Formation and Reduction of Carbon Monoxide in a Burning Cigarette*

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SUMMARY

The total amounts of carbon monoxide (CO) and carbon dioxide (CO2) in the mainstream smoke of a burning cigarette during a steady draw were measured by a non-dispersive infrared (IR) technique for a variety of flow rates. The temperature profiles in the cigarette were also measured under the same flow conditions. The data were used in a diffusion model to estimate the concentrations of these gases downstream of the pyrolysis zone. The contribution of pyrolysis in the generation of these gases was calculated using a kinetic model. The remaining CO and CO2 are attributed to processes occurring in the combustion zone. The calculated mean concentrations of carbon oxides behind the pyrolysis zone are in reasonable agreement with the experimental data. The contributions of pyrolysis and combustion to the formation of CO were found to be approximately 1/3 and 2/3 respectively. The results show that the peak temperature rises with an increase in the mainstream flow rate in the limited range of 0 to 200 mL/min. As a result, the concentrations of carbon oxides behind the pyrolysis zone also increase with the flow rate and reach plateaus at higher flow rates. [Beitr. Tabakforsch. Int. 20 (2003) 439–447]

ZUSAMMENFASSUNG


RESUME

La teneur en monoxyde de carbone (CO) et dioxyde de carbone (CO2) de la fumée du courant principal d’une cigarette allumée au cours d’un fumage à tirage constant a été mesurée au moyen d’une technique infrarouge (IR) non-dispersive pour plusieurs débits d’air. Les profils thermiques dans une cigarette ont également été mesurés dans les mêmes conditions de débits d’air. Les données ont été utilisées avec un modèle de diffusion pour estimer les concentrations de ces gaz en aval de la zone de pyrolyse. La teneur en CO et CO2 restante est attribuée aux processus de la zone de combustion. Les concentrations moyennes calculées en oxydes de carbones en arrière de la zone de pyrolyse sont en accord avec les données expérimentales. Il a été trouvé que les contributions de la pyrolyse et la combustion à la formation de CO étaient respectivement de 1/3 et 2/3. Les résultats montrent que la température maximale accroît en relation avec une augmentation du débit du courant principal dans la marge restreinte de 0 à 200 mL/min. En conséquence, les concentrations d’oxydes de carbone en arrière de la zone de pyrolyse augmentent également en relation avec le débit d’air et plafonnent aux débits les plus élevés. [Beitr. Tabakforsch. Int. 20 (2003) 439–447]
INTRODUCTION

The amount of carbon monoxide (CO) in mainstream smoke varies with the type of tobacco and cigarette design and is generally reported between 12 and 23 mg/cigarette under standard Federal Trade Commission (FTC) smoking conditions. The corresponding value for carbon dioxide (CO₂) varies from 45 to 65 mg/cigarette. These gaseous species cannot be efficiently removed from the mainstream smoke with available filter technologies. The only mechanism by which a fraction of these gases are removed from the mainstream smoke is by diffusion through the paper.

There have been many studies of the gas composition from a burning cigarette, but most researchers sample from the exit gas stream of the cigarette and do not analyze the gas phase composition within a cigarette. BAKER and KILBURN (1) were the first to report the distribution of low molecular weight gases in the burning (pyrolysis + combustion) zone of a cigarette. Both axial and radial distributions of CO, CO₂, oxygen (O₂) and other gases were reported in this study. The measurement was done with a mass spectrometer coupled to a sampling probe within a cigarette. LANZILLOTTI and WAYTE (2) measured the concentration of O₂, nitrogen (N₂), CO, CO₂ and methane (CH₄) along the axis of a cigarette during a two-second, 35-cc puff. Earlier, NEWSOME and KEITH (3) measured the variation of the gas phase composition within a burning cigarette. They reported that the concentrations of O₂, CH₄, CO, hydrogen (H₂), and CO₂ dropped along the length of a cigarette. They pointed out that diffusion contributes to only 30 to 40 percent of the reductions, the rest being due to diluting air which enters into the mainstream through the permeable cigarette paper. Other investigators (4–9) have also measured the concentration of several chemical constituents including CO in mainstream smoke. BAKER and CRELLIN (10) also presented an equation for the diffusion of CO, which was derived from a one-dimensional analysis similar to that of OWEN and REYNOLDS (5).

RILEY et al. (11) reported a more comprehensive mathematical modeling of the diffusion of the gases through the paper. The radial diffusion and convection in both directions were included in this model. The nature of the problem does not allow an explicit solution, hence a finite-difference numerical technique had to be used to solve the equations. Experimental data from an unlit cigarette were used to validate the model. Excellent agreement between predictions and experimental data for the outlet mean (bulk) concentration was reported. The report included a parametric study of the effects of various parameters on the diffusion of gases.

BAKER and ROBINSON (12) introduced a semi-theoretical model for the prediction of smoke delivery including CO on a puff-by-puff basis. This model requires inputs such as physical dimensions of the tobacco rod, the filter, the paper, and the diffusion coefficients of CO as well as the smoking conditions. A good agreement between the model prediction and experimental data was observed.

In this work, the total amounts of CO and CO₂ are measured for a given period of time in the mainstream smoke of a burning cigarette during a steady draw using a non-dispersive infrared (IR) technique. The temperature profiles in the cigarette are also measured under the same flow conditions. These data are then used in a diffusion model to estimate the concentrations of these gases downstream of the pyrolysis zone. The model incorporates radial and axial diffusions as well as axial convection of the gas species in a porous media. An explicit solution is obtained that eliminates the need for the numerical solution of the partial differential equations. The contribution of pyrolysis in the generation of these gases is then calculated using a kinetic model.

EXPERIMENTAL

Gas concentration measurement

The mainstream smoke was generated by continuous puffing of an unconditioned 1R4F reference cigarette, which is an industry standard cigarette obtained from the University of Kentucky. A schematic diagram of the experimental setup is shown in Figure 1. The draw was created by the bench top vacuum and the flow rate was regulated with a Hastings Instruments digital flow meter (model HFC 202). To prevent the interference of gases from a match or propane lighter, the cigarette was lit with
a Borgwaldt Technik electric cigarette lighter. Once the cigarette was lit, the mainstream smoke continuously drawn by the vacuum at a fixed flow rate first passed through a Cambridge pad. The smoke aerosol and heavier condensable products were trapped by the Cambridge pad; gases, including CO, CO$_2$, O$_2$, and the lighter organic compounds, passed through the Cambridge pad and entered a NGA2000-MLT multi-gas analyzer from Rosemount Analytical. The inlet gases passed through the CO, CO$_2$ and O$_2$ measurement chambers in the analyzer consecutively. The NGA2000-MLT multi-gas analyzer uses two non-disperse near infrared detectors to measure the concentration (by volume percentage) of CO and CO$_2$ respectively and one paramagnetic detector to measure the concentration (also by volume percentage) of O$_2$ in the continuous flow. The presence of other organic compounds does not interfere with the measurements. Measurements were taken every second to ensure a closely monitoring of the concentration changes. The measured concentration data along with time were logged on a computer for analysis.

In this study 1R4F cigarettes were used. This experimental cigarette is 84 mm in length, 25 mm in circumference, has a 17-mm cellulose acetate filter with 20% dilution, 32 mm of tipping paper and is marked for a 35-mm butt length. Two lines were marked on the cigarette before the smoking. One is 10 mm from the tip of the cigarette, another is 10 mm from the tipping line, as shown in Figure 1 (dashed lines). The distance between the two dashed lines is 32 mm.

The time for a cigarette to burn between the lines was recorded and used to calculate the linear burn rate. When the paper burn line reached the second dashed line, the cigarette was removed from the holder and extinguished. The ash was collected in an aluminum tray and weighed for each smoked cigarette. The Cambridge pad was weighted before and after the experiment for the mass of wet total particulate (WTPM).

A typical CO, CO$_2$ and O$_2$ concentration trace is shown in Figure 2. Before lighting the cigarette, the O$_2$ concentration is 21% as in the air, while the CO and CO$_2$ concentrations are very close to zero. During the burning of a cigarette, CO and CO$_2$ are produced and O$_2$ is consumed. Once the cigarette is burnt, the concentrations of CO and CO$_2$ return to zero and the concentration of O$_2$ rises back to 21%. The integration of the concentration vs. time gives quantities proportional to CO, CO$_2$ production and O$_2$ consumption during the burning process. The integral of concentration vs. time can be converted by the following equation to the milligrams of the specific gas produced or consumed:

$$\text{Gas produced or consumed (mg)} = \frac{\text{Integration (ppm} \cdot \text{s)} \times \text{Flowrate (mL/s)} \times \text{MW (mg/mmol)} \times 10^6 (\text{ppm}) \times 24.45 (\text{mL/mmol})}{\text{mg/mmol}}$$

The value 24.45 mL/mmol is calculated based on the ideal gas law at room temperature. To calculate an average value at each flow rate, tests are repeated for five times. A typical set of data is shown in Table 1, where the amount of WTPM, nitric oxide (NO), and ash content as well as the linear burn rate are also reported. The maximum gas flow was limited to 200 mL/min partly because the experiment was conducted under continuous draw and higher flow rates resulted in rapid cigarette burning and changing shape of the coal during the process.

**Temperature measurement**

A schematic diagram of the experimental setup for the temperature measurement is shown in Figure 3. Several thermocouples are mounted on a system that can be adjusted to sense the temperature at different radial and...
Figure 3. Schematic diagram for temperature measurement

Figure 4. Surface, midpoint and centerline temperature as a function of time at a flow rate of 200 mL/min

The results for continuous draw for the standard experimental cigarette 1R4F are reported herein. The experimental procedure consists of marking the axial positions on the cigarette for the thermocouples, making holes to insert the thermocouples, mounting the cigarette horizontally on the holder, inserting the thermocouples, lighting the cigarette, and running the program to collect data. Marking for the first set of thermocouples is done at 12 mm away from the lit tip of the cigarette to give the cigarette enough time to have a stable coal established. The positions of subsequent sets of thermocouples are marked at 8 mm axial intervals. At each axial location, three holes are made for the insertion of thermocouples. The holes are made radially at three peripheral locations 90 degrees apart, one on the top and two others on the sides. The remaining space in the holes, after the insertion of thermocouples, is filled with cellulose powder to minimize excessive flow of oxygen towards the combustion zone during smolder.

MODELING

Diffusion

Figure 6 shows the physical model of the problem. The computational domain begins approximately 5 mm behind the paper burn line, where the gas temperature does not change appreciably with axial position (13). Furthermore, at this location we can assume that pyrolysis reactions are complete. It is also assumed that the mean axial velocity of gas in the tobacco rod does not change appreciably along axial positions inside a burning cigarette. The signals from thermocouples are sent to a VXI mainframe through a circuit board, and the mainframe is connected to a personal computer so that the measurements can be recorded with the aid of HP VEE 5.0 software. A circuit board hp1419 is used in one of the slots of an E8408A 4-slot C-size VXI mainframe made by Agilent®, which is the interface unit between the thermocouples and the computer that is used to collect data and monitor the operation of the thermocouples. HP VEE is a visual programming language optimized for building test and measurement applications. HP VEE has a compiler, a professional development environment suited for large and complex programs, and advanced instrument management capabilities.

The thermocouples used in this experiment are sheathed K-type thermocouples with a diameter of 0.01 inch (250 μm) made by Omega®. The sheath is made of ceramic materials so that to withstand the high temperatures involved in the cigarette combustion zone. It protects the thermocouples against mechanical impacts and also acts as a thermal insulator which reduces the heat losses from the bare wire and hence the measurement error. Three thermocouples are used at each axial location: one at the centerline, one at midpoint between the surface and the center, and the last one on the surface (see Figure 3).
the cigarette during the continuous draw. This is the most questionable assumption and deserves more attention. There are three factors that affect the gas mean velocity as the cigarette shortens as well as at any time along the cigarette. One of these is the variation of filter ventilation variation with the remaining length of the cigarette. However, this variation is small; changing from 20% to 17% of the total flow when the length varies from 80 mm to 30 mm (14). At a given time, there are also two competing factors; one is the increase in the velocity towards the filter as a result of the air infiltration through the paper and the other is the decrease due to cooling of the gas. Therefore, there are some qualitative justifications for a constant mean gas velocity assumption along the rod.

A gas species \( i \) enters the rod at \( x = 0 \) with a given concentration. Part of it diffuses out of the paper; the rest leaves the rod at \( x = L \). Assuming that \( L >> a \), the diffusion equation for any species is given by (16)

\[
U_0 \frac{\partial C}{\partial x} = D \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C}{\partial r} \right) + D \frac{\partial^2 C}{\partial x^2} \quad [1]
\]

subject to the following boundary conditions:

\[
x = 0, \quad 0 < r < a, \quad C = C_0; \quad x \rightarrow \infty, \quad C = \text{finite} \quad [2a]
\]

\[
r = 0, \quad \frac{\partial C}{\partial r} = 0
\]

\[
r = a, \quad -\rho D \frac{\partial C}{\partial r} |_{r=a} = \frac{(C - C_0)}{R_m} \quad [2b]
\]

The solution to Equation [1] is as follows (15,16):

\[
\frac{C - C_\infty}{C_0 - C_\infty} = \sum_{1}^{w} \frac{2BJ_0(\beta_n/a)}{(\beta_n^2 + B^2)J_0(\beta_n)} e^{-S_n x/a} \quad [3]
\]

where

\[
S_n = \gamma \left( \sqrt{1 + (\beta_n^2 \gamma)^2} - 1 \right), \quad \gamma = \frac{U_0 a}{2D}
\]

and \( B = a^2 (\rho DR_m^3) \) is a dimensionless quantity, and \( \beta_n \)'s are the roots of the following equation:

\[
\beta J_1(\beta) - BJ_0(\beta) = 0 \quad [4]
\]

The mass flow rate of a gas diffusing out of a porous rod of radius \( a \) and length \( L \) may be calculated from:

\[
\dot{m}_{L} = \int_{0}^{L} 2\pi a \left( -\rho D \frac{\partial C}{\partial r} \right) dx = (4\pi a^2 U_0 (C_0 - C_\infty) B/2\gamma) \sum_{1}^{w} \frac{J_1(\beta_n)}{(\beta_n^2 + B^2)J_0(\beta_n)} \left( \beta_n/S_n \right) (1 - e^{-S_n L/a}) \quad [5]
\]

Assuming that the burning front in a steady draw case travels uniformly and the time needed for the length of a cigarette to change from the initial value of \( L_0 \) to the final value of \( L_f \) is \( t_f \), the following equation may be used to obtain the total mass of a gas in the mainstream during this period of time:

\[
\frac{m_{L}}{\rho U_0 \pi a^2 (C_0 - C_\infty) t_f} = (4B/2\gamma) \sum_{1}^{w} \frac{J_1(\beta_n)}{(\beta_n^2 + B^2)J_0(\beta_n)} \left( \beta_n/S_n \right) \left( 1 - e^{-S_n L_f/a} \right) \quad [6]
\]

This equation may be used to calculate the concentration of each gas specie, \( C_\infty \), behind the pyrolysis zone from the measured mass of the gas in the mainstream during a given period of time. Equation [6] is derived based on the assumption that the concentration of the gas \( C_0 \) is constant during the entire period of burning. This is a reasonable
assumption because the temperature field in a coordinate frame attached to the paper burn line does not change with time in a continuous draw. This has been observed from the measurement of the temperature at four axial locations (Figure 3), but the results are not included here. The parameters in Equation [6] may be evaluated from the thermophysical data of the gas, cigarette design parameters, the flow and thermal conditions.

**Pyrolysis**

Once the concentration of a gas behind the pyrolysis zone is determined, we would like to know what fraction results from the tobacco pyrolysis itself. In order to carry out these calculations, the kinetic parameters for the formation of the individual gas species from tobacco as well as the heating rate and the time during which the tobacco undergoes heating prior to combustion are required. The kinetic parameters strongly depend on the tobacco type and are available for certain tobacco types and for only a small number of gas species that resulted from pyrolysis. Baker (17,18) provided kinetic parameters for the evolution of CO and CO$_2$ from thermal decomposition of tobacco. The overall kinetic parameters that are available in the literature (19) cannot be used here because they are only useful for total weight loss calculations.

The kinetic parameters for the thermal degradation of several biomass materials including tobacco samples have been estimated and provided to Philip Morris USA by Advance Fuel Research Inc. (20). The samples were pyrolyzed in a thermogravimetry Fourier transformed infrared spectrometry (TG-FTIR) system. The TG-FTIR data were then used in a kinetic model to obtain the kinetic parameters. The functional group (FG) biomass-pyrolysis model was used to estimate the evolution of several gaseous species from the thermal decomposition of a given biomass sample for a given heating rate. More details about this pyrolysis model can be found in (21). This model is used to estimate the production of CO and CO$_2$ from the pyrolysis of the tobacco samples.

In order to calculate the contribution of tobacco thermal decomposition to the formation of CO and CO$_2$, we need to know the temperature-time history of the sample in the actual continuous draw cases. Typical data of this type from the temperature measurements are shown in Figures 4 and 5.

**RESULTS AND DISCUSSION**

Results of temperature measurements at one axial location are shown in Figure 4 for a flow rate of 200 mL/min. The temperature of tobacco at the centerline rises from the ambient to about 800 °C in a short period of time, while the surface temperature fluctuates. Large fluctuations in the surface thermocouple reading may be attributed to unsteady heat transfer mechanisms. The fluctuation of the surface thermocouple readings may be explained as follows. The thermocouple junction is in equilibrium with the local inflow of ambient cold air, the outgoing hot gas and thermal radiation with its surroundings. It is possible that due to the transient and inhomogeneous nature of the material density and porosity near the surface, complicated by the presence of paper, that these effects are highly transient causing the local temperature to fluctuate with time.

The effects of flow rate on the centerline temperature history are shown in Figure 5. Generally, increasing the
Figure 7. Effect of steady flow rate on the linear burn rate

Figure 8. Concentrations of CO and CO\textsubscript{2} and their ratio behind the pyrolysis/combustion zone

Flow rate increases the peak temperature slightly as well as the heating rate (or the T-t slope), both of which play important roles in the evolution of gases by pyrolysis reactions. The increase in the peak temperature from the no-flow case to a flow of 200 mL/min is about 100 °C. Note that the maximum flow rate in Figure 5 is 200 mL/min, which is less than a fifth of the standard puffing rate, i.e., 1050 mL/min. Figure 7 shows the effects of flow rate on the linear burn rate (LBR), which is defined as the linear velocity of the paper burn line. At intermediate flow rates, LBR varies linearly with the flow rate. A linear relationship between the burn rate and the volume flow of air entering the cone of a cigarette during puffing has been reported earlier (22). At lower flow rates, the linear relationship breaks down because the combustion process is also affected by the diffusion of oxygen to the coal rather than the forced air flow through the coal. However, at low flow rates, the LBR data approach the smoldering value. Extrapolation of the data of Figure 7 to a zero flow rate results in a value of 0.075 mm/s (4.5 mm/min) for the smoldering case. At intermediate flow rates, LBR data approach the smoldering value.

CONCLUSIONS

The oxides of carbon are generated through pyrolysis and combustion reactions in a cigarette. A portion of these shape changes from a short cone to a long cone during the burning process. As stated earlier, the cross-sectional average concentrations of CO and CO\textsubscript{2} behind the pyrolysis/combustion zone may be calculated from Equation [6]. These data as well as the ratio of CO/CO\textsubscript{2} are shown in Figure 8 as a function of flow rate. The mean concentrations of CO and CO\textsubscript{2} as well as the CO/CO\textsubscript{2} ratio increase initially and then approach plateaus. The initial increase is due to the decline of the outward diffusion as a result of stronger forced air flow. In fact at low flow rates, a substantial amount of the gases generated in the combustion-pyrolysis zone diffuse out of the cigarette because of strong buoyancy effects in the combustion zone, which is caused by the concentration and temperature gradients. At higher flow rates the forced flow of air dominates the flow and reduces the buoyancy effects. This flow effect results in an increase in the concentration of gaseous species in the mainstream as the flow rate increases. The gas concentrations remain unchanged at higher flow rates mainly due to the fact that the heating rate and the peak temperature do not vary considerably with the flow rate. The heating rate and temperature are in fact the main two parameters which determine the rate of formation of a gas from pyrolysis and combustion reactions. We can only make a rough comparison between the present results and data reported in the literature. This is due to a number of differences in the test conditions including the flow rate, cigarette designs and materials used in this study and those reported in the literature. The calculated mean concentrations on a mass basis behind the pyrolysis zone are approximately 7% for CO and 32% for CO\textsubscript{2}. The corresponding experimental value for CO concentration at this location varies from a low value at the surface to approximately 9% at the centerline (24). The experimental value for the average CO\textsubscript{2} concentration behind the pyrolysis zone is around 15% (v/v%), which corresponds to about 22% (mass basis). The ratio of CO/CO\textsubscript{2} in the mainstream smoke reported in the literature varies from 0.16 to 0.36 depending on the flow rate and the ventilation level; for a cigarette with 33% ventilation, it is 0.24 at a flow rate of 525 mL/min and 0.32 at 1050 mL/min. In this work, the calculated ratio of CO/CO\textsubscript{2} behind the pyrolysis zone approaches a value of 0.25 as the flow rate increases. The contributions of pyrolysis and combustion processes to the formation of CO and CO\textsubscript{2} are shown in Figures 9 through 11. Generally, the rate of formation (mg/min) increases linearly with the flow rate. The main reason for this is the higher mass burn rate of tobacco with increasing flow rate. Figure 11 shows that at higher flow rates, almost one third of the total CO generated is due to the pyrolysis reactions and the remaining two thirds is due to combustion of char and the reduction of CO\textsubscript{2} to CO in the combustion zone. This is in good agreement with other available data (23–26). The contribution of pyrolysis to the formation of CO\textsubscript{2} at flow rates above 150 mL/min, as can be seen from Figures 10 and 11, is around 45%.
gaseous species diffuses out of the paper as they flow through the cigarette rod towards the filter. The rest remain in the mainstream smoke. In this work, the concentrations of CO and CO$_2$ in the mainstream smoke under different continuous flow rates are measured by infrared spectroscopy (IR). The data on mainstream smoke concentrations are used in a mathematical model to estimate the amount of diffusion and the concentrations behind the pyrolysis zone, which leads to the estimation of generation of CO and CO$_2$ in the pyrolysis and combustion zones. The calculated mean concentrations of the carbon oxides behind the pyrolysis zone are in reasonable agreement with the experimental data. The contributions of pyrolysis and combustion to the formation of CO were found to be approximately 1/3 and 2/3, respectively, which is in agreement with the literature data. The peak temperature varies from 750°C to 850°C as the mainstream flow rate increases from 0 to 200 mL/min. As a result the concentration of carbon oxides behind the pyrolysis zone changes accordingly and reach plateaus at higher flow rates.

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