Chemistry of Cigarette Burning Processes*

by

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SUMMARY

Cigarette-burning and the smoke-formation processes and smoke composition are important topics for understanding cigarette performance. This paper proposes the molecular formulas representing the active components of bright, burley, and Oriental tobaccos and a basic chemistry model of the cigarette burning processes. Previous knowledge of the cigarette burning processes and smoke formation helped to establish parameters in deriving the basic chemistry equations. The proposed chemistry provides a brief view of the mechanisms of the cigarette burning during puffing and interpuff smoldering, and can be used to interpret and predict the smoke composition for cigarettes made from bright, burley, and Oriental tobaccos. Based on the proposed chemistry, the effect of ventilation on smoke component deliveries is discussed and the reaction heat of the puffing process is estimated. [Beitr. Tabakforsch. Int. 21 (2004) 105–110]

ZUSAMMENFASSUNG


RESUME


INTRODUCTION

Cigarette-smoke formation and smoke composition are major characteristics of cigarette performance. Fundamental research on the mechanisms of cigarette burning and smoke formation has been performed by a number of
investigators over several decades (1–15). The research has been targeted to the following basic questions: What affects cigarette smoke formation and composition? How much air participates in the reaction? What is the contribution of each cigarette component in the combustion process? What is the mass balance when a cigarette is smoldering or being puffed? BOYD et al. (3) studied the dependence of the gas-phase composition of smoke on the combustion temperature of tobacco products. JOHNSON et al. (6) studied the distributions of some components in tobacco smoke including ammonia, carbon monoxide, carbon dioxide, carbonyls, and hydrocarbons. They used the hydrocarbon information to predict combustion temperatures. JENKINS et al. (11) used C14 to study the contribution of carbon to each smoke phase from ingredients in the 1R1 Kentucky reference cigarette. The smoke distribution of radioactivity from each of the labeled cigarettes was measured and multiplied by the actual amount of carbon consumed during burning to obtain the carbon distribution in smoke phases. YAMAMOTO et al. (15) studied the effect of chemical constituents on the formation rate of carbon monoxide in bright tobacco. BAKER et al. (16), BROWN et al. (17), and NORMAN (18) studied ventilation effects on the smoke composition. These efforts significantly improved the understanding of cigarette burning processes and smoke formation. However, a more comprehensive understanding of the chemistry of cigarette burning processes and smoke formation is necessary to extend these research achievements for predicting the chemical composition of cigarette smoke.

This paper proposes the molecular formulation of the active component of tobacco materials and uses the mass balance involved in cigarette burning processes to propose a model chemistry of cigarette burning processes. Previous knowledge of cigarette burning and smoke formation helped to establish the parameters used in deriving the chemistry equations. The chemical reactions proposed can be used to interpret and predict the mainstream and sidestream smoke composition of a defined cigarette and offers a simple method to explore the effects of cigarette parameters such as tobacco components, ventilation, coal temperature, and other factors on cigarette-smoke composition.

### CHEMISTRY OF CIGARETTE BURNING PROCESSES

When a cigarette is smoked, it undergoes puffing and inter-puff smoldering processes. As the cigarette is burning, a receding burning front is observed, which has a constant temperature (approx. 450 °C) and divides the burning cigarette into two zones, the burning zone and the pyrolysis zone (20). During smoldering, the main reaction – among distillation, pyrolysis and pyrosynthesis – in the burning zone is high-temperature (600–850 °C) char combustion. The oxygen participating in the reaction in the burning zone is coming through diffusion and natural convection. In the pyrolysis zone behind the paper char line, due to the heat transferred from the burning zone, the moisture in the tobacco evaporates and tobacco undergoes a series of pyrolysis reactions and is continuously converted into volatile and semivolatile smoke components and char. Hot gas flows out of the burning zone at the top of the coal near the paper char line with a temperature of about 350 °C. Due to the sudden drop of the temperature of the hot gas, semivolatiles and some volatiles will condense to the sidestream smoke aerosol. As a result of relatively long contact times between incoming air and the burning coal, the chemical reactions occurring during smoldering may reach a steady state. The chemical composition of the sidestream smoke is affected by tobacco components, coal length, and coal temperature.

During puffing, the hot gases generated in the burning zone flow through the tobacco column to heat the tobacco and carry the pyrolysis and distillation products to form the mainstream smoke. Since the contact time of air in the burning coal is relatively short and hot gas flows through the tobacco column and filter, the chemical composition of the mainstream smoke will be affected not only by tobacco components, coal length, and coal temperature, but also the puff volume, ventilation level, and the filter design. JENKINS et al. (11) used C14 to study the contribution of carbon in each smoke phase from each gradient in the 1R1 Kentucky reference cigarette in 1980. The smoke distribution of radioactivity from each of these labeled cigarettes was measured in all of the smoke components, resulting in the carbon distribution of each cigarette in all the smoke phases as shown in Table 1.

Based on the analytical results of carbon and nitrogen contents in tobacco, it is proposed here that the molecular formula of the active component of tobacco material can be represented as CnHmOxNz. For burley, n equals 2, for bright and Oriental, n equals 1. The rest or the inactive component of tobacco material is ash. The tobacco ash contents as shown in Table 2 were calculated from the measured C and N contents and the formula above. For example, if the carbon content of a bright cigarette is 40.8%, the content of CnHmOx will be 38.2%, the nitrogen content is 1.6%, therefore, the ash content is 10.2%.

Experimental cigarettes were fabricated 8.4 cm long, 2.5 cm in circumference, and made of bright, burley, or Oriental tobaccos. The cut-widths of the tobacco fillers were 30 cuts per inch. The filters used in the cigarettes were 2.1-cm long cellulose acetate filters (8.0 denier per filament, 40,000 total denier) with filtration efficiencies of 27% for “tar” and 22% for nicotine. All cigarettes were smoked under Federal Trade Commission (FTC) conditions.
(with 35 cc puff volume, 2 s puff duration, and 1 puff per minute), the total length burnt during smoking, $L_{bt}$, is 5.6 cm. The smoking performances of these cigarettes are shown in Table 3 and the sidestream data of these cigarettes are shown in Table 4. The volatiles in the tables include hydrocarbons, NO, HCN, and the volatile organic compounds measured (the data shown in Tables 3 and 4 are the average of five replicates using the Fourier Transform Infrared (FTIR) method for vapor-phase analysis and the Gas Chromatography (GC) method for nicotine and “tar” analysis [22,23]). The total mass consumed $W_{bt}$ includes both burnt tobacco and paper.

If a cigarette is smoked under FTC conditions, the total mass consumed during the interpuff smoldering process, $W_s$ (mg), may be estimated by

$$W_s = (pfn - 0.5) \times \frac{58}{60} \times W_{bt} \times LBR$$  \[1\]

where $pfn$ is puff count, $L_{bt}$ and $W_{bt}$ are total length (cm) and mass burned (mg) during smoking, respectively. The number of puff intervals for a single cigarette is the integer part of the puff number. However, the puff count of a designed cigarette $pfn$ is an average value of several tests, so the simplest estimate of the number of puff intervals is $(pfn - 0.5)$. Thus, the total mass consumed during puffs, $W_p$ (mg), will be

$$W_p = W_{bt} - W_s = W_{bt} - (pfn - 0.5) \times \frac{58}{60} \times W_{bt} \times LBR$$  \[2\]

By using the above information and the experimental data from burley, bright, or Oriental cigarettes, the chemistry of the cigarette burning processes is proposed. During a puff, the chemical reactions of the burning processes can be written as follows:

For burley cigarettes (Bu. cig.),

$$C_9H_8O_2N + 5.5O_2 \rightarrow 3CO + 6CO_2 + 17H_2O + C_{12}H_8O_2N + C_{11}$$  \[3\]

where M.W. denotes the molar weight of reactants and products of the reaction. The pseudo-molar weights of the experimental cigarettes should include its ash content (17.4%) and moisture content (12%). The burned mass of the cigarettes calculated from Eqn. [2] can be used to calculate the oxygen amount consumed and the weight of the products in Eqn. [3]. The fourth term on the right hand side of the equations is the lump-sum of organic and inorganic products which includes “tar”, nicotine, and volatiles in the vapor phase given in Table 3. It should be noted that the major components of the lump-sum products are “tar” and nicotine. “Tar” and nicotine count for 83–88% of the lump-sum products in mainstream smoke, and 73–77% in sidestream smoke. The char derived during puffing is not all consumed due to the short contact time between air and the coal.

For bright cigarettes (Bt. cig.),

$$C_{10}H_8O_2N + 3O_2 + 6CO + 17H_2O + C_{12}H_8O_2N + C_9$$  \[4\]

For Oriental cigarettes (Or. cig.),

$$C_9H_8O_2N + 8O_2 + 3CO + 8CO_2 + 17H_2O + C_{12}H_8O_2N + C_9$$  \[5\]
\[
C_{35}H_{22}O_2N_2 + C_{6} + \beta_2O_2 \rightarrow (3.5 + \frac{1}{7}\alpha_2)CO + (20.5 + \frac{6}{7}\alpha_2)CO_2 + 17H_2O + C_{6}H_4O_2N_2 + \frac{2}{3}NH_3
\]  
Equation 6. Chemistry in interpuff smoldering for burley cigarettes

\[
C_{35}H_{20}O_2N_2 + C_{6} + \beta_2O_2 \rightarrow (3.5 + \frac{1}{7}\alpha_2)CO + (20.5 + \frac{6}{7}\alpha_2)CO_2 + 17H_2O + C_{6}H_4O_2N_2 + \frac{2}{3}NH_3
\]  
Equation 7. Chemistry in interpuff smoldering for bright cigarettes

\[
C_{35}H_{20}O_2N_2 + C_{6} + \beta_2O_2 \rightarrow (3.5 + \frac{1}{7}\alpha_2)CO + (20.5 + \frac{6}{7}\alpha_2)CO_2 + 17H_2O + C_{6}H_4O_2N_2 + \frac{2}{3}NH_3
\]  
Equation 8. Chemistry in interpuff smoldering for Oriental cigarettes

**Table 5. Puff count calculation**

<table>
<thead>
<tr>
<th>Ventilation</th>
<th>0%</th>
<th>20%</th>
<th>40%</th>
<th>60%</th>
<th>80%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cigarette A</td>
<td>7.4</td>
<td>7.7 (7.8)</td>
<td>8.0 (8.3)</td>
<td>8.5 (8.9)</td>
<td>9.1 (9.5)</td>
</tr>
<tr>
<td>Cigarette B</td>
<td>5.4</td>
<td>5.7 (5.8)</td>
<td>6.1 (6.2)</td>
<td>6.7 (6.8)</td>
<td>7.2 (7.4)</td>
</tr>
<tr>
<td>Cigarette C</td>
<td>7.9</td>
<td>8.7 (8.4)</td>
<td>8.9 (9.0)</td>
<td>9.8 (9.7)</td>
<td>10.4 (10.5)</td>
</tr>
</tbody>
</table>

* A = \( L_{bt} \): 5.6 cm, \( LBR \): 0.57 cm/min; B = \( L_{bt} \): 4.8 cm, \( LBR \): 0.62 cm/min; C = \( L_{bt} \): 5.6 cm, \( LBR \): 0.51 cm/min. The numbers in brackets are calculated values.

For bright cigarettes, the number of carbon molecules to be burnt in the interpuff smoldering \( \alpha_2 = 9 \times \frac{W_p}{W_s} = 3.6 \), and the number of oxygen molecules consumed, \( \beta_2 = 20.3 + 0.93 \cdot \alpha_2 \), Eqn. 7.

For Oriental cigarettes, the number of carbon molecules to be burnt in the interpuff smoldering \( \alpha_2 = 7 \times \frac{W_p}{W_s} = 2.1 \), and the number of oxygen molecules consumed \( \beta_2 = 20.3 + 0.93 \cdot \alpha_2 \), Eqn. 8.

For cigarettes with filter ventilation, the number of carbon molecules \( \alpha \) should be determined by the ratio of \( W_p \) to \( W_s \) of the ventilated cigarettes to reflect the effect of ventilation. As \( W_s \) approaches zero, \( \alpha \) becomes zero, Eqns. [6] to [8] become the chemistry of free smoldering processes. The proposed chemical reactions take into account the carbon distribution data in smoke phases by JENKINS et al. (11). For example, for burley cigarettes, the calculated carbon distributions in the gas phase and TPM of the mainstream smoke are 13% and 12%; and that of the sidestream smoke are 63% and 12%, respectively. Including the original moisture in tobacco, the total delivery of water is about 42% of the tobacco weight. It can be seen from these equations that the composition of the tobacco types, including the nitrogen content, has an obvious impact on the cigarette burning process.

**VENTILATION EFFECT**

Based on the ventilation-effect studies by BAKER et al. (12,16), BROWN et al. (17), and NORMAN (18), the effect of ventilation level, \( v \), on the puff count of a given cigarette (under FTC smoking conditions) may be empirically expressed as,

\[
pfn = \frac{pfn_{\text{init}}}{(1 - kv)} \quad k = 1 - \frac{pfn_{\text{init}}}{\left( \frac{L_{bt}}{LBR} + 0.483 \right)}
\]  
Equation 9

Once the puff number of the non-ventilated cigarette, \( pfn_{\text{init}} \), is known, the puff number of cigarettes with any ventilation level can be calculated. Table 5 illustrates the calculated puff count under FTC smoking conditions and the experimental values for Cigarettes A, B, and C. The total weight consumed during puffing and interpuff smoldering can be determined using Eqns. [1] and [2]. The corresponding smoke component delivery in mainstream smoke can then be determined by the proposed chemical reactions of the burning processes using Eqns. [3] to [5].

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Figure 1 shows the effect of ventilation on the relative deliveries of smoke components in mainstream smokes, such as CO₂, NH₃, “tar”, and nicotine. As can be seen from Figure 1, the impact of tobacco type on the relative delivery of mainstream components is very little. However, the impact of tobacco type on the relative delivery of sidestream components is significant as shown in Figure 2. The impact of tobacco type on sidestream CO or CO₂ delivery is less than that on other components, as determined by the proposed chemistry for the interpuff smoldering processes, Eqs. [6] to [8].

It should be noted that Figure 1 and Figure 2 only consider the effects of dilution and puff count, but not any other effects. For example, the CO diffusion through the cigarette paper during puffs is not accounted for in the mainstream CO delivery and most of the water vapor in the mainstream smoke condensed onto the tobacco filler will eventually go to the sidestream smoke. It was observed that CO delivery was reduced more as compared with CO₂ delivery when the ventilation level increases (4,17,18). This is because, as the incoming air flow rate is low or the ventilation level is high, the contact time between the air and the coal becomes longer, and part of the sidestream smoke might be drawn to mix with mainstream smoke. CO delivery was reduced more as compared with CO₂ delivery when the ventilation level increases.

HEAT OF CIGARETTE COMBUSTION

BOYD et al. (3) studied the dependence of the gas-phase composition of smoke on the combustion temperature of tobacco products. JOHNSON et al. (6) used the smoke component information obtained to predict the coal temperature. In a previous paper, a mathematical model of the cigarette smoldering process was developed (20). This model predicts the free smoldering speed, or linear burn rate, and the temperature and density profiles in the pyrolysis zone of the smoldering cigarettes. The model also estimates the coal length and the maximum coal temperatures during free smoldering. The results show that air consumed in the smoldering process is about 2.6 times the mass of tobacco burnt. WAYMACK et al. (21) found the heat of smoldering combustion for tobacco, ΔH(tobacco), is about 1.68 cal/mg for the 78 cigarette designs that were investigated.

For a free smoldering cigarette, if the burn weight of tobacco is 1000 mg, the air consumed will be 2600 mg, or 619 mg of oxygen (19.3 mmol). Therefore, the heat generation based on oxygen consumed, ΔH(O₂), will be:

\[ ΔH(O_2) = ΔH(tobacco) \times 1000/19.3 = 87.1 \text{ cal/mmol oxygen}. \]

This value is similar to the literature value of 89.0 cal/mmol of oxygen consumed (9).

The char derived during puffing is not all consumed, so it is not suitable to estimate the reaction heat during puffing based on the heat of smoldering for tobacco. Therefore, it is better to estimate the reaction heat during puffing based on oxygen consumption, by assuming the same heat generation based on oxygen consumed as in free smoldering. The estimated reaction heat during puffing for these cigarettes is shown in Table 6. The values were calculated by Eqs. [3] to [5] using the fixed heat generation of 87.1 cal/mmol oxygen consumed.

CONCLUSIONS

The chemical reactions of cigarette burning processes during puffing and smoldering are proposed based on the mass balance in cigarette burning processes and earlier studies in the literature. The predicted deliveries of some
smoke components agree fairly well with the experimental data for bright, burley, and Oriental experimental cigarettes. The effect of ventilation is obvious on relative delivery of smoke components in both mainstream and sidestream smoke. The impact of tobacco components on the relative delivery of mainstream constituents is small, but it is significant on the relative delivery of sidestream constituents. Based on the heat generation in free smoldering, the reaction heats of the burning process during puffing are estimated to be 0.43, 0.52, and 0.65 cal/mg for burley, bright, and Oriental experimental cigarettes, respectively.

REFERENCES

7. Rathkamp, G., T.C. Tso, and D. Hoffmann: Chemical studies on tobacco smoke XX: Smoke analysis of cigarette made from bright tobacco differing in variety and stalk positions; Beitr. Tabakforsch. 7 (1973) 179–189.
22. FTIR vapor phase analysis of mainstream and sidestream smoke; Battelle SOP No. AC.V-030.

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Table 6. Calculated reaction heat of cigarette during puffing (based on 87.1 cal/mmol oxygen consumed)

<table>
<thead>
<tr>
<th>Cigarette</th>
<th>Calculated ash %</th>
<th>Reaction heat during puffing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Burley</td>
<td>17.0</td>
<td>0.43 cal/mg</td>
</tr>
<tr>
<td>Bright</td>
<td>10.2</td>
<td>0.52 cal/mg</td>
</tr>
<tr>
<td>Oriental</td>
<td>15.6</td>
<td>0.65 cal/mg</td>
</tr>
</tbody>
</table>