

Numerical simulation of heat and mass transport phenomena on the flavor generating cellulose porous medium

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A detailed kinetic model is applied to simulate the evaporation-pyrolysis of cellulosic material, a structured isotropic porous medium inside an electrically heated smoking article via ceramic heater. Heat and mass transfer in the flavor-generating cellulosic materials are coupled with moisture evaporation and precursor pyrolysis which are influenced by a strong interaction between transport phenomena and chemical reactions. A two-dimensional transient model is presented in this study to predict the physico-chemical processes of the pyrolysis and evaporation in the porous medium. This model considers pyrolysis of the cellulosic materials as obeying a kinetic scheme based on the functional groups (FG) and described with a single-step multi-reaction model, evaporation of water following a mass-transfer and rate-determined process. Physical processes involve the convection, conduction (including radiation if heat transfer) and the momentum resistivity due to the porous medium. In the study for momentum transfer, the Navier-Stokes equation including viscous loss and inertial loss is compared with a pressure evolution equation obtained through a combination of continuity, state and momentum equations. Moreover, in the case of energy balance, convective and conductive heat transfer rates at the boundaries are compared to figure out the relative importance of the different heat transfer mechanisms. This model is implemented in the commercial computational fluid dynamics (CFD) code, FLUENT, using user-defined-functions (UDFs).

Key words: mathematical model, isotropic porous medium, multi-reaction, pyrolysis, ceramic heater.

Introduction

The flavor-generating cellulosic material used is a mixture of pectine, glycerin, tobacco particles, water and tobacco soluble. The heat from the ceramic heater supplied to the cellulosic material will be sufficient to volatilize, but not to burn, these components. The flavor from the material is produced by applied controlled heat from a ceramic heater. Therefore, the temperature distribution inside a cellulosic material plays an important role in the formation of flavor [1].

As the cellulosic material degrades by the heat from the heat source, it produces a mixture of gases, aerosols, condensable organic components (tar), a reactive char and ash from the char oxidation. Since the majority of smoke constituents are formed by pyrolysis, to reduce the hazardous smoke constituents, physico-chemical processes occurring inside the degrading cellulosic material are studied. It is very desirable to understand product formation and distribution, which depend on smoking conditions and material properties. However, it is extremely difficult to determine the rate of reactions and the mechanisms of formation of individual flavor constituents and their yields.

Many researchers have made significant attempts to

model the process of a burning cellulosic porous medium. In particular, Sandusky [2] and Summerfield et al. [3] have developed a one-dimensional, heterogeneous, time-dependent model of cigarette combustion for the steady-draw case. The model predicts well the burning velocity as a function of air flow rate and gas temperature. A more realistic and detailed model is that of Muramatsu et al. [4]. They developed a one-dimensional, steady-state model for the evaporation-pyrolysis of a smoldering cigarette. However, product distribution is neglected in these studies. More recently, Mitler and Walton [5] developed a two-dimensional, time-dependent, heterogeneous model which used a single-step reaction for pyrolysis of tobacco.

In this study a numerical simulation of transport phenomena and chemical processes in the porous medium is presented to predict the production of volatile species during the pyrolysis in the cellulosic material. The contribution of the different heat transfer mechanisms is investigated on porous medium boundaries.

Mathematical Model

The flavor-generating cellulosic material has a two-dimensional planar geometry where the void volume is initially filled with gas. As thermal degradation takes place the volumes occupied by pyrolysis products, though total volume of the shred is not changed. The numerical simulations of physico-chemical processes in

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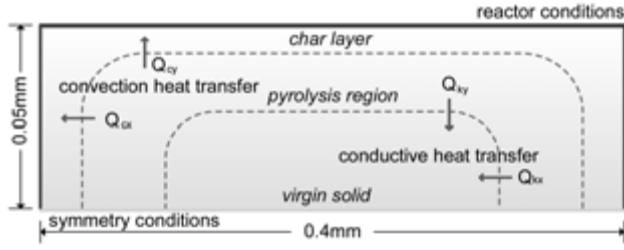


Fig. 1. Schematic of physico-chemical processes in the cellulosic material.

the porous medium are developed using the following assumptions: (1) local thermal equilibrium between solid and gas phases, (2) negligible condensation of tars, (3) internal energy replaced by enthalpy, (4) negligible inertial term in momentum balance. Transport phenomena and chemical process scheme of the model is described in Figure 1. Because of the symmetry of the problem only a half of the cellulosic material is considered.

Transport phenomena

Mass and momentum transport phenomena in the isotropic porous medium account for conduction, and convection. Similarly, heat transport phenomena consist of conduction, convection and also radiation. In the case of momentum conservation, two mathematical models are presented and compared for the accuracy of the solution and the efficiency of numerical computation. The one is a pressure evolution equation considering continuity and state equations with Darcy's law. The other is a standard Navier-Stokes equation including the viscous and inertial resistance in a porous medium.

The continuity equation for total gas-phase species is considered as:

$$\frac{\partial(\epsilon \rho_g)}{\partial t} + \frac{\partial}{\partial x}(\rho_g u) + \frac{\partial}{\partial y}(\rho_g v) = \Omega_g \quad (1)$$

in which the total volumetric generation rate of gaseous material in the cellulosic material is given by:

$$\Omega_g = \sum_{i=1}^{21} \left. \frac{\partial \rho_i}{\partial t} \right|_{pyr} + \left. \frac{\partial \rho_{H_2O}}{\partial t} \right|_{evap} \quad (2)$$

In the case of a pressure evolution equation, momentum balance will be described according to the Darcy's law:

$$u = -\frac{\kappa \partial p}{\mu \partial x}, \quad v = -\frac{\kappa \partial p}{\mu \partial y} \quad (3)$$

and the mixture of gases inside the porous medium behaves according to the ideal gas law:

$$\rho_g = \frac{p M_g}{R T} \quad (4)$$

This equation is substituted into a continuity equation,

then a pressure evolution equation is obtained through a combination of the continuity equation, the state equation and Darcy's law:

$$\frac{\partial}{\partial t} \left(\frac{\epsilon p}{T} \right) = \frac{\partial}{\partial x} \left(\frac{\kappa p}{\mu T} \frac{\partial p}{\partial x} \right) + \frac{\partial}{\partial y} \left(\frac{\kappa p}{\mu T} \frac{\partial p}{\partial y} \right) + \frac{R}{M_g} \Omega_g \quad (5)$$

In the case of a standard Navier-Stokes equation, momentum equations will be solved for obtaining velocity components in the porous medium. The presence of the porous medium will be considered through an additional momentum sink term. The momentum equations are given by the following relations:

$$\begin{aligned} \frac{\partial(\rho_g u)}{\partial t} + \frac{\partial}{\partial x}(\rho_g u u) + \frac{\partial}{\partial y}(\rho_g v u) = & -\frac{\partial p}{\partial x} + \frac{\partial}{\partial x} \left(\mu \frac{\partial u}{\partial x} \right) + \frac{\partial}{\partial y} \left(\mu \frac{\partial u}{\partial y} \right) \\ & - \left(\frac{\mu u}{\kappa} + C \rho_g |u| u \right) \end{aligned} \quad (6)$$

$$\begin{aligned} \frac{\partial(\rho_g v)}{\partial t} + \frac{\partial}{\partial x}(\rho_g u v) + \frac{\partial}{\partial y}(\rho_g v v) = & -\frac{\partial p}{\partial y} + \frac{\partial}{\partial x} \left(\mu \frac{\partial v}{\partial x} \right) + \frac{\partial}{\partial y} \left(\mu \frac{\partial v}{\partial y} \right) \\ & - \left(\frac{\mu v}{\kappa} + C \rho_g |v| v \right) \end{aligned} \quad (7)$$

where, μ is the fluid viscosity, C is an empirical constant governing the magnitude of the inertial term, which is relevant only for turbulent flows [4].

The permeability in both the cases varies with the composition according to a linear dependence:

$$\kappa = \eta \kappa_{unburnt} + (1 - \eta) \kappa_{burnt} \quad (8)$$

where, $\eta = \rho_s / \rho_{s,0}$

The energy conservation can be expressed in terms of total enthalpy, which includes accumulation of enthalpy of the cellulosic material and gas-phase-species, the convective transport of gas-phase species, the conductive transport of heat and the heat release associated with chemical reactions [6].

$$\begin{aligned} \frac{\partial}{\partial t}(\rho_p h_p + \rho_w h_w + \rho_i h_i + \epsilon \rho_g h_g) + \frac{\partial}{\partial x}(\rho_g u h_g) + \frac{\partial}{\partial y}(\rho_g v h_g) \\ = \frac{\partial}{\partial x} \left(k_{eff} \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(k_{eff} \frac{\partial T}{\partial y} \right) - \frac{\partial p}{\partial t} (\Delta H_{pyr}) - \frac{\partial \rho_w}{\partial t} (\Delta H_{evap}) \end{aligned} \quad (9)$$

in which the specific enthalpies of chemical species are defined as:

$$h_p = C_{p,p} T, \quad h_w = C_{p,w} T, \quad h_i = C_{p,i} T, \quad h_g = C_{p,g} T \quad (10)$$

hence the energy balance equation becomes:

$$\begin{aligned} \frac{\partial}{\partial t} \{ (\rho_p C_{p,p} + \rho_w C_{p,w} + \rho_i C_{p,i} + \epsilon \rho_g C_{p,g}) T \} \\ + \frac{\partial}{\partial x}(\rho_g u C_{p,g} T) + \frac{\partial}{\partial y}(\rho_g v C_{p,g} T) \\ = \frac{\partial}{\partial x} \left(k_{eff} \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(k_{eff} \frac{\partial T}{\partial y} \right) - \frac{\partial p}{\partial t} (\Delta H_{pyr}) - \frac{\partial \rho_w}{\partial t} (\Delta H_{evap}) \end{aligned} \quad (11)$$

The effective thermal conductivity, k_{eff} in the porous medium can be represented by the following equation [7]:

$$k_{eff} = (1 - \varepsilon^{2/3})k_s + \varepsilon^{1/3} \left(1 + \frac{2}{3} h_r D_p / k_g \right) k_g \quad (12)$$

where, $h_r = 4 \times \sigma \varepsilon_i T^3$

In this study fourteen different gaseous species will be considered. They are air, water vapor, tars, carbon dioxide, carbon monoxide, nicotine etc. Separate transport equations of the following form will be respectively solved for the mass fraction of all species but air:

$$\begin{aligned} & \frac{\partial(\varepsilon \rho_g Y_i)}{\partial t} + \frac{\partial(\rho_g u Y_i)}{\partial x} + \frac{\partial(\rho_g v Y_i)}{\partial y} \\ & = \frac{\partial(\varepsilon \rho_g D_e \frac{\partial Y_i}{\partial x})}{\partial x} + \frac{\partial(\varepsilon \rho_g D_e \frac{\partial Y_i}{\partial y})}{\partial y} + \Omega_i \end{aligned} \quad (13)$$

where, Y_i is mass fraction and Ω_i is source or sink term for species i .

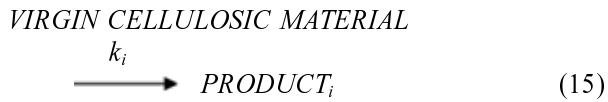
Air mass fraction is calculated by the following relation:

$$Y_{air} = \left(1 - \sum_{i=1}^{14} Y_i \right) \quad (14)$$

The molecular weight of the gaseous mixture is assumed to be constant, 0.029 kg/m^3 and an incompressible ideal gas law is used for calculating density.

Cellulosic material pyrolysis

Pyrolysis can be described according to a one-step, multi-reaction scheme:



The virgin cellulosic material is gradually consumed by pyrolysis. The rate of pyrolysis is equal to the sum of forty-eight different pyrolysis reactions.

The kinetics is modeled by a uni-molecular first-order reaction rate equation with a Gaussian distribution of activation energies [8] which can be expressed as:

$$\frac{dV_i}{dt} = \int_{-\infty}^{\infty} A_i \exp\left(-\frac{E_i}{RT}\right) \frac{\exp\left[-\frac{1}{2} \left(\frac{E_{m,i} - E_i}{\sigma_i}\right)^2\right]}{\sigma_i \sqrt{2\pi}} dE_i (V_i^* - V_i) \quad (16)$$

where, V_i is the yield of product i , and A_i , E_i and σ_i are the pre-exponential factors, activation energy, and the width of the Gaussian distribution, respectively. The quantity V_i^* is the ultimate attainable yield, that is, the yield at high temperatures for long residence times and E_m is the mean activation energy.

The conversion of precursors can be represented by the following reactions:

$$\frac{\partial \rho_p}{\partial t} = -\rho_{s,0} \times \sum_{i=1}^{21} \frac{dV_i}{dt} \quad (17)$$

This model based on kinetic parameters resulting from Advanced Fuel Research (AFR)'s Functional Group (FG) model for pyrolysis in the cellulosic material, correlates with the available TG-FTIR data. The kinetic parameters and physical properties of the cellulosic material are given in Tables 1-2.

Water evaporation

As the temperature of the material increases, the water content in the cellulosic material will be evaporated. A detailed description of the formulation of the water evaporation can be found from the work done by

Table 1. Physical properties and initial values for the cellulosic material

	parameter	unit	value
Physical properties	$C_{p,g}$	$J/kg \cdot K$	1096.0
	$C_{p,p}$		1715.0
	$C_{p,w}$		4182.0
	$C_{p,i}$		1096.0
	k_g	$W/m \cdot K$	0.0452
	k_s		0.3160
	$K_{unburnt}$	m^2	9.869E-15
	K_{burnt}		9.869E-14
	μ	$kg/m \cdot s$	3.0E-5
	D_p	m	5.75E-4
	σ_s	$W/m^2 \cdot K^4$	5.67E-8
	ε_i	—	0.97
	C	—	0
Water evaporation parameters	N_a	m^2/m^3	6870.0
	α	$kg/m^2 \cdot s$	1.345E+8
	θ	—	8430.0
	β	—	1.81
	a	—	5.12
	b	—	8.46
	c	—	14.16
Heat of reaction	ΔH_{evap}	J/kg	2.2572E+6
	ΔH_{pyr}		0
Initial values	ρ_p	kg/m^3	830.5
	ρ_w		126.5
	ρ_i		22.0
	ε	—	0.3

Table 2. Kinetic parameters and yield of the cellulosic material

Species	A [s ⁻¹]	E _m /R [K]	σ/R [K]	V* [wt.% daf]
Carbon Dioxide	5.0E+11	18598.0	1500.0	12.17
	4.4E+18	34042.0	1500.0	2.10
	4.6E+13	33837.0	1000.0	1.95
Carbon Monoxide	5.2E+11	18598.0	1500.0	1.75
	2.8E+11	35042.0	1500.0	0.43
	1.4E+11	29429.0	1000.0	3.50
Water	5.2E+11	18598.0	1500.0	9.69
	4.4E+18	35042.0	1500.0	0.20
Methane	6.5E+11	25070.0	1000.0	0.80
Tar	5.2E+11	18598.0	3500.0	45.20
	4.4E+11	35042.0	3000.0	1.50
Ethylene	6.5E+11	25070.0	500.0	0.25
Methanol	5.2E+11	18598.0	500.0	0.35
Hydrogen Cyanide	4.4E+11	34042.0	5000.0	0.56
Ammonia	5.0E+11	15375.0	1500.0	0.00
	5.2E+11	18598.0	3000.0	0.55
Formaldehyde	5.2E+11	18598.0	500.0	0.18
Formic acid	5.2E+11	18598.0	500.0	0.60
Acetaldehyde	5.2E+11	18598.0	500.0	2.60
Acetic acid	5.2E+11	18598.0	500.0	1.50
Nicotine	5.2E+11	15375.0	1500.0	2.20

Muramatsu et al. [4].

The evaporation rate of water from tobacco can be expressed by the empirical equation:

$$\frac{\partial \rho_w}{\partial t} = -N_a \alpha \exp\left(-\frac{\theta}{T}\right)(w - w_{eq})^\beta = (\rho_{s,0} - \rho_{w,0}) \frac{\partial w}{\partial t} \quad (18)$$

where, N_a is the total surface area of tobacco particles per unit volume of a cigarette, θ is an experimental constant, and w_{eq} is related to the water vapor pressure, p_w by:

$$w_{eq} = \frac{(p_w/p_{ws})}{a + b(p_w/p_{ws}) - c(p_w/p_{ws})^2} \quad (19)$$

The saturated vapor pressure of water p_{ws} can be expressed by Calingaert and Davis's equation [9] as follows;

$$\log p_{ws[mmHg]} = 7.991 - \frac{1687}{T - 43} \quad (20)$$

In this model, the transport equation for water vapor mass fraction is solved as follows:

$$\frac{\partial(\epsilon \rho_g Y_{H_2O})}{\partial t} + \frac{\partial(\rho_g u Y_{H_2O})}{\partial x} + \frac{\partial(\rho_g v Y_{H_2O})}{\partial y} = \frac{\partial}{\partial x} \left(\epsilon \rho_g D_e \frac{\partial Y_{H_2O}}{\partial x} \right)$$

$$+ \frac{\partial}{\partial y} \left(\epsilon \rho_g D_e \frac{\partial Y_{H_2O}}{\partial y} \right) + \frac{\partial \rho_{H_2O}}{\partial t} \Big|_{pyr} - \frac{\partial \rho_w}{\partial t} \Big|_{evap} \quad (21)$$

The kinetic data and associated parameters of Muramatsu et al. [4], indicated in Table 1 are used.

Initial and Boundary Conditions

Initially, the cellulosic material is set at ambient conditions, with temperature and system pressure are at room conditions and all solid components in the cellulosic material have initial values as listed in Table 1.

$$T = T_0, \rho_s = \rho_{s0}, \rho_c = \rho_{c0}, V_i = 0 \quad (22)$$

At the solid surface, the boundary condition on energy balance is specified by the pyrolysis environment. For this simulation, the surface of the solid is taken to be linearly heated from the ceramic:

$$T(t) = T_0 + mt \quad \text{where, } m \text{ is heating rate.} \quad (23)$$

the spatial conditions at the centerline are determined by symmetry:

$$\frac{\partial T}{\partial y} = 0, \frac{\partial V_i}{\partial y} = 0 \quad (24)$$

and outlet conditions for gaseous species are used.

Heat analysis

In order to evaluate the role played by the different heat transfer mechanisms during the physico-chemical process, the enthalpy equation is calculated over the whole domain [10]:

$$H_i = Q_{kx} - Q_{cx} + Q_{ky} - Q_{cy} + Q_r \quad (25)$$

where, Q_{kx} and Q_{ky} are the contributions due to conduction, Q_{cx} and Q_{cy} are those due to convection and Q_r is the heat needed for the reactions to occur in the cellulosic material. They can be described as follows [10]:

$$H_i = \int_0^{\tau_x} \int_0^{\tau_y} \left((\rho_p C_{p,p} + \rho_w C_{p,w} + \rho_i C_{p,i} + \epsilon \rho_g C_{p,g}) \frac{\partial T}{\partial t} \right) dy dx \quad (26)$$

$$Q_{kx} = \int_0^{\tau_y} \left(k_{eff} \frac{\partial T}{\partial x} \right)_{x=\tau_x} dy, \quad Q_{ky} = \int_0^{\tau_x} \left(k_{eff} \frac{\partial T}{\partial y} \right)_{y=\tau_y} dx \quad (27)$$

$$Q_{cx} = \int_0^{\tau_x} (u C_{p,g} \rho_g (T - T_{ambient}))_{x=\tau_x} dy,$$

$$Q_{cy} = \int_0^{\tau_y} (v C_{p,g} \rho_g (T - T_{ambient}))_{y=\tau_y} dx \quad (28)$$

$$Q_r = \int_0^{\tau_x} \int_0^{\tau_y} \left(-\frac{\partial \rho_p}{\partial t} (\Delta H_{pyr}) - \frac{\partial \rho_w}{\partial t} (\Delta H_{evap}) \right) dy dx \quad (29)$$

Model Implementation

The implementation of the models described above was done in a commercial computational fluid dynamics (CFD) code, FLUENT 6.0. All equations were solved sequentially and iteratively in keeping with the FLUENT algorithms. Most of the processes occurring inside the cellulosic material cannot be simulated using the standard version of FLUENT software. Therefore, the equations described above are incorporated with the user-defined-functions (UDFs) available in FLUENT by solving new sets of scalar equations. The UDFs are written in the C programming language.

Results and Discussions

Mathematical models are presented for pyrolysis of a cellulosic porous medium. The product yields and evolution of the main variables are calculated for high and low heating rates of 500 K/s and 15 K/s with a final pyrolysis temperature of 758 K. Due to the symmetry condition, the half of the porous medium is shown in Figure 1. The kinetic parameters and physical properties are listed in Table 1 and 2. All value used in this study will be specified in SI units. Figure 2 shows overpressure profiles computed by the Navier-Stokes equation and by the pressure evolution equation. Both profiles show a nearly equal accuracy of solution but the convergent time of the pressure evolution equation takes five times longer than for the Navier-Stokes equation. Hence all results in this study have been computed by Navier-Stokes equation.

Pyrolysis precursor starts to decompose as the temperature at the boundary reaches about 400 K. Then three main regions are present in the cellulosic material: a virgin cellulose region, a pyrolysis region and a char region for times from 0.2 to 0.9 s at the high heating rate and from 6.7 to 30.5 s at the low heating rate. Three regions exist in the cellulosic material during pyrolysis: a virgin cellulose region, a pyrolysis region

and a char region. Initially the whole domain is virgin cellulose region. The pyrolysis region is developed from the heating boundary wall when the temperature of the heating wall reaches 400 K. When the temperature at the symmetry condition wall is above 400 K, decomposition occurs in the whole heating zone so that virgin cellulose does not exist in heating zone. Then the char region appears where pyrolysis of the precursor is completed.

Figure 3 shows temporal changes of area-weighted averaged temperature and overpressure in the whole domain. As reported by Muramatsu et al. [4] and Valverde [11], volatiles in the cellulose could be divided into several non interacting mass-loss events clearly shown in Figure 3. Figure 4 shows area-weighted gas velocity magnitude. Velocities increase with generation of pyrolysis products and fall off with a decrease the amount of virgin solid. Flow is developed gradually as the void fraction is increasing and maximum velocities are about 0.10 m/s and 0.0037 m/s at high and low heating rates respectively. As expected the overpressure and velocity in the shred at the high heating rate are much larger than those at the low heating rate because of shorter reaction time.

The dynamics of weight loss of pyrolysis precursor

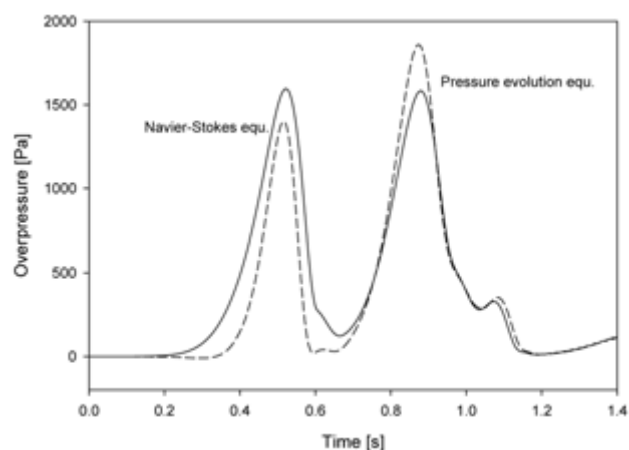


Fig. 2. Over pressure profiles for the pressure evolution equation and Navier-Stokes equation with ideal gas law at puffing condition (at heating rate $m=500$ K/s).

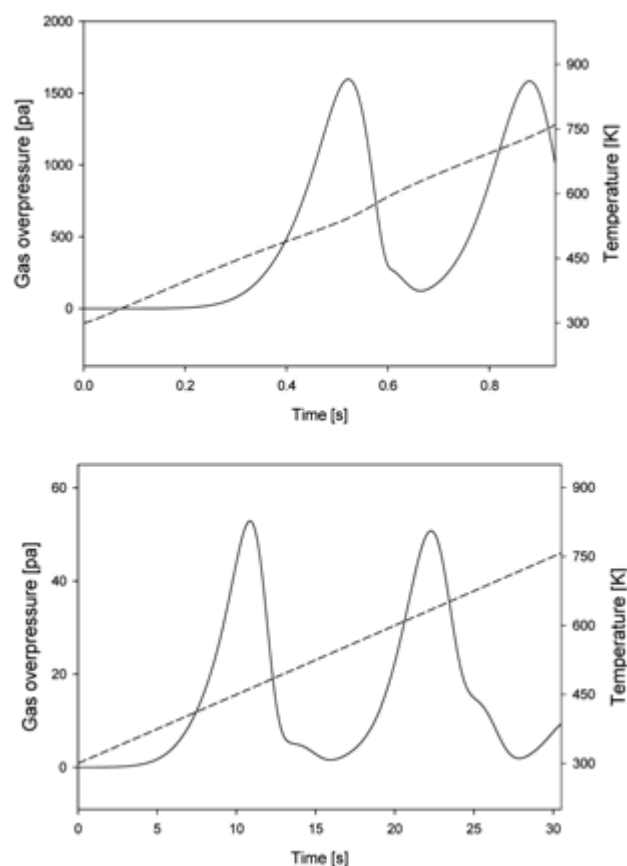


Fig. 3. Overpressure (solid lines) and temperature change profiles (dashed lines) in the cellulosic material as a function of time at a heating rate $m=500$ K/s (above), and $m=15$ K/s (below). The final temperatures are 759.5 K and 757.4 K respectively.

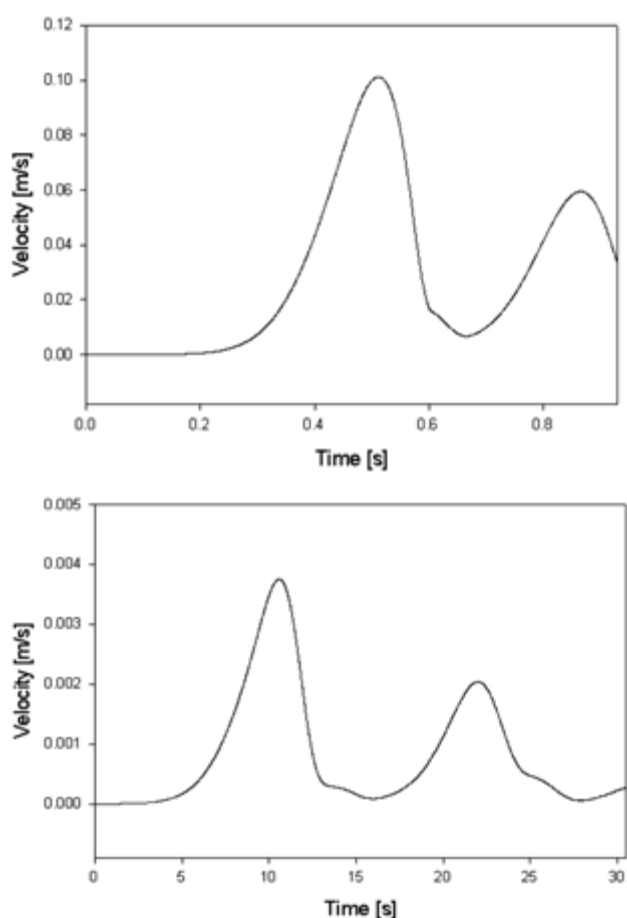


Fig. 4. Dynamics of area-weighted average gas velocity at a high heating rate, $m=500$ K/s, final temperature, $T_p=759.5$ (above) and a low heating rate, $m=15$ K/s, final temperature, $T_p=757.4$ (below).

and its rate at two different heating rates are shown in Figure 5. An initial period of fast weight loss is followed by a slow weight loss for both conditions.

Figures 6 and 7 show how each gas species concentration varied with temperature at different heating rates, $m=500$ K/s and $m=15$ K/s respectively. In particular, the concentration of water gas is obtained from the precursor pyrolysis and evaporation which occurred around 350 K as shown. This clearly shows that each species reacts in its own temperature range.

It is predicted that the degradation of the pyrolysis precursor starts above 400 K at 0.2 s for a high heating rate and at 6.7 s for the low heating rate. As the temperature rises, the overpressure increases up to 0.5 s as shown in Figure 3. The pyrolysis rate has the highest value at 0.5 s in Figure 5. Therefore, overpressure and gas velocity have the highest value at 0.5 s.

In Figure 8 the area-weighted average solid density and porosity change are shown as a function of time. The pyrolysis precursor degraded from 743.6 kg/m^3 to 193.6 kg/m^3 and the water density change from 126.5 kg/m^3 to 0.15 kg/m^3 at the high heating rate. At the low heating rate the pyrolysis precursor degraded from 743.6 kg/m^3 to 164.0 kg/m^3 and the water density change

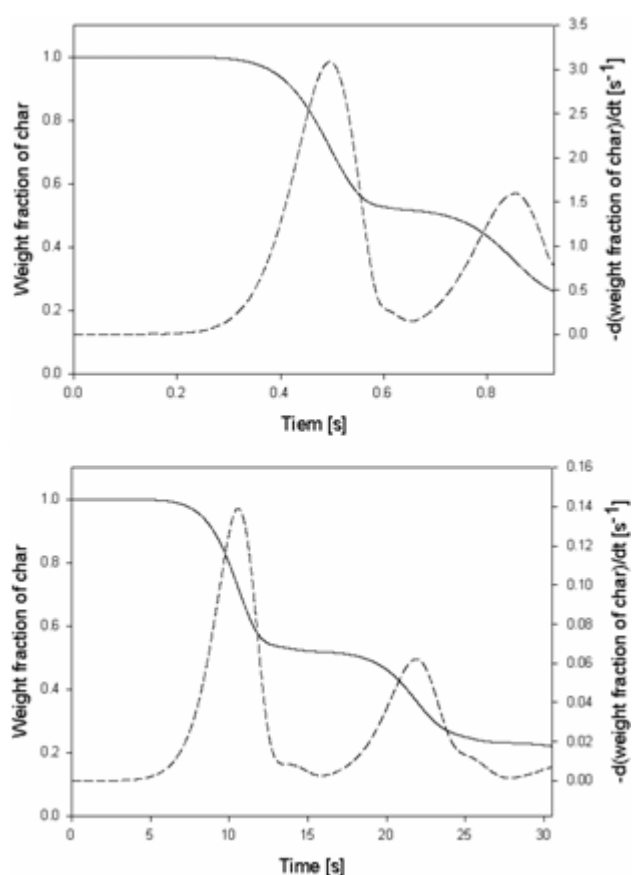


Fig. 5. Weight fraction and time derivative of char as a function of pyrolysis time at a high heating rate, $m=500$ K/s, final temperature, $T_p=759.5$ (above) and a low heating rate, $m=15$ K/s, final temperature, $T_p=757.4$ (below).

from 126.5 kg/m^3 to 0.001 kg/m^3 .

In Figure 9 the relative contributions of the different heat transfer mechanisms are plotted. The contribution of conductive heat transfer (Q_k) in the y-direction is predicted to be always larger than in the x-direction and both of them decrease as time increases. The length of the porous medium which is one hundred times shorter than the width, restricts in gas flow in the x-direction, and convective heat transfer (Q_c) is larger in the y-direction than in the x-direction. Figure 10 shows the overall enthalpy of reaction (H_i) and the heat needed for the reaction to occur (Q_r). Q_r has negative values due to the fact that pyrolysis of tobacco is an endothermic reaction in the whole domain so to use the same scale $-Q_r$ is plotted.

Conclusions

A two-dimensional, transient model presented in this study has predicted the heat and mass transport phenomena during the pyrolysis and evaporation in a cellulosic material. In this model, a kinetic scheme based on the functional groups (FG) and described with a single-step multi-reaction model accounts for the complex

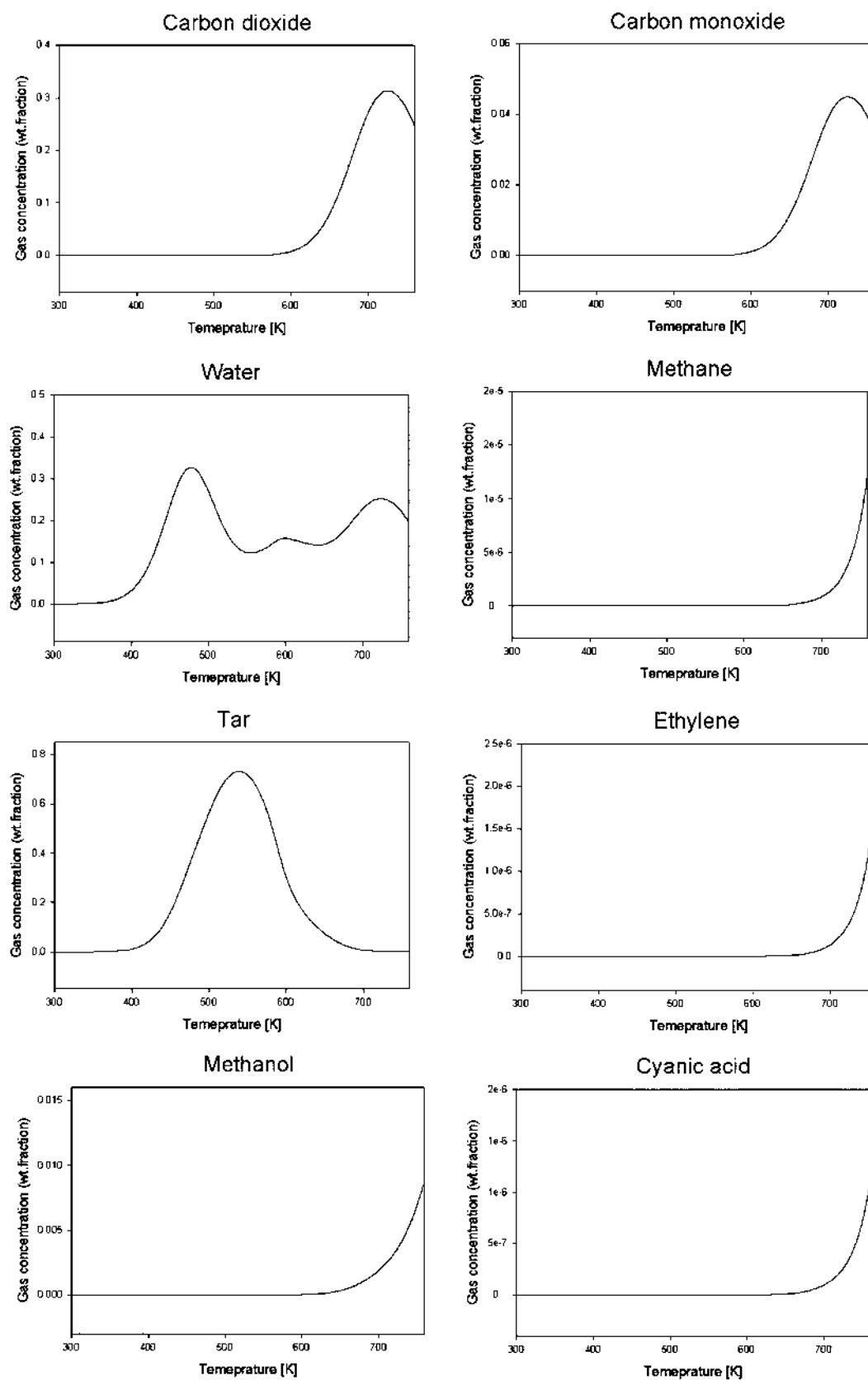


Fig. 6. Gas concentration for the degrading cellulosic material at a high heating rate, $m=500$ K/s, final temperature, $T_p=759.5$.

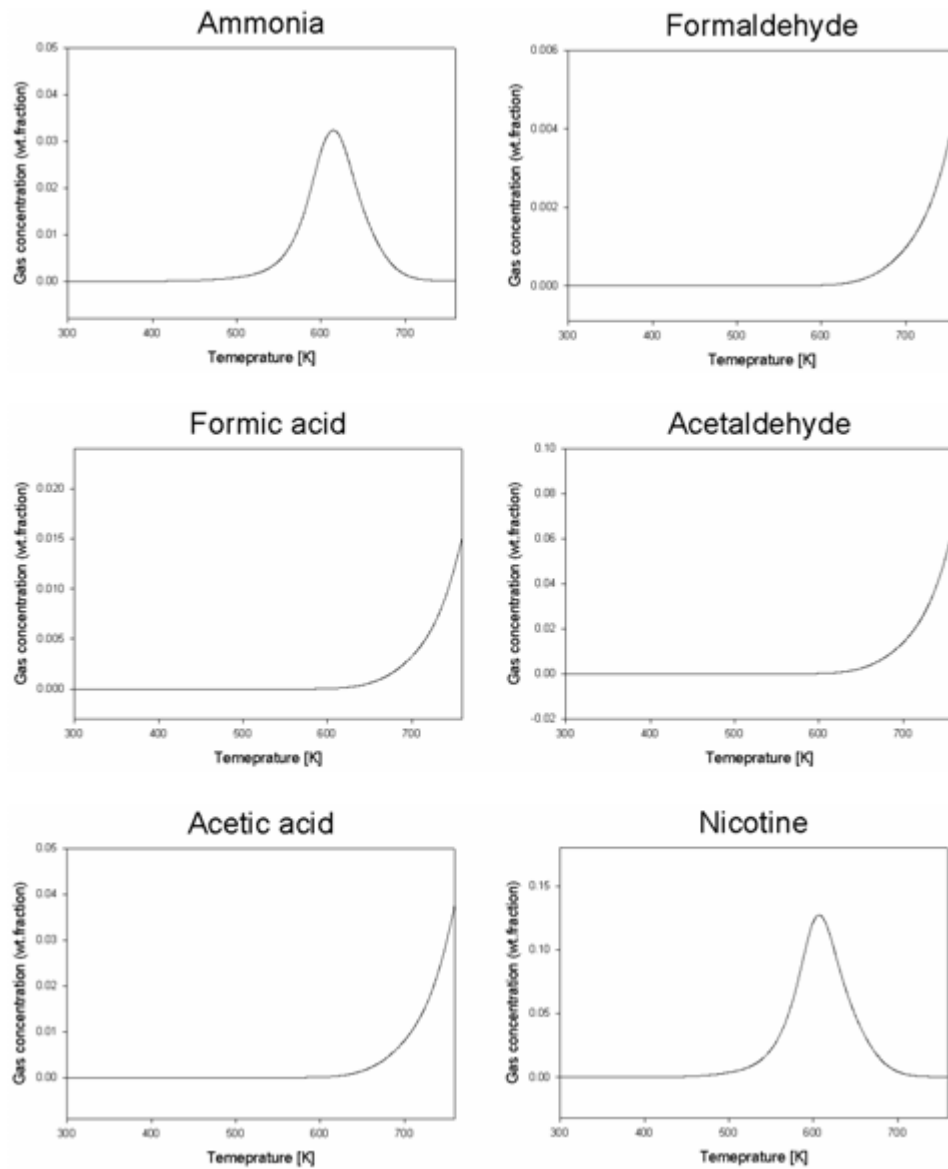


Fig. 6. Continued.

processes of pyrolysis. For the momentum conservation equation, the Navier-Stokes equation is compared with the pressure evolution equation through overpressure profiles. The Navier-Stokes equation predicts a similar overpressure to the pressure, however, it is more efficient in numerical convergent time. In the case of the heat transfer, convective and conductive heat transfer rates at the boundaries are compared through heat analysis to predict the relative importance of the different heat transfer mechanisms.

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Nomenclature

A	pre-exponential factor for Gaussian activation energy model [1/s]
a, b, c	experimental constants for equilibrium water content
C_p	specific heat [J/kg·K]
D_e	effective diffusion coefficient [J/kg·K]
D_p	pore diameter [m]
E_i	activation energy of species i [J/mole]
H	specific enthalpy [J/kg]
h_c	free convective heat-transfer coefficient [W/m ² ·K]
k	thermal conductivity [W/m·K]
k_{eff}	effective thermal conductivity [W/m·K]
k_{gc}	mass transfer coefficient [m/s]
M	molecular weight [kg/mole]
N_a	total surface area of tobacco particle per unit volume [m ² /m ³]

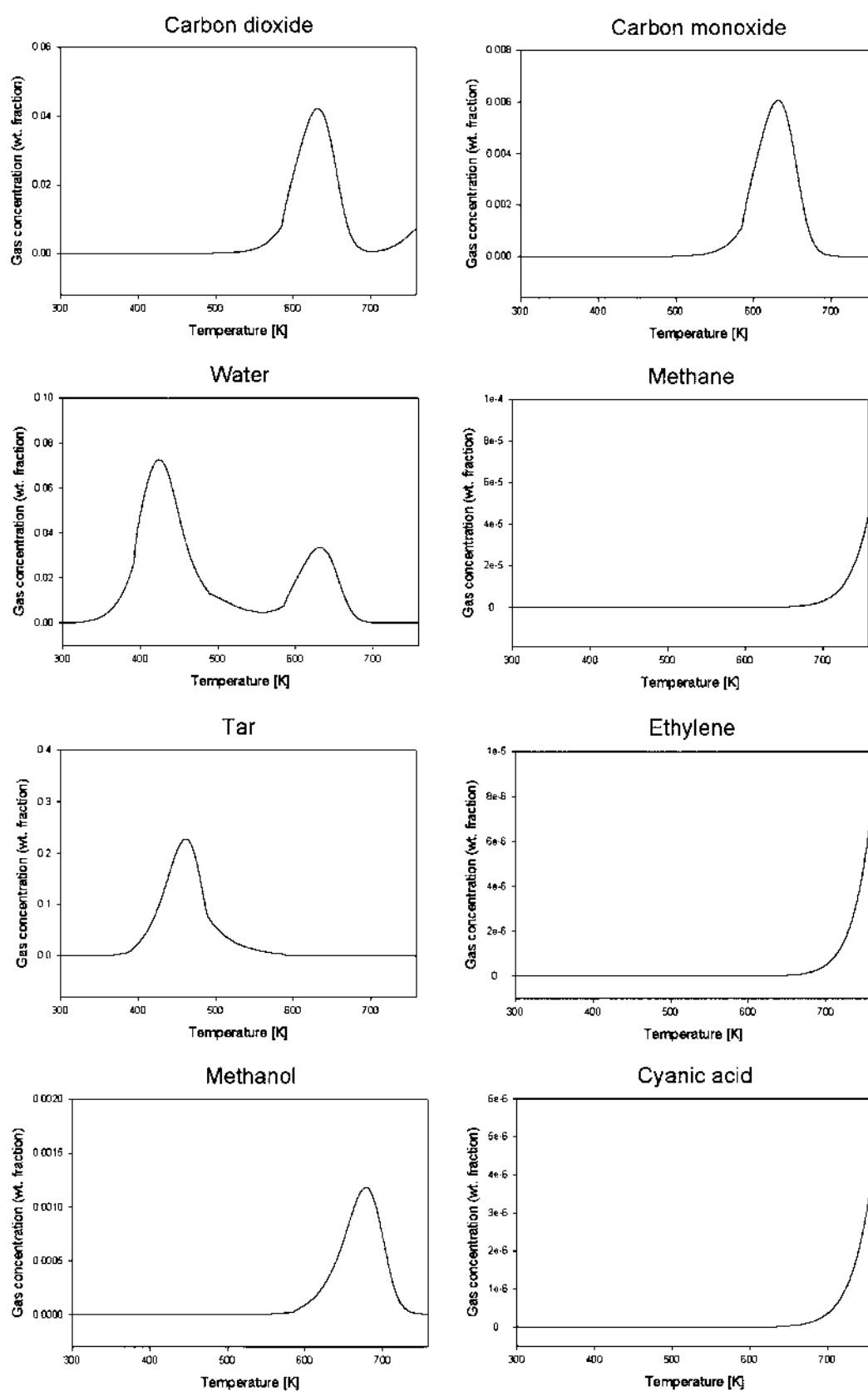


Fig. 7. Gas concentration for the degrading cellulosic material at a low heating rate, $m=15$ K/s, final temperature, $T_p=757.4$.

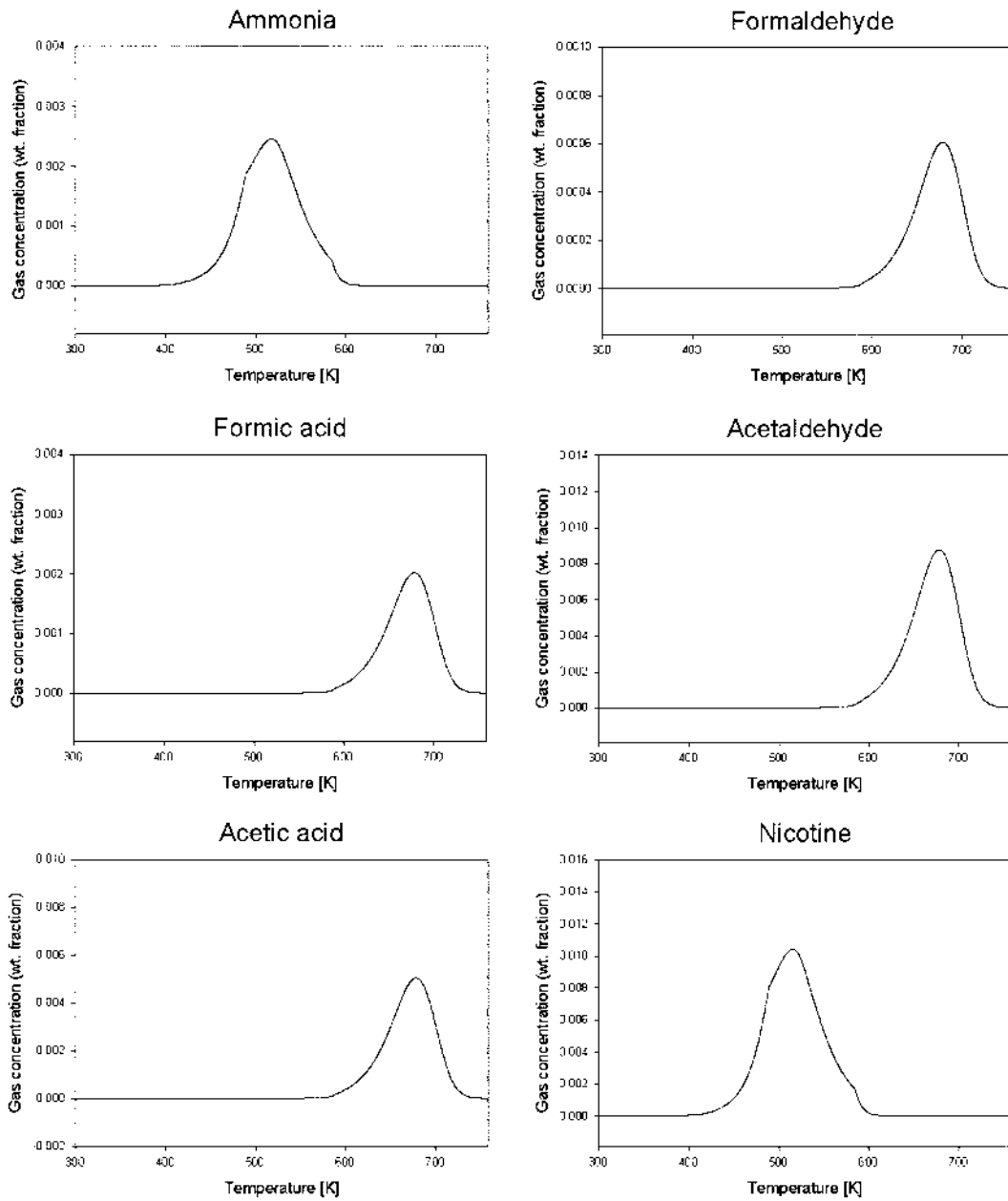


Fig. 7. Continued.

p	pressure [Pa]
p_w	water vapor pressure [Pa]
p_{ws}	saturated water vapor pressure [mmHg]
R	universal gas constant [J/mole·K]
T	temperature [K]
t	time (s)
u	x-component of velocity vector [m/s]
V_i	product yield of species i [–]
V_i^*	ultimate yield of species i [–]
v	y-component of velocity vector [m/s]
w	water content [kg water/kg virgin cellulosic material]
w_{eq}	equilibrium water content [kg water/kg virgin cellulosic material]
t	time (s)

Greek Symbols

α	experiment constant for water evaporation rate [kg/m ² ·s]
β	experiment constant for water evaporation rate [–]
ε	porosity or void fraction [–]
ε_s	surface radiative emissivity [–]
η	ratio of the instantaneous to the initial value of the cellulosic mass [–]
θ	experiment constant for water evaporation rate [–]
κ	permeability [m ²]
μ	viscosity [kg/m·s]
ρ	density [kg/m ³]

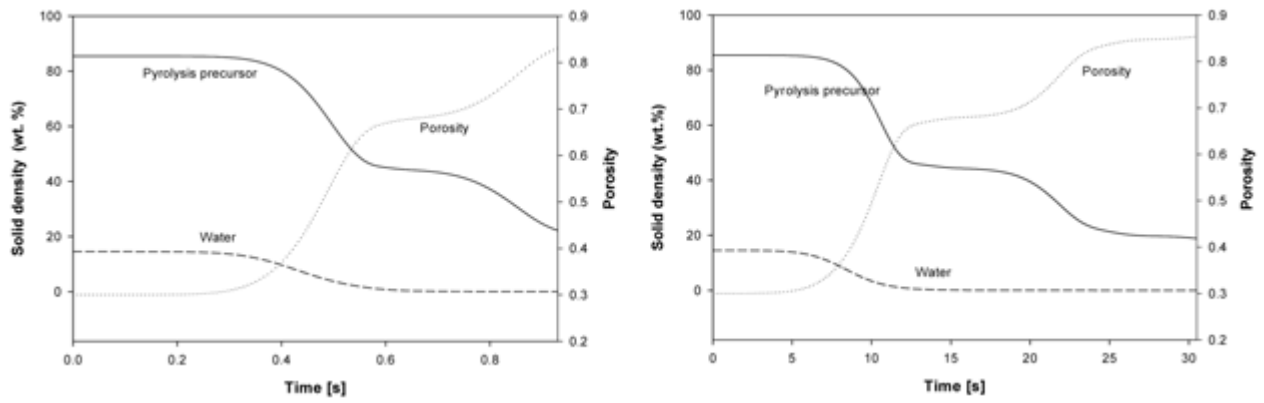


Fig. 8. Solid density and porosity change profiles in the cellulosic material as a function of time at a high heating rate, $m=500$ K, final temperature, $T_p=759.5$ K (above) and a low heating rate, $m=15$ K/s, $T_p=757.4$ K (below).

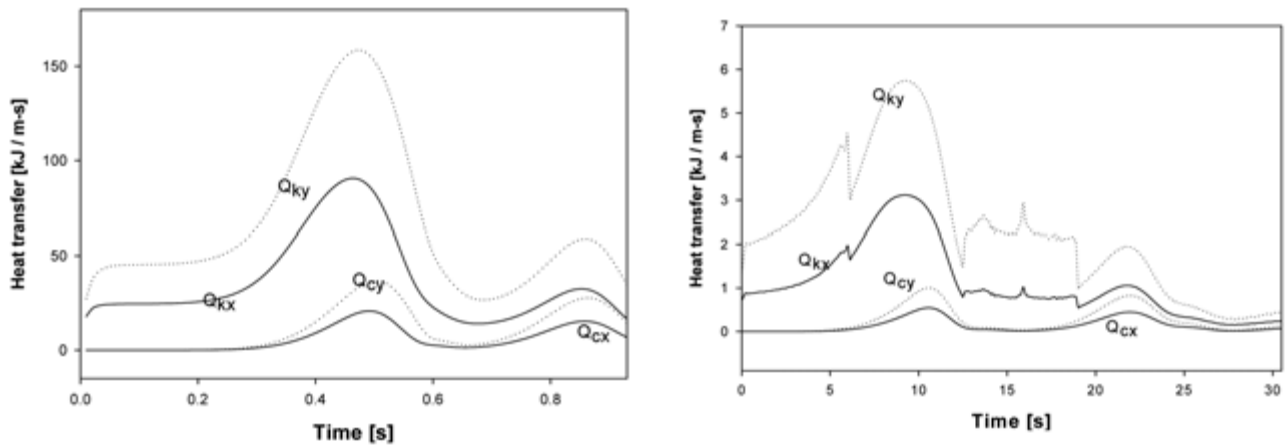


Fig. 9. Heat transfer rates at boundaries and temperature in the cellulosic material at a high heating rate, $m=500$ K, final temperature, $T_p=759.5$ K (above) and a low heating rate, $m=15$ K/s, $T_p=757.4$ K (below).

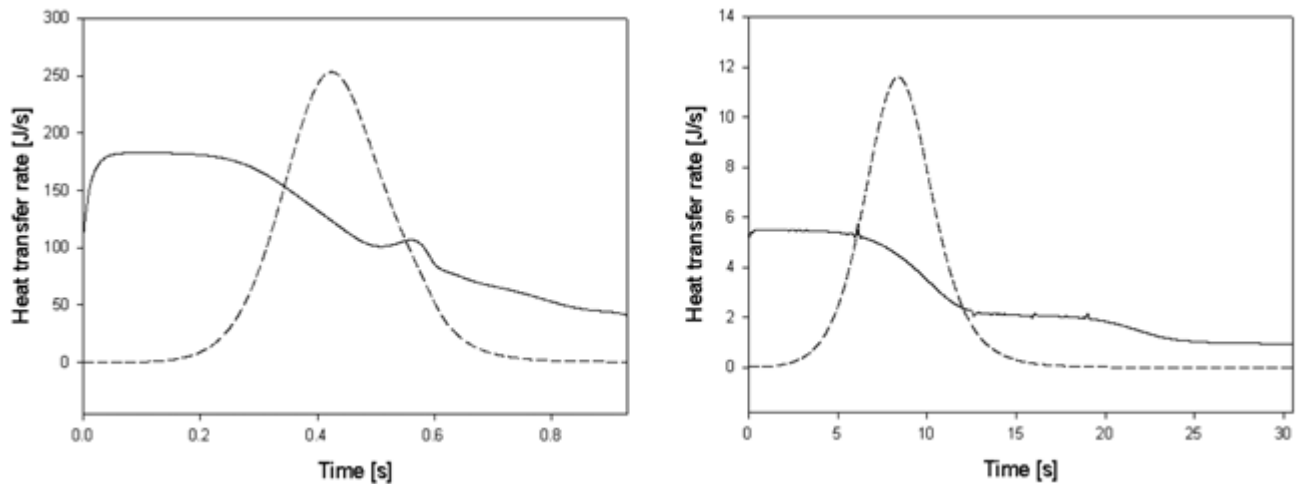


Fig. 10. Enthalpy (solid line) and the heat needed for the reactions to occur (dashed line) at a high heating rate, $m=500$ K, final temperature, $T_p=759.5$ K (above) and a low heating rate, $m=15$ K/s, $T_p=757.4$ K (below).

σ Stefan-Boltzmann constant [5.67×10^{-8} W/m²·K⁴]
 σ_i width of the Gaussian distribution for species i [J/mole]

Subscripts
 $_{eff}$ effective
 $_{evap}$ evaporation reaction
 $_i$ inert

H_2O	water vapor
p	pyrolysis precursor
pyr	pyrolysis reaction
w	water
0	initial value

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