DRYING TECHNOLOGY, 17(7&8), 1603–1612 (1999)

A NEW TREATMENT FOR A FILTER TIP TO DECREASE FLAVOR AND WATER MIGRATONS DURING STORAGE OF A TOBACCO PRODUCT

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Key Words: adsorption; flavor; migration; tobacco; water

ABSTRACT

Volatile flavors are playing an increasingly important role in the quality control of cigarettes to enhance their smoke taste and odor. The cigarettes which contain a filter tip having an activated carbon for reducing the irritant and physiological effects of the smoke are popular in the Japanese market. We found that the flavors migrate from the tobacco column to the filter tip, while spontaneously water moves backwards, depending on the adsorption equilibrium of cigarettes and its packaging materials during storage. A new "Ethanol Adsorption Treatment" for a filter tip has been presented to decrease this undesirable flavor and water migrations. The treatment is performed by applying the binary vapor of water and ethanol to the filter tip before connecting it with a tobacco column. Then during storage, the presence of ethanol vapor decreased the flavor migration mainly by decreasing the amounts of flavors adsorbed on the activated carbon within the filter tip. The treatment was confirmed to be effective for decreasing both flavor and water migrations simultaneously.

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INTRODUCTION

Various volatile flavors are being applied to food and tobacco products for the enhancement of taste and smoke odor. In the food industry, it is widely recognized that significant loss of flavor occurs in stored products when polymer films have been used as outer packaging materials. In our previous study (Miyauchi et al., 1995a, 1995b), it was found that water migrates from the filter tip to the tobacco column, while flavors transfer backwards, depending on the selectivity as well as the mechanism of adsorption. Especially, the flavor migration to the charcoal filter which contains the activated carbon is greater than that to the plain filter without it.

The purpose of the "Ethanol Adsorption Treatment" (EAT) is to add some substance to the charcoal filter for controlling the adsorption equilibria between the activated carbon and the volatile compounds. Ethanol was selected and examined as an adsorbed agent for the EAT because it has been used as a solvent in the flavoring process. The EAT has two beneficial characteristics; i.e., (a) the control of the water content within the filter tip and (b) the depression of flavor migration due to the increase in ethanol vapor in the spaces between the cigarettes.

The objectives of this study were to (a) measure the adsorption equilibria of binary water-flavor and ternary water-flavor-ethanol vapors for typical materials used for the tobacco product and (b) evaluate the effect of the EAT on decreasing the water and flavor migration during storage, based on these adsorption equilibria.

EXPERIMENTAL

Materials

Tobacco, paper, filter and activated carbon were used as typical materials contained in a box of the tobacco product. The filter was formed by the cellulose acetate fiber. From measurements of nitrogen adsorption, the specific micropore volume or surface area for activated carbon in the filter were determined to be 0.22 cm^3/g or 529m^2/g, respectively.

Adsorption measurements

As shown in Figure 1, the experimental apparatus was a flow-type multi-component adsorption system used in a previous study (Miyauchi et al., 1995a).

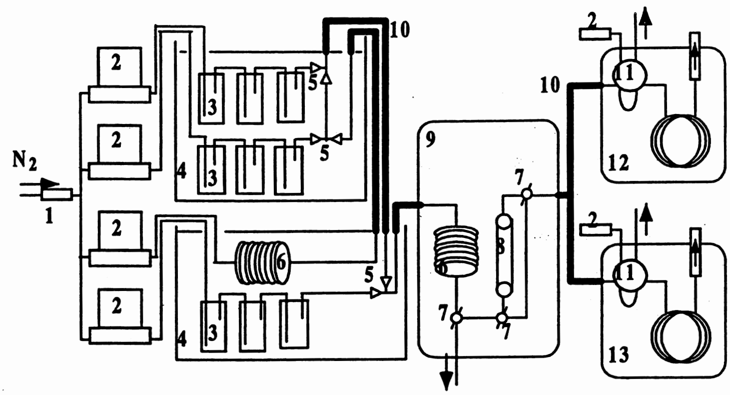

Figure 1 Flow-type multi-component adsorption system

The main functions of the system were the control of gas flow rates, water-vapor supplying, operation of adsorption, and analysis of vapor concentrations. Because the removal of the intrinsic volatile compounds and any adsorbed vapor was required to get reproducible values of adsorption equilibria, each material was pre-treated by vacuum drying, and was held in equilibrium with a constant vapor pressure of pure water, p_w = 2.5kPa, corresponding to p_w/p_w^o = 0.6. During the measurements, the material was kept in the adsorption cell until it reached equilibrium with the desired mixtures of flavor and water vapor at a constant temperature of 303 K. The adsorbed flavor and water were desorbed by vacuum heating and their amount was analyzed using a thermal conductivity detector (FID) or a flame ionization detector (TCD) for the gas chromatographs, respectively, in the same manner mentioned in a previous study (Miyauchi et al., 1995b).

Ethanol Adsorption Treatment (EAT)

The adsorption of binary water-ethanol vapors on the charcoal filter tip was carried out until their equilibria were attained. The binary adsorption of a temperature at 303 K was carried out under the vapor pressure conditions of 2.1 kPa for water and 0.1~2.1 kPa for ethanol to prevent condensation.

Storage tests

Ethyl acetate was used as model flavors and applied to the tobacco column as ethanolic solutions. The loading amount was 2.5 mg for ethyl acetate and 8 mg for ethanol. The cigarettes were prepared by connecting the flavored tobacco column to the filter tip with tipping paper after the EAT. They were stored in a sealed glass jar at a constant temperature of 295 K for over 2 weeks until an equilibrium was attained within the jar (Samejima, 1983). The amounts of compounds among each material were measured by means of their desorptions as mentioned above.

RESULTS AND DISCUSSION

Binary adsorption equilibria

For tobaccos, papers and filter, the amount of adsorbed water was nearly constant, except that some of the water adsorbed on the filter was slightly desorbed as the ethyl acetate was adsorbed, while the amount of adsorbed flavors was expressed as follows;

$$q_i = k \times p_i \tag{1}$$

For activated carbon, the amount of adsorbed water was nearly zero. These results were explained in terms of substitution for some adsorbed water as well as adsorption of flavor into the micropores. Therefore, if the binary adsorption treatment of water and ethanol was selected as the EAT, the amount of water was controlled at its desirable level, corresponding to the water content within the practical filter tip after its connection. These results lead to the fundamental concept of the EAT, and the application of binary adsorption of water and ethanol vapor was found to be desirable for the EAT. The following Dubinin-Astakhov (DA) equation was known to correlate with the adsorption data of organic solvents on activated carbon (Dubinin, 1960,1967) i.e.;

$$w_i = w_i^o \exp\left(-\left(\frac{A}{E}\right)^n\right) \tag{2}$$

$$w_i = \frac{q_i \times M}{\rho} \tag{3}$$

where w_i^o is the micropore volume and A is the adsorption potential $[=RT\ln(p_i^o/p_i)]$. The recommended value of n is 2 for the organic solvent adsorption on activated carbon. The values of k, w_i^o and E of the flavor presented for the binary adsorption equilibria of the water and flavor are listed in Table 1.

Ternary adsorption equilibria

From the measurements of the ternary adsorption equilibria of the water-ethanol-ethyl acetate system, it was found that ethanol exerted a great influence on the adsorption of ethyl acetate onto activated carbons, demonstrating a negligibly small effect on the tobacco as well as the filters. The ternary adsorption equilibria of ethyl acetate for the activated carbon are shown in Figure 2. As shown in the figure, the value of q_f decreased by both decreasing the vapor pressure of ethyl acetate (p_f) and increasing that of ethanol (p_e). Here, Lewis et al. (1950) presented the following equation to correlate the quantities of a hydrocarbon gas mixture adsorbed on silica gel and activated carbon;

$$\sum\left(\frac{q_i}{q_i^*}\right)=1 \tag{4}$$

where q_i* is the adsorbed amount of the pure component corresponding to the total pressure ($\sum p_i$). This correlation was valid for our experimental concentration range.

Evaluation of the EAT

The ratio of flavor distribution within the tobacco column (D_t) is defined by the following technical term.

$$D_t=\frac{W_f^t}{W_f^t+W_f^{fil}} \tag{5}$$

where W_f^t and W_f^{fil} are the amounts of flavor within the tobacco column and the filter tip, respectively. The ratio (D_t/D_{to}) was represented in Figure 3 as a function of the total amount of ethanol (W_e^T) which was the sum of the ethanol amounts added in the flavoring and the EAT process.

Further, the ratio of flavor distribution (D_t/D_{to}) was estimated based on the following assumptions and using the adsorption equilibria obtained above and Equation (4). The assumptions are as follows; (a) the effect of adsorbed water on the adsorption of ethyl acetate for activated carbon was negligible (Miyauchi et al., 1995b), (b) the distribution of ethanol could be evaluated by the binary adsorption equilibria of ethanol and water vapor, and (c) ethanol exerts no influence on the

Table 1. The constants of equations (1) and (2) for adsorption equilibria of ethanol and ethyl acetate

Material	Ethanol		Ethyl acetate	
	k [mol/(kg·kPa)]		k [mol/(kg·kPa)]	
Tobacco column				
Bright yellow tobacco	0.20[a]		0.022	
Burley tobacco	0.13[a]		0.022	
Cigarette paper	0.04		0.011	
Filter tip				
Acetate filter	0.51		0.285	
Tipping paper	0.05		0.010	
Wrapping paper	0.04		0.009	
Package				
Hard pack	0.05		0.012	
Aluminum foil	0.03		0.009	
	w^o [cm^3/g]	E [kJ/mol]	w^o [cm^3/g]	E [kJ/mol]
Activated carbon	0.22	11.5	0.26	12.4
(pure ethanol system)	0.25	12.7		

[a]Nakanishi & Kobari, 1989

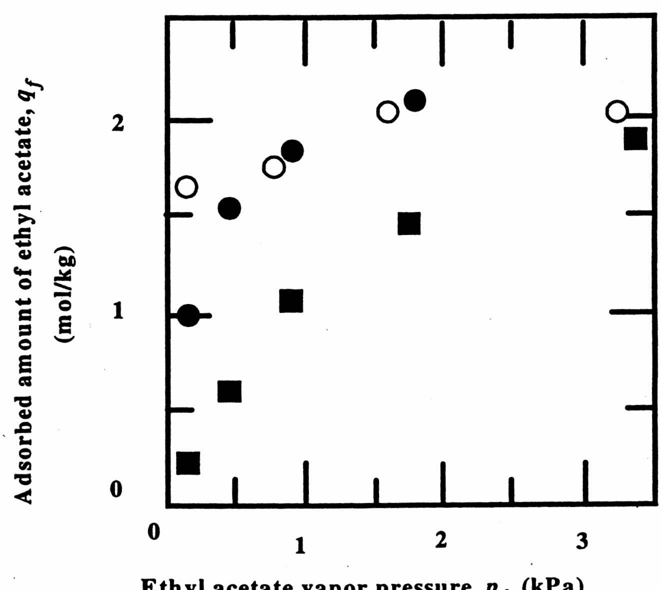

Figure 2 Adsorbed amounts of ethyl acetate from water-ethanol ethyl acetate mixtures from coconut activated carbon in filter

adsorption of ethyl acetate on tobacco and the filter as mentioned above. Thus the calculation proceeded as follows;

(1) According to assumption (b), q_e for each material at the specific p_e was calculated utilizing the binary adsorption equilibria of water and ethanol vapor, and the values of W_e^T were given by the sum of q_e ($W_e^T = \sum q_e$). The values of p_e and q_e among each material were then obtained relative to the various W_e^T.

(2) The value of D_t where p_w and p_e were specified was estimated as follows. The total vapor pressure ($\sum p_i = p_w + p_e + p_f$) was calculated by assuming the p_f of ethyl acetate. The quantities of q_i^* for the activated carbon corresponding to the total vapor pressure were obtained by DA equations for pure water, ethanol and ethyl acetate. However, the DA equation for ethyl acetate obtained from the binary adsorption equilibria was used according to assumption (a). Because the value of (q_w/q_w^*) was assessed to be 0.1 from the ternary adsorption equilibria, q_f of ethyl acetate for the activated carbon was then calculated using Equation (5). Ignoring the ethanol vapor according to assumption (c), the q_f of ethyl acetate for the tobacco, papers and filter was given from the p_f of ethyl acetate by utilizing the binary adsorption equilibria of water and ethyl acetate vapor (Miyauchi et al., 1995b). W_f^T was then estimated from the sum of q_f of ethyl acetate for the tobacco, papers, filter and activated carbon. The assumption of p_f of ethyl acetate was repeated until W_f^T was equal to the initial values (2.5 mg). By satisfying this limitation, the value of D_t at the specific p_e was obtained by Equation (5).

(3) This procedure (2) was carried out within the whole range of our experimental ethanol vapor pressure.

The values of (D_t/D_{t0}) are shown as a solid curve in Figure 3. As shown in Figure 3, the ratio (D_t/D_{t0}) increased with an increasing amount of ethanol added to the filter tip, indicating the decreased flavor migration by the EAT. The calculated values show good agreement with the experimental ones; therefore, the validity of the assumptions was certified. These results lead to the conclusion that the depression of flavor migration in the activated carbon was caused by increasing the ethanol vapor pressure.

Ethanol migration

In Figure 4, the amounts of ethanol within the tobacco column (W_e^t) as well as the filter tip (W_e^{fil}) for the cigarettes after their storage tests are plotted against the total amount of ethanol (W_e^T). In the calculation, the amount of ethanol for each material was determined against p_e, using the binary adsorption equilibria

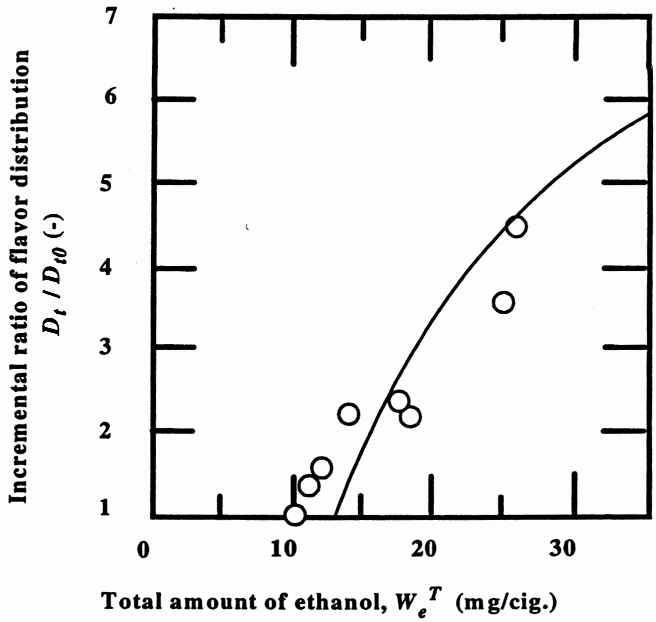

Figure 3 Effect of total amount of ethanol on ratio of flavor distribution

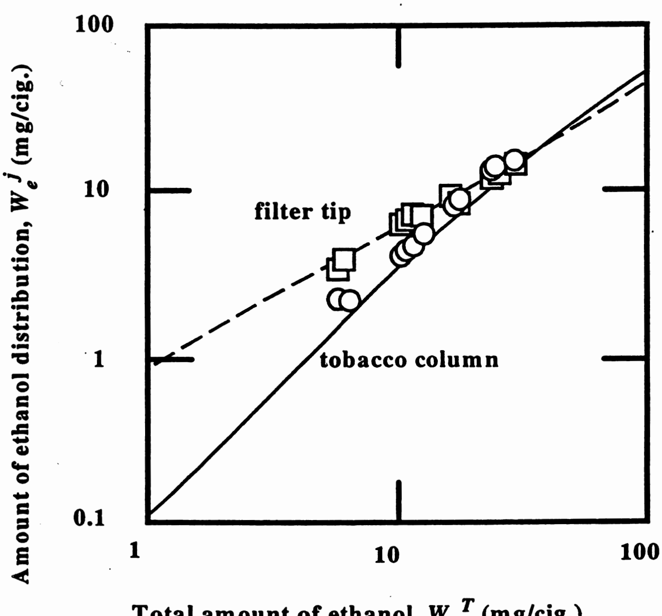

Figure 4 Ethanol distribution between tobacco column and filter tip as a function of total amount of ethanol

obtained, and these values were then grouped and summed to estimate the amounts of ethanol contained in the tobacco columns (W_e^t), the filter tips (W_e^{fil}) and the whole products or cigarettes (W_e^T). The calculated values of W_e^t or W_e^{fil} were plotted against W_e^T as a solid or broken curve, respectively. Because no marked differences were found between the experimental and calculated values, the equilibrium distribution of ethanol was recognized to be capable of being evaluated by the binary adsorption equilibria of water and ethanol. The calculation of flavor distribution indicated that p_f ranged in the lower level of one-tenth that of p_e; therefore, the ethanol distribution was almost independent of the flavor vapor. Therefore, this condition between p_f and p_e in the spaces between the cigarettes led to the effective depression of flavor migration.

NOTATION

A	free energy of adsorption	J/mol
D_t	ratio of flavor distribution amount	-
D_{t0}	ratio of flavor distribution amount when ethanol does not exist in products	-
E	characteristic free energy of adsorption	J/mol
k	constant in Equation (1)	mol/(kg·kPa)
M	molecular weight	kg/mol
n	constant in Equation (2)	-
p	vapor pressure	Pa
p^o	saturated vapor pressure	Pa
q	amount of adsorbed component	mol/kg
q^*	amount of adsorbed component, as in pure isotherm	mol/kg
R	gas constant	J/(K·mol)
T	temperature	K
W	amount	mg/cig.
w	volume of adsorbed component	m^3/kg
w_e^o	constant in Equation (2) (=micropore volume)	m^3/kg
ρ	density	kg/m^3
Subscripts		
e	ethanol	
f	ethyl acetate	

i	species in binary or ternary compounds
w	water
Superscripts	
fil	filter tip
i	species in binary or ternary component system
j	part of cigarette (tobacco column or filter tip)
T	total (=the sum of tobacco column and filter tip)
t	tobacco column

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