

A Mathematical Model for Pyrolysis Processes During Unforced Smoldering of Cigarette

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비흡입시 연소하는 담배의 열분해 작용에 관한 수학적 모델

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ABSTRACT : A mathematical model for the pyrolysis processes during unforced smoldering of cigarette was proposed in this study by analyzing the physical model of the smoldering cigarette (including the establishment of burning front between burning zone and pyrolysis zone, and analyzing the involvement of main factors such as pyrolysis of virgin tobacco, evaporation of water, and internal heat transport in the processes). Thermal conduction of cigarette paper and convective and radiative heat transfer at the outer surface were also considered via the thermal resistance law for the competitive heat transfer mechanisms. The governing partial differential equations were solved using an integral method. Model predictions of smoldering speed, or linear burn rate, as well as temperature and density profiles in the pyrolysis zone for different kinds of cigarettes were found to be close to the experimental data in the literature (Muramatsu, 1981). The model provides a relatively fast and efficient way to simulate the pyrolysis processes and offers a practical tool for exploring important parameters for a smoldering cigarette, such as blended tobacco composition, properties of cigarette paper, and heat flux from the burning zone to the pyrolysis zone.

Key words : mathematical model, smoldering, pyrolysis, heat flux

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Cigarette ignition of furniture is one of the leading cause of fire worldwide. For this reason, the Fire Safe Cigarette Act of 1990 was passed in the United States of America : its goal was to determine whether safer (from the point of view of fires) cigarettes were technically feasible. To predict theoretically whether an upholstered furniture item will be ignited to smoldering or not when a lit cigarette is dropped on it, the heating of the substrate by the heat source must be accurately modeled, and a criterion established for the ignition. In order to examine how the ignition properties will be influenced by changing one or more properties of the cigarette, it is also necessary to understand the behavior of a smoldering cigarette. This includes knowing the heat flux from the burning zone to the pyrolysis zone.

In order to study the fundamental mechanisms of smoldering and the important factors governing smoldering speed, the cigarette smoldering processes have been studied by a number of investigators. Jenkins et al. (1977) measured the changes in the density of a smoldering cigarette and correlated them with the temperature distribution reported by Baker (1975, 1977). A theoretical and experimental investigation of the smoldering mechanism of tobacco was carried out by Muramatsu (1981). Muramatsu et al. (1979) proposed a pseudo steady state model of pyrolysis processes inside a naturally smoldering cigarette and solved the one dimensional differential equations numerically.

In the present paper, the pyrolysis processes of a smoldering cigarette are analyzed and a receding burning front is defined. In a smoldering cigarette, two major reaction zones may be distinguished : (1) the high-temperature burning zone (above 450 °C) and (2) the pyrolysis zone (below 450 °C). These two zones are separated by a burning front, which is marked by the paper char line and characterized by a constant temperature of about 450 °C (Muramatsu, 1979). A mathematical model for the pyrolysis zone has been developed and solved by an integral method. The smoldering speed, or linear burn rate, and the

distribution profiles of both temperature and density calculated from the integral method were close to the experimental data provided in the literature.

MATERIALS AND METHODS

Model Formulations

The physical model for the analysis is shown in Figure 1. Originally, a cigarette is assumed to have uniform initial temperature T_0 and a moisture content of w_0 . As soon as the temperature of one end is raised to above 450 °C by ignition, the burning front, $S(t)$, appears, which has a constant temperature ($\cong 450$ °C) and divides the cigarette into two zones, the burning zone and the pyrolysis zone. The main reactions included in the burning zone are high temperature oxidative pyrolysis and char combustion which create a large amount of heat. In the pyrolysis zone, the main processes included are water evaporation and tobacco non-oxidative pyrolysis. Due to the heat transferred from the burning zone, the temperature of tobacco in the pyrolysis zone increases, the moisture in the tobacco evaporates, and virgin tobacco is continuously converted into volatile smoke components and residual char. Consequently, the material in the pyrolysis zone consists of three major components, virgin tobacco, water, and char. The heat transferred from the burning zone to the pyrolysis zone is used to raise the tobacco temperature, and loses as energy to the atmosphere. Finally, a steady state will be reached where both the heat flow to the pyrolysis zone and the linear burn rate become constant.

Assumptions : The mathematical analysis of pyrolysis processes in a smoldering cigarette is also based on the following assumptions : (1) The reaction of atmospheric oxygen with tobacco, char, and smoke in the pyrolysis zone is negligible. (2) The temperature of the solid phase is the same as that of the gas phase, which is reasonable because the gas flow inside the pyrolysis zone is negligible in the case of natural

smoldering. (3) Heat loss from the outer surface of the smoldering cigarette is caused by free convection and radiation. (4) The thermal conduction inside the pyrolysis zone is characterized by an effective thermal conductivity, a combination of the multiphase conduction and radiation. Validation of these assumptions can be found by Muramatsu (1979, 1981).

Physical model of smoldering cigarettes : Since the temperature profiles measured in the radial direction in the pyrolysis zone of smoldering cigarettes were relatively flat (Baker, 1977), an one-dimensional heat transfer equation which includes a term for heat loss through the tobacco cylinder and the outer surface may be suitable to describe the pyrolysis processes. The x-coordinate is taken along the longitudinal axis of the cigarette in the direction opposite to the velocity of the burning front as shown in Figure 1.

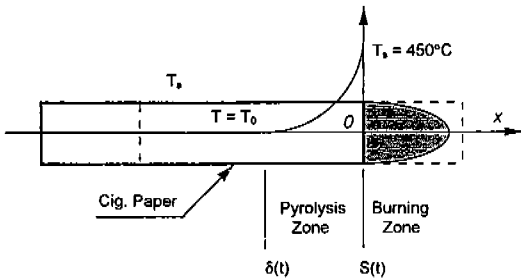


Figure 1. The physical model for a smoldering cigarette

Heat transfer equation : By performing the heat balance on a basic element in the pyrolysis zone, the following heat transfer equation (Bird et al., 1960) can be obtained :

$$\rho C_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} (K_{eff} \frac{\partial T}{\partial x}) - \frac{2h}{r} (T - T_a) + Q_p \quad (1)$$

where ρC_p is the product of material density and specific heat in the element, K_{eff} is the effective thermal conductivity of the cigarette column, h is the overall heat transfer coefficient in the radial direction,

and Q_p is the heat source term due to pyrolysis reactions. The left side of the equation is the heat accumulation term. The terms on the right side are the effective thermal conduction term, the heat loss term through the outer surface, and the heat source term due to the pyrolysis reactions, respectively. The effective thermal conductivity, K_{eff} , can be determined by the Kunii's equation (Kunii, 1961) :

$$K_{eff} = (1 - \Phi_t^{2/3}) k_{sf} + \Phi_t^{1/3} (k_g + \frac{2}{3} h_r D_p) \quad (2)$$

and

$$h_r = 5.433 \times 10^{-12} \varepsilon_t T^3 \quad (3)$$

In the present study, the furthest end of the pyrolysis zone from the burning front is defined as the penetration boundary. It is assumed that, beyond this boundary, $\delta(t)$, the temperature remains at its initial value and no heat is transferred. Thus, the temperatures at the both boundaries of the pyrolysis zone are :

If can be assumed,

$$T = T_s = 450^\circ C \quad \text{at } x = S(t) \quad (4)$$

$$T = T_0 \approx T_a \quad \text{at } x = \delta(t) \quad (5)$$

The density change in the pyrolysis zone can be described by the mass continuity equations. The consumption of mass in the pyrolysis zone is mainly due to pyrolysis reactions of virgin tobacco and the evaporation of water. The pyrolysis reactions are usually described in four major steps, as studied by Muramatsu et al. (1979). Therefore, the change of solid density in the pyrolysis zone may be represented by the sum of four different n-th order Arrhenius reaction equations :

$$\frac{\partial \rho_i}{\partial t} = - \sum_{i=1}^4 A_i \exp\left(-\frac{E_i}{RT}\right) \rho_i^n \alpha_i \quad (6)$$

$$\frac{\partial w}{\partial t} = -A_w \exp\left(-\frac{E_w}{RT}\right) \rho_w^{n_w} \quad (7a)$$

where α_i is the contribution of i th pyrolysis step.

or

The evaporation rate of water from tobacco laminars is expressed by the following empirical equation (Muramatsu et al., 1979 ; Kamei et al., 1941) :

$$\frac{\partial \rho_w}{\partial t} = -A_w \exp\left(-\frac{E_w}{RT}\right) \rho_w^{n_w} \quad (7b)$$

Table 1. Kinetic parameters for pyrolysis and water evaporation (Muramatsu et al., 1979)

Kinetic parameter	Flue Cured	Burley	Oriental
Pyrolysis of Reaction Kinetics			
i=1			
n	1	1	1
E (kcal/mol)	20.2	20.8	20.8
A (s ⁻¹)	6.27 × 10 ⁷	1.0 × 10 ⁸	1.0 × 10 ⁸
Contribution to pyrolysis	0.25	0.08	0.05
i=2			
n	1	1	1
E (kcal/mol)	24.5	25.6	20.1
A (s ⁻¹)	1.69 × 10 ⁸	7.31 × 10 ⁸	4.08 × 10 ⁸
Contribution to Pyrolysis	0.28	0.32	0.35
i=3			
n	1	1	1
E (kcal/mol)	45.7	39.8	40.2
A (s ⁻¹)	5.99 × 10 ¹⁴	1.32 × 10 ¹³	8.65 × 10 ¹²
Contribution to pyrolysis	0.17	0.30	0.30
i=4			
n	3	3	3
E (kcal/mol)	25.2	27.9	29.1
A (s ⁻¹)	4.69 × 10 ⁶	2.64 × 10 ⁷	6.12 × 10 ⁷
Contribution to pyrolysis	0.3	0.3	0.3
Water Evaporation			
n	1.81		
E (kcal/mol)	16.75		
A	1.057 × 10 ⁹		

Table 2. Heat transfer properties for cut tobaccos (Muramatsu et al., 1979)

Heat transfer property	Flue Cured	Burley	Oriental
C_{pv} (cal/g K)	0.41	0.34	0.35
C_{pc} (cal/g K)	0.25	0.25	0.25
C_{pw} (cal/g K)	1.00	1.00	1.00
k_f (cal/sec cm K)	7.56×10^{-4}	7.56×10^{-4}	7.56×10^{-4}
k_g (cal/sec cm K)	1.08×10^{-4}	1.08×10^{-4}	1.08×10^{-4}
ϵ_s, ϵ_i	0.97	0.97	0.97
D_p (cm)	0.0575	0.0395	0.0535
Φ	0.798	0.822	0.849
Q_w (cal/g)	540.0	540.0	540.0
Q_p (cal/g)	0	0	0
k_v (cal/sec cm K)	0.046	0.046	0.046
d (cm)	0.64	0.64	0.65
r (cm)	0.4	0.4	0.4

The apparent kinetic parameters for the pyrolysis steps, the contribution to the pyrolysis of each step, water evaporation and the heat transfer properties of cut tobacco for cigarette are listed in Tables 1 and 2 (Muramatsu et al., 1979). The overall heat source term due to pyrolysis reactions is determined by

$$Q_p = \sum_{i=1}^4 (\Delta H)_i \frac{\partial \rho_i}{\partial t} \quad (8)$$

The thermal analysis of tobacco and its constituents in a helium atmosphere using a differential scanning calorimeter (DSC) suggested that the pyrolysis of α -cellulose in tobacco is endothermic, whereas the pyrolysis of pectin is exothermic (Muramatsu et al., 1979). Since exothermic and endothermic reactions tend to compensate for each other, endothermic peaks observed on DSC curves of tobacco pyrolysis are very small. Therefore, the overall heat source term for tobacco pyrolysis, Q_p , is usually neglected in the calculation.

Model Formulations

An integral method similar to that described by

Goodman (1964) has been used to solve the above differential equations. In this method, temperatures in the pyrolysis zone are assumed to have a given functional form, and this assumed profile is integrated across the region and is required to match the overall mass and energy balance constraints and boundary conditions.

At the burning front, $S(t)$, the temperature is assumed to be constant at 450°C . The distance between the burning front and the penetration boundary, $(S(t) - \delta(t))$ is defined as the pyrolysis zone length. It is also assumed that the heat flow from the burning zone becomes constant when a steady state is reached. Therefore, at the steady state, as a result of a constant heat flow to the pyrolysis zone, the pyrolysis zone length and the linear burn rate become constant.

In the present integral formulation, the temperature profile in the pyrolysis zone is assumed to have a cubic form, i.e.,

$$T = T_o + (T_s - T_o) \left[\frac{x - \delta}{S - \delta} \right]^3 \quad (9)$$

At an unsteady state the position of the penetration boundary, $\delta(t)$, is determined by integrating equation (1) from δ to S using the assumed temperature profile given in Eqn. (9) with the boundary conditions (4) and (5)

$$-\frac{\partial \delta}{\partial t} = \frac{6K_{eff}}{\rho C_p (S - \delta)} - \frac{h(T_s - T_a)}{r \rho C_p (T_s - T_o)} (S - \delta) \quad (10)$$

The smoldering speed or linear burn rate at the moving front, S , is determined by

$$\frac{dS}{dt} = -\frac{\left. \frac{\partial T}{\partial x} \right|_S}{\left. \frac{\partial T}{\partial x} \right|_\delta} \quad (11)$$

$$-\frac{dS}{dt} = \frac{2K_{eff}}{\rho C_p (S - \delta)} - \frac{2h(T_s - T_a)}{3r \rho C_p (T_s - T_o)} (S - \delta) \quad (12)$$

Once the temperature profile is determined for each time step introducing δ and S obtained from Eqns. (10) and (12) into Eqn. (9), the change in density at a certain location is then calculated by Eqns. (6) and (7).

Physical properties which vary with time include overall heat transfer coefficients h and the product of material density and specific heat, ρC_p . In this model, they are determined by

$$h = h' \left(1 + \frac{k_p}{dh} + \frac{K_{eff}}{0.693rh} \right) \quad (13)$$

where h' is the surface heat transfer coefficient, taking the natural convection (McAdams, 1942) and radiation into account, i.e.,

$$h' = 0.00008 \left(\frac{T_s - T_a}{r} \right)^{0.25} + 5.422 \times 10^{-12} \varepsilon_s \left(\frac{T_s + T_a}{2} \right)^3 \quad (14)$$

and

$$\rho C_p = \rho_v C_{pv} + \rho_w C_{pw} + \rho_c C_{pc} \quad (15)$$

The equations developed above were coded in FORTRAN for solution on a computer with a typical time step of 0.01 second. The heat transfer properties are calculated for each time step. Once the positions of two ends of the pyrolysis zone are determined, the temperature and density profiles and hence the instantaneous smoldering speed can be defined.

RESULTS AND DISCUSSION

Figure 2 shows the model predicted history of the linear burn rate, LBR, and the pyrolysis zone length, PZL, for a typical smoldering cigarette. The curves in Figure 2 show that the smoldering process reaches steady state about thirty seconds after ignition. The predicted model and experimental temperature and density profiles in the pyrolysis zone of a smoldering cigarette containing flue-cured tobacco at steady state are shown in Figures 3 and 4. The predicted model and experimental temperature and density profiles for a Burley cigarette are shown in Figures 5 and 6. As can be seen from these figures, the profiles calculated from this model are close to experimental data in the literature (Muramatsu et al., 1979). This model was

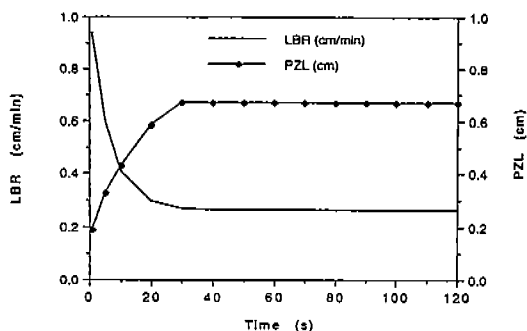


Figure 2. Linear burn rate and pyrolysis zone length for a smoldering cigarette (BY-L1)

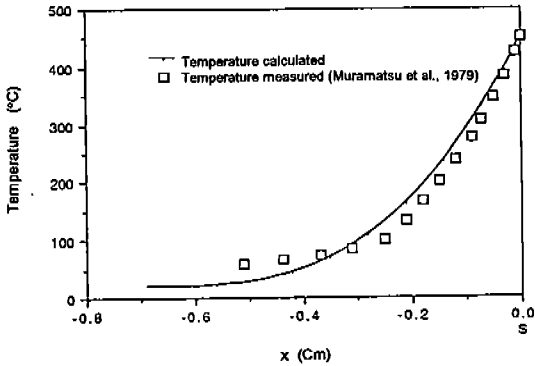


Figure 3. Temperature profile in the pyrolysis zone of a smoldering cigarette (BY-L1) at steady state ; S is the position of burning front

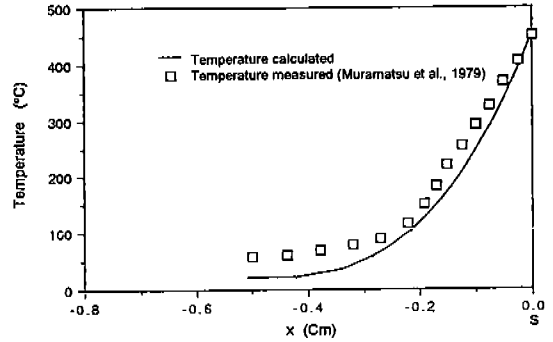


Figure 5. Temperature profile in the pyrolysis zone of a smoldering cigarette (BUR-L1) at steady state ; S is the position of burning front

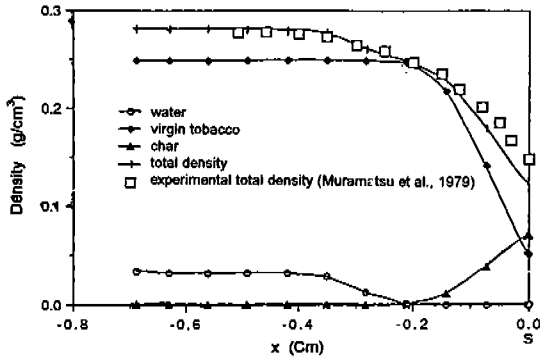


Figure 4. Density profiles in the pyrolysis zone of a smoldering cigarette (BY-L1) at steady state ; S is the position of burning front

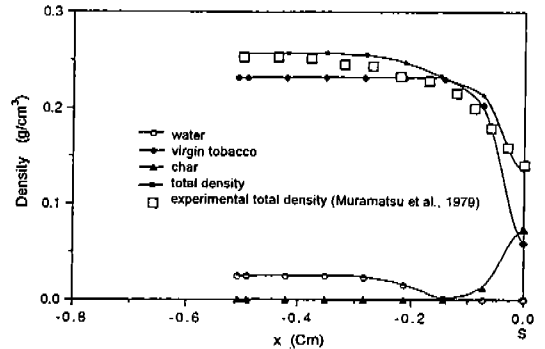


Figure 6. Density profiles in the pyrolysis zone of a smoldering cigarette (BUR-L1) at steady state ; S is the position of burning front

also used to calculate the heat flow from the burning zone to the pyrolysis zone, HF, for different cigarette designs. Table 3 shows the calculated LBR, MBR, and HF of different type of crude tobacco from the proposed model, and it is observed that, for the almost same packing density, ρ_0 , Burley cigarettes show a faster mass burn rates, MBR, than those of others. This may be a result of the high yield of char a_c for Burley tobacco.

Following the above results, the integral model is able to simulate the smoldering processes for flue-cured, burley, and oriental cigarettes. With this model, it is also possible to explore important parameters for a smoldering cigarette, such as blended tobacco composition, thermal properties of cigarette paper, and heat flow from the burning zone to the pyrolysis zone.

A relationship was found when the heat flow to the pyrolysis zone was plotted against the mass burn rate for the above cigarettes. As shown in Figure 7, the heat flow to the pyrolysis zone is almost proportional

Table 3. Physical properties of test tobaccos and calculated linear burn rate and mass burn rate

Cigarette	W_0^* (%)	ρ_0 (g/cm ³)	α_c^{**} (%)	LBR (cm/min)	MBR ^{***} (mg/min)	HF ^{****} (cal/min)
Flue Cured						
BYC2	12.9	0.259	34.1	0.321	41.7	14.47
BYL1	13.4	0.281	32.2	0.266	37.6	13.12
BYL2	12.7	0.295	31.3	0.248	36.8	12.77
Burley						
BURC2	11.9	0.236	40.0	0.455	53.9	18.64
BURL1	10.9	0.256	39.0	0.380	48.9	16.84
BURL2	11.5	0.248	38.9	0.341	42.5	14.73
Oriental						
MTKC2	11.5	0.215	40.9	0.461	50.7	17.00
MTKL1	11.9	0.239	36.1	0.323	38.2	13.57
MTKL2	11.6	0.225	36.1	0.308	39.5	13.77

* w_0 , initial mass fraction moisture ; ** α_c , yield of char ; *** $MBR = LBR \cdot \pi r^2 \cdot \rho_0$; **** $HF = 60 \cdot \pi r^2 \cdot K_{eff} dT/dx|_s$

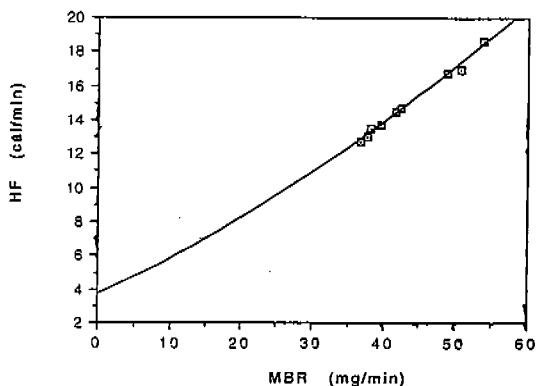


Figure 7. Heat flux (HF) to pyrolysis zone vs. mass burn rate (MBR)

to the mass burn rate for all cigarettes. The curve obtained from the calculations by this model shows the form of the relationship is represented as follows :

$$HF = 8.05 + 0.14 \times MBR + 0.00026 \times MBR^2 \quad (16)$$

which indicates the minimum heat flow required to maintain the smoldering process is about 8 cal/min for these 8 mm diameter cigarettes. The physical meaning of this criterion is that, if the heat transferred to the pyrolysis zone is equal to the heat lost to the environment, there is no energy to raise the material temperature in the pyrolysis zone or to maintain the smoldering speed.

CONCLUSIONS

An integral model of pyrolysis processes in a smoldering cigarette has been proposed to simulate the smoldering process. The model predictions of the smoldering speed and the temperature and density profiles in the pyrolysis zone of smoldering cigarettes were found to be close to the experimental data in the literature. The model allows rapid simulation of the smoldering process on an inexpensive computer and

offers a practical tool for exploring important parameters of the pyrolysis processes in a smoldering cigarette. A minimum in the heat flow to the pyrolysis zone required to maintain the smoldering process was estimated to be 8 cal/min.

요 약

비흡입시 연소하는 담배의 열분해 작용에 관한 수학적 모델을 개발함으로써 담배의 열전달 작용을 수학적으로 해석하였다. 본 모델에서는 비흡입시 연소하는 담배를 열분해 영역과 연소 영역을 약 450℃가 되는 지점을 중심으로 나누어서 고찰하였다. 열전달 현상을 이해하기 위하여 담배의 열분해 과정, 습도의 증발 및 열전달을 유효 열전달 계수를 이용하여 모델을 개발하였다. 담배 표면에서의 열전달은 대류와 복사에 의하여 이루어지며, 주어진 편미분 방정식은 적분법에 의하여 풀어내었다. 여러 다른 종류의 담배에 대한 열분해 영역에서의 온도 및 밀도 분포, 연소 속도 등이 실험치와 비교하여 잘 일치하였으며, 연소 영역에서 열분해 영역으로 필요한 에너지가 약 8cal/min으로 예측되었다.

NOMENCLATURE

A	pre exponential factor (s^{-1})
C_p	specific heat (cal/g K)
d	paper thickness (cm)
D_p	apparent average diameter of pores inside a cigarette (cm)
E	activation energy (kcal/mol)
f	constant in Eqn. (2) (-)
h	convective heat transfer coefficient (cal/cm ² sK)
h_r	radiation heat transfer coefficient (cal/cm ² sK)
h	overall heat transfer coefficient (cal/cm ² sK)
HF	heat transferred to the pyrolysis zone (cal/min)
K_{eff}	effective thermal conductivity of a cigarette column (cal/cm s K)
k_g	thermal conductivity of gas inside a cigarette (cal/cm s K)
k_p	thermal conductivity of paper (cal/cm s K)

k_s	thermal conductivity of tobacco shred inside a cigarette (cal/cm s K)
LBR	linear burn rate, or smoldering speed (cm/min)
MBR	mass burn rate of a smoldering cigarette (mg/min)
n	reaction order (-)
PZL	pyrolysis zone length (cm)
Q_p	heat source term of pyrolysis reactions (cal/cm ³ s)
r	radius of a cigarette (cm)
R	gas constant (cal/mol K)
S	the burning front (cm)
t	time (s)
T	temperature (K)
w	moisture content in tobacco (g H ₂ O/g tobacco)

Greek Letters

ΔH	reaction heat of a pyrolysis reaction (cal/g)
α_c	yield of char (%)
α_i	contribution of the <i>i</i> th pyrolysis step (%)
δ	the penetration boundary (cm)
σ	Steffan-Boltzmann constant (1.355×10^{-12} cal/cm ² s K ⁴)
ϵ_s	radiative emissivity of out surface (-)
ϵ_t	radiative emissivity of tobacco shred inside a cigarette (-)
$\bar{\phi}_t$	total void fraction (-)
ρ	density (g/cm ³)

Subscripts

o	initial value
a	air
c	char
s	out surface
v	virgin tobacco
w	water

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