A model to predict carbon monoxide of woods under external heat flux –
Part I: Theory

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Abstract
Carbon monoxide (CO) is always a significant judgment criterion in fire risk evaluation. Therefore, a model to predict CO of woods under external heat flux was developed in this study. To improve modeling accuracy, fire processes such as water evaporation, volume shrinkage, liquid and gas transport inside wood slab were considered in this model. Three reactions such as water evaporation, oxidation of virgin wood and char were included. For oxidation reactions of virgin wood and char, CO yields of each reaction were considered constant even under various external heat fluxes. This will expand the applications of this model as limited experimental data of CO yields under different external heat flux. Temperature and moisture dependent thermal properties were used for modeling input.

Comparisons between experiment and modeling showed that CO production of woods under different external heat flux can be well predicted by this model. This model intends to provide a practical tool to predict toxic gases of combustible materials under fire conditions.

This two-part study contains theory, validation and application of a mathematical model. This paper serves as a precursor for Part II: Validation and application of a model to predict CO of woods under external heat flux.

Keywords: Wood; Carbon monoxide; Toxic gas; Water evaporation; Shrinkage; Mass transport

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>pre-exponential factor (1/s)</td>
</tr>
<tr>
<td>$C_p$</td>
<td>specific heat capacity (J/kg K)</td>
</tr>
<tr>
<td>$D$</td>
<td>diffusion coefficient (m$^2$/s)</td>
</tr>
<tr>
<td>$E$</td>
<td>activation energy of reaction (J/mol)</td>
</tr>
<tr>
<td>$h$</td>
<td>specific enthalpy (J/kg)</td>
</tr>
<tr>
<td>$k$</td>
<td>rate of reaction (1/s)</td>
</tr>
<tr>
<td>$L$</td>
<td>thickness of specimen (m)</td>
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<tr>
<td>$m$</td>
<td>mass (kg)</td>
</tr>
<tr>
<td>$n$</td>
<td>number of grids</td>
</tr>
<tr>
<td>$N$</td>
<td>number of species or reactions</td>
</tr>
<tr>
<td>$\beta_v$</td>
<td>volume change coefficient (-)</td>
</tr>
<tr>
<td>$\Delta h$</td>
<td>heat of reaction (J/kg)</td>
</tr>
<tr>
<td>$\gamma^*$</td>
<td>gas yield in Eq. (4b) (kg/kg)</td>
</tr>
<tr>
<td>$\phi^*$</td>
<td>gas production rate in Eq. (4b) (kg/s)</td>
</tr>
<tr>
<td>$\phi^*$</td>
<td>gas production rate in Eq. (4c) (kg/s)</td>
</tr>
</tbody>
</table>

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1. Introduction

Carbon monoxide (CO) in enclosure fires is the most important factor in fire risk evaluation. Roughly two-thirds of all deaths resulting from enclosure fires can be attributed to the presence of CO, which is known to be the dominant toxicant in fire deaths [1]. Carbon monoxide is always a key issue of fire research, playing a very important role in Performance-Based Design (PBD) of buildings. Occupational Safety and Health Administration (OSHA) set exposure limits of CO at 35 ppm, and the exposure to higher concentrations can be detrimental to human health and possibly result in death [2].

Few models have considered CO of woods under external heat flux. He and Behrendt [3] developed a method to simulate combustion of large biomass particle. Gas volatiles were predicted by pyrolysis reaction of virgin wood. Lautenberger and Fernandez-Pello [4] used Gpyro to simulate pyrolysis of white pine slab irradiated under non-flaming conditions. Gas volatiles were predicted by gaseous species yield in heterogeneous and homogeneous reactions.

Some models used multiple-steps reactions to predict CO of combustible materials under external heat flux. Haseli et al. [5], for example, used more than 10 reactions to predict CO of woody biomass particle. One of the reactions is the oxidation of CO. A model even used 58 reactions with 16 species to describe combustion of methane. This is a level of complexity that is undesirable for a practical fire model as tracking 16 species would greatly increase the computational resources required and many of the reactions would occur at length scales never encountered in a typical large-scale simulation [6].

As modeling results are very sensitive to oxygen, applications of multiple-steps reactions are limited because of the difficulty in describing oxygen level inside wood slab. Weng et al. [7] assumed a linear function to describe partial oxygen pressure from surface to char front. Gupta et al. [8] assumed that carbon oxidation occurs at the surface of the char particle. He et al. [9] considered an oxidation front between ash layer and char layer in natural downward smoldering of piled char powder.

Under the situation mentioned above, challenges still exist to predict CO of woods under external heat flux. These challenges are summarized as follows: (1) modeling results from previous models haven’t been validated by experiments; (2) applications of multiple-steps reactions are limited as the difficulty in describing oxygen level inside wood slab; (3) CO yields are sensitive to external heat flux as CO release rate is highly dependent on ignition and flameout time [10,11]; (4) experiments [2, 12-16] have obtained a broad range of CO yields, resulting in various modeling results; (5) some models have ignored gas transport inside wood slab, indicating that CO is assumed to exhaust to the air immediately after production; and (6) oxidation reaction of wood char is sometimes ignored.

An one-dimensional model to predict CO of woods under external heat flux was developed. To improve the modeling accuracy, this model was developed with following considerations or features:

- Oxidation reactions of both virgin wood and char;
- Constant CO yields of each reaction even under various external heat flux;
- Transport processes of gas volatiles and liquids inside solid phase;
- Volume shrinkage of woods under external heat flux;
- Water evaporation of woods under different moisture content; and
- Temperature and moisture dependent thermal properties for modeling input.
2. Mathematical model

2.1. Governing equations

This model is developed to predict CO of wood samples under external heat flux. Several assumptions are made in this model, which are:

- One-dimensional computational domain;
- Thermal properties such as diffusion coefficient, specific heat capacity, surface emissivity, thermal conductivity are temperature dependent;
- All the new produced CO during the presence of visible flame change into CO2 immediately after production;
- Solid phase contains virgin wood, char and ash, and all the virgin wood will finally change into ash;
- Volume shrinkage is determined by mass loss, including mass loss of water evaporation;
- Flameout happens when mass of solid phase is equal to the mass of produced char by consuming all the virgin wood; and
- All gases have equal diffusion coefficient which is dependent on temperature, and diffusion coefficient of water is considered temperature and moisture dependent.

Energy conservation equation can be expressed as:

\[
\sum_{i=1}^{N_s+N_l+N_g} m_i C_{p,i} \frac{\partial T}{\partial t} = \nabla \cdot \left( \hat{\mathbf{j}} \nabla T \right) \Delta V - \sum_{j=1}^{N_r} k_j \Delta h_j + \sum_{k=1}^{N_s+N_l+N_g} \nabla \cdot \left( \hat{\mathbf{j}}_k h_k \right) \Delta V
\]

(1)

where \( N_s, N_l, \) and \( N_g, N_r \) are the numbers of solid, liquid, gas species and reactions. The L.H.S. of this equation is the absorbed heat for heating up. The first term on R.H.S. describes heat transfer inside solid phase, the second term is the heat balance of reactions, and the last term is the heat taken away by gas and liquid species.

Mass conservation equation for solid species can be expressed by:

\[
\frac{\partial m_i}{\partial t} = \dot{\phi}_i
\]

(2)

Mass conservation equation for gas and liquid species inside wood slabs can be given by:

\[
\frac{\partial m_i}{\partial t} = \nabla \cdot \hat{\mathbf{j}}_i + \dot{\phi}_i
\]

(3)

The L.H.S. term is transient gas or liquid species. The first term on R.H.S. describes mass transportation, and the second term is a source term representing produce of gas or liquid species.

2.2. General reaction scheme

Reaction scheme of woods under external heat flux is shown in Fig. 1. Three reactions in the solid phase are considered in this model. The first reaction represents evaporation process of water. Temperature inside wood slab keeps increasing under external heat flux. Water then start to evaporate as temperature is higher than 373 K. Wet wood converts to dry wood during this process. For the second reaction, virgin wood first change to char at specific temperature. Besides the CO, some other gas volatiles such as CO2, methane and hydrogen are produced during this process [3]. Produced char undertake oxidation reaction at the same time.

![Fig. 1. Reaction scheme of woods under external heat flux.](image-url)
Chemical reactions in solid phase are given as:

\[ R_1 : \text{Water} \xrightarrow{k_1} H_2O \]  
(4a)

\[ R_2 : \text{Wood} + O_2 \xrightarrow{k_2} CO + Char + G_i \]  
(4b)

\[ R_3 : \text{Char} + O_2 \xrightarrow{k_3} CO + Ash + G_j \]  
(4c)

where \( G_i \) and \( G_j \) are other gas products besides CO during oxidation processes of virgin wood and char, respectively.

Production rate of water vapor during water evaporation process in Eq. (4a) is expressed by:

\[ \dot{\phi} = -k_1 m_w \]  
(5)

Production rate of gas species during pyrolysis is reaction of virgin wood in Eq. (4b) is given as:

\[ \dot{\phi}^* = y_i k_2 m_w \]  
(6)

During oxidation process of char in Eq. (4c), production rate of gas volatiles is expressed:

\[ \dot{\phi}^* = y_j k_2 m_w \]  
(7)

Experimental results [10, 11] showed a sharp decrease of CO release rate shortly after ignition and a second peak near the end of experiments. So it is assumed that the new produced CO during the presence of visible flame change into CO2 immediately after production. The \( \dot{\phi}_{CO}^* \) in Eqs. (6) and (7) can be expressed by:

\[ y_{CO}^* > 0, y_{CO}^* > 0 \quad \text{or} \quad t_{ext} \geq t_{flameout} \]  
(8a)

\[ y_{CO}^* = y_{CO}^* = 0 \quad \text{or} \quad t_{ext} < t_{flameout} \]  
(8b)

Ignition time of woods under various moisture content and external heat flux can be obtained by [17, 18]:

\[ t_g = \left( 87 + 518 X_w \right) \rho^{0.73} \left( 4 \dot{\phi}_{ext}^* - 28.0 \right)^{0.32} \]  
(9)

And flameout time is obtained by the remained mass. It is assumed that flameout happens when the mass of solid phase is equal to the mass of produced char by consuming all the virgin wood. The flameout time can be expressed by:

\[ t_{flameout} = t_{m_w = m_{char}} \]  
(10)

Global production rate of gas species can be obtained by Eqs. (5) to (7):

\[ \dot{\phi} = \dot{\phi}^* + \dot{\phi}_{CO}^* + \dot{\phi}_{CO}^* \]  
(11)

2.3. Reaction rate

Water evaporation cannot be ignored as moisture has significant impact on the overall biomass combustion process, including changing the pyrolysis products and increasing the overall combustion time [19]. Water evaporation process is assumed to happen when temperature is higher than 373 K, which can be expressed by a first-order Arrhenius equation:
\[
\frac{\partial m_r}{\partial t} \bigg|_{T<373K} = 0
\]  
\[
\frac{\partial m_r}{\partial t} \bigg|_{T>373K} = -k_i m_r
\]

where \( k_i \) is the rate of reaction, which is given as:

\[
k_i = A_i \exp\left(-\frac{E_i}{RT}\right) \quad i = 1, 2, 3
\]

Several schemes about tar, gas and intermediate solid during pyrolysis reaction of woods have been investigated [20]. These pyrolysis schemes may improve modeling accuracy. However, applications are hampered as limited experimental data, such as kinetic data for the produce of gas volatiles, tar and other products. A review [21] showed that kinetic data in most previous studies were expressed by first-order Arrhenius equation. So a first-order Arrhenius equation is used to describe the pyrolysis process:

\[
\frac{\partial m^*_s}{\partial t} = -k_s \left( m^*_r - m_{f,s} \right)
\]

where \( m^*_s \) is the total mass of solid phase during the oxidation process of virgin wood, which can be expressed by:

\[
m^*_r(t) = m_r(t) + m_c(t) = m_{t,0} + \left[ m_{t,0} - m_{t,1} \right] y^*_c
\]

According to the reaction in Eq. (4b), a proportional relationship between mass loss of virgin wood and produced char can be gained:

\[
\frac{\partial m_c}{\partial t} = -y^*_c \frac{\partial m_r}{\partial t}
\]

Based on Eqs. (14), (15), and (16), it is gained that:

\[
\frac{\partial m_r}{\partial t} = -k_c m_c
\]

\[
\frac{\partial m^*_s}{\partial t} = y^*_c k_s m_c
\]

Similarly, pyrolysis reaction of wood char can be expressed as:

\[
\frac{\partial m^*_c}{\partial t} = -k_c \left( m^*_c - m_{f,s} \right)
\]

where \( m^*_c \) is the total mass of solid phase during oxidation reaction of char.

Reaction rate of consumed char and produced ash during oxidation of char can be gained in the same way:

\[
\frac{\partial m^*_c}{\partial t} = -k_y m_c
\]
\[
\frac{\partial m^*}{\partial t} = y^* k_t m_t
\] (19b)

where \(m^*\) is the mass of char during the oxidation process of char.

### 2.4. Mass transport

Transport processes in solid phase include liquid water and gas volatiles. Based on Fick’s law, transport mass flux of gas or liquid water under diffusive force can be expressed by:

\[
J_i = D_i \nabla m_i / (\phi \Delta V)
\] (20)

where \(J_i\) is the upward mass flux of species \(i\), kg/m²·s; and \(D_i\) is the diffusion coefficient of species \(i\), m²/s.

Diffusion coefficient of water is considered as temperature and moisture dependent, and diffusion coefficient of gas volatiles in wood slab as temperature dependent. These two coefficients can be expressed by:

\[
D_w = A_{D,w} \exp\left[(-E_{D,w1} + E_{D,w2} X)/(RT) + E_{D,w3}\right]
\] (21a)

\[
D_g = A_{D,g} \exp\left[(-E_{D,g1}/(RT) + E_{D,g2}\right]
\] (21b)

Global transport flux of species \(i\) is expressed by:

\[
\hat{J}_i = \max (J_i, 0)
\] (22)

### 2.5. Shrinkage

Volume change of woods under external heat flux has been described by mass loss [22-24], pore volume [25], and external heat flux [19]. Pore volume is difficult to be expressed along the time under external heat flux. And few experiments have been taken on shrinkage factor under different external heat flux. It is known that external heat flux results in mass loss, and change of pore volume can be also described by mass loss [26]. So the shrinkage of woods under external heat flux may be predicted by mass loss individually. A simple scheme is assumed to describe the shrinkage of woods under external heat flux:

\[
\frac{\partial \Delta x}{\partial t} = -\beta_v \frac{L_0 \Delta m_{v_0}}{m_0 \Delta t}
\] (23)

where \(\beta_v\) is the volume change coefficient, which can be obtained by experiment:

\[
\beta_v = -m_0 \Delta L / (\Delta m_{L_0})
\] (24)

### 2.6. Initial and boundary conditions

Initial conditions of this model are:

\[
\begin{align*}
m_{v_0} &= m_0 (1 - X_0)/n, & m_{v_o} &= m_{a_0} = 0, & m_{v_o} &= X_0 m_0/n, & \Delta x &= \Delta x_0 \\
m_{g,i} &= \rho_{g,i} \phi \Delta V, & X &= X_0, & \hat{J}_i &= 0, & T &= T_0\end{align*}
\] (25)

Boundary conditions are:
\[
\begin{align*}
-\hat{\lambda} \cdot \nabla T \bigg|_{x=0} &= \hat{q}_m^e \hat{q}^e - \hat{q}_m^c - \hat{q}_m^{\text{rad}} \\
-\hat{\lambda} \cdot \nabla T \bigg|_{x=L} &= \hat{q}_m^c \\
\hat{j}_m \bigg|_{x=L} &= 0
\end{align*}
\] (26a) (26b) (26c)

Thermal conductivity of solid phase is expressed by temperature dependent thermal conductivity of both virgin wood and char, which is expressed by:

\[
\hat{\lambda} = \left( \frac{m_m}{m_{m,0}} \lambda_c(T) + \left(1 - \frac{m_m}{m_{m,0}} \right) \lambda_v(T) \right)
\] (27)

3. Modeling approach

3.1. Solution methodology

A set of nonlinear partial differential equations was solved numerically. Due to the large number of temperature and moisture dependent variables and complexity of the problem, an explicit formulation was adopted for the solution of all equations. To improve the stability, all the equations have been nondimensionalized before discretization. And the discretized time step met the requirement that: $\Delta t < 0.5 \left[ \min (\Delta x) \right]^2$. The entire domain was divided into $n$ grids, and variables of next time step were predicted by the data from last time step. As the boundary conditions of temperature are nonlinear, temperature of next time step were obtained by iteration. Mass of solid, liquid and gas species, transport mass flux of liquid and gas species, temperature, shrinkage can then be predicted. Fig. 2 shows a flow chart of numerical procedure.

Fig. 2. Flow chart of numerical procedure.
<table>
<thead>
<tr>
<th>Property</th>
<th>Symbol</th>
<th>Unit</th>
<th>Correlation/value</th>
<th>References</th>
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</thead>
<tbody>
<tr>
<td>Yield of char in Eq. (4b)</td>
<td>( y'_{c} )</td>
<td>kg/kg</td>
<td>0.26</td>
<td>[27]</td>
</tr>
<tr>
<td>Yield of ash in Eq. (4c)</td>
<td>( y'_{a} )</td>
<td>kg/kg</td>
<td>0.10</td>
<td>[27]</td>
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<tr>
<td>Yield of CO in reaction Eq. (4b)</td>
<td>( y'_{CO} )</td>
<td>kg/kg</td>
<td>0.30 Estimated</td>
<td></td>
</tr>
<tr>
<td>Yield of CO in reaction Eq. (4c)</td>
<td>( y''_{CO} )</td>
<td>kg/kg</td>
<td>0.10 Estimated</td>
<td></td>
</tr>
<tr>
<td>Water evaporation rate</td>
<td>( k_{1} )</td>
<td>l/s</td>
<td>4.29×10^{3}\exp(-43,800/RT)</td>
<td>[4]</td>
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<tr>
<td>Oxidation rate of virgin wood</td>
<td>( k_{2} )</td>
<td>l/s</td>
<td>2.47×10^{6}\exp(-106,500/RT)</td>
<td>[28]</td>
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<tr>
<td>Oxidation rate of char</td>
<td>( k_{3} )</td>
<td>l/s</td>
<td>9.79×10^{3}\exp(-192,400/RT)</td>
<td>[4]</td>
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<td>Heat of reaction for water evaporation</td>
<td>( \Delta h_{1} )</td>
<td>kJ/kg</td>
<td>2440</td>
<td>[29]</td>
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<td>Heat of reaction for virgin wood pyrolysis</td>
<td>( \Delta h_{2} )</td>
<td>kJ/kg</td>
<td>418</td>
<td>[14]</td>
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<td>Heat of reaction for oxidation of char</td>
<td>( \Delta h_{3} )</td>
<td>kJ/kg</td>
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<td>Diffusion coefficient of water</td>
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<td>m^{2}/s</td>
<td>7.0×10^{6}\exp(-38,500/RT+29,000X/RT)</td>
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<tr>
<td>Diffusion coefficient of gas</td>
<td>( D_{g} )</td>
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<td>1.55×10^{6}\exp(-19,248/RT+7.7686)</td>
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<td>Specific heat capacity of virgin wood</td>
<td>( C_{p,v} )</td>
<td>J/kg K</td>
<td>4.85T-212.1</td>
<td>[28]</td>
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<tr>
<td>Specific heat capacity of char and ash</td>
<td>( C_{p,i} )</td>
<td>J/kg K</td>
<td>2.09T+432.6</td>
<td>[28]</td>
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<td>Specific heat capacity of gas</td>
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<td>University gas constant</td>
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<td>Surface emissivity</td>
<td>( \varepsilon )</td>
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<td>Thermal conductivity of virgin wood</td>
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<td>W/m s</td>
<td>0.096+6×10^{3}T</td>
<td>[28]</td>
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<tr>
<td>Thermal conductivity of char</td>
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<td>[28]</td>
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<td>Stefan-Bolzmann constant</td>
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<td>Volume change coefficient</td>
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<td>Experiment</td>
</tr>
<tr>
<td>Initial moisture content</td>
<td>( X_{0} )</td>
<td>-</td>
<td>0.113</td>
<td>Experiment</td>
</tr>
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</table>

3.2. Thermal properties

A dynamical porosity is assumed related to the mass, which is estimated by [26]:

\[
\phi = 1 - \frac{\rho}{\rho_{\text{theo}}}
\]  \hspace{1cm} (28)

where \( \rho_{\text{theo}} \) is the theoretical density of a compact solid wood free from voids, and is assumed as 1500 kg/m^{3}.

The surface emissivity can be expressed by:

\[
\varepsilon = \varepsilon_{0} + \tilde{\varepsilon} T
\]  \hspace{1cm} (29)

where \( \tilde{\varepsilon} \) is the dependent coefficient expressing the change of surface emissivity by temperature.

Temperature dependent thermal properties are used for modeling input, shown in Table1. Estimated values are determined by optimization algorithm. A point need to be mentioned is that CO yields of each reaction are considered constant even under different external heat flux. This will expand the applications of this model as the limited experimental data of CO yields under various external heat fluxes.

4. Conclusions

A one-dimensional model to predict CO production of woods under external heat flux was developed. Fire processes such as water evaporation, volume shrinkage, transport of liquid water and gas volatiles can also be predicted by this model. To improve modeling accuracy, temperature and moisture dependent thermal properties are used for modeling input. Three
reactions are included in this model, namely evaporation reaction of water, oxidation reactions of virgin wood and char. For the prediction of CO, it is assumed that the new produced CO during the presence of visible flame change into CO2 immediately after production. Carbon monoxide yields of each reaction are considered constant even under various external heat flux. This will expand the applications of this model as the limited experimental data of CO yields under different external heat flux.

In Part II of this study, modeling results such as mass loss rate and CO release rate will be validated by experimental data. And modeling results such as shrinkage, transport processes of liquid water and gas volatiles inside wood slab will be included as well.

References