for the reference tobacco and tobacco plus catalyst systems. The probability in the assignation according to the Wiley MS library and the assigned family are also shown.

ASIGNATION	FAMILY	P	REFERENCE TOBACCO	HUSY	Hβ	HZSM-5	AL-MCM41
Pyridine, 4-methyl-	pyridine	93	3.8	2.3	2.0	2.2	3.0
Pyrazine, methyl-	pyridine	94	3.3	2.0	1.9	1.9	2.9
Furfural	carbonyl	93	34.9	18.3	19.2	17.2	27.9
2-Pentanone, 4-hydroxy-4-methyl-	carbonyl	72	3.3	2.7	1.4	3.3	2.7
2-Furanmethanol	epoxy	76	8.0	3.4	5.1	4.0	5.0
Pyridine, 3-methyl-	pyridine	95	7.7	4.7	4.1	4.7	5.6
2-Propanone, 1-(acetyloxy)-	carbonyl	72	17.6	9.8	9.3	9.0	13.1
4-Cyclopentene-1,3-dione	carbonyl	81	13.5	6.8	5.6	5.0	10.5
Styrene	aromatic	81	2.4	1.6	1.9	1.1	1.7
2-Cyclopenten-1-one, 2-methyl-	carbonyl	91	14.1	7.6	8.9	7.3	10.7

2-Acetylfuran	carbonyl	64	13.1	6.9	7.8	6.1	7.3
2(5H)-furanone	carbonyl	80	8.7	4.8	4.6	4.2	6.7
2-Hydroxycyclopent-2-en-1-one	carbonyl	83	8.2	6.0	5.1	5.1	6.4
Pyridine, 3,5-dimethyl-	pyridine	87	4.7	2.6	2.9	3.2	4.4
2,5-Dimethyl-2-cyclopentenone	carbonyl	80	4.0	3.1	1.9	3.1	4.5
4-Acetylcyclopentane	carbonyl	72	2.4	1.8	1.2	2.4	0.4
Butanoic acid, 3-methyl-	carbonyl	72	5.2	4.4	4.4	4.5	3.1
Benzaldehyde	carbonyl	60	5.8	3.8	3.2	3.7	5.0
Furfural, 5-methyl-	carbonyl	90	26.3	12.5	14.1	11.7	21.0
Pyridine, 3-ethenyl-	pyridine	90	8.5	2.4	4.6	1.1	4.2
2(5H)-Furanone, 3-methyl-	carbonyl	74	7.8	3.8	4.0	3.2	4.0
Phenol	phenolic	95	40.5	26.4	26.7	24.1	34.4
2-isopropylfuran	epoxy	80	6.3	5.2	4.7	3.6	4.7
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	carbonyl	96	16.2	11.9	10.7	10.3	12.7
Limonene	otros	93	5.8	3.9	3.8	4.0	4.8
Benzenemethanol	otros	89	8.9	9.3	7.1	8.2	9.4
2,3-Dimethyl-2-cyclopenten-1-one	carbonyl	90	20.9	14.7	14.2	13.6	13.8
Indene	PAH	81	6.3	4.3	3.8	3.3	3.3
o-Cresol	phenolic	97	19.0	14.1	13.7	13.3	15.2
2-Acetylpyrrole	pyridine	87	3.5	1.6	2.0	1.9	2.6
Ethanone, 1-phenyl-	carbonyl	53	3.7	2.3	1.7	2.4	2.2
3-Ethylcyclopent-2-en-1-one	carbonyl	87	4.2	2.9	2.1	2.9	2.4
p-Cresol	phenolic	96	23.2	17.7	17.8	17.3	14.1
2 ethyl tiophene	otros	47	5.7	3.9	3.5	3.6	1.8
Phenol, 2-methoxy-	phenolic	90	13.2	8.7	9.0	8.6	10.4
2,4-Dimethyl-4-cyclohexen-1,3-dione-one	carbonyl	49	5.0	2.9	3.2	3.3	4.3
Nicotinamide	pyridine	76	6.5	5.3	4.6	4.4	4.2
3-Ethyl-2-hydroxy-2-cyclopenten-1-one	carbonyl	92	9.1	5.8	4.4	3.6	6.3
Benzeneacetonitrile	pyridine	95	6.7	4.7	5.1	3.4	4.6
2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	carbonyl	91	18.9	13.9	14.0	12.7	17.0
Phenol, 2,4-dimethyl-	phenolic	90	6.3	5.3	8.3	5.0	2.3
Phenol, 2,3-dimethyl-	phenolic	96	6.7	4.2	5.4	4.0	3.8
Phenol, 4-ethyl-	phenolic	93	9.6	6.2	4.9	7.2	7.1

Naphthalene	PAH	90	1.2	1.2	0.9	0.8	0.7
Ethanone, 1-(3-methylphenyl)-	carbonyl	64	5.6	5.4	4.8	4.4	2.3
p-cresol 2 methoxy	phenolic	64	7.1	4.0	6.2	5.9	7.1
2,3-Dihydro-benzofuran	epoxy	90	11.9	10.1	10.6	11.9	9.0
2-furancarboxaldehyde, 5-(hydroxymethyl)-	carbonyl	52	3.2	2.1	3.0	2.8	3.5
1H-Inden-1-one, 2,3-dihydro-	carbonyl	76	4.3	4.0	3.7	4.3	2.4
Hydroquinone	phenolic	76	13.3	10.2	3.6	5.2	13.2
1H-Indole	pyridine	87	14.1	13.0	14.3	13.5	8.4
4-vinyl-2-methoxy-phenol	phenolic	91	8.4	6.8	7.4	7.2	7.8
Nicotine	pyridine	96	614.6	459.5	542.8	544.1	407.5
1H-Indole, 3-methyl-	pyridine	87	5.8	5.5	7.8	6.1	3.6
Myosmine	pyridine	94	6.4	7.5	5.9	5.7	4.7
Phenol, 2-methoxy-4-(2-propenyl)-	phenolic	55	3.2	2.7	2.3	2.6	2.7
Nicotyrine	pyridine	45	2.8	4.0	2.5	2.6	1.1
Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl-	phenolic	72	1.2	1.8	2.4	3.0	0.9
2,3'-Bipyridine	pyridine	72	4.1	4.7	4.3	5.5	1.9
1,4-dihydrophenantrhene	PAH	74	4.4	6.4	6.1	5.8	3.8
Diethyl phatalate	carbonyl	93	1.8	2.4	3.9	2.4	0.0
Megastigmatrienone	carbonyl	90	4.5	4.2	5.4	4.9	2.5
2,4 dimethyl-6-(2-furyl) pyridine	pyridine	45	0.0	0.0	0.0	0.0	0.0
N-propyl nornicotine	pyridine	45	3.9	2.6	3.0	2.4	2.3
Cotinine	pyridine	86	7.0	6.8	6.0	7.3	6.2
1H-Indene, 2,3-dihydro-1,1,3-trimethyl-3-phenyl-	aromatic	96	2.1	1.7	1.6	1.5	3.9
5-Tetradecen	aliphatic	70	2.7	3.1	3.0	2.9	1.9
N(b)-formylnornicotine	pyridine	80	2.2	2.4	2.7	3.0	2.7
2,4-Diphenyl-4-methyl-penten-1ene	phenolic	91	5.5	3.9	6.2	6.5	6.8
Neophytadiene	aliphatic	96	40.8	40.8	39.0	44.7	36.4
Farnesol	otros	60	3.2	3.0	3.2	3.3	2.9
8-Quinolinemethanol	pyridine	53	4.2	4.4	4.2	4.4	3.4
Methyl 3-(3-pyridazinyl)-2-cyanoacrylate	pyridine	74	10.0	10.5	10.0	10.9	17.6
Dibutyl phthalate	carbonyl	45	2.8	2.6	3.8	3.5	2.4
Hexadecanoic acid, ethyl ester	carbonyl	46	3.4	3.2	4.0	3.9	3.2

Pentadecane	aliphatic	93	3.0	2.1	2.2	2.5	2.5
Octadecane	aliphatic	96	25.7	19.8	20.6	20.3	21.7
Eicosane	aliphatic	76	2.8	2.6	2.8	2.5	2.8
Docosane	aliphatic	86	3.8	3.4	3.7	3.5	5.3
Citric acid, tributyl ester	carbonyl	87	4.0	3.1	2.7	4.6	2.4
Dioctyl adipate	carbonyl	68	4.4	2.6	6.4	6.5	6.7
Bezoic acid 2,5 dimethyl	carbonyl	64	3.3	3.0	4.1	2.6	2.4
Tricosane	aliphatic	95	7.9	6.0	6.0	6.3	7.6
2,6,10,14,18,22-Tetracosahexaene, 2,6,10,15,19,23-hexamethyl-	aliphatic	96	16.1	4.0	9.5	10.2	10.4
Heptacosane	aliphatic	89	8.5	6.6	6.9	7.4	7.2
Triacontane	aliphatic	70	10.3	9.3	7.9	7.9	8.9
Tocopherol	phenolic	83	26.5	21.3	18.5	19.6	14.7

Table 6. Yield of the different compounds (μg/g of smoked tobacco) identified in the TPM-T for the reference tobacco and tobacco plus catalyst systems. The probability in the assignation according to the Wiley MS library and the assigned family are also shown.

ASIGNATION	FAMILY	P	REFERENCE TOBACCO	HUSY	Hβ	HZSM-5	AL-MCM41
Pyridine, 4-methyl-	pyridine	93	0.9	0.7	0.6	1.0	0.0
Pyrazine, methyl-	pyridine	94	0.7	0.6	0.9	1.1	0.0
Furfural	carbonyl	93	5.1	4.4	4.6	4.9	4.0
2-Pentanone, 4-hydroxy-4-methyl-	carbonyl	72	1.3	2.4	6.5	3.2	0.0
2-Furanmethanol	epoxy	76	0.0	0.0	0.0	0.0	0.0
Pyridine, 3-methyl-	pyridine	95	0.2	1.4	1.2	1.1	0.2
2-Propanone, 1-(acetyloxy)-	carbonyl	72	1.8	1.6	1.7	1.6	1.2
4-Cyclopentene-1,3-dione	carbonyl	81	1.4	1.2	1.3	1.2	1.0
Styrene	aromatic	81	0.8	0.4	0.8	0.5	0.0
2-Cyclopenten-1-one, 2-methyl-	carbonyl	91	1.5	1.5	1.7	1.8	1.5
2-Acetylfuran	carbonyl	64	0.7	0.1	0.9	0.5	0.0
2(5H)-furanone	carbonyl	80	1.1	0.8	0.7	0.8	1.0
2-Hydroxycyclopent-2-en-1-one	carbonyl	83	1.8	1.4	1.4	1.5	0.8
Pyridine, 3,5-dimethyl-	pyridine	87	0.0	0.0	0.0	0.0	0.0
2,5-Dimethyl-2-cyclopentenone	carbonyl	80	0.0	0.0	0.0	0.0	0.0
4-Acetylcyclopentane	carbonyl	72	0.0	0.0	0.0	0.0	0.0
Butanoic acid, 3-	carbonyl	72	2.9	2.6	2.8	2.2	0.0

methyl-							
Benzaldehyde	carbonyl	60	0.9	0.7	0.5	0.6	0.0
Furfural, 5-methyl-	carbonyl	90	1.7	1.7	1.7	1.5	1.5
Pyridine, 3-ethenyl-	pyridine	90	0.5	0.6	1.1	0.6	0.0
2(5H)-Furanone, 3-methyl-	carbonyl	74	0.0	0.0	0.0	0.0	0.0
Phenol	phenolic	95	8.4	5.0	5.8	4.1	5.5
2-isopropylfuran	epoxy	80	0.0	0.0	0.0	0.0	0.0
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	carbonyl	96	3.8	2.6	2.8	2.2	2.6
Limonene	others	93	1.3	1.2	1.3	1.4	1.3
Benzenemethanol	others	89	0.0	0.0	0.0	0.0	0.0
2,3-Dimethyl-2-cyclopenten-1-one	carbonyl	90	2.3	1.5	2.7	2.2	0.0
Indene	PAH	81	0.2	0.6	0.4	0.4	0.0
o-Cresol	phenolic	97	6.9	4.5	5.0	3.7	4.8
2-Acetylpyrrole	pyridine	87	0.0	0.0	0.0	0.0	0.0
Ethanone, 1-phenyl-	carbonyl	53	0.0	0.0	0.0	0.0	0.0
3-Ethylcyclopent-2-en-1-one	carbonyl	87	0.0	0.0	0.0	0.0	0.0
p-Cresol	phenolic	96	8.0	5.9	6.4	5.0	4.4
2 ethyl tiophene	others	47	2.7	2.8	2.1	2.0	1.5
Phenol, 2-methoxy-	phenolic	90	1.9	1.5	1.6	1.7	1.3
2,4-Dimethyl-4-cyclohexen-1,3-dione-one	carbonyl	49	0.0	0.0	0.0	0.0	0.0
Nicotinamide	pyridine	76	1.5	0.8	1.1	0.7	0.0
3-Ethyl-2-hydroxy-2-cyclopenten-1-one	carbonyl	92	1.5	1.7	1.5	1.3	0.3
Benzeneacetonitrile	pyridine	95	0.7	0.8	0.5	0.4	0.0
2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	carbonyl	91	14.8	13.1	13.5	11.1	8.9
Phenol, 2,4-dimethyl-	phenolic	90	6.1	7.3	4.8	4.3	3.2
Phenol, 2,3-dimethyl-	phenolic	96	3.2	2.8	3.1	2.5	0.9
Phenol, 4-ethyl-	phenolic	93	7.4	3.6	4.6	3.7	4.9
Naphthalene	PAH	90	0.0	0.0	0.0	0.0	0.0
Ethanone, 1-(3-methylphenyl)-	carbonyl	64	3.3	2.7	2.6	2.4	2.1
p-cresol 2 methoxy	phenolic	64	3.6	3.5	4.2	3.0	2.5
2,3-Dihydro-benzofuran	epoxy	90	8.9	9.3	6.6	7.1	5.6
2-furancarboxaldehyde, 5-(hydroxymethyl)-	carbonyl	52	7.6	11.5	10.2	5.9	3.4
1H-Inden-1-one, 2,3-	carbonyl	76	1.1	0.5	0.0	0.7	0.0

dihydro-							
Hydroquinone	phenolic	76	11.8	12.2	12.5	8.1	4.5
1H-Indole	pyridine	87	9.1	7.4	7.5	4.7	6.8
4-vinyl-2-methoxy-phenol	phenolic	91	6.7	7.9	6.6	4.8	6.1
Nicotine	pyridine	96	663.1	635.7	680.3	673.8	392.1
1H-Indole, 3-methyl-	pyridine	87	6.7	5.6	3.9	3.7	3.9
Myosmine	pyridine	94	5.6	7.2	7.2	5.6	3.6
Phenol, 2-methoxy-4-(2-propenyl)-	phenolic	55	4.8	4.2	4.9	4.4	2.6
Nicotyrine	pyridine	45	4.7	10.1	10.5	9.0	2.7
Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl-	phenolic	72	5.0	11.8	9.7	9.3	5.2
2,3'-Bipyridine	pyridine	72	2.7	6.5	5.6	4.3	1.8
1,4-dihydrophenantrhene	PAH	74	4.0	7.3	5.2	5.3	2.9
Diethyl phatalate	carbonyl	93	2.3	3.2	3.9	4.7	2.8
Megastigmatrienone	carbonyl	90	5.0	6.1	5.9	6.0	3.0
2,4 dimethyl-6-(2-furyl) pyridine	pyridine	45	3.6	2.1	3.6	3.2	3.2
N-propyl nornicotine	pyridine	45	3.8	4.7	4.6	4.0	3.5
Cotinine	pyridine	86	10.3	11.8	12.9	10.1	5.2
1H-Indene, 2,3-dihydro-1,1,3-trimethyl-3-phenyl-	aromatic	96	0.0	0.0	0.0	0.0	0.0
5-Tetradecen	aliphatic	70	2.3	3.3	3.2	2.4	2.3
N(b)-formylnornicotine	pyridine	80	8.6	9.8	8.8	9.7	6.8
2,4-Diphenyl-4-methyl-penten-1ene	phenolic	91	0.0	0.0	0.0	0.0	0.0
Neophytadiene	aliphatic	96	42.9	47.7	43.0	46.3	27.8
Farnesol	others	60	5.2	5.0	6.1	5.2	4.0
8-Quinolinemethanol	pyridine	53	0.0	0.0	0.0	0.0	0.0
Methyl 3-(3-pyridazinyl)-2-cyanoacrylate	pyridine	74	0.0	0.0	0.0	0.0	0.0
Dibutyl phthalate	carbonyl	45	3.4	3.7	3.0	3.4	2.4
Hexadecanoic acid, ethyl ester	carbonyl	46	8.3	4.8	5.7	6.7	3.6
Pentadecane	aliphatic	93	1.5	1.8	1.8	1.6	2.2
Octadecane	aliphatic	96	35.8	35.2	39.1	37.1	34.3
Eicosane	aliphatic	76	2.1	1.9	1.4	1.6	1.8
Docosane	aliphatic	86	3.1	3.0	3.0	3.2	3.8
Citric acid, tributyl ester	carbonyl	87	1.8	2.5	1.8	1.4	2.4
Dioctyl adipate	carbonyl	68	4.5	4.3	3.1	3.5	6.3
Bezoic acid 2,5 dimethyl	carbonyl	64	8.1	7.9	8.6	7.8	4.5

Tricosane	aliphatic	95	12.1	11.8	11.0	11.9	13.5
2,6,10,14,18,22-Tetracosahexaene, 2,6,10,15,19,23-hexamethyl-	aliphatic	96	9.6	7.4	7.0	7.4	7.2
Heptacosane	aliphatic	89	12.4	12.9	11.1	12.6	14.4
Triacontane	aliphatic	70	14.9	15.5	16.3	14.5	15.4
Tocopherol	phenolic	83	31.6	39.6	40.0	38.5	27.5

Comparing the results of the filters (Table 5) and the traps (Table 6) for the reference cigarettes, it is expected that the more heavy compounds may condense firstly. Nevertheless, the amount of the compounds with lower retention time (usually the lowest molecular weight compounds) found in the filters is much higher than in the traps. See, for example, the amount of furfural (34.9 and 5.1 μg/g of smoked tobacco in the filter and the traps, respectively); phenol (40.5 and 8.4); nicontinamide (6.5 and 1.5) or 2,3-dihydro-benzofuran (11.9 and 8.9). These relatively low molecular weight compounds are preferably retained by the filter, but as the molecular weight increases compounds are delivered more uniformly between the filter and the trap. For example, the amount of or nicotine is 614.6 and 663.1 μg/g of smoked tobacco in the filter and the traps. For higher retention times the amount of some compounds in the traps is higher than in the filter, as is the case for example of diethyl phthalate (0,9 and 1,2 μg/g of smoked tobacco in the filter and the traps, respectively); cotinine yield is 7.0 and 10.0, N(b)-formyl nornicotine is 1.1 and 4.3 μg/g of smoked tobacco in the filter and the traps. This is true for most of compounds with high retention time, but some hydrocarbons are an exception, see for example 5-tetradecene, (2.7 and 2.3 μg/g of smoked tobacco in the filter and the traps, respectively), pentadecane (3.0 and 1.5) or eicosane (2.8 and 2.1), while others high molecular weight hydrocarbons are delivered quite uniformly.

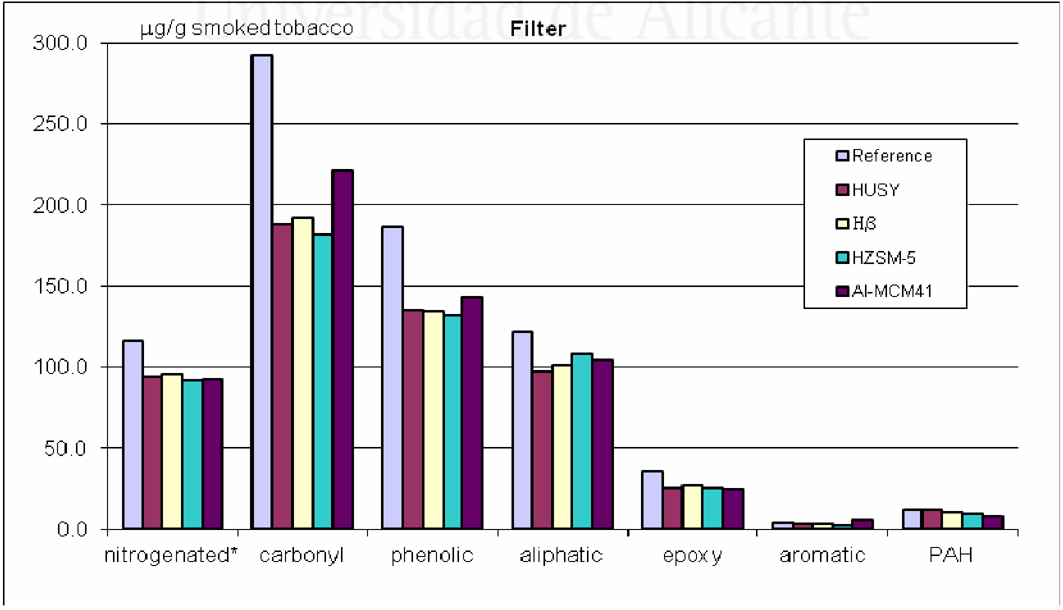
The way chemical compounds are delivered between filter and traps is similar for all the catalyst+tobacco systems (Tables 5 and 6). The explanation to this observation may involve aspects as the different affinity of the different compounds by the filter or their relative concentration and vapour pressures. Other authors [17], when studying active carbon filters, also found some compounds with the mentioned behaviour, departing from the expected trend. They attributed such results to the contribution of the adsorption enthalpy. The difference in the pressure drop when modifying the cigarettes could produce also changes, making more difficult the interpretation.

On another hand, for every compound detected, the yields vary strongly depending on the catalyst, but opposite to the results found in gases, all the catalysts, including Hβ, show at least some activity for most of compounds. According to the results shown in Tables 5 and 6, the decrease of the yields is a common fact for most of the compounds of the particulate fraction. The extent of such reductions is somewhat different for each compound and, in this way, it can be observed that some components show reductions higher than others. In order to facilitate the comparison of the effect of the different catalysts on the compounds found in the filter and in the traps, the compounds analysed in Tables 5 and 6 have been grouped by families, according to their chemical functionality. The families considered, ordered according to the established priority, are the following:

nitrogenated compounds > carbonyls > phenolics > epoxy > aromatics > aliphatics > PAHs

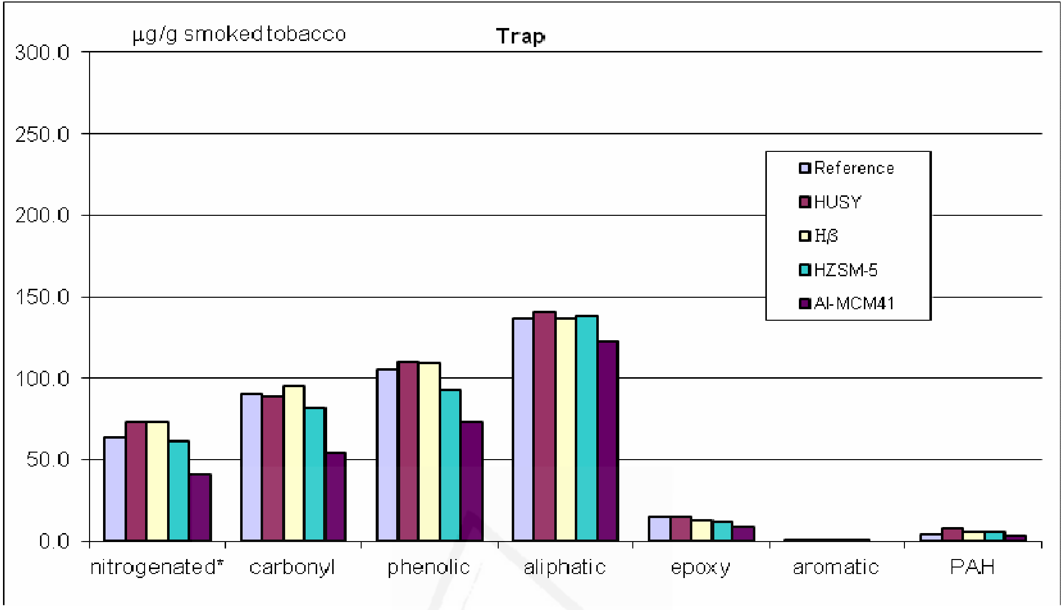
The family of the "nitrogenated compounds" analysed is mainly constituted by pyridine derivatives, and some pyrazine and a pyrrol have also been included in this group. "Carbonyls" are mainly composed by furfural derivatives and other aldehydes and ketones. The "phenolics" group includes phenols and substituted phenols. The "epoxy" group is mainly composed by furan derivatives and other cyclic or linear epoxy. Some alcohols such as 2-furanmethanol or 2-(1-methylethoxy)-ethanol, have been included in the epoxy group. Alcohols were not considered as an independent group since they were minority compounds and they have not been reported as specialty toxic in the tobacco smoke. Among "aliphatics" there is a series of linear or branched alkanes and alkenes from tetradecane to longer chains. The only "aromatics" found were styrene and 1H-indene, 2,3-dihydro-1,1,3-trimethyl-3-phenyl-. The "PAH" group is constituted exclusively by indene, naphthalene and 1,4-dihydrophenantrhene. Alcohols not included as epoxy (benzenemethanol and farnesol) appears in the group "Others". The group "Others" also includes 2-ethyl-tiophene and limonene.
Figures 1 and 2 show the amount obtained for each family of compounds in the filters and the traps, respectively. Nicotine yields were shown in Table 2 and commented there in and they have been excluded from the nitrogenated compounds group in these Figure, since nicotine behaves as the other nitrogenated compounds but its yield is as high as the sum of all the other compounds and if included, the other nitrogenated compounds or the other families could not be observed clearly. In the case of the filters (Figure 1) carbonyls are the major compounds found followed by phenolics, aliphatics, nitrogenated and epoxy. All these families of compounds are fairly reduced when using catalysts. Aromatics and PAH are the minors and both of them are not reduced with HUSY.

Figure 1. Yield of nitrogenated (excluding nicotine), carbonyl, phenolic, aliphatic, epoxy, aromatic and PAH compounds retained in the filters for all the systems studied.*



In Figure 2 the results for the traps are shown. Aliphatics are the major compounds found in the traps, followed by phenolics, carbonyls, nitrogenated compounds and epoxy. The total yield for PAH and aromatics is very low.

*Figure 2. Yield of nitrogenated (*excluding nicotine), carbonyl, phenolic, aliphatic, epoxy, aromatic and PAH compounds retained in the traps for all the systems studied.*

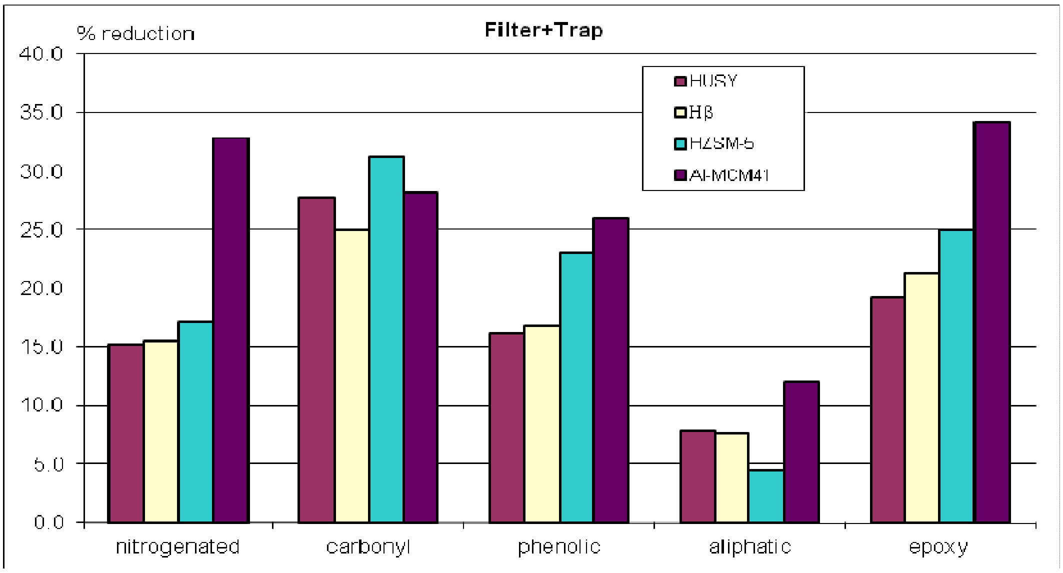


Comparing Figures 1 and 2 it can be observed that carbonyls are mainly retained in the filter (most of them are polar low molecular weight compounds as can be seen in Tables 5 and 6) while aliphatics are preferably retained in the traps (are linear non polar high molecular weight compounds). The other families of compounds are delivered more similarly between the filter and the traps.

As mentioned above, TPM-T (Figure 2) is the fraction usually reported since it is the one that could be inhaled by a smoker (it is important to point out that ISO conditions do not represent the behaviour of smokers). From this point of view the Al-MCM41 catalysts is, by far, the catalyst showing the lowest yield in all the families of compounds. On other hand, the HUSY and Hβ zeolites give quite similar results and their yields for nitrogenated, phenols and aliphatics are even higher than with the reference cigarette, while results for and HZSM-5 are intermediate.

In order to compare the actual activity of each catalyst, Figure 3 shows the percentage of reduction of the total yield (filter plus traps) for the majority families. Aromatics and PAH are not included in this figure due to their low yield. In this case nicotine has been included among the nitrogenated compounds.

Figure 3. Total reduction of the yield (TPM-F+TPM-T) for nitrogenated, carbonyl, phenolic, aliphatic and epoxy compounds for all the systems tobacco plus catalyst studied.



Al-MCM41 proportionates by far the highest reduction in nitrogenated compounds (32.8%), phenolic (26.0%), aliphatic (12.0%) and epoxy compounds (34.2%), while HZSM-5 is the best catalyst in reducing the yield of carbonyl compounds (32.1%). HUSY and Hβ behave quite similarly and proportionate the lowest reductions for nitrogenated (15.2 and 15.5%), carbonyl (27.7 and 25.0) phenolic (16.2 and 16.8%) and epoxy compounds (19.2 and 21.2).

In Figure 3 all the catalysts show a high ability for reducing carbonyl compounds. As seen in tables 5 and 6, most of carbonyls are polar and relatively small molecules as furfural derivatives or substituted aldehydes and ketones. Phenolic compounds (phenol, o-cresol, p-cresol, hydroquinone, and other substituted phenols) are larger molecules and their yield is satisfactorily reduced by HZSM5 and Al-MCM41 and to a lower extent by Hβ and HUSY. The bulky nitrogenated compounds (most of them sustituted pyridines such as nicotine, myosmine, 2,3 bipyridine or cotinine) are fairly reduced by Al-MCM41 while the other catalysts show a moderate activity for these compounds. Aliphatics are non polar large molecules and are poorly reduced by all the catalysts. The best global behaviour is for AlMCM-41 catalyst. The textural properties and acidity of the catalysts may account for their activity [29] and [30] and also the particle morphology, as it has been recently pointed out by Gao who studied the reduction of nitrosamines yields in tobacco smoke by zeolite-like calcosilicates [14]. Table 1 shows the properties of the catalysts studied. Al-MCMC41 is the catalyst showing the largest pore volume, pore size and BET area and also the lowest acidity. In fact Al-MCM41 is a mesoporous material while the other catalyst are in the range of the microporous. The large pore size of Al-MCM41 enables bulky molecules to enter the pores and interact more closely with the catalyst, while the small pore size of the other catalysts does not. Accordingly Branton [17] stated that the removal efficiencies of mesoporous materials were substantially better than for the microporous materials with identical pore volume when studying the removal of vapour phase compounds in the mainstream smoke of tobacco by activated carbons. In fact not only the pore size but the whole structure of the catalysts may account by their activity, but among those studied here only the Al-MCM41 catalyst is able to reduce the yield of the more bulky molecules obtained in the tobacco smoke.

4. CONCLUSIONS

The results obtained in this work show that the zeolites HUSY, Hβ and HZSM5 are able to reduce to some extent the yields of some known toxic and carcinogenic compounds studied in the main stream of cigarettes smoke. Especially interesting is the case of the mesoporous Al-MCM41 catalyst, which reduces CO by 23%, nicotine and TPM in the traps by 41% (in a per gram of smoked tobacco base) and also reduces the yield most compounds analysed in traps. The ability of Al-MCM41 to reduce the yield of nitrogenated compounds is especially remarkable. Therefore, it can be concluded that this catalyst would be an interesting alternative to be considered as an additive of tobacco in order to reduce the yield of the different components of the tobacco smoke.

A distinct behaviour of the compounds retained in the filter has been observed depending on the molecular weight of the compounds. Among condensable products, the lowest molecular weight and polar compounds are preferably retained by the filter tip while those with the highest molecular weight are more uniformly delivered between the filter cigarette and the traps.

FUNDING

Financial support for this investigation has been provided by the Spanish “Comisión de Investigación Científica y Tecnológica” of the “Ministerio de Ciencia e Innovación” and the European Community (FEDER refunds) (CTQ2008-01023/PPQ).

REFERENCES

[1] R.R. Baker, L.J. Bishop. J. Anal. Appl. Pyrol. 74 (2005) 145-170.

[2] World Health Organization. WHO Framework Convention on Tobacco Control. WHO Document Production Services. Geneva, Switzerland. 2003. ISBN 978 92 4 159101 0 (LC/NLM classification: HD 9130.6).

[3] M.F. Borgerding, J.A. Bodnar, H.L. Chung, P.P. Mangan, C.C. Morrison, C.H. Risner, J.C. Rogers, D.F. Simmons, M.S. Uhrig, F.N. Wendelboe, D.E. Wingate and L.S. Winkler. Food and Chem. Toxic. 36 (1997) 169-182.

[4] F. Seeofer and E. Kausch. Removal of Nitric Oxide and Carbon Monoxide from Tobacco Smoke. US patent 4182348 (1980).

[5] P. Rongved. Catalytic Cigarette Smoke Cleaning Devise and Process. US patent 5671758 (1997).

[6] P. Li and M. Hajaligol. Oxidant/Catalyst Nanoparticles to Reduce Carbon Monoxide in The Mainstream Smoke of a cigarette. US Patent 2003/0075193 A1 (2003).

[7] P. Li and M. Hajaligol. Oxidant/catalyst nanoparticles to reduce tobacco smoke constituents such as carbon monoxide. US Patent 2007/0113862 A1 (2007).

[8] P. Li; F. Rasouli, M. Hajaligol. Beitr. Tabakforsch. Int. 21(1) (2004) 1-8.

[9] C. Liu and A. Parry. Beitr. Tabakforsch. Int. 20(5)(2003) 341-347.

[10] N. Cvetkovic, B. Adnadjevich, M. Nikolic. Beitr. Tabakforsch. Int. 20(1) (2002) 43-48.

[11] W.M. Meier and K. Siegmann. Micropor. Mesopor. Mat. 33(1) (1999) 307-310.

[12] M.W. Meier. Process for Treating Tobacco with Catalytically Active Material for Reducing Toxic Components in Tobacco Smoke. European Patent EP 1234511 A1 (2001).

[13] Q.H. Xu, and J.H. Zhu. Acta Phy. Chem. 31,1–2 (1985) 181-187

[14] L. Gao, Y. Cao, S.L. Zhou, T.T. Zhuang, Y. Wang and J.H. Zhu. J. Hazard. Mater. 169, (2009)1034-1039.

[15] G. Yong, Z. Jin, H. Tong, X. Yan, G. Li, S. Liu. Micropor. Mesopor. Mat. 91 (2006) 238-243.

[16] Z. Chen, L. Zhang, Y. Tang, Z. Jia. Appl. Surf. Sci. 252 (2006) 2933-2937.

[17] P. Branton, A. Lu, F. Schüth. Carbon. 47 (2009) 1005-1011.

[18] A. Marcilla, A. Gómez-Siurana, D. Berenguer. Appl. Catal. A: Gen. 301 (2) (2006) 222–231.

[19] A. Marcilla, A. Gómez-Siurana, M. Beltrán, I. Martínez, D. Berenguer. Applied Catalysis A: General. 378 (2010) 107-113.

[20] A. Marcilla, M. Beltrán, A. Gómez-Siurana, I. Martínez, D. Berenguer. Chem. Eng. Res. Des. (2011) doi:10.1016/j.cherd.2011.04.015

[21] A. Marcilla, M. Beltrán, A. Gómez-Siurana, I. Martínez, D. Berenguer. Thermochim. Acta. 518 (2011) 47-52.

[22] T.R Gaydhankar, V. Samuel, R.K Jha, R. Kumar. Mater. Res. Bull. 42(8) (2007) 1473-1484.

[23] R.H. Perry and D.W. Green. Manual del Ingeniero Químico. Vol. 1. Séptima Edición. Mc Graw Hill. 2001.

[24] M.E. Counts, M.J. Morton, S.W. Laffoon, R.H. Cox and P.J. Lipowicz. Regulatory Toxicology and Pharmacology. 41 (2005) 185-227.

[25] R.R. Baker. Prog. Energ. Combust. 32 (2006) 373-385.

[26] M. Goldstein. J. Emerg. Nurs. 34 (2008) 538-542.

[27] D. Hoffmann and I. Hoffmann. J Toxicol. Environ. Health. 50(4) (1997) 307-364.

[28] M. Borgerding and K. Hubert. Exp. Toxicol. Pathol. 57(1) (2005) 43-73.

[29] A. Marcilla, A. Gómez-Siurana, F.J. Valdés. Micropor. Mesopor. Mat. 109 (2008) 420-428.

[30] A. Marcilla, A. Gómez-Siurana, F. J. Valdés. Appl. Catal A. Gen. 352 (2009) 152-158.

Publicación V. *Comparative study of the main characteristics and composition of the mainstream smoke of ten cigarettes brands sold in Spain. I. Martínez, D. Bereguer, A. Gómez-Siurana, M.I. Beltrán and A. Marcilla. En revisión, Food and Chemical Toxicology.*

En trabajos previos se había empleado tabaco tipo Virginia procedente de una marca comercial de cigarrillos para realizar los experimentos de fumado, de modo que se consideró interesante establecer el comportamiento de otros cigarrillos comerciales y cómo podía afectar el tipo de tabaco y la configuración del cigarrillo a la composición del humo del tabaco.

En este trabajo se han realizado experimentos de fumado y se ha analizado la composición de la corriente principal del humo del tabaco de diez marcas comerciales de cigarrillos seleccionadas de entre las más vendidas en España. Las condiciones experimentales para el proceso de fumado y análisis fue similar a la descrita en trabajos previos.

Se ha tratado de establecer la relación entre las principales características de diseño de los cigarrillos, tales como cantidad de tabaco inicial, longitud del filtro y del papel, con la cantidad de tabaco fumado durante un número fijo de caladas y con la relación CO_2/CO obtenida. Estas variables se han correlacionado satisfactoriamente mediante análisis multivariante. Se han analizado 35 compuestos presentes en los gases y 85 en los líquidos y se ha observado que el rendimiento de algunos componentes de la fase vapor y de la materia particulada sigue una tendencia similar en las diferentes marcas estudiadas, lo que ha sido confirmado mediante análisis multivariante.

Los resultados obtenidos en este trabajo han permitido cubrir los siguientes objetivos específicos:

-Estudio de las características de diseño y de la composición de la corriente principal del humo del tabaco de marcas comerciales de cigarrillos entre las más vendidas en España.

COMPARATIVE STUDY OF THE MAIN CHARACTERISTICS AND COMPOSITION OF THE MAINSTREAM SMOKE OF TEN CIGARETTES BRANDS SOLD IN SPAIN

A. MARCILLA, I. MARTÍNEZ, D. BERENGUER, A. GÓMEZ-SIURANA AND M.I. BELTRÁN

Dpto. Ingeniería Química, Universidad de Alicante, Apdo. 99, 03080 Alicante, Spain. e-mail: maribel.beltran@ua.es

ABSTRACT

In this study 10 commercial top selling cigarette brands in Spain have been machine smoked and the mainstream smoke has been analyzed. Multifunctional analysis has been satisfactorily employed to correlate the effect of the main design features of the cigarettes including amount of tobacco, filter size or paper weight with the amount of smoked tobacco and with the ratio CO_2/CO. The composition of the vapor phase and that of the particulate matter have been analyzed. A general trend for the relative yield of some compounds in the different brands have been identified and confirmed by multifunctional analysis. The particulate matter retained in the filter of the cigarettes has also been analyzed showing a distinct behavior of the compounds condensed in the cigarette filters and in the traps, related to their retention time.

1. INTRODUCTION

Tobacco is a natural product that consists of more than 3800 constituents. The chemical composition of the tobacco leaf will depend to varying extents upon tobacco variety, leaf stalk position, geographic region in which the leaf is grown, the climate during growing, local cultivation practices, among others (Tso, 1990). Tobacco constituents range from small molecules such as hydrocarbons, terpenes, carbonilics, phenols, or nitriles, to macromolecules as cellulose, lignin or nucleic acids. During the smoking process, this complex biomass is subjected to high temperatures (up to 950ºC) and a varying concentration of oxygen, producing an incomplete combustion which generates a large amount of components, any of them toxic and carcinogenic compounds. The smoke composition varies not only with tobacco constituents but also with cigarette varieties, cigarette design, additives employed during processing of tobacco and smoking conditions (Baker, 2006; Borgerding and Klus, 2005). About 4800 compounds have been identified in tobacco smoke. Moreover, the ageing effects and artifact formation may complicate the analysis of these complex mixtures.

The tobacco smoke is composed by a particulate phase and a vapor phase. Low molecular weight hydrocarbons, such as benzene, 1,3-butadiene, or toluene or small aldehydes such as acrolein or butiraldehyde are primarily constituents of the vapor phase, nicotine, polyciclyc aromatic compounds or nitrosamines are associated primarily with the particulate phase (PM), while others are found in both phases (Counts et al. 2005). Potentially harmful smoke constituents have been identified and reviewed (Fowles and Dybing, 2003; Hoffmann and Hoffmann, 1997). Unfortunately there is no scientific consensus on specific smoke constituents and harm induction relationships [Rodgman and Green, 2003].

Recently some papers have been published on the relationship of the design features of commercial cigarettes (such as tobacco blend type, cigarettes length, filter type, ventilation holes...) and the tar, nicotine and CO content of the smoke. Osamu et al.

(2009) studied the nicotine, tar and mutagenicity of the mainstream smoke generated under two smoking regimes for the ten major Japanese cigarette brands. Calafat et al. (2004) obtained nicotine, tar and CO of smoke deliveries from 77 cigarettes brands purchased in 35 countries under ISO conditions. They also determined physical parameters such as filter length and weight, cigarette weight or filter ventilation levels. Relatively few studies have included a comparable range of smoke constituents for a variety of commercial cigarettes. Several brands and types of cigarettes sold in Italy were studied by Pieraccini et al. (2008) employing SPME-GC-MS under two smoking regimes. Counts et al. (2005) tested smoke composition of 48 Philip Morris commercial cigarettes from numerous international market regions under three smoking regimes. They analyzed a considerable number of smoke constituents and established some predicting relationships between tar yield and the smoke constituents for each smoking regime.

In this work the composition of the smoke obtained under the ISO smoking conditions for 10 cigarette brands among the best selling in Spain in 2010 have been analyzed and compared. Multivariant analysis (software PASW Statistics 18, version 18.0.0) has been applied to establish the relationships among the main features of the cigarettes design, the amount of smoked tobacco and the ratio CO_2/CO. 34 compounds were identified in the vapor fraction while 85 were identified in the particulate matter, and a general trend for the relative yield of most of compounds in the different brands has been established and confirmed by multifunctional analysis. The particulate matter retained in the filter of the cigarettes has also been analyzed and compared with the particulate matter retained in the traps. The results obtained for the cigarettes sold in Spain have been compared and the results for other international commercial cigarettes available in the literature have been commented.

2. MATERIALS AND METHODS

2.1 Materials

The twelve best selling brands in Spain for the year 2010, by market share, were: Marlboro, Winston, Fortuna, Chesterfield, Ducados Negro, Ducados Rubio, Camel, L&M, Nobel, Lucky Strike, Pall Mall and John Player SP. Among them, the ten brands shown in Table 1 were chosen for this study. Table 1 also shows information of the type of tobacco blend, as provided by the tobacco companies. For privacy reasons in the following Figures and Tables, brands have been nominated with letters from A to J in a different order than that shown in Table 1.

Table 1. Information available on the studied brands.

	TOBACCO COMPANY	TYPE OF BLEND	MARKET SHARE % euros
Marlboro	Philip Morris	American Blend	15.21
Winston	R.J. Reynolds	American Blend	10.75
Fortuna	Imperial Tobacco	American Blend	10.53
Chesterfield	Philip Morris	American Blend	9.49

Ducados Rubio	Imperial Tobacco		6.16
Camel	R.J. Reynolds	Turkish and Virginia	6.13
L&M	Philip Morris	American Blend	6.00
Nobel	Imperial Tobacco		5.14
Lucky Strike	BAT	European Blend	4.82
John Player SP	BAT	American Blend	2.24

Isopropanol (99.9% purity) for the extraction of the compounds retained in the filter of cigarettes and in the traps was purchased from Fluka. The standards gaseous mixtures of CO_2 and CO (Reference 501670) and the gaseous hydrocarbons (References 501816, 22567 and 501662) were obtained from Scott Specialty Gases and they were used to identify and quantify these compounds in the tobacco smoke. Nicotine standard (99.9% purity) was purchased from Merk. Other compounds such as benzene (Ref. 21803.291), toluene (Ref.1.08325.1000) and acetone (Ref. 1.00014.1000) were purchased form VWR while acetaldehyde (Ref. 00070), furan (Ref. 185922) and acetonitrile (Ref. 34967) were from Sigma.

2.2 Experimental Procedure

Before performing the smoking experiments, 200 cigarettes of each brand 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. The cigarettes were conditioned for at least 48 h at 22ºC and a relative humidity of 60%.

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. The puff volume was 35 mL, taken during 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. In this work the effect of the amount of tobacco in the commercial cigarettes was also considered among the variables under study. That is the reason why differently to the ISO standard, the puff number was 8 in all cases, while the ISO establishes to smoke up to a butt length of filter tipping overwrap plus 3 mm. Each smoking experiment was repeated for 3 times and average values are shown.

According to the ISO 3308, a condensing trap was located after the mouth end of the cigarettes. Therefore, the less volatile compounds of the mainstream smoke may condense in two points, i.e., in the filter of the smoking cigarette and in the trap, while the rest of the mainstream smoke was collected in a Tedlar bag. 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 condensed products retained in the trap, as well as those in the filter of the cigarettes, were extracted separately with isopropanol and analyzed by GC/MS.

34 and 85 compounds were identified 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 analytes have been carried out as follows. CO was quantified by GC with a TCD detector in a Shimadzu GC-14, with a CTRI column. The temperature of the injector was 28ºC and the temperature of the detector was 110ºC. Helium was used as a carrier gas, with a flow rate of 40 mL/min. The volume of sample injected was 2.5 mL. Other components of the vapor phase collected in the Tedlar bag were identified and analyzed by GC with MS and FID detectors in an Agilent 6890N gas chromatograph, with a GS-GASPRO column. The temperature of the injector was 150ºC, and the GC oven temperature program was: 35 ºC for 10 min, 5 ºC/min up to 100ºC, 15ºC/min up to 200ºC and 10 min at the final temperature. Helium was used as carrier gas (2 mL/min) and the volume of sample injected was 150 µL. To quantify 1,3-butadiene, HCN, isoprene, acrolein, propionaldehyde, crotonaldehyde and isobutiraldehyde, the response factors were calculated from a standard gaseous hydrocarbons (Scott Speciality Gases). To obtain the calibration curves for benzene, toluene, acetone and acetaldehyde, different amounts of the vapor in equilibrium with the corresponding pure liquid at 8ºC were injected. The area of the corresponding peak for each compound was represented versus the injected amounts, and the response factor (RF, area per gram) was calculated from the slope of the regression lines. Five points calibration curves were constructed and regression coefficients higher than 0.999 were obtained in all cases. For the other compounds identified in the gaseous fraction the RF of the compound with the closest retention time was employed. The results corresponding to these compounds have not been considered for comparison among other studies but they have been employed to compare the different brands in this study.

The particulate matter condensed in both, the trap and the filter of the cigarettes, was extracted separately with isopropanol, dried and analyzed by GC/MS in an Agilent 6890N gas chromatograph, with a HP-5-MS column. The injector temperature was 250ºC, and the GC oven program used in this case was: initial temperature of 40ºC for 5 min, ramp of 12 ºC/min up to 320ºC and 25 min at the final temperature. The carrier gas was helium with a flow rate of 2 mL/min, and the volume of sample injected was 1µL. The assignation of peaks to compounds was done by comparison with the Wiley MS library. 85 peaks were assigned to compounds with probability close to or higher than 90%. A calibration curve with standards of nicotine was used. The response factor of nicotine was employed for all the compounds identified in the particulate matter. Except for nicotine, the results shown for the particulate matter have to be considered as semiquantitative and suitable for comparative purposes among the different brands studied.

3. RESULTS AND DISCUSSION

3.1 Preliminary analysis

The physical properties of the cigarettes under study are shown in Table 2. It includes the initial amount of tobacco, the overall cigarette, filter and paper length, the cigarette diameter , the filter and paper weight, and the filter ventilation, evaluated as the number of holes rows. All the filters were cellulose acetate tips.

Table 2. Physical properties of the cigarettes under study.

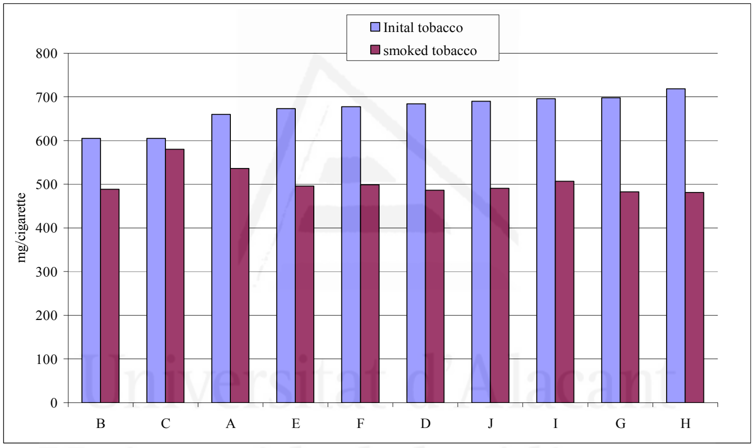
CIGARETTE BRAND	TOBACCO AMOUNT mg/cigarette	CIGARETTE LENGTH mm	FILTER LENGTH mm	PAPER LENGTH mm	CIGARETTE DIAMETER mm	FILTER WEIGHT mg/cigarette	PAPER WEIGHT mg/cigarette	VENTILATION (HOLE ROWS)
A	660	82.2	19.9	57.3	7.7	120.0	41.0	4
B	605	82.7	26.7	50.3	7.6	157.8	35.6	2
C	605	82.1	20.8	57.4	7.1	114.1	39.4	3
D	684	83.6	21.2	58.7	7.6	126.9	43.8	1
E	673	83.2	21.1	58.7	7.1	120.8	40.3	3
F	677	84.1	21.0	59.7	7.4	117.7	42.4	4
G	698	83.9	21.1	59.2	7.6	114.0	41.7	4
H	718	82.5	22.2	56.6	7.4	116.7	35.5	4
I	696	83.7	21.1	59.3	7.3	120.4	42.9	1
J	690	83.9	21.0	59.6	7.4	122.4	40.7	4

Results of the average amount of tobacco smoked for each brand, the particulate matter delivered, and the CO_2/CO ratio are shown in Table 3. According to ISO 4387 the particulate matter (TPM) is that collected immediately after the mouth end of the cigarette. In this work we have also considered the particulate matter retained in the filter of the cigarettes (TPM-F), determined and extracted in the same way than TPM-T. TPM-F is retained in the filter cigarette and consequently it is not frequently reported but, as it will be shown below, an interesting behavior of the composition of both, TPM-T and TPM-F, can be observed when individually analyzed.

The ratio CO_2/CO might indicate the extent of incomplete combustion reactions (i.e., the ratio decreases as the extent of incomplete combustion increases). As the incomplete combustion transforms carbon in CO and other species that may be toxic, high values of CO_2/CO are desirable. All tobacco brands show values within the range 3.3 to 3.8 except brands B and H which present higher ratios.

Large differences in the amount of tobacco smoked were observed, despite, as mentioned above, 8 puffs were always taken. Figure 1 represents the amount of initial tobacco contained in the cigarettes and the smoked tobacco.

Figure 1. Amount of tobacco in the cigarette and smoked tobacco for each brand.



The general trend is the higher the amount of initial tobacco the lower the amount of tobacco consumption during smoking, probably due to the tightest packing of tobacco. The more obvious exception to the rule is the case of brand B which presents by far the longest filter and the shortest paper length (Table 2), so oxygen permeability must be low and the pressure drop across the filter tip very high, both factors contributing to a lower consumption of tobacco. In fact, brands B and C present the same initial weight of tobacco but the volume of cigarette occupied by tobacco in B is much lower than in C, which may aid to explain that they both are also the brands showing the lowest and highest consumption of tobacco during smoking.

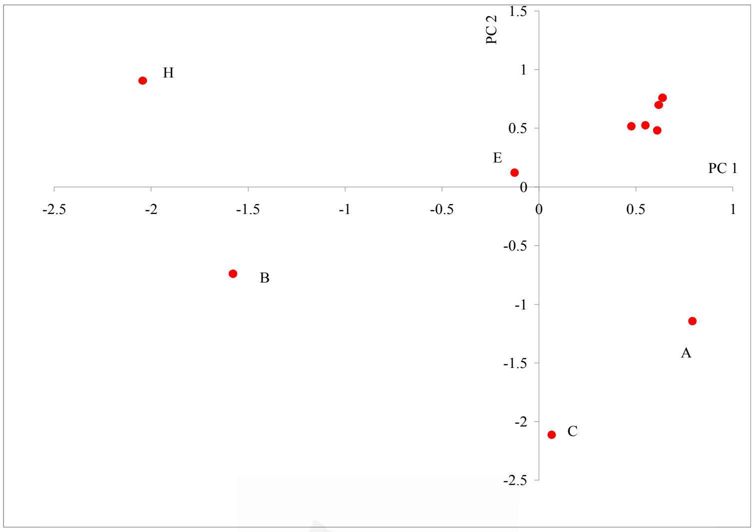
A statistical principal component analysis (PCA) has been performed using the software PASW Statistics 18, version 18.0.0., and considering the variables shown in Table 2, which reflect the morphological characteristics of the studied cigarettes (i.e., tobacco amount, length of cigarette, weight and length of filters and paper, diameter and ventilation of filters), together with the amount of tobacco smoked and the ratio of the yields of CO_2 and CO, (Table 3). The results obtained indicate that, among these variables, CO_2/CO shows the highest correlation with the length of filter (positive correlation) and with the weight of paper (negative correlation), which is in agreement the comments above. On the other hand, four principal components can be extracted, which account for the 92.0% of the total variance of the studied samples. The first principal component (PC1) represents the 32.3% of the total variance and includes, mainly, the contribution to the variability of the length of filter, weight and length of paper, and CO_2/CO, showing the length of filter and CO_2/CO negative contributions and the other two variables, positive contributions. The second principal component (PC2) includes the amount of tobacco smoked (with negative contribution) and the weight of tobacco in the cigarettes and the length of cigarette (both with positive contributions), and represents the 24.3% of total variance. The third principal component (PC3) explains the 18.4% of total variance, and mainly depends (positively) on the weight of the filter and the perimeter. Finally, the fourth principal component (PC4) includes the ventilation (with positive contribution) and represents the 17% of the variance. These results mean that the variables contributing in higher extent to the variability among samples are those represented in PC1, and that the highest values of PC1 correspond to samples with high values of length and weight of paper, whereas samples with high values of length of filter and CO_2/CO exhibit low values of PC1. Similar considerations can be carried out for the other principal components. In this way, PCA permits us to reduce the dimensions of this problem, with a very low loss of information, by passing from the original 10 variables to the 4 principal components.

Table 3. Smoked tobacco amount, TPM-F, TPM-T, TPM-F+TPM-T and CO_2/CO ratio for the different brands.

CIGARETTE BRAND	SMOKED TOBACCO AMOUNT mg/cigarette	TPM-F mg/cigarette	TPM-T mg/cigarette	TPM-F+TPM-T mg/cigarette	CO_2/CO
A	536.4	4.6	6.9	11.5	3.3
B	488.7	3.4	4.8	8.2	4.0
C	579.9	11.4	11.2	22.6	3.7
D	486.7	3.7	5.5	9.2	3.8
E	495.7	3.2	5.8	9.0	3.7
F	499.0	2.9	5.2	8.1	3.6
G	482.5	1.8	5.3	7.1	3.4
H	480.7	4.1	4.5	8.6	4.5
I	506.4	2.7	4.1	6.8	3.7
J	491.1	3.8	5.5	9.3	3.4
Mean value	504.7	4.2	5.9	10.0	3.7

Figure 2 shows the graphical representation of the two first principal components, both representing the 56.6% of the total variance.

Figure 2. Graphical representation of the first and the second principal components obtained from the PCA of the morphological characteristics of the samples and the amount of tobacco and the CO_2/CO ratio.



As it can be seen, the samples H and B show the lowest values of PC1, i.e., the highest values of CO_2/CO, probably related with their higher values of length of filter and lower length and weight of paper, which favor a better combustion process and, therefore, higher yield of CO_2 at expenses of CO. In fact, according to Table 2, effectively, samples H and B have the lowest values of length and weight of paper, the highest values of the CO_2/CO ratio and sample H has low length of filters too, thus supporting the validity of PCA to assist in the interpretation of the results in the cases where the number of variables considered is high. C and A samples, and in less extent B sample, show the lowest values of PC2, thus suggesting that they have the highest values of amount of tobacco smoked, the shortest cigarettes and the highest amount of tobacco smoked. Finally, PCA indicates that there is a homogeneous group of tobacco brands, in relation to their morphological characteristics and their CO_2/CO ratio, which includes the other studied brands, i.e.: D, F, G, I and J.

3.2 Analysis of the vapor phase

Table 4 shows the yields of the compounds analyzed in the vapor fraction for the studied brands. Among them, the compounds showing the major amount are by far CO and CO_2. CO is a well known poison and Spanish regulations allow a maximum quantity of CO of 10 mg/cigarette (Ministry of Health, BOE 19-10-2002). All tobacco brands are within the value allowed except C, which slightly exceeds.

Table 4. Gases yield for the 10 commercial brands and average values. All amounts are in μg/cigarette except those corresponding to CO and CO_2 that are in mg/cigarette.

COMPOUND	A	B	C	D	E	F	G	H	I	J	Average
CO	9.0	4.9	10.8	7.8	8.3	6.9	6.5	5.0	6.5	7.4	7.3
CO_2	30.0	19.7	39.5	29.4	30.4	24.7	22.4	22.3	23.8	25.4	26.8
Methane	499.2	393.2	742.8	514.6	580.2	494.9	433.2	465.6	511.2	498.6	513.1
Ethane	194.0	166.1	299.2	212.7	234.1	201.7	177.0	188.2	202.3	198.6	207.4

Ethylene	115.7	89.0	195.1	120.3	134.1	114.8	99.5	106.2	112.5	117.1	120.4
Ethyne	13.5	10.4	27.5	14.8	17.0	16.4	12.9	12.7	14.6	16.0	15.6
Propane	85.7	77.5	136.3	99.0	107.2	93.4	81.1	86.3	92.7	91.5	95.1
Propene	104.1	85.7	176.3	113.9	124.7	107.7	94.4	100.5	107.1	111.6	112.6
Iso-butane	8.8	7.2	14.1	9.2	19.0	8.5	7.9	8.7	8.6	33.8	12.6
Chloromethane	30.0	21.6	43.8	25.1	41.5	22.0	18.6	24.9	25.5	22.9	27.6
Butane	26.1	23.3	42.6	30.1	33.1	28.6	25.8	26.6	27.3	28.4	29.2
1-Butene	25.3	21.2	42.4	27.7	29.2	26.3	23.2	23.8	25.7	27.2	27.2
1,2-Propadiene	6.6	4.5	12.2	6.6	7.0	7.0	5.6	5.1	5.8	6.6	6.7
1,3-Butadiene	15.2	12.2	27.6	16.7	17.9	15.2	14.0	14.1	15.8	16.2	16.5
Isobutene	23.0	20.8	38.1	26.9	30.7	24.4	22.6	24.5	26.3	26.9	26.4
cis-2-Butene	17.6	16.6	30.7	20.7	22.5	13.5	15.3	18.2	17.5	21.0	19.4
Pentane	7.2	6.9	12.2	8.6	8.7	8.4	7.3	7.6	7.9	9.6	8.4
Methanethiol	13.3	6.4	22.6	10.4	12.0	10.7	9.8	10.5	12.9	10.6	11.9
Hydrogen cyanide	5.7	5.0	9.4	7.2	7.7	5.5	5.2	6.4	6.8	7.0	6.6
1-Pentene	8.0	8.3	15.5	8.9	9.9	7.0	7.4	8.1	8.3	8.4	9.0
Furan	8.9	7.2	16.1	11.0	10.1	9.8	8.3	8.2	8.7	9.2	9.8
Isohexane	12.9	17.4	34.6	23.0	17.7	20.7	18.7	14.3	21.2	22.7	20.3
Isoprene	116.5	35.0	119.8	140.1	163.5	107.3	119.1	113.0	126.4	140.2	118.1
Hexane	6.3	5.8	11.0	8.9	8.0	4.9	8.0	5.6	6.8	7.4	7.3
1-Hexene	1.3	0.9	1.4	2.0	2.0	2.0	1.7	1.7	1.7	1.9	1.7
Benzene	68.6	45.7	119.5	64.3	73.1	68.9	56.3	53.6	62.1	68.3	68.0
Acetaldehyde	285.2	249.5	528.3	302.8	361.1	314.5	283.3	270.2	309.6	307.8	321.2
Acetone	172.6	164.6	270.6	260.0	287.3	254.3	184.7	207.4	251.1	180.0	223.3
Acrolein	14.5	10.1	20.0	10.1	16.0	18.3	7.8	10.9	9.5	12.0	12.9
Propionaldehyde	12.3	8.3	15.6	8.9	11.4	14.9	7.5	10.1	12.0	9.7	11.1
Acetonitrile	37.1	29.4	66.9	27.3	48.9	55.8	28.0	30.7	53.2	70.5	44.8
Toluene	18.2	43.0	113.3	102.8	96.0	14.3	12.6	12.5	15.8	16.6	44.5
2,5-Dimethylfuran	5.1	8.3	10.5	10.1	11.9	5.4	6.2	4.5	5.3	4.8	7.2
Crotonaldehyde	2.9	2.2	4.5	2.1	4.7	3.0	2.0	3.3	2.8	3.5	3.1
Isobutyraldehyde	3.1	3.2	5.9	3.7	4.1	4.6	3.5	3.3	3.4	3.7	3.8
Sum	2005	1703	3394	2291	2601	2139	1842	1921	2156	2166	2222

Excluding CO and CO_2, the major compound present in the vapor fraction is methane. Other light hydrocarbon molecules are also present in high amounts such as ethane, ethylene, propane and propene. It is worth mentioning that the relative yield of most of the gaseous hydrocarbons in the different brands follows a similar pattern. For example, Figure 3 shows the hystograms of ethane, propene and isobutene, all of them showing very similar trends for all brands.

Figure 3. Hystograms of ethane (a), propene (b) and isobutene (c) in the different brands (µg/cigarette).

Figure 3a)

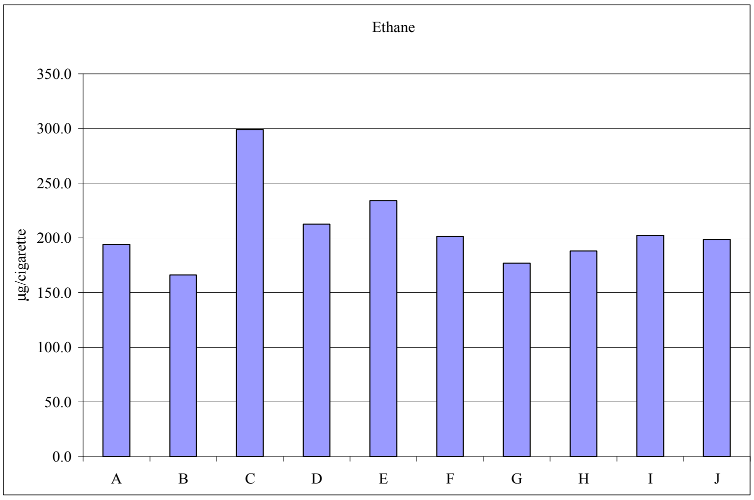


Figure 3b)

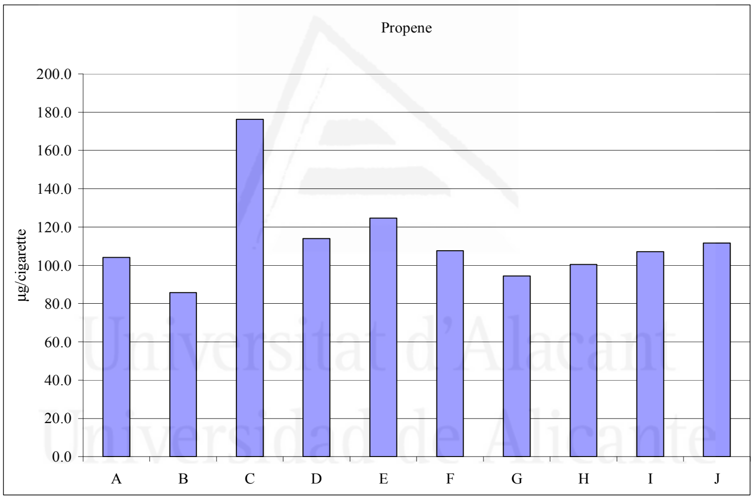
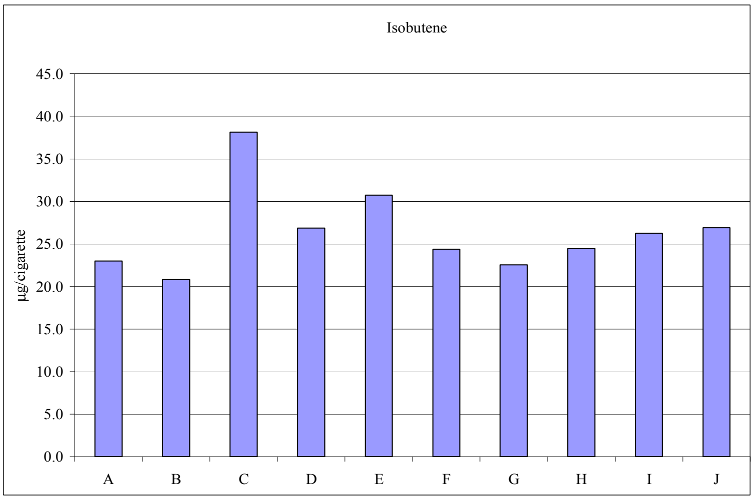


Figure 3c)



The same situation can be found for methane, ethylene, ethane, propane, butane, 1-

butene, isobutane and most of the compounds in the gaseous fraction. In all these cases brand C followed by E show the highest amount of the analytes while B and G yield the lowest amounts. The amount of smoked tobacco follows the same pattern shown for these compounds, and probably, the relative amount of the precursors involved in the formation of these compounds is the same in all the tobacco brands studied. Counts et al. (2005) found that linear functions strongly correlate tar yield with any individual smoke constituent yield, when smoke was obtained under the ISO conditions. For the mentioned hydrocarbons we have found that the pattern obtained is very similar but, there are some compounds that depart from this “general trend” as will be shown.

Small aldehyde molecules present in the tobacco smoke are particularly harmful, and according to EPA these are the major contributor to cancer risk (Fowles and Dybing, 2003). Among aldehydes, acetaldehyde is that with the highest cancer risk and shows values as high as 528.3 μg/cigarette in brand C, being the lowest value 249.5 in brand B. The average amount of acetaldehyde for all the brands studied is 321.2 μg/cigarette. Isobutiraldehyde presents much lower yields but behaves similarly to acetaldehyde and to the other compounds previously commented on in the vapor fraction, where brand C presents the highest concentration while brand B the lowest and the pattern is similar to that shown in Figure 3. An exception to this general trend is the behavior of some aldehydes such as propionaldehyde, acrolein and crotonaldehyde (Figure 4). Brands C, F, E and A present the higher amounts of acrolein and propionaldehyde, while G followed by B yield the lowest amounts.

Figure 4. Hystograms of some aldehydes acrolein (a), propionaldehyde (b) and crotonaldehyde (c) in the different brands (μg/cigarette).

Figure 4a)

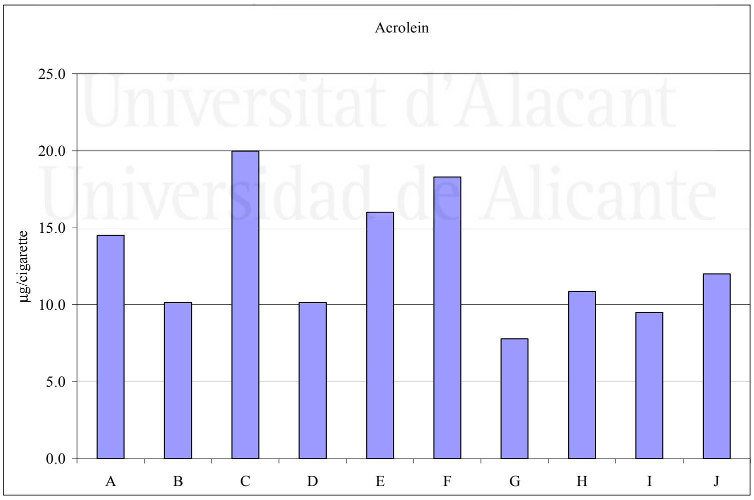


Figure 4b)

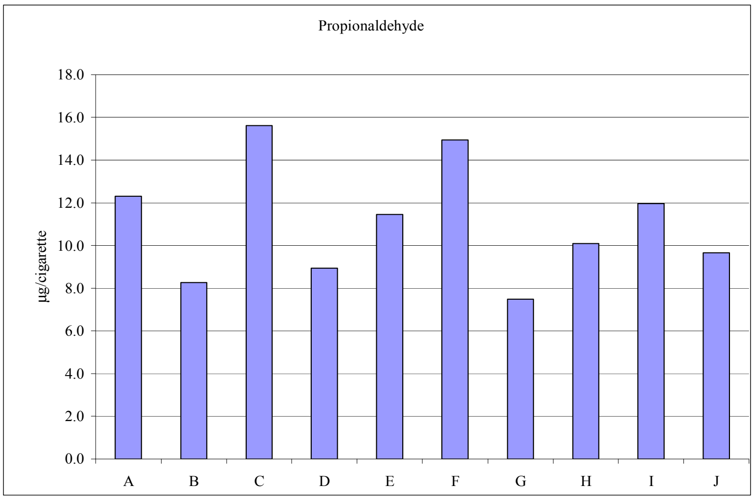
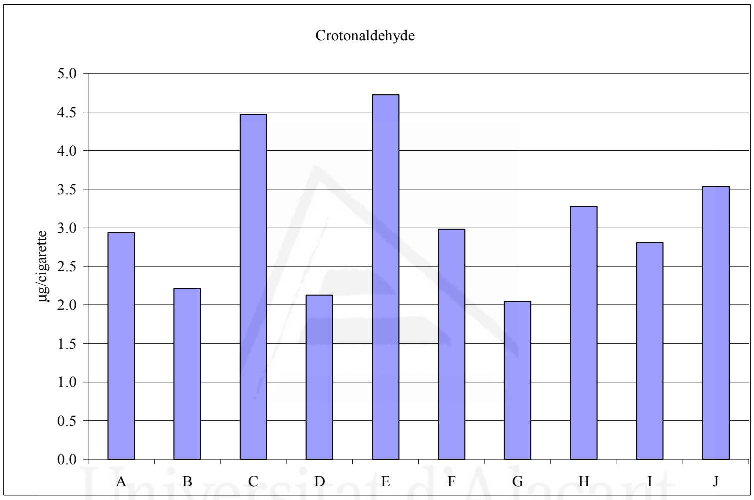


Figure 4c)



Other remarkable compounds shown in Table 4 are 1,3-butadiene and hydrogen cyanide. According to Fowles and Dybing (2003), 1,3-butadiene presents the highest cancer risk index of all constituents of cigarettes smoke. Excluding brand C which doubles the amount obtained in some other brands, all brands show very close values. HCN is the smoke constituent representing the highest index for cardiovascular effects. The average value for this compound in the studied cigarettes is 6.6 µg/cigarette, being brand C that showing the largest value of 9.4 µg/cigarette.

Acetone and isoprene present very high yields in all brands, reaching values as high as 287.3 and 163.5 µg/cigarette, respectively. Both compounds present patterns departing from the general trend commented above, with brand E proportionating the highest yields and brand B the lowest (Figure 5).

Figure 5. Amount of isoprene (a), toluene (b) and 2,5-dimethyl furan (c) for the brands studied (µg/cigarette).

Figure 5a)

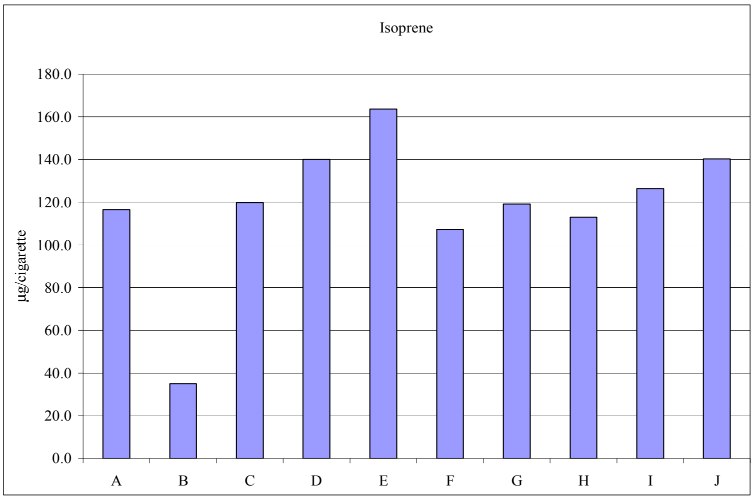


Figure 5b)

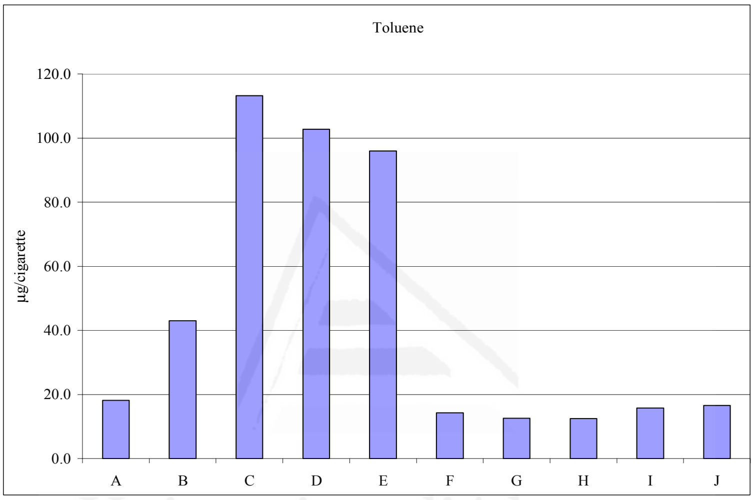
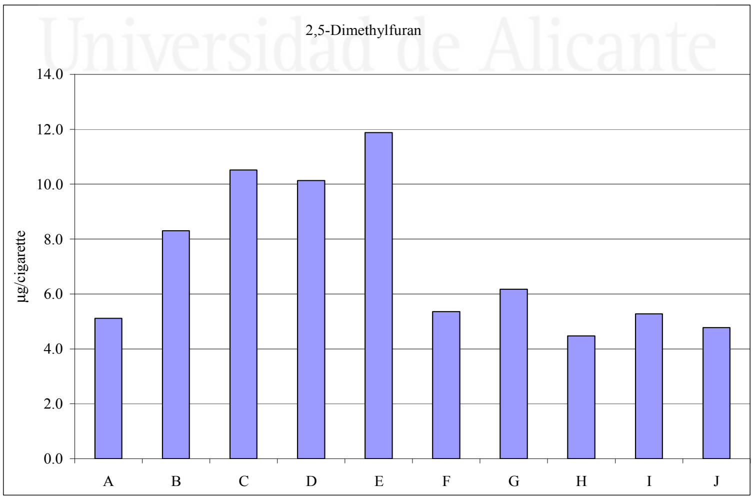


Figure 5c)



Other compounds which appear in the vapor phase at high concentration and that are known by their high toxicity are benzene and toluene. Benzene follows a general pattern similar to light hydrocarbons and small aldehydes, with amounts that vary from 45.7 to 119.5 µg/cigarette (brands B and C, respectively). The toluene behavior is much different (Figure 5). Brands C, D and E have concentrations of toluene around 100 µg/cigarette, while the other brands (excluding B) are around 14 µg/cigarette.

Other compound that is worth mentioning is 2,5-dimethylfuran that has been commonly used as tracer compound of the ETS (environmental tobacco smoke) (Bi et al. 2005) The behavior of the different brands for 2,5-dimethylfuran is much different than for other compounds as can be seen in Figure 5.

Summarizing, the vapor fraction of smoke of brand C is that presenting the highest amount of most of the analytes studied. For isoprene, crotonaldehyde and 2,5-dimethylfuran, brand E is the one providing the more concentrated gases, and for iso-butane and acetonitrile, is the smoke from brand J is the more concentrated. The lowest yield for most of the analytes in the vapor fraction is obtained for brand B but in some particular cases, for example aldehydes (acrolein, propionaldehyde, crotonaldehyde) brand G has the lowest concentration. Brands A, D, F and H show the lowest concentration for a few analytes. Attending to the global yield of gases (Table 4), brands B and G provide the lowest yields, while by far brand C, followed by E give the highest.

PCA has been applied to the 34 variables included in Table 4, corresponding to the composition of the not condensed fraction of the mainstream smoke obtained from the 10 studied cigarette brands. The above-mentioned software (PASW Statistics 18, version 18.0.0) permit us to reduce the dimensionless of the problem passing from the 35 original variables to only 5 principal components, which represents the 94.9% of the total variance of the problem. Table 5 shows the coefficients of the rotated component matrix, which indicate the contribution of each one of the original variables to each principal component. The percentage of the total variance explained by each principal component is also shown.

Table 5. Rotated component matrix corresponding to PCA of the original variables shown in Table 4.

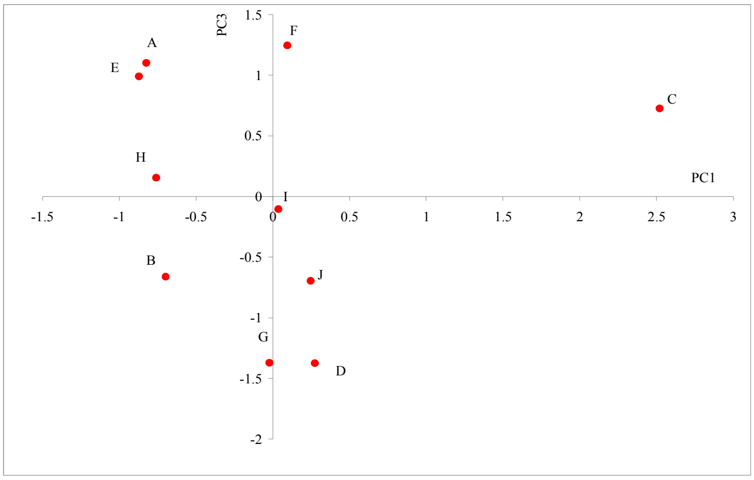
Original variable	PC1	PC2	PC3	PC4	PC5
CO	0.625	0.37	0.407	0.097	0.193
CO_2	0.673	0.494	0.415	0.092	0.127
Methane	0.758	0.401	0.446	0.156	0.169
Ethane	0.781	0.427	0.407	0.159	0.116
Ethylene	0.813	0.374	0.408	0.065	0.148
Ethyne	0.87	0.217	0.393	0.112	0.153
Propane	0.794	0.426	0.371	0.186	0.101
Propene	0.828	0.369	0.372	0.1	0.162
Iso-butane	0.161	-0.023	-0.028	0.19	0.93
Chloromethane	0.4	0.673	0.575	0.029	0.202
Butane	0.801	0.423	0.352	0.175	0.127
1-Butene	0.856	0.34	0.349	0.077	0.147
1,2-Propadiene	0.863	0.242	0.408	0.026	0.095
1,3-Butadiene	0.856	0.365	0.326	0.048	0.143
Isobutene	0.762	0.44	0.318	0.205	0.247
cis-2-Butene	0.696	0.581	0.151	-0.057	0.358
Pentane	0.879	0.196	0.217	0.129	0.311

Methanethiol	0.791	0.225	0.449	-0.022	0.102
Hydrogen cyanide	0.691	0.493	0.221	0.238	0.317
1-Pentene	0.789	0.506	0.24	-0.171	0.131
Furan	0.876	0.346	0.289	0.11	0.005
Isohexane	0.966	0.097	-0.038	0.096	0.052
Isoprene	0.127	0.247	0.124	0.78	0.41
Hexane	0.736	0.572	-0.201	0.102	0.173
1-Hexene	-0.033	-0.058	-0.033	0.983	0.119
Benzene	0.84	0.252	0.437	0.033	0.151
Acetaldehyde	0.843	0.331	0.38	0.055	0.114
Acetone	0.392	0.386	0.354	0.669	-0.206
Acrolein	0.458	0.099	0.819	0.048	0.04
Propionaldehyde	0.507	-0.117	0.83	0.105	-0.095
Acetonitrile	0.561	-0.262	0.416	0.175	0.557
Toluene	0.477	0.817	0.043	0.145	-0.074
2,5-Dimethylfuran	0.293	0.857	0.023	0.125	-0.121
Crotonaldehyde	0.299	0.36	0.649	0.15	0.513
Isobutyraldehyde	0.842	0.126	0.404	0.131	-0.05
% of variance explained	48.8	16.5	15.3	7.2	7

As it can be seen, the main contributors to the first principal component (PC1) are 25 of the 35 studied variables, and includes CO, CO_2, the major part of the analyzed hidrocarbons, methanethiol, hydrogen cyanide, furane, acetaldehyde, acetonitrile and isobutiraldehyde, and represents the 48.8% of total variance. This compounds are those showing the general trend previously commented on for the most of light hydrocarbons and small aldehydes. The second principal component (PC2) includes chloromethane, toluene and 2,5-dimethylfurane (with positive contributions). Toluene and 2,5-dimethylfurane have been above-mentioned as compounds showing a different pattern than those grouped in PC1 (see Figures 3 and 5). Therefore, in this case, PCA is also in agreement with the statements carried out after the visual inspection of the experimental results and, moreover, also has permitted us to distinguish other compound with similar behavior (chloromethane). The third principal component (PC3) includes acroleine, propionaldehyde and crotonaldehyde (with positive contributions), which were marked as exceptions of the general pattern shown by aldehydes. Both, PC2 and PC3 explain similar percentages of the total variance, 16.5% and 15.3%, respectively, which are significantly lower that explained by PC1. The fourth and fifth principal components (PC4 and PC5, respectively) represent, each one of them, around 7% of total variance and include, respectively isoprene, hexene and acetone, and isobutene (note that isoprene has been also mentioned as compound departing from the general trend) . These results, besides confirming the validity of PCA to systematize and to simplify the analysis of data sets with high number of variables, highlight the interest of the new variable PC1, because this component accounts for a lot of information accumulated in the most of the single variables. PC3 also is interesting because includes compounds noticeably toxic.

Figure 6 shows the graphical representation of PC3 versus PC1.

Figure 6. Graphical representation of the first and the third principal components obtained from the PCA of the variables shown in Table 5.



As it can be seen, in good agreement with the considerations pointed out previously, sample C appears apart from the other samples, due to its higher value of PC1, related with its highest global yield of the compounds appearing in PC1 (see Tables 4 and 5), and its relatively high value of PC3. Samples A, E, H and B exhibit the lowest values of PC1, and among this group, samples A and E differentiate from the rest by their higher value of PC3. Samples A, E and F show the highest values of PC3, and G and D have the lowest values of PC3. In order to summarize these results, a hierarchical cluster analysis has been performed with PASW Statistics 18, version 18.0.0. The dendrogram obtained is shown in Figure 7, and is a graphical summary of the cluster solution which reflects a grouping of the samples based in the measurement of the euclidean distance among samples and/or clusters in the 35-dimmensional space defined by the variables shown in Table 4. In Figure 7, cases are listed along the horizontal axis and the left vertical axis shows the distance between clusters when they are joined. The dendogram reflects the existence of a cluster which includes samples H, I, G, A, F and J, being sample B joined to this cluster at a higher distance, and another cluster which only includes samples D and E. According with Figure 7, sample C is quite different from the rest. The characteristics of the clusters can be easily deduced from the values of the principal components. Figure 7 permits us to conclude that sample C has a noticeably high value of PC1, accordingly with its higher global yields of the analytes included in such principal component (Figure 6), whereas the differences between the two observed clusters are reflected in a better way by the corresponding values of PC1 and PC2: as it is shown in Figure 8, the first group (samples H, I, G, A, F, J and B) have low values of PC1 and PC2, whereas the other cluster (samples D and E) also have low values of PC1, but higher values of PC2.

Figure 7. Dendogram corresponding to the hierarchical cluster analysis of variables of Table 5.

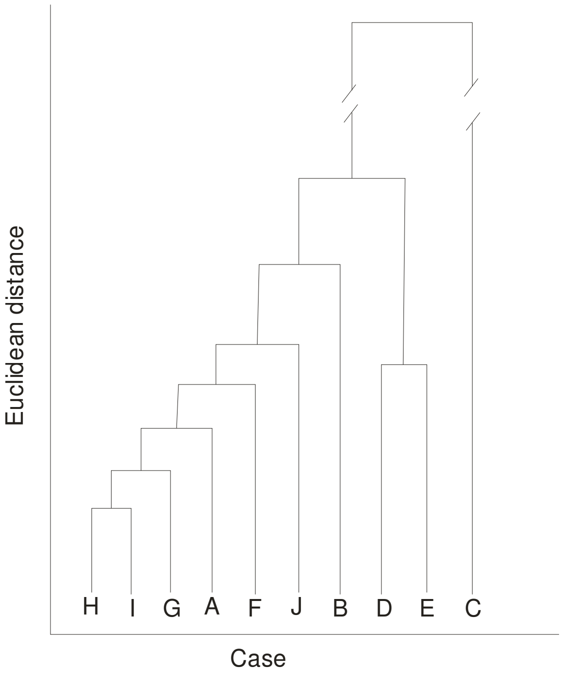
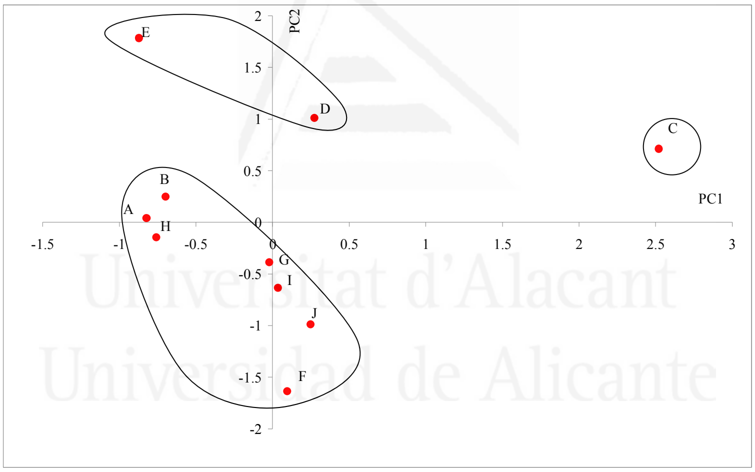


Figure 8. Graphical representation of the first and the second principal components obtained from the PCA of the variables shown in Table 5.



Finally, the previous PCA and cluster analysis have been repeated, adding to the original variables the initial amount of tobacco in each cigarette and the percentage of tobacco smoked in each case. The results obtained are quite similar to that commented on in the previous paragraphs. Five principal components are extracted, which explain the 94.6% of total variance. The contribution of the original variables to each component are very similar to those appearing in Table 5. Moreover, the initial amount of tobacco in the cigarette is included in PC4, with a positive contribution, and the percentage of tobacco smoked appears in PC1 (with positive contribution) and in PC4 (with positive contribution). The percentage of tobacco smoked is positively correlated with all the variables (see Table 6), with the exceptions of isobutane, isoprene, and hexene, and also negatively correlated with the amount of tobacco in the cigarette. The positive correlations indicate that the increase of the yield of such components could be related with an increase in the percentage of tobacco smoked, being more important this relationship as the coefficient of correlation increases (see Table 6). Contrarily, the compounds which are not highly correlated with the percentage of tobacco smoked could be more characteristic of the type of brand. The dendogram obtained by application of hierarchical cluster analysis is also very similar to that obtained without considering the amount of tobacco and the percentage smoked as variables included in the statistical analysis.

Table 6. Coefficient of multiple correlation of the percentage of tobacco smoked with the yield of different compounds appearing in the not condensed fraction of the mainstream smoke.

CO	0.673
CO_2	0.702
Methane	0.673
Ethane	0.679
Ethylene	0.731
Ethyne	0.698
Propane	0.658
Propene	0.703
Iso-butane	-0.042
Chloromethane	0.641
Butane	0.649
1-Butene	0.724
1,2-Propadiene	0.772
1,3-Butadiene	0.734
Isobutene	0.589
cis-2-Butene	0.652
Pentane	0.604
Methanethiol	0.732
Hydrogen cyanide	0.492
1-Pentene	0.802
Furan	0.709
Isohexane	0.597
Isoprene	-0.257
Hexane	0.495
1-Hexene	-0.598
Benzene	0.762
Acetaldehyde	0.739

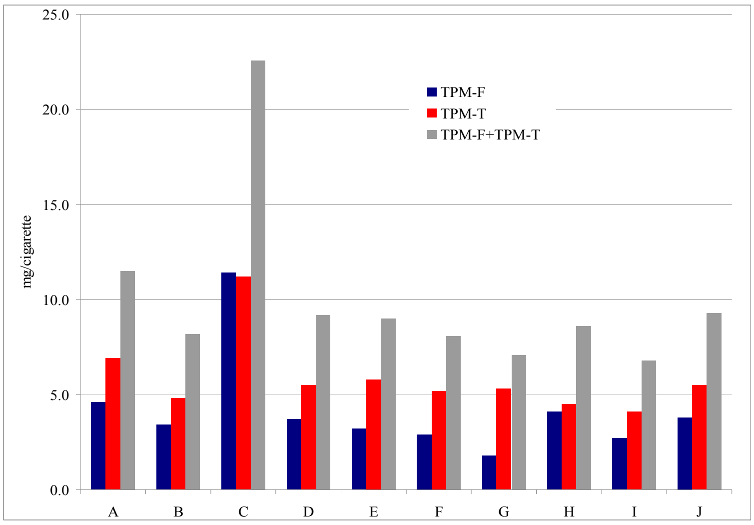
Acetone	0.149
Acrolein	0.641
Propionaldehyde	0.589
Acetonitrile	0.373
Toluene	0.506
2,5-Dimethylfuran	0.424
Crotonaldehyde	0.396
Isobutyraldehyde	0.661
Initial amount of tobacco	-0.885

3.3 Particulate matter

The main fraction of the smoke is formed by condensable products. In this work 85 components were identified in the particulate matter. Only the yield of the products retained in the traps is commonly reported, but in this work our interest was to compare the differences in the behavior of the most common commercial cigarettes, not only the differences in the smoke collected in the traps but the whole evolved products. In this way and differing from other works, the particulate matter condensed in the filter of the cigarettes have also been extracted and analised in the same way than that condensed in the traps. A very interesting behavior has been observed that will be commented hereafter.

Figure 9 shows the yield of total particulate matter condensed in the filters and the traps and the sum of both for the ten brands. For all brands the TPM-F is much lower than TPM-T except for brand C. The nature of the filters and traps employed is the same in all the samples despite the size of the filter may vary slightly (Table 2), but this does not seem to be responsible for the big differences found among brands in the relative amount of matter condensed in the filters and the traps. The way in which the condensed products are delivered between filters and traps may depend on a big number of factors and the nature of the compounds may play an important role as will be shown.

Figure 9. Yield of the total particulate matter condensed in the filters and the traps and the sum of both for the ten cigarettes brands.



It is worth mentioning that the yield of TPM-F+TPM-T (Figure 9), and consequently that of most of the compounds condensed in the filters, follows a similar pattern to that commented previously for most of the gaseous compounds and shown in Figure 3. The highest value of TPM-F+TPM-T is obtained for brand C, while the lowest is for brand I and, excluding C, the differences in the TPM yields are relatively small among the brands. The behavior is also valid for TPM-T that would be the particulate matter leaving the mouth end of the cigarette.

Table 7 contains the yield of the 85 compounds for the ten brands for the filters, while Table 8 contains the data of compounds condensed in the traps. Compounds have been ordered according to their retention time. In order to facilitate comparisons, both tables show the same compounds despite some of them were not found in the traps. It is worth mentioning, by its high toxicity, the case of naphthalene, that has been commonly reported as a component of tar, but it was probably under our detection limits in the traps.

Table 7. Yield of the compounds identified in the filter (TPM-F) for the 10 commercial brands. All amounts are in μg/cigarette.

Compound	A	B	C	D	E	F	G	H	I	J	Average
Pyridine, 4-methyl-	2.52	2.14	4.15	3.25	3.97	3.05	1.92	2.72	2.28	3.65	2.96
Pyrazine, methyl-	2.74	2.18	4.26	2.66	3.50	2.77	1.38	1.75	1.87	3.06	2.62
Furfural	29.84	17.41	42.37	21.62	27.43	24.43	13.36	14.71	16.45	24.10	23.17
2-Pentanone, 4-hydroxy-4-methyl-	0.90	2.24	1.68	2.61	2.52	1.86	2.11	3.70	2.10	1.85	2.16
2-Furanmethanol	6.12	3.03	14.80	3.70	5.95	6.49	0.00	0.68	1.20	0.00	4.20
Pyridine, 3-methyl-	7.52	4.69	11.20	5.52	7.28	6.62	2.61	4.46	3.70	6.02	5.96
2-Propanone, 1-(acetyloxy)-	13.13	8.09	17.90	8.88	12.13	10.47	5.81	6.58	6.62	9.62	9.92
4-Cyclopentene-1,3-dione	10.66	6.22	14.23	7.16	8.63	9.47	5.43	5.68	9.18	10.99	8.76
Styrene	1.11	1.58	2.92	2.10	2.75	2.36	1.20	1.19	1.59	1.75	1.85
2-Cyclopenten-1-one, 2-methyl-	9.04	6.82	15.57	8.60	10.73	8.95	5.09	6.14	6.26	8.72	8.59
2-Acetylfuran	5.33	3.89	10.65	5.28	7.84	4.74	2.79	4.70	3.61	4.95	5.38
2(5H)-furanone	6.95	4.29	12.20	4.29	7.08	4.97	2.89	3.27	3.88	4.68	5.45
Pyrazine, 2,3-dimethyl-	1.30	0.56	2.82	1.14	1.48	1.33	0.56	0.90	0.94	1.10	1.21
2-Hydroxycyclopent-2-en-1-one	5.50	3.52	9.95	3.92	5.06	5.02	2.86	3.19	3.41	4.94	4.74
Pyridine, 3,5-dimethyl-	2.58	1.38	4.49	1.54	1.93	0.96	1.12	1.25	1.50	2.19	1.89

2,5-Dimethyl-2-cyclopentenone	0.00	0.72	3.12	1.42	1.45	0.61	0.43	0.81	0.85	1.47	1.09
2(3H)-furanone, 5-methyl-	0.86	0.00	1.06	0.95	1.24	0.98	0.40	0.65	0.47	0.00	0.66
Butanoic acid, 3-methyl-	1.01	1.36	1.66	0.53	2.17	0.36	0.62	1.43	0.56	1.82	1.15
Ethanol, 2-butoxy-	1.54	1.83	3.51	1.54	2.77	2.43	1.22	1.11	1.08	2.29	1.93
Benzaldehyde	3.40	1.89	4.80	2.61	3.31	2.59	1.76	1.84	2.03	2.83	2.71
Furfural, 5-methyl-	17.32	11.00	28.25	11.82	16.00	14.01	7.47	8.01	9.85	13.13	13.69
Pyridine, 3-ethenyl-	3.37	2.18	6.14	2.52	1.75	3.30	1.10	1.67	1.74	3.38	2.71
2(5H)-Furanone, 3-methyl-	4.40	2.35	7.76	2.69	4.08	3.48	1.73	2.15	2.24	3.10	3.40
Phenol	26.20	18.48	49.78	22.17	26.08	23.57	15.57	16.67	16.52	23.08	23.81
2-Isopropylfuran	2.58	0.00	5.86	3.47	4.35	3.01	1.25	1.77	2.31	2.55	2.71
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	7.91	7.21	22.94	8.83	10.89	9.10	4.58	5.59	6.19	8.91	9.22
Limonene	2.53	3.76	4.01	4.17	5.08	4.08	1.51	2.81	2.90	3.49	3.43
Benzenemethanol	4.77	4.30	0.00	6.15	0.00	0.00	0.00	0.98	0.95	0.00	1.72
2,3-Dimethyl-2-cyclopenten-1-one	6.45	5.96	11.08	5.93	5.99	5.25	3.26	3.98	3.53	5.82	5.72
Indene	2.55	2.50	5.97	2.68	3.07	3.89	1.32	1.78	1.48	2.79	2.80
o-Cresol	8.10	6.89	16.01	6.92	8.87	7.86	5.47	5.62	5.58	9.37	8.07
2-Acetylpyrrole	2.10	1.27	3.63	1.45	1.93	2.30	0.93	1.07	1.17	1.62	1.75

Ethanone, 1-phenyl-	1.91	1.26	3.98	1.59	2.24	1.73	0.90	1.16	0.95	1.29	1.70
p-Cresol	15.18	12.45	34.15	13.76	17.65	15.46	8.32	10.23	9.08	14.41	15.07
2-Ethyl tiophene	0.76	1.65	3.05	0.70	3.25	1.46	0.84	0.45	0.76	0.93	1.38
Phenol, 2-methoxy-	7.33	5.74	14.72	6.28	7.92	7.73	3.63	4.33	4.77	6.63	6.91
2-Propanamine	4.85	4.93	9.64	4.94	5.90	5.75	2.42	3.05	1.60	3.56	4.66
2,4-Dimethyl-4-cyclohexen-1,3-dione-one	2.77	2.30	5.23	1.51	3.02	3.50	0.59	1.46	0.00	1.40	2.18
Nicotinamide	7.50	5.32	9.88	0.00	6.98	6.46	3.09	0.00	2.13	4.07	4.54
3-Ethyl-2-hydroxy-2-cyclopenten-1-one	2.83	2.65	8.00	2.86	3.74	3.51	1.94	2.51	1.28	3.38	3.27
Benzeneacetonitrile	3.66	4.54	7.30	3.36	7.74	2.89	1.89	2.10	2.08	3.43	3.90
2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	5.33	5.44	11.04	6.52	7.81	7.73	1.67	2.57	0.55	1.99	5.06
Phenol, 2,4-dimethyl-	5.01	5.65	2.59	5.78	5.35	4.71	2.31	3.33	0.95	1.54	3.72
Phenol, 4-ethyl-	3.73	2.76	9.11	3.03	3.99	3.30	1.22	1.92	1.49	3.22	3.38
Naphthalene	1.73	1.04	3.34	1.60	2.04	1.46	0.85	1.34	1.34	1.64	1.64
Ethanone, 1-(3-methylphenyl)-	2.17	2.40	5.14	2.71	3.20	2.94	1.32	1.92	1.67	2.67	2.62
p-Cresol 2 methoxy	3.94	2.48	5.72	3.27	3.85	3.91	1.38	2.19	2.36	3.18	3.23
2,3-Dihydro-benzofuran	3.12	2.69	6.95	4.26	4.77	3.57	3.02	2.70	2.63	2.73	3.64
2-Furancarboxaldehyde, 5-(hydroxymethyl)-	4.85	1.73	5.98	3.59	7.84	4.69	1.43	2.27	0.97	0.00	3.34

1H-Inden-1-one, 2,3-dihydro-	4.20	2.37	4.64	2.24	2.94	2.24	0.00	0.84	1.83	3.40	2.47
Hydroquinone	7.68	7.60	14.38	4.71	2.66	3.80	6.00	2.17	0.00	2.86	5.19
1H-Indole	9.27	10.29	16.70	10.38	9.19	8.79	5.20	7.20	4.86	9.20	9.11
4-Vinyl-2-methoxy-phenol	3.27	3.95	7.96	3.75	4.72	4.45	2.19	2.84	2.48	3.34	3.89
Nicotine	350.2	294.5	656.9	352.6	439.9	418.1	230.8	333.6	295.6	392.9	376.5
1H-Indole, 3-methyl-	3.47	2.63	4.64	3.44	4.58	2.78	2.08	2.72	2.02	3.41	3.18
Myosmine	4.32	3.98	7.91	3.77	5.86	4.87	2.42	4.83	2.39	4.68	4.50
Phenol, 2-methoxy-4-(2-propenyl)-	1.05	1.48	4.02	2.27	2.16	1.79	0.62	1.06	0.91	1.34	1.67
Nicotyrine	2.67	1.21	3.56	1.90	1.68	2.15	0.92	1.03	2.11	2.72	1.99
Norsolanadiona	1.63	1.71	1.49	1.86	1.86	2.45	0.68	2.06	1.73	2.84	1.83
Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl-	0.73	0.73	1.43	0.86	1.73	1.14	0.28	0.46	0.80	1.79	0.99
2,3'-Bipyridine	3.14	3.32	5.24	2.83	3.70	3.29	1.93	2.99	1.62	3.00	3.11
1,4-Dihydrophenantrhene	1.27	1.29	3.75	2.92	2.24	0.73	0.56	1.21	0.84	1.90	1.67
Diethyl phatalate	1.33	0.81	0.84	0.00	0.84	4.14	0.43	0.00	0.71	0.00	0.91
Megastigmatrienone	1.37	1.29	2.01	1.81	1.97	1.72	0.47	0.00	1.33	1.37	1.33
N-propyl nornicotine	0.94	1.33	1.16	1.41	2.17	1.01	0.91	0.87	0.91	1.19	1.19
Cotinine	2.42	3.19	6.16	4.21	4.92	4.07	2.02	3.36	1.90	3.31	3.56

1H-Indene, 2,3-dihydro-1,1,3-trimethyl-3-phenyl-	0.27	1.50	0.42	0.00	1.12	0.00	0.00	0.42	0.00	0.00	0.37
5-Tetradecene	1.09	1.01	3.57	1.17	2.32	1.68	0.95	0.65	1.21	1.39	1.50
N(b)-Formylnornicotine	0.85	1.47	1.88	0.91	2.05	1.80	0.64	1.72	0.00	0.75	1.21
2,4-Diphenyl-4-methyl-penten-1ene	0.52	2.66	0.00	0.00	2.91	0.00	0.00	0.49	0.00	0.00	0.66
Neophytadiene	18.38	22.10	55.11	38.39	35.35	31.38	18.43	20.83	33.23	28.59	30.18
Farnesol	1.32	1.31	2.43	1.43	1.54	4.12	0.00	0.64	1.79	1.48	1.61
8-Quinolinemethanol	1.13	0.84	2.31	0.00	0.98	2.07	1.15	0.00	0.00	2.08	1.06
DBP	0.00	2.23	1.71	0.76	0.00	0.46	0.00	0.00	0.00	0.00	0.52
Hexadecanoic acid, ethyl ester	1.81	1.21	2.40	2.96	2.07	1.52	1.31	0.80	1.90	4.24	2.02
Pentadecane	0.00	3.53	1.12	1.83	0.94	1.28	1.75	0.68	1.24	1.23	1.36
Octadecane	3.29	9.77	14.07	8.68	12.09	9.70	5.18	8.67	6.24	8.79	8.65
Eicosane	1.05	3.96	2.21	1.11	2.14	0.00	2.31	1.76	1.38	1.10	1.70
Docosane	2.12	3.07	0.54	4.87	3.50	4.78	4.43	2.91	2.97	3.66	3.29
Citric acid, tributyl ester	0.64	1.46	16.57	32.43	0.81	38.26	10.02	25.23	31.73	49.36	20.65
Tricosane	2.23	1.81	6.87	4.45	5.89	4.78	3.15	4.29	2.99	3.60	4.01
2,6,10,14,18,22-Tetracosahexaene, 2,6,10,15,19,23-hexamethyl-	2.47	1.67	2.57	1.00	5.13	2.76	2.06	2.53	1.65	3.11	2.49
Heptacosane	3.25	5.36	7.56	4.83	5.22	4.50	2.86	5.35	4.40	6.41	4.97

Triacontane	1.63	4.14	6.22	3.92	5.74	4.71	2.53	4.48	2.35	2.36	3.81
Tocopherol	2.16	2.47	7.40	4.17	6.80	3.26	0.00	2.81	0.00	1.97	3.10

Table 8. Yield of the compounds identified in the trap (TPM-T) for the 10 commercial brands. All amounts are in μg/cigarette.

Compound	A	B	C	D	E	F	G	H	I	J	Average
Pyridine, 4-methyl-	0.49	0.16	1.95	0.09	0.39	0.00	0.00	0.00	0.072	0.00	0.38
Pyrazine, methyl-	0.58	0.29	1.97	0.30	0.72	0.36	0.00	0.00	0.55	0.00	0.47
Furfural	3.51	1.80	14.15	2.00	2.72	1.76	1.78	0.88	3.41	1.50	3.35
2-Pentanone, 4-hydroxy-4-methyl-	1.39	1.29	3.43	1.70	2.08	1.12	1.19	2.78	1.73	1.58	1.82
2-Furanmethanol	0.00	0.00	2.76	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.27
Pyridine, 3-methyl-	0.28	0.13	0.85	0.00	0.40	0.23	0.10	0.00	0.42	0.24	0.26
2-Propanone, 1-(acetyloxy)-	0.80	0.21	2.39	0.50	0.58	0.48	0.47	0.27	0.69	0.56	0.69
4-Cyclopentene-1,3-dione	2.42	1.00	3.98	1.23	1.49	1.27	1.15	0.87	1.48	1.27	1.61
Styrene	0.25	0.96	1.93	1.16	1.07	1.03	0.29	0.21	0.29	0.25	0.74
2-Cyclopenten-1-one, 2-methyl-	0.86	0.67	4.52	0.65	0.82	0.70	0.49	0.37	0.99	0.49	1.05
2-Acetylfuran	0.37	0.18	1.98	0.26	0.38	0.40	0.21	0.22	0.53	0.14	0.46
2(5H)-furanone	1.84	0.69	1.98	0.81	1.01	0.69	0.84	0.55	0.90	0.91	1.02

Pyrazine, 2,3-dimethyl-	0.00	0.00	0.59	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05
2-Hydroxycyclopent-2-en-1-one	1.45	0.65	2.12	0.93	0.75	0.98	0.66	0.64	0.48	0.74	0.93
Pyridine, 3,5-dimethyl-	0.00	0.00	0.41	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04
2,5-Dimethyl-2-cyclopentenone	0.00	0.00	0.69	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06
2(3H)-furanone, 5-methyl-	0.42	0.00	0.0 0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04
Butanoic acid, 3-methyl-	1.20	0.00	1.04	0.00	0.45	0.90	0.53	1.19	0.65	1.32	0.72
Ethanol, 2-butoxy-	1.60	0.91	2.52	1.11	1.31	1.56	0.85	0.82	0.74	1.35	1.27
Benzaldehyde	0.56	0.40	1.44	0.37	0.44	0.55	0.35	0.42	0.68	0.31	0.54
Furfural, 5-methyl-	1.41	0.53	3.70	0.66	0.82	0.82	0.65	0.43	1.04	0.76	1.08
Pyridine, 3-ethenyl-	0.66	0.23	1.04	0.00	0.00	0.00	0.00	0.00	0.24	0.00	0.21
2(5H)-Furanone, 3-methyl-	0.70	0.00	1.17	0.00	0.00	0.00	0.16	0.00	0.00	0.00	0.20
Phenol	5.82	2.59	8.30	3.60	3.65	5.28	3.35	2.95	2.24	2.91	4.06
2-Isopropylfuran	0.00	0.00	0.61	0.00	0.46	0.00	0.00	0.00	0.00	0.00	0.10
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	3.10	0.55	3.72	1.18	2.51	1.77	1.07	0.87	0.81	0.99	1.65
Limonene	1.47	0.73	1.52	0.77	1.59	0.89	0.52	0.58	0.93	0.85	0.98
Benzenemethanol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2,3-Dimethyl-2-cyclopenten-1-one	0.84	0.33	1.77	0.68	0.00	0.88	0.51	0.55	0.38	0.33	0.62
Indene	0.86	0.17	1.14	0.18	0.00	0.42	0.25	0.19	0.23	0.14	0.35

o-Cresol	2.98	1.26	3.69	1.45	2.10	2.11	1.91	1.98	1.28	2.18	2.09
2-Acetylpyrrole	0.57	0.00	0.45	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10
Ethanone, 1-phenyl-	0.00	0.00	0.63	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06
p-Cresol	5.47	2.65	7.38	3.72	3.11	5.30	2.62	2.81	1.67	2.99	3.77
2-Ethyl tiophene	0.76	1.03	1.22	1.18	1.77	1.52	0.83	0.41	0.79	0.73	1.02
Phenol, 2-methoxy-	1.58	0.77	2.42	0.81	0.92	1.27	0.54	0.47	0.53	0.56	0.98
2-Propanamine	3.32	1.15	3.47	2.63	0.64	3.72	1.50	1.59	0.69	1.48	2.22
2,4-Dimethyl-4-cyclohexen-1,3-dione-one	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Nicotinamide	10.04	0.00	0.00	0.00	4.99	5.35	3.73	5.42	1.25	0.00	3.07
3-Ethyl-2-hydroxy-2-cyclopenten-1-one	1.92	0.34	1.94	0.76	0.00	1.40	0.54	0.58	0.00	0.79	0.82
Benzeneacetonitrile	0.00	0.00	0.00	0.00	0.00	0.00	0.34	0.00	0.00	0.00	0.03
2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	5.97	3.08	4.86	5.14	5.96	7.04	2.13	3.96	1.14	2.95	4.22
Phenol, 2,4-dimethyl-	1.70	0.87	2.70	1.04	0.65	1.81	3.41	1.02	1.29	3.43	1.79
Phenol, 4-ethyl-	1.62	0.50	2.95	1.38	2.04	2.62	0.93	1.02	0.75	1.09	1.49
Naphthalene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ethanone, 1-(3-methylphenyl)-	0.00	0.00	2.21	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.22
p-Cresol 2 methoxy	1.56	0.36	1.11	0.26	0.00	0.00	0.72	0.57	0.96	0.89	0.64
2,3-Dihydro-benzofuran	2.98	1.32	3.79	3.28	2.10	3.08	1.64	1.73	2.13	2.92	2.49

2-Furancarboxaldehyde, 5-(hydroxymethyl)-	3.88	1.85	2.11	3.65	4.56	4.86	0.00	0.00	0.67	0.70	2.22
1H-Inden-1-one, 2,3-dihydro-	0.78	0.57	1.76	0.00	0.00	0.85	0.46	0.51	0.66	1.45	0.70
Hydroquinone	15.40	7.33	22.20	13.61	7.02	10.85	10.26	7.55	7.60	11.84	11.36
1H-Indole	9.31	2.57	9.80	3.59	2.63	4.11	2.64	3.55	1.90	4.41	4.45
4-Vinyl-2-methoxy-phenol	2.54	1.04	3.42	1.70	2.59	3.51	1.43	0.99	1.29	1.59	2.00
Nicotine	613.2	282.5	612.3	419.2	482.3	557.0	352.8	390.9	408.4	475.3	459.3
1H-Indole, 3-methyl-	2.76	1.49	3.57	2.04	2.29	2.62	1.99	2.59	2.18	2.31	2.38
Myosmine	5.37	2.40	5.66	3.44	4.09	4.66	2.74	4.97	2.89	3.96	4.01
Phenol, 2-methoxy-4-(2-propenyl)-	2.34	1.46	4.51	2.34	2.58	2.78	1.32	2.70	0.93	1.91	2.28
Nicotyrine	4.56	1.05	5.48	2.31	1.51	1.66	1.07	1.68	1.88	2.43	2.36
Norsolanadiona	4.45	1.23	5.43	2.28	1.67	2.14	1.58	2.29	2.17	3.09	2.63
Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl-	8.44	4.03	5.09	5.24	6.13	7.45	6.13	7.33	8.10	8.66	6.65
2,3'-Bipyridine	4.24	2.15	5.41	3.35	3.62	3.59	2.60	3.60	2.79	3.70	3.50
1,4-Dihydrophenantrhene	3.58	0.00	2.26	1.86	2.94	3.56	2.37	2.64	2.60	3.19	2.49
Diethyl phatalate	4.25	1.02	1.25	1.84	3.14	6.50	3.10	3.40	3.51	2.51	3.05
Megastigmatrienone	2.10	0.40	3.17	1.90	1.31	1.48	0.77	1.29	1.48	1.45	1.53
N-propyl nornicotine	2.43	0.97	2.31	2.37	2.08	2.58	1.15	1.84	1.35	1.83	1.89
Cotinine	6.66	3.39	9.90	7.02	5.72	6.24	3.79	4.87	3.28	5.26	5.61

1H-Indene, 2,3-dihydro-1,1,3-trimethyl-3-phenyl-	3.67	0.00	0.00	1.55	3.22	2.99	2.45	3.23	3.07	3.62	2.38
5-Tetradecene	1.92	0.65	2.66	1.99	1.83	1.35	1.25	1.18	1.29	1.48	1.56
N(b)-Formylnornicotine	5.03	0.00	5.19	3.54	6.60	5.31	3.73	3.17	4.40	4.50	4.14
2,4-Diphenyl-4-methyl-penten-1ene	0.72	0.00	0.00	2.66	5.91	5.31	3.86	4.20	4.69	4.95	3.22
Neophytadiene	30.81	15.21	51.53	33.12	26.77	27.91	20.46	22.57	31.31	26.77	28.64
Farnesol	2.16	1.87	3.23	2.00	3.06	2.90	1.54	1.79	2.10	2.24	2.28
8-Quinolinemethanol	0.00	0.00	0.00	0.00	0.96	0.72	0.61	0.74	0.92	0.85	0.48
DBP	0.00	1.36	0.00	0.38	0.00	0.00	0.00	0.00	0.00	0.00	0.17
Hexadecanoic acid, ethyl ester	3.46	1.36	3.11	3.60	2.24	2.82	1.92	2.04	2.38	3.19	2.61
Pentadecane	1.31	1.56	3.12	1.51	1.03	1.09	0.72	1.04	0.81	0.96	1.31
Octadecane	11.36	8.74	19.96	16.23	13.04	15.29	10.44	14.99	10.93	14.30	13.52
Eicosane	1.70	1.29	3.25	1.67	1.69	1.70	1.50	2.02	1.39	1.26	1.74
Docosane	2.73	4.64	4.41	3.95	3.55	3.38	2.67	2.50	2.49	2.45	3.27
Citric acid, tributyl ester	0.00	2.51	5.35	1.85	0.00	0.00	0.00	0.00	0.00	0.00	0.97
Tricosane	6.26	5.26	8.97	6.88	5.83	6.83	5.41	7.09	6.28	6.71	6.55
2,6,10,14,18,22-Tetracosahexaene, 2,6,10,15,19,23-hexamethyl-	4.16	0.53	2.83	1.53	3.24	4.47	2.41	4.49	1.70	3.81	2.91
Heptacosane	7.53	5.64	10.27	7.15	6.78	8.16	5.41	8.83	7.09	8.24	7.50
Triacontane	5.53	3.81	9.92	6.12	8.25	6.43	4.71	6.09	5.19	5.70	6.17

Tocopherol	4.45	3.09	13.02	8.52	8.32	7.12	2.31	4.60	2.40	3.35	5.71

A remarkable aspect that can be appreciated in Tables 7 and 8 is the way compounds are delivered between the filter and the trap according to their retention time. The amount of most of compounds with low retention time (i.e., compounds with relatively low molecular weight) is higher in the filters than in the traps, while the very opposite is true for the heaviest compounds. For the compounds with the lowest retention time, the yield in the filters is two or three times higher than in the traps and for example for furfural, phenol or indene the yield in the filter can be even 10 times higher than in the traps. Compounds with medium retention times such as nicotine or 2,3'-bipyridine are more uniformly delivered between filters and traps, while the heaviest compounds such as cotinine, octadecane and heptacosane present higher amounts in the traps than in the filter. This rule is true for most of the compounds and the brands but there are some exceptions such as hydroquinone among the relatively low molecular weight compounds, and pentadecane and eicosane among the compounds which present the highest retention time. The explanation to this observation may involve aspects as the different affinity of any particular compound by the filter or their relative concentration and vapor pressures. The difference in the pressure drop when modifying the cigarettes could produce also changes, making more difficult the interpretation.

Figures 10 to 12 shows the hystograms of some compounds condensed in the filters and the traps. These compounds have been selected because they were present in high amounts or because they have been reported to be implied in human diseases.

Figure 10. Hystograms of phenol (a), p-cresol (b) and hydroquinone (c) in TPM-F and TPM-T for the different brands.

Figure 10a)

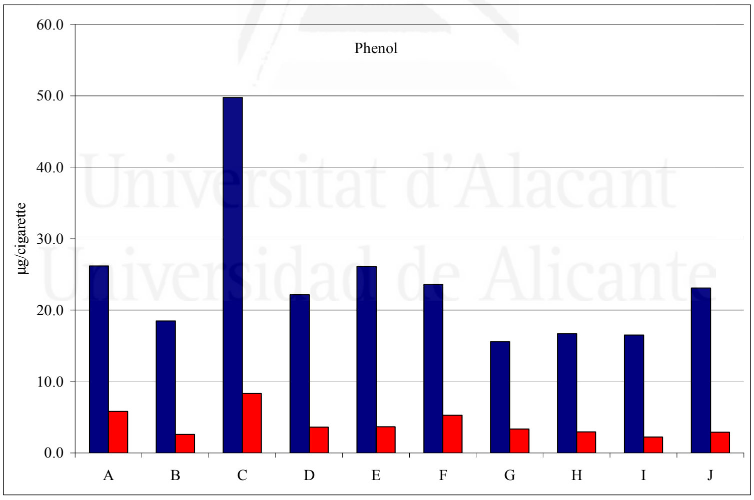


Figure 10b)

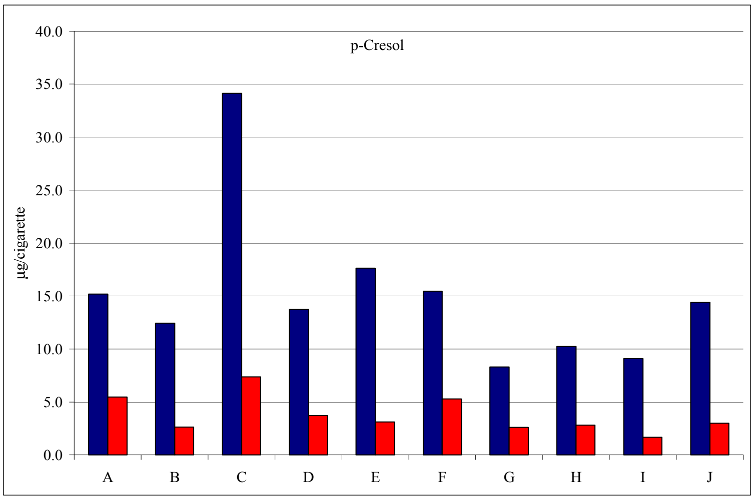


Figure 10c)

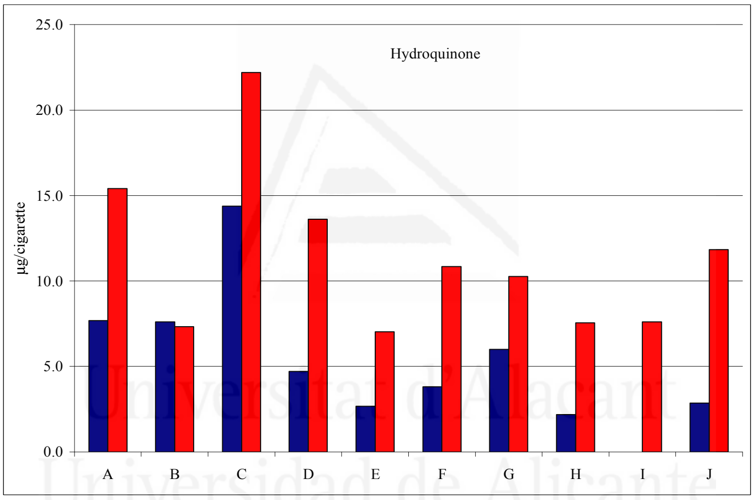


Figure 11. Hystograms of nicotine (a), myosmine (b) and cotinine (c) in TPM-F and TPM-T for the different brands.

Figure 11a)

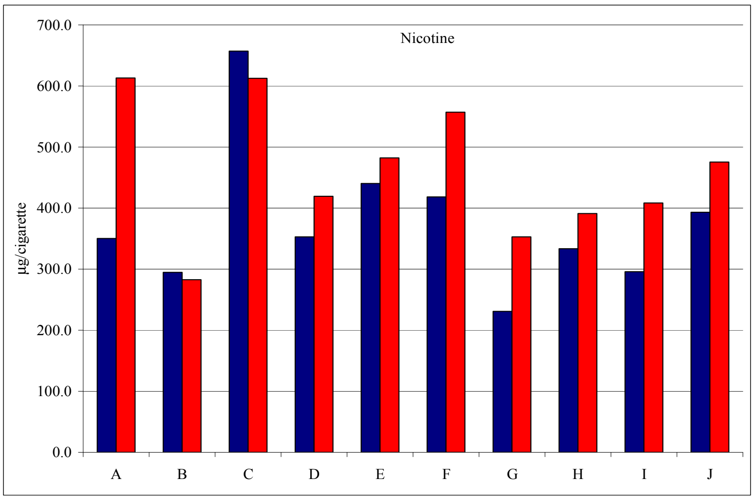


Figure 11b)

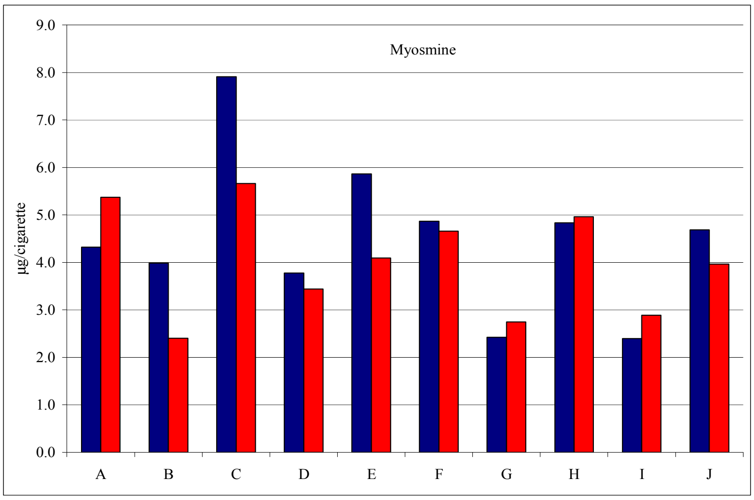


Figure 11c)

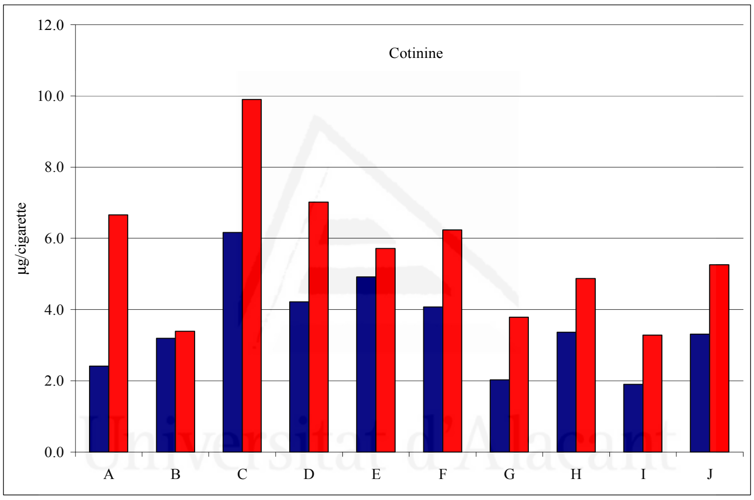


Figure 12. Hystograms of octadecane (a), heptacosane (b) and triacontane (c) in TPM-F and TPM-T for the different brands.

Figure 12a)

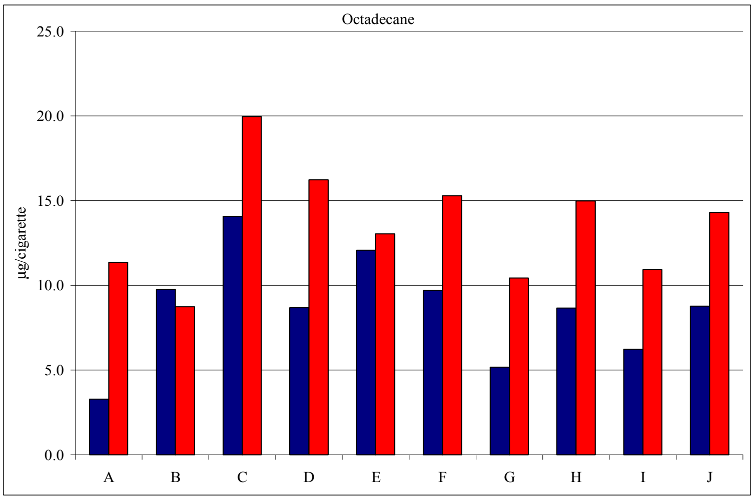


Figure 12b)

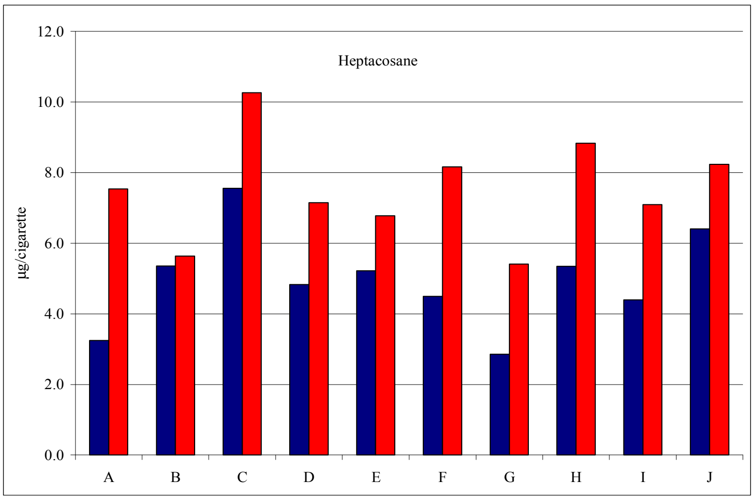
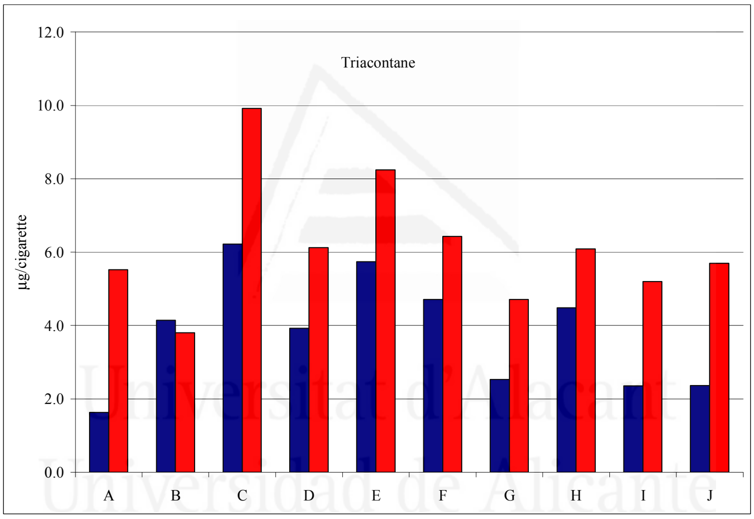


Figure 12c)



Apart from water, nicotine is the major individual compound contained in the particulate matter and it is also the main responsible for the addictive behavior of smokers. The hystogram for nicotine, cotinine and myosmine are shown in Figure 11. Nicotine in the TPM-T for the 10 brands under study varies from 282.5 to 613 µg/cigarette (brands B and C, respectively) in the traps, and presents a relatively low variation coefficient for all the brands. Brands A and C present nearly the same amount of nicotine despite TPM-T is much higher for C than for A. The hystogram for myosmine is quite similar to that of nicotine. In fact molecular weight and chemical structure of both pyridine derivatives are very similar. The behavior of cotinine is much different as it structure does, and its concentration in traps is higher than in filters, as it corresponds to the general way that most of compounds are delivered in filters and traps.

In tar there are some compounds with higher toxicity than nicotine and directly responsible for lung cancer and other diseases. Some phenols are included in the Hoffmann list by their high toxicity. Figure 10 and Tables 7 and 8 include the results for the phenolic compounds of the Hoffmann list (Hoffmann and Hoffmann, 1997), i.e. phenol, p-cresol, o-cresol, and excluding brand C, the relative amount of phenols produced by the different brands is quite similar. The hydroquinone behavior (Figure

10) is quite different and major relative differences can be found among brands. According to Borgerding and Klus (2005) the hydroquinone yield is more sensitive to tobacco blend type than other smoke constituents and is delivered in much higher extent in traps.

Figure 12 shows the hystograms for some hydrocarbons present in the particulate matter. The hydrocarbons shown present very similar behaviors among brands and, as it was shown for hydrocarbons in the vapor phase, it could be said that this is the general trend for these compounds in TPM-F and TPM-T but there are other hydrocarbons such as eicosane and pentadecane that present a different pattern.
It is relatively frequent to assume that if a cigarette yields more tar than others it may be more toxic, and in general it may be true, and current European Comunity Regulations are limiting exclusively the CO, nicotine and "tar" content. At this respect, Borgerding and Klus (2005) reviewed some studies that demonstrated R^2 values greater than 0.9 for most of the individual Hoffmann analytes and tar, nicotine or CO, and they pointed out that these relationships depend mainly on tobacco blend and other cigarette design features. When comparing commercial cigarettes where these design features vary considerably, as can be seen in the results shown in the present work, the relative production of a compound or family of compounds may vary differently to tar. For example, brand E presents a content of TPM-F and TPM-T lower to the average of all brands and a nicotine yield very close to the average. Nevertheless the content of brand E in some well know toxic compounds such as isoprene, crotonaldehyde or toluene is the highest of all brands. Brand I is that with the lowest TPM and the lowest yield for most of the condensed compounds reported, while the lowest yields in gases are produced by brand B for most of compounds followed by G. On another hand, according to Counts et al. (2004) the yield of any compound of the vapor phase tends to be more similar for the different cigarettes than the TPM constituents yield. This would be also our case if among vapor phase constituents crotonaldehyde, isobutiraldehyde and toluene are excluded. The other components of the vapor phase present variation coefficients lower than those of the particulate matter. Attending to the global yield of TPM-T (Figure 9), brands I and H provide the lowest yields, while by far brand C, followed by A are those providing the highest.

The application of multivariate statistical analysis would be especially valuable in this case where there are a large amount of variables and experimental results, as Tables 7 and 8 reflect. The low variability of the studied variables also supports the need of applying some technique in order to simplify the analysis of results. In fact, the unvariate statistics of each variable analyzed in the traps show that the most of them (78 variables) have coefficient of variation, calculated as 100 x standard deviation/mean, lower than 100, and the coefficient of variation for the remaining seven variables is lower than 200. Similar results have been obtained for the filters. The PCA permits us to reduce de dimensionless of the problem, and 8 and 9 principal components, respectively, have been obtained for traps and filters. The percentage of the variance explained is very high in both cases: in the PCA of the results of traps, the 8 principal components selected account for the 98.8% of the total variance, despite a 71% of variance is already represented by the three first principal components, which indicates that these would provide a satisfactory interpretation of the results. The PCA of the results of filters provides 9 principal components which represent the 100% of total variance. In this case, the first principal component (PC1) accounts for the 57% of total variance, the second one (PC2) the 9%, and the third, fourth and fifth ones around 6%.

The tables corresponding with the rotated component matrix resulting from PCA of the original variables analyzed in filters and traps are noticeably large and it has been considered more interesting to present the resume and interpretation of such tables for both, filters and traps. In this way, it has been simultaneously taken into consideration the variables appearing with high loadings in each principal component, and also the possible grouping of these variables considering the correlation degree (i.e., the correlation coefficient calculated as the ratio of the covariance and the square root of the product of variances). Thus, Table 9 shows the groups of variables according their correlation coefficient (thus, with similar behavior), and the principal components where they are represented in the PCA of the results corresponding to the traps. In order to avoid an excess of low relevant information, only the fourth first principal components are shown. According with these results, the study of the differences among tobacco brands could be performed by centering the attention in the interpretation of the results corresponding to the variables included in these tables and, moreover, only one variable as representative of each group of correlated variables could be chose. In general, the PCA analysis of the results corresponding to the chemical analysis of the materials retained in the filters shows similar results to that of the traps. In this cases a single group of variables highly correlated are obtained, which includes most of the variables of groups 1, 2 and 3 of the traps (see Table 9). The other groups of correlated variables only include two variables and do not provide too much interesting information. In this case, PC1 (57% of total information of the samples) includes the most of the studied variables.

Table 9. Variables included in the fourth first principal components resulting from the PCA of the chemical analysis of the compounds retained in the traps. The variables within each group are higly correlated.

	PC1	PC2	PC3	PC4
Group 1	Pyridine, 4-methyl-			
	Pyrazine, methyl-			
	Furfural			
	2-Furanmethanol			
	Pyridine, 3-methyl-			
	2-Propanone, 1-(acetyloxy)-			
	4-Cyclopentene-1,3-dione			
	2-Cyclopenten-1-one, 2-methyl-			
	2-Acetylfuran			
	Pyrazine, 2,3-dimethyl-			
	Pyridine, 3,5-dimethyl-			
	2,5-Dimethyl-2-cyclopentenone			
	Benzaldehyde			
	Furfural, 5-methyl-			
	Ethanone, 1-phenyl-			
	Ethanone, 1-(3-methylphenyl)-			

Group 2	2(5H)-furanone			2-Acetylpyrrole
	2-Hydroxycyclopent-2-en-1-one			
	Pyridine, 3-ethenyl-			
	2(5H)-Furanone, 3-methyl-			
	Indene			
	Phenol, 2-methoxy-			
	1H-Indole			
	Nicotyrine			
	Norsolanadiona			
Group 3	Ethanol, 2-butoxy-			
	Phenol			
	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-			
	o-Cresol			
	p-Cresol			
	Cotinine			
Group 4	2-Isopropylfuran			
	Triacontane			
Group 5		2-Propanamine		

		2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one		
Group 6	Megastigmatrienone			
	5-Tetradecene			
	Neophytadiene			
Group 7	Myosmine			
	2,3'-Bipyridine			
Group 8	Phenol, 2-methoxy-4-(2-propenyl)-			
	Tocopherol			
Group 9			1,4-Dihydrophenantrhene	
			DBP	
Group 10	Pentadecane			
	Eicosane			
	Citric acid, tributyl ester			
Group 11	Octadecane			
	Tricosane			
	Heptacosane			
Uncorrelated	2-Pentanone, 4-hydroxy-4-methyl-	2-Ethyl tiophene	Butanoic acid, 3-methyl-	2(3H)-Furanone, 5-methyl-

	Styrene	Phenol, 4-ethyl-	Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl-	Nicotinamide
	Limonene	2-Furancarboxaldehyde, 5-(hydroxymethyl)-	1H-Indene, 2,3-dihydro-1,1,3-trimethyl-3-phenyl-	3-Ethyl-2-hydroxy-2-cyclopenten-1-one
	1H-Inden-1-one, 2,3-dihydro-	4-Vinyl-2-methoxy-phenol	N(b)-Formylnornicotine	p-Cresol 2 methoxy
	1H-Indole, 3-methyl-	Nicotine	2,4-Diphenyl-4-methyl-penten-1ene	
		N-Propyl nornicotine	8-Quinolinemethanol	

The results obtained from the PCA of the chemical analysis of the liquids retained in the filters and in the traps indicate that PC1 could be a good indicator of the overall yields, because the main part of the analyzed compounds are represented in such principal component and because it represents the greater part of the information of the variables.

Figure 13. Graphical representation of the two first principal components obtained in the PCA of the results from the analysis of the liquids retained in a) the traps and b) the filters.

Figure 13a)

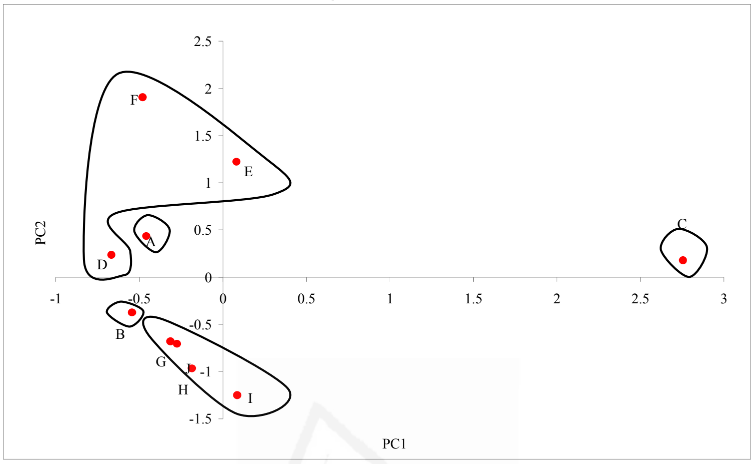


Figure 13b)

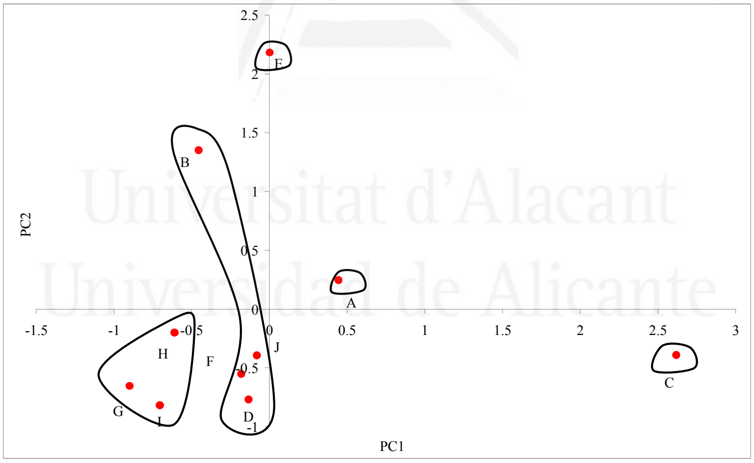


Figure 13a shows the graphical representation of the two first principal components obtained from the PCA analysis of the results of the liquids retained in the traps. As it can be seen, in good agreement with the results obtained in the analysis of the gaseous fraction, sample C is noticeably separated from the rest, due to its high value of PC1 (i.e., its relatively high yields of products). The groups provided by the cluster analysis have been marked in Figure 13a. As it can be seen, there appears a group with brands D, E and F with positive and relatively high values of PC2, another group with brands G, H, I and J, with negative and relatively high absolute values of PC2, and samples A and B appear as individual clusters, with intermediate values of PC2. All the brands, with the only exception of C, have negative or near zero values of PC1. The differences among brands A and B and the other groups lie in the positive and high values of PC4 of these brands, in front of the other samples, which show negative values of PC4 in all the cases. These results also agree, with the groups of brands obtained from the analysis of the gases, which reflected the existence of three groups. In fact, as has been above commented on, the "group" of sample C has been detected from both analysis, samples E and D showed similarities in the composition of the gases, and also in the composition of the liquids retained in traps and, finally, the rest of brands could not be differentiated from the chemical analysis of the gases, but the liquids retained in the traps permit us to observe some additional differences.

With respect to the filters (Figure 13b), the following groups of tobacco brands could been considered:
- brand C, with a positive and noticeably high value of PC1. In good agreement with the results obtained for the gases and for the liquids retained in traps, this is the brand yielding the highest amount of products.
- brands G, H and I, characterized by negative and relatively high absolute values of PC1, and negative values of PC2. These samples also appear within homogeneous groups when the chemical composition of gases and liquids retained in the traps was considered, and appear as the brands yielding the lowest concentrated products.
- brand A appears in an individual groups because has positive PC1 (but noticeably lower than brand C).
-brand E appears in an individual group because it has the highest positive value of PC2.
- the rest of brands (B, D, F and J) appear in another group, with intermediate negative values of PC1. B has positive PC2 and the other samples of this group have negative values of PC2.

3.4 Comparison with other studies on commercial cigarette brands

Comparisons must be done with care, taken into account the differences commonly reported when comparing tobacco smoke yields among different laboratories (Counts et al. 2004; Gregg et al. 2004). These differences have been found even for reference cigarettes smoked under the same normalized conditions, and they may account for different variables largely affecting the smoking process and sometimes underestimated, such as pressure drop and compacting of the tobacco in the cigarette, block of ventilation holes, collection method of smoke or even the lighten method, as have been thoroughly discussed by different authors (Borgerding and Klus, 2005; Baker 2006; Adam et al. 2009; Li et al. 2003). Moreover, there are no internationally recognized standard methods for the determination of other compounds different from CO, water, nicotine and tar. As it was explained in the experimental section, quantification has been done for CO, CO_2, 1,3-butadiene, HCN, isoprene, acrolein, propionaldehyde, crotonaldehyde, isobutiraldehyde, benzene, toluene and acetaldehyde in the vapor fraction and nicotine in the particulate matter, while the results for the rest of compounds have been calculated with the response factor of others and they have been reported just for comparison purposes among the studied brands. Moreover the results reported here are for a fixed number of puffs. Comparison for the particulate matter (nicotine) refers to that condensed in the trap, since is the only one reported by other works.

Table 10 contains the minimum and maximum values for some compounds reported by other researchers who studied international tobacco brands. Calafat et al. (2004) examined levels of nicotine, carbon monoxide and tar of 77 cigarette brands purchased in 35 countries which were divided in different regions according to the World Health Organization. According to these authors the European cigarette deliveries varied widely in the brands they studied, from 0.5 to 1.6 mg of nicotine/cigarette and 5.9 to 17.4 mg of CO/cigarette. Osamu-Endo et al. (2009) tested nicotine and tar for the ten top selling Japanese cigarettes with the ISO and the Health Canada Intense method. They found that the nicotine value under the ISO method varied from 0.19 to 1.11

mg/cigarette. Counts et al. (2005) tested forty-eight Philip Morris USA and Philip Morris International commercial filtered cigarettes with three smoking regimes (ISO, Canadian Intense and Massachusetts Department of Public Health). With the ISO method they reported variations of nicotine from 0.1 to 1.13 mg/cigarette and of carbon monoxide from 1.1 to 13.4 mg/cigarette in the different brands. In our work, for the ten top selling brands in Spain, the nicotine varies from 0.28 to 0.61 mg/cigarette, while carbon monoxide does from 5,1 to 11,1 mg/cigarette. Pieraccini et al. (2008) studied 13 top selling cigarette brands in Italy. They results were reported in μg/puff as shown in Table 10, where our values in the same units are also shown. The reported values in our work are within those obtained by other workers, and assuming the risk of comparisons, CO content would be in the medium to high level in Spanish cigarettes as compared to commercial cigarettes from other countries, while nicotine would be in the low to medium level. Another remarkable fact is that there are relatively low differences among the Spanish brands studied, despite, as the multivariate statistical analysis has pointed out, in general brand C differentiates from the rest by its higher yields, and samples G, H and I seem to show higher similarities (and lower yields).

Table 10. Lower and maximum values of different components of smoke reported in the literature for commercial cigarettes under the ISO method.

	Calafat 2004		Endo Osamu 2009		Counts 2005		Pieraccini 2008		This work	
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
Nicotine (mg/cigarette)	0.5	1.6	0.19	1.11	0.1	1.13			0.28	0.61
Nicotine (µg/puff)							24.12	98.22	35.31	76.65
CO (mg/cigarette)	5.9	17.4			1.1	13.4			5.1	11.1
Isoprene (µg/cigarette)					70	484			35	163.5
HCN (µg/cigarette)					3.4	194.4			5	9.4
1,3-Butadiene (µg/cigarette)					6.4	54.1			12.2	27.6
Acetaldehyde (µg/cigarette)					32	643			249	528
Acrolein (µg/cigarette)					2.4	61.9			7.8	20
Propionaldehyde (µg/cigarette)					3.3	60.4			7.5	15.6
Crotonaldehyde (µg/cigarette)					1	28.3			2	4.7
Butyraldehide (µg/cigarette)					2.7	47.5			3.1	5.9
Toluene (µg/cigarette)					8.3	69.9			12.5	113.3
Toluene (µg/puff)							0.88	5.14	1.56	14.13
Benzene (µg/cigarette)					6.1	44.6			45.7	119.5
Benzene (µg/puff)							0.73	3.06	5.71	14.94

Differently to other authors, Counts et al. (2005) determined the yield of an important range of smoke constituents and proposed predicting relationships between mainstream smoke, tar and the yield of individual constituents. The maximum and minimum yields for some compounds reported by these authors for the 48 Philip and Morris commercial cigarettes are also included in Table 10 together to our minimum and maximum values. All the compounds shown for the Spanish brands are within the values reported by Counts, and ranging from low to medium values, except for acetaldehyde, which varies from the medium to the high level.

4. CONCLUSIONS

The design features of the 10 commercial brands of cigarettes sold in Spain has been reported. In general, the higher the amount of tobacco initially contained in the cigarette the lower the tobacco consumption during smoking at a fix number of puffs. Other variables such as filter and paper length may play an important role during the smoking process as has been demonstrated.

Gaseous hydrocarbons and most of compounds of the vapor phase present similar relative proportions among brands, but there are some noticeable compounds such as crotonaldehyde, isoprene or toluene which depart from the “general trend” found for other compounds in the vapor fraction. The brands that present the lowest total yield for the compounds in the vapor fraction are not coincident with does showing the lowest yield in TPM-T.

In general, the amount of most of compounds with low retention time is higher in the filters than in the traps, while the very opposite is true for most of the heaviest compounds. Any case the importance of filters in retaining toxic compounds has been once again observed.

Multivariate statistical analysis has demonstrated its ability for aid and facilitates the interpretation of results in this kind of studies, where a noticeable amount of variables have to be simultaneously taken into account. In this work, the analysis of principal components and the cluster analysis have been satisfactorily used for reducing the dimensions of the problem, for the identification of the variables with higher variability and with higher influence in the variability among samples and for the definition of groups or clusters of similar samples.

The tobacco brands studied present similarities in the composition of the compounds studied but there are also some important differences. The relative yield of some known toxic compounds may vary substantially from brand to brand. Since the toxicity of any individual compound can be very different and the relative proportion of them is not always proportional to tar, CO or nicotine, more adequate parameters to determine tobacco toxicity must be established.

Comparatively and assuming the risks in doing so, Spanish top selling brands are in the low to medium range of the compounds quantified in this study except for nicotine (medium range), CO and acetaldehyde (medium to high range).

ACKNOWLEDGMENTS

Financial support for this investigation has been provided by the Spanish “Secretaría de Estado de Investigación” del Ministerio de Ciencia e Innovación (CTQ2008-01023 and MAT2011-24991).

REFERENCES

Adam, T., McAughey, J., McGrath, C., Mocker, C., Zimmermann, R., 2009. Simultaneous on-line size and chemical analysis of gas phase and particulate phase of cigarette mainstream smoke. Anal. Bioanal. Chem. 394, 1193-1203.

Baker Richard, R., 2006. Smoke generation inside a burning cigarette: Modifying combustion to develop cigarettes that may be less hazardous to health. Prog. Energy Comb. Sci. 32, 373-385.

Bi, X., Sheng G., Feng, Y., Fu, J., Xie, J., 2005. Gas- and particulate-phase specific tracer and toxic organic compounds in environmental tobacco smoke. Chemosphere, 61(10), 1512-1522.

Borgerding, M., Klus, H., 2005. Analysis of complex mixtures – Cigarette smoke. Exp. Toxicol. Pathol. 57, 43-73.

Calafat, A.M., Polzin, G.M., Saylor, J., Richter, P., Ashley, D.L., Watson, C.H., 2004. Determination of tar and carbon monoxide yields in the mainstream smoke of selected international cigarettes. Tob. Control. 13, 45-51.

Counts, M.E., Hsu, F.S., Laffoon, S.W., Dwyer, R.W., Cox, R.H., 2004. Mainstream smoke constituent yields and predicting relations from a worldwide market sample of cigarette brands: ISO smoking conditions. Regul. Toxicol. Pharmacol., 39, 111–134.

Counts, M.E., Morton M.J., Laffoon, S.W., Cox, R.H., Lipowicz, P.J., 2005. Smoke composition and predicting relationships for international commercial cigarettes smoked with three machine smoking conditions. Regul. Toxicol. Pharmacol. 41, 185-227.

Fowles, J., Dybing, E., 2003. Application of Toxicological Risk Assessment Principles to the Chemical Constituents of Cigarette Smoke. Tob. Control. 12(4), 424-430.

Gregg, E., Hill, C., Hollywood, M., Kearney, M., McAdam, K., McLaughlin, D., Purkis, S., Williams, M., 2004. The UK smoke constituents testing study. Summary of results and

Hoffmann, D., Hoffmann, I., 1997. The changing cigarette. J. Toxicol. Environ. Health. 50, 307-364.

Li, S., Olegario, R.M., Banyasz, J.L., Shafer, K.H., 2003. Gas chromatography–mass spectrometry analysis of polycyclic hydrocarbons in single puff of cigarette smoke. J. Anal. App. Pyrolysis. 66, 155–163.

Pieraccini, G., Furlanetto, S., Orlandini, S., Bartolucci, G., Giannini, I., Pinzauti, S., Moneti, G., 2008. Identification and determination of mainstream and sidestream smoke components in different brands and types of cigarettes by means of solid-phase microextraction–gas chromatography–mass spectrometry. J. Chromatogr. A. 1180 (1-2), 138-150.

Osamu Endo, Mariko Matsumoto, Yohei Inaba, Kazutoshu Sugita, Daisuke Nakajima, Sumio Goto, Hiromitsu Ogata, Gen Suzuki. 2009. Nicotine, tar and mutagenicity on mainstream smoke generated by machine smoking with international organization for standardization and health Canada intense regimens of major Japanese cigarette brands. J. Health Sci. 55(3), 421-427.

Rodgman, A., Green, R.G., 2003. Toxic chemicals in cigarette mainstream smoke-Hazard and hoopla. Beitr. Tabakforsch. Int. 20, 481-545.

Tso, T.C., 1990. Production, physiology and biochemistry of tobacco plant. IDEALS, Inc. Belstville.

CONCLUSIONES

6

Las principales conclusiones obtenidas en las diferentes publicaciones que constituyen esta Tesis Doctoral se muestran a continuación.

6.1. Publicación I: Catalytic effect of MCM-41 on the pyrolysis and combustion processes fo tobacco. Effect of the aluminium content.

1. Los catalizadores MCMC-41 sintetizados sin aluminio y con diferentes proporciones del mismo son capaces de reducir el rendimiento de la mayoría de los compuestos obtenidos en el proceso de fumado de tabaco.

2. De los materiales sintetizados en este trabajo, el que ofrece mejores resultados para reducir los productos generados durante el proceso de fumado es el que contiene una cantidad intermedia de aluminio (nominado 2AM que presenta una relación Si/Al de 50 y una acidez de 0.28 mmol/g).

3. La actividad catalítica de estos materiales en el proceso de fumado de tabaco dependen tanto de las propiedades texturales como de la acidez.

6.2. Publicación II: Evaluation of the efficiency of solvent extraction for template removal in the synthesis of MCM-41 type materials to be used as tobacco additives for smoke toxicity reduction

1. Los procesos de extracción con disolventes estudiados (HCl/EtOH y H_2O_2) son capaces de eliminar la mayor parte del tensioactivo del material MCM-41 y los catalizadores obtenidos presentan una actividad aceptable cuando son utilizados como aditivos en el tabaco para reducir la toxicidad asociada al humo generado.

2. Cuando la extracción del tensioactivo se realiza en varias etapas, la mayor eliminación tiene lugar en la primera etapa y decrece sucesivamente en posteriores etapas, lo que sugiere que el proceso de extracción en contracorriente sería el más eficiente. En cualquier caso para conseguir la eliminación completa del tensioactivo es necesaria una última etapa de calcinación.

3. La eliminación del tensioactivo llevada a cabo con HCl/Etanol produce cambios en la estructura del material durante la primera etapa de contacto, que son mayores cuanto más drásticas son las condiciones experimentales y que suponen la destrucción al menos parcial de la estabilidad hidrotérmica del material.

4. La extracción con H_2O_2 no genera cambios en la estructura del catalizador, aunque la eliminación del tensioactivo es algo menor. La acidez y las propiedades finales del catalizador cuando se emplea H_2O_2 como disolvente son más parecidas a las de la muestra calcinada por el proceso habitual.

5. La reducción de la cantidad de tensioactivo contenido en el material sintetizado MCM-41 mediante los procesos de extracción analizados permitiría su recuperación y reutilización y disminuiría la energía requerida en la etapa de calcinación. Un estudio económico global permitiría decidir la elección del proceso de eliminación del tensioactivo más conveniente.

6.3. Publicación III: Template removal in MCM-41 type materials by solvent extraction. Influence of the treatment on the textural properties of the material and the effect on its behaviour as catalyst for reducing tobacco smoking toxicity

1. Las propiedades texturales de los catalizadores preparados mediante eliminación del tensioactivo con disolventes dependen del disolvente utilizado, de la relación disolvente/sólido, del número de etapas de extracción y del proceso utilizado.

2. A través del análisis de las isotermas de adsorción de nitrógeno de los catalizadores sintetizados se ha podido comprobar el efecto estabilizador del aluminio sobre la estructura del catalizador MCM-41.

3. La caracterización fisicoquímica de los catalizadores se ha llevado a cabo mediante TGA, XRF, XRD y ^{27}AlNMR. Se confirma que el tratamiento con mezclas de HCl/etanol causan daños estructurales en el catalizador, que dependen de las condiciones experimentales, mientras que es tratamiento con H_2O_2 resulta más adecuado para la eliminación del tensioactivo.

4. El análisis de la corriente principal del humo del tabaco muestra que todos los catalizadores MCM-41 estudiados mantienen un buen comportamiento como aditivos del tabaco, y que el catalizador que presenta las mejores propiedades texturales y la mejor estabilidad hidrotérmica, es también el que tiene mayor actividad.

6.4. Publicación IV: Reduction of tobacco smoke components yields by zeolites and synthetysed Al-MCM-41.

1. Las zeolitas HUSY, Hβ y HZSM-5 son capaces de reducir, al menos en cierta medida, el rendimiento de algunos de los compuestos tóxicos y cancerígenos presentes en la corriente principal del humo del tabaco.

2. El catalizador Al-MCM-41 es el que presenta un mejor comportamiento de todos los estudiados. En las condiciones empleadas en los experimentos de fumado, es capaz de reducir el rendimiento de CO en un 23% y de nicotina y materia total particulada en un 41%. Su capacidad para reducir el rendimiento de derivados nitrogenados es especialmente notable.

3. Los compuestos condensados en filtros y trampas presentan un comportamiento llamativo, de modo que los compuestos de menor peso molecular y más polares son preferentemente retenidos en el filtro, mientras que los de mayor peso molecular se distribuyen más uniformemente entre el filtro y las trampas del humo.

6.5. Publicación V: Comparative study of the main characteristics and composition of the mainstream smoke of ten cigarettes brands sold in Spain

1. Cuanto mayor es la cantidad de tabaco inicial contenida en el cigarrillo menor es la cantidad de tabaco consumida por calada. La longitud del filtro y del papel también son variables importantes en el proceso de fumado.

2. En general todos los hidrocarburos y la mayoría de los compuestos presentes en la fase vapor presentan proporciones similares entre todas las marcas. Algunos compuestos como crotonaldehído, isopreno o tolueno tienen un comportamiento que se aparta de la tendencia general encontrada para otros compuestos presentes en la fase vapor.

3. La composición del humo en todas las marcas estudiadas es muy similar, pero existen también algunas diferencias importantes. La cantidad relativa de algunos compuestos tóxicos presentes en el humo varía entre las diferentes marcas y no es siempre proporcional a la cantidad de alquitranes, CO y nicotina, de modo que se pone de manifiesto la necesidad de establecer otros parámetros para determinar la toxicidad del tabaco. Las marcas de cigarrillos que presentan bajos rendimientos para los compuestos presentes en la fase vapor no coinciden con aquellas que muestran bajos rendimientos en los líquidos condensados en las trampas de humo.

4. Se ha observado la importancia del filtro para retener compuestos tóxicos. Por otra parte, la mayoría de los compuestos con bajos tiempos de retención se encuentran en mayor proporción en filtros que en trampas, mientras que lo opuesto pasa para los compuestos más pesados.

5. Al comparar los resultados obtenidos con los encontrados en la bibliografía, y teniendo en cuenta los riesgos asociados a esta comparación, se ha observado que las marcas de tabaco analizadas se encuentran en el rango medio-bajo de los rendimientos obtenidos para los compuestos estudiados, a excepción de la nicotina, CO y acetaldehído que presentan rendimientos en el rango medio-alto.

6. Se ha demostrado la utilidad del análisis multivariante para facilitar la interpretación de los resultados obtenidos en estudios de este tipo, donde se debe considerar un gran número de variables simultáneamente. En este trabajo, el análisis de las componentes principales y de los clusters se ha empleado satisfactoriamente

para reducir las dimensiones del problema, para la identificación de las variables con mayor variabilidad entre las muestras, y para la definición de grupos de clusters de muestras similares.

7

BIBLIOGRAFÍA

Aguado, J., Serrano D.P. y Escola, J.M. "A sol-gel approach for the room temperature synthesis of Al-containing micelle-templated silica", Microporous and Mesoporous Materials, 34, (2000), 43-54.

Argauer, R.J. y Landolt, G. R. Patente US 3,702,886 (1972), Mobil Oil.

Baker R.R. "Smoke generation inside a burning cigarette: Modifying combustion to develop cigarettes that may be less hazardous to health", Progress in Energy and Combustion Science, 32 (2006) 373-385.

Baker R.R. y L. J. Bishop. "The pyrolysis of non-volatile tobacco ingredients using a system that simulates cigarette combustion conditions", Journal of Analytical and Applied Pyrolysis, 74 (2005), 145-170.

Baker R.R., Pereira da Silva J.R. y Smith G. "The effect of tobacco ingredients on smoke chemistry. Part I: Flavourings and additives", Food and Chemical Toxicology, 42S (2004), S3–S37.

Barrett E.P., Joyner L.G. y Halenda P.P. "The determination of pore volume and area distributions in porous substances. I. computations from nitrogen isotherms", Journal of the American Chemical Society, 73 (1951), 373–380.

Beck J.S., Journal of the American Chemical Society, 114, (1992), 10834.

BOE-A-2005-21436. LEY 28/2005, de 26 de diciembre, de medidas sanitarias frente al tabaquismo y reguladora de la venta, el suministro, el consumo y la publicidad de los productos del tabaco.

BOE-A-2010-20138. Ley 42/2010, de 30 de diciembre, por la que se modifica la Ley 28/2005, de 26 de diciembre, de medidas sanitarias frente al tabaquismo y reguladora de la venta, el suministro, el consumo y la publicidad de los productos del tabaco.

Borgerding M. F.,. Bodnar J. A., Chung H. L., Mangan P. P., Morrison C. C., Risner C. H., Rogers J. C., Simmons D. F., Uhrig M. S., Wendelboe F. N., Wingate D. E. Y Winkler L. S. "Chemical and biological studies of a new cigarette that primarily heats tobacco.: Part 1. Chemical composition of mainstream smoke"**,** Food and Chemical Toxicology , 36 (1998), 169-182.

Borgerding M. y Klus H. “Analysis of complex mixtures-cigarette smoke”, Experimental and Toxicologic Pathology, 57(2005), 43-73.

Branton, P., Lu, A. y Schüth, F. “The Effect of Carbon Pore Structure on the Adsorption of Cigarette Smoke Vapour Phase Compounds”. Carbon., 47, (2009) 1005-1011.

Breck, D.W. Zeolite Molecular Sieves, (1974), 771.

Brunauer S., Emmett P. H. y Teller E. “Adsorption of gases in multimolecular layers”, Journal of the American Chemical Society, 60 (1938), 309-319.

Calafat A.M., Polzin G.M., Saylor J., Richter P., Ashley D.L. y Watson C.H. “Determination of tar, nicotine, and carbon monoxide yields in the mainstream smoke of selected international cigarettes”, Tobacco Control, 13 (2004), 45-51.

Chen L.Y., Ping Z., Chuah G.K., Jaenicke S. y Simon G. “A comparison of post-synthesis alumination and sol-gel synthesis of MCM-41 with high framework aluminun content”, Microporous and Mesoporous Materials, 27 (1999), 231-242.

Chen Z., Zhang L., Tang Y. y Jia Z. “Adsorption of nicotine and tar from the mainstream smoke of cigarettes by oxidized carbon nanotubes”. Applied Surface Science, 252 (2006), 2933-2937.

Connolly G.N., Wayne G.D., Lymperis D. y Doherty M.C. “How cigarette additives are used to mask environmental tobacco smoke”, Tobacco Control, 9 (2000), 283–291.

Corma, C. A.; Navarro, V. M. T. y Pérez, P. J. “Material de estructura tipo zeolita de poros ultragrandes con un red constituida por óxidos de silicio y titanio; su síntesis y utilización para la oxidación selectiva de productos orgánicos”. Patente 2 092 428 A1 (1996).

Counts M.E., Morton M.J., Laffoon S.W., Cox R.H. y Lipowicz P.J. “Smoke composition and predicting relationships for international commercial cigarettes smoked with three machine-smoking conditions”, Regulatory Toxicology and Pharmacology, 41 (2005), 185-227.

Cvetkovic, N, Adnadjevich, B. Y Nikolic, M. "Catalytic reduction of NO and NOx content in tobacco smoke", Beitraege zur Tabkforschubg International 20 (1) (2002), 43-48.

Davison Chemical Division of W. R. Grace, Inc: U.S. Pat. No. 3,449,070, (1969).

Ding Y.S., Zhang L., Jain R.B., Jain N., Wang R.Y., Ashley D.L. y Watson C.H. "Levels of Tobacco-Specific Nitrosamines and Polycyclic Aromatic Hydrocarbons in Mainstream Smokefrom Different Tobacco Varieties", Cancer Epidemiology, Biomarkers and Prevention, 17 (2008) 3366-3371.

DIRECTIVA 2001/37/CE DEL PARLAMENTO EUROPEO Y DEL CONSEJO de 5 de junio de 2001 relativa a la aproximación de las disposiciones legales, reglamentarias y administrativas de los Estados miembros en materia de fabricación, presentación y venta de los productos del tabaco. DO L 194, 18.7.2001.

Fowles J. y Dybing E. "Application of toxicological risk assessment principles to the chemical constituents of cigarette smoke", Tobacco Control, 12 (2003), 424–430.

Gao L., Cao Y., Zhou S.L., Zhuang T.T., Wang Y. y Zhu J.H. "Eliminating carcinogenic pollutants in environment: Reducing the tobacco specific nitrosamines level of smoke by zeolite-like calcosilicate", Journal of Hazardous Materials, 169 (2009), 1034-1039.

Gaydhankar T.R., Samuel V., Jha R.K., Kumar R. y Joshi P.N. " Room temperature synthesis of Si-MCM41 using polymeric version of ethyl silicate as a source of silica", Materials Research Bulletin, 42 (2007), 1473-1484.

Green C. R., Schumacher J.N. y Rodgman A. "The expansion of tobacco and its effect on cigarette mainstream smoke properties", Beiträge zur Tabakforschung International. 22 (5) (2007), 317-345.

Hammond D., Fong G.T., Cummings K.M., O'Connor R.J., Giovino G.A. y McNeill A. "Cigarette Yields and Human Exposure: A Comparison of Alternative Testing Regimens", Cancer Epidemiology, Biomarkers and Prevention, 15 (2006), 1495-1501.

Hoffmann D. y Hoffman I. "The changing cigarette, 1950-1995", Journal of Toxicology and Environmental Health , 50(4) (1997) 307-364.

Hoffmann D., Djordjeveic M.V. y Hoffmann I. "The changing cigarette", Preventive Medicine, 26 (1997), 427-434.

Hua Z., Shi J., Wang L. y Zhang W. "Preparation of mesoporous silica films on a glass side: surfactant template removal by solvent extraction", Journal of Non-Crystalline Solids, 292 (2001), 177-183.

Internacional Agency for Research on cancer (IARC).

Jianhua, Z., Ying, W. y Yilun, W. "Mesopore solid alkali, mesopore functional material, its preparation method and application", CN 1460641, 2003.

Kresge, C. T., Leonowicz, M. E., Roth, W. J., Beck, J.S. y Vartuli, J.C. "Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism". Nature, 359, (1992), 710.

Li, C. y Parry, A. "Potassium organic salts as burn additives in cigarettes", Beitraege zur Tabkforschubg International 20 (5) (2003), 341-340.

Li, P. y Hajaligol, M. "Oxidant/catalyst nanoparticles to reduce carbon monoxide in the mainstream smoke of a cigarette", US Patent Application 20030075193, Kind Code A1, 2003.

Li, P. y Hajaligol, M. "Oxidant/catalyst nanoparticles to reduce tobacco smoke constituents such as carbon monoxide", US Patent Application 2003/013118759, Kind Code A1, 2003.

Li, P., Rasouli, F. y Hajaligol, M. "Application of nanoparticle iron oxide in cigarette for simultaneous CO and NO removal in the mainstream smoke", Beitraege zur Tabkforschubg International 21 (1) (2004), 1-8.

Li, P., Rasouli, F. y Hajaligol, M. "Catalysts to reduce carbon monoxide and nitric oxide from the mainstream smoke of cigarette", PCT WO 2004/110184 A2, 2004.

Li, P., Rasouli, F. y Hajaligol, M. "Manganese oxide mixtures in nanoparticle form to lower the amount of carbon monoxide and/or nitric oxide in the mainstream smoke of a cigarette", US Patent Application 6,782,892, 2004.

Marcilla, A., Gómez-Siurana, A. y Berenguer, D. "Study of the influence of the characteristics of different acid solids in the catalytic pyrolysis of different polymers". Applied Catalysis A: General. 301 (2) (2006). 222–231.

Meier M. W., Jost W. y Scanlan, F. "Smoker's article", EP 0 740 907 A1, 1995.

Meier W.M. y Siegmann K. "Significant reduction of carcinogenic compounds in tobacco smoke by the use of zeolite catalysts", Microporous and Mesoporous Materials, 33 (1999), 207-310.

Meier, M.W. "Process for treating tobacco with catalitically active material for reducing toxic componentes in tobacco smoke", European Patent Application EP 1 234 511 A1, 2001.

Radojicic, V., Nikolic, M., Adnadevic, B. y Jovanovic, A. "Selective reduction of PAH content in cigarette tobacco smoke by catalytic cracking process", Physical Chemistry, 2004.

Rasouli, F., Li, P., Zhang, W.J. y Gedevanishvili, S. "Use of oxyhydroxide compounds in cigarette paper for reducing carbon monoxide in the mainstream smoke of a cigarette", PCT WO 2005/039326 A2, 2005.

Rongved P. "Catalytic cigarette smoke cleaning devise and process", US005671758A, 1997.

Rosen, W.E. "Method of treating tobacco", US patent 3,840,026, 1974.

Rustemeier K., Stabbert R., Haussmann H.J., Roemer E. y Carmines E.L. "Evaluation of the potential effects of ingredients added to cigarettes. Part 2: chemical composition of mainstream smoke", Food and Chemical Toxicology, 40 (2002) 93-104.

Seeofer, F. y Kausch, E. “Removal of nitric oxide and carbon monoxide from tobacco smoke”, US patent 4,182,348, 1980.

Shahryar R. R., Firooz Rasouli M. y Hajaligol R.M. “Tobacco cut filler including metal oxide supported particles”, US 2005/0126583 A1, 2005.

Snarskis M. J. “Compendio de Agronomía Tropical”, Volumen II. Publicado por el Instituto Interamericano de Cooperación para la Agricultura de San José de Costa Rica, 1989.

Stanbridge K.A. “Incorporating additives into cigarette rods”, UK Patent Application GB 2229079 A, 1990.

Suoza M.J.B., Silva A.O.S., Joana M.F., Aquino B., Fernandes Jr. V.J. y Araújo A.S. “Kinetic study of template removal of MCM-41 nanostructured material”, Journal of Thermal Analysis and Calorimetry, 75 (2004), 693-698.

Treacy M.M.J. y Newsam J.M. “Two new three-dimensional twelve-ring zeolite frameworks of which zeolite beta is a disordered intergrowth”. Nature, 332, (1988), 249-251.

Varmuza K. y Filzmoser P. “Introduction to multivariable statistical análisis in chemometrics”. Publicado por CRC Press. 2009

Wadlinger, G.T. *US Patent*, **3**, 308 069, (1967).

Xiao L., Li J., Jin H. y Xu R. “Removal of organic templates from mesoporous SBA-15 at room temperature using UV/dilute H_2O_2”, Microporous and Mesoporous Materials, 96 (2006), 413-418.

Xu Y., Zhu J.H., Ma L.L., Ji A., Wei Y.L. y Shang X.Y. “Removing nitrosamines from mainstream smoke of cigarettes by zeolites”, Microporous and Mesoporous Materials, 60 (2003), 125-138.

Yong G., Jin Z., Tong H., Yan X., Li G. y Liu S. “Selective reduction of bulky polycyclic aromatic hydrocarbons from mainstream smoke of cigarettes by mesoporous materials”. Microporous and Mesoporous materials, 91 (2006), 238-243.

http://www.agronet.com

http://www.cmtabacos.es/wwwcmt/paginas/ES/mercadoEstadisticas.tmpl

http://www.lapshin.org/cultivar/N36/Pogany/Nicotiana-tabacum.jpg

http://www.personal.utulsa.edu/~geoffrey-price/zeolite/

http://www.tabaqueria-martin.com/images/maya.jpg

http://yesmoke.eu/brand/selected-tobaccos/expanded-tobacco/

ÍNDICE DE TABLAS

ÍNDICE DE FIGURAS