
Seyed Ziaedin Miry a*, Marco A.B. Zanoni a, Tarek L. Rashwan a,b, José L. Torero c, Jason I. Gerhard a

a Department of Civil and Environmental Engineering, The University of Western Ontario, London, Ontario N6A 5B9, Canada

b Department of Civil Engineering, Lassonde School of Engineering, York University, Toronto, Ontario, M3J 1P3, Canada

c Department of Civil, Environmental and Geomatic Engineering, University College London, London WC1E6BT, UK

* Corresponding author at: Department of Civil and Environmental Engineering, The University of Western Ontario, Claudette Mackay-Lassonde Pavilion, Rm. 1317, London, Ontario, Canada N6A 5B9. E-mail address: smiry@uwo.ca (S.Z. Miry)
1. Appendix A. Pneumatic Conductivity, Permeability, and Porosity Measurement

The bed intrinsic permeability was measured following a previous methodology [1] based on ASTM D6539 00 [2]. The packed bed was subjected to cold air injection at several air fluxes (i.e., 5.00, 10.0, 15.0, 20.0, 27.5, and 30.0 L/min) before smouldering (i.e., the permeability of the sand/GAC mixture) and after smouldering (i.e., the permeability of clean sand-only). Pneumatic conductivity was determined by Eq. (A.1) [3]:

\[ K = \frac{k_p \rho_g g}{\mu} \]  

where \( k_p \), \( \mu \), \( \rho_g \), and \( g \) represent the intrinsic permeability, viscosity, density, pressure, and gravity, respectively. Experimental results show that the average pneumatic conductivity increased from 5.4\times10^{-4} to 1.2\times10^{-3} m/s when the permeability increased from 8.7\times10^{-10} m^2 to 1.95\times10^{-9} m^2, which corresponds to before and after smouldering. Because these differences are small, an average permeability of 1.4\times10^{-9} m^2 was used in the numerical model for computational efficiency.

![Figure A.1. Measurements of pneumatic conductivity and intrinsic permeability before and after smouldering for two different experiments.](image)
The GAC particle density was measured based on the mass of each grain divided by its volume. 109 particles were investigated using a digital calliper (Tritan) to measure the particle diameters and a high-precision scale (METTLER TOLEDO, Balance XSR205DU) to weigh the GAC particles. This resulted in an average GAC particle density of 1311 ± 190 kg/m$^3$. The GAC porosity, which corresponds to the pore volume occupied by GAC, was calculated by:

$$
\phi_{GAC} = Y_{GAC}C_{GAC}(1 - \phi)\rho_{sand} \cdot \frac{1}{\rho_{GAC}}
$$

where $Y_{GAC}$ and $C_{GAC}$ are the GAC mass fraction and concentration, respectively. This resulted in a GAC porosity equal to 0.05 ± 0.006 for a GAC concentration of 0.03 kg$_{GAC}$/kg$_{sand}$. 
2. Appendix B. Experimental Results, Inverse Modelling, and H Sensitivity Analysis

Figure B.1 shows the temperature evolution at centerline for heat transfer-only and smouldering with 0.03 kg_{GAC}/kg_{sand} experiments where the centreline TCs were placed 1 to 70 cm from the plenum. For heat transfer-only and smouldering experiments, the air was turned on when the TC at z = 1 and 4 cm reached 300 °C (i.e., at $t_g$) and the heater was turned off when the TC at z = 4 and 7 cm peaked (i.e., at $t_h$) (see Table 5). Note that the peak temperature in Fig. B.1b was nearly constant throughout smouldering (i.e., $T_p = 732 \pm 6$ °C), which shows how the oxidation energy rate compensates for local losses in the reaction zone (i.e., at the smouldering front).

![Figure B.1](image)

Figure B.1. Experimental temperature evolution for a) heat transfer-only, b) smouldering at the centerline at different heights from 1 to 70 cm.

The heat influx delivered at the bottom boundary ($\dot{q}$ (W/m²)) was determined using inverse modelling in which the error between model-predicted temperatures and heat transfer-only experimental results (average of three repeats) of the first centerline thermocouple at Z = 1 cm was minimized. The rest of the thermocouples at the centerline and wall were used for determining the radial heat loss coefficient ($H$) via a sensitivity analysis. The objective function for the heat flux optimization takes into account both the temperature evolution ($T(t)$) and peak temperature ($T_p$) as shown in [4]:

\[
\text{Objective Function} = \min \left\{ \sum_{i=1}^{n} \left( T_i(t) - T_{i,\text{model}}(t) \right)^2 + \left( T_p - T_{p,\text{model}} \right)^2 \right\}
\]
\[ \text{Error} [\%] = (0.5 \times \text{NRMSD}_{T(t)}|_{Z=1 \text{ cm}} + 0.5 \times \left| \frac{T_{p,\text{exp}} - T_{p,\text{num}}}{T_{p,\text{num}}|_{Z=1 \text{ cm}}} \right| ) \times 100 \]  

(B.1)

where \( T_{p,\text{exp}} \) and \( T_{p,\text{num}} \) are the peak temperature in the experiment and numerical simulation, respectively. NRMSD is the Normalized Root-Mean-Square Deviation between experimental \( (T_{s,\text{exp}}) \) and numerical sand temperature \( (T_{s,\text{num}}) \) [5]:

\[ \text{NRMSD}_{T(t)} = \frac{\sqrt{\sum_{i=1}^{n}(T_{s,\text{exp}} - T_{s,\text{num}})^2}}{n}(T_{s,\text{max}} - T_{s,\text{min}}) \]  

(B.2)

The data logger measured the temperature every 2 s during the experiment where \( n \) is the number of measurements taken by data logger. \( T_{s,\text{max}} \) and \( T_{s,\text{min}} \) are the maximum and minimum temperature of sand. \( T(t) \) shows that NRMSD is defined based on the difference of temperature changing with time. The “pattern search optimization algorithm” was used to minimize the error calculated by Eq. (B.1) built into MATLAB. The algorithm found a sequence of points that approach an optimal point [6]. The value of error either decreased or remained the same from each point in the sequence to the next iteration; the optimal point was that with the lowest value after 100 iterations. The optimal value for \( \dot{q} \) was equal to 35000 (W/m\(^2\)) with an error equal to 6\% providing an excellent agreement (see thermocouple at \( Z = 1 \text{ cm} \) in Figure B.2. a). Figure B.2 also shows a sensitivity analysis of \( H \) where the numerical temperatures from \( Z = 13 \text{ cm} \) to \( Z = 61 \text{ cm} \) were used to compare with the experiment. This sensitivity analysis shows that \( H = 3 \text{ W/m}^2 \text{ K} \) results in the best estimation of experimental data with errors equal to 6\% and 5.7\% at the centerline and wall, respectively.
Figure B.2. Various heat transfer simulations. The shaded region represents 95% confidence interval of three repeats of experimental results; the dashed-dot, solid, and dashed lines represent numerical model predictions with $H$ equal to 1, 3, and 5 W/m$^2$ K, respectively, along the a) centerline and b) wall.

Figure B.3 shows the sensitivity analysis of $\dot{q}$ for smouldering at 0.03 GAC concentration. By increasing $\dot{q}$ from 23080 to 35000 (W/m$^2$K), a negligible difference in the cooling zone was observed due to boundary effects that are propagated along the system. Moreover, the energy rate of GAC oxidation ($\dot{E}_{ox}$) is much higher than energy rate of the heater ($\dot{E}_{in}$) (see Figure 7). Therefore, $\dot{q} = 23080$ (W/m$^2$K) was considered for the smouldering simulation in this research.
Figure B.3. Temperature evolution at multiple radial positions: a) centerline, b) wall, c) $r = 1.5$ cm, and d) $r = 2.8$ cm. The solid and dashed-dot lines represent numerical results with $q^\prime = 23080$, and $35000$ (W/m$^2$). Shaded region shows three repeats of experimental results.

The sensitivity of the heat loss coefficient ($H$) on the temperature evolutions for smouldering 0.03 and 0.02 GAC concentrations is presented in Figs. B.4 and B.5, respectively. $H$ determines the rate of radial heat loss between the column wall and ambient air, which includes the effect of insulation; therefore, $H$ is a complicated parameter that required a separate sensitivity analysis for each GAC concentration. In fact, $H$ is expected to change under different smouldering conditions with different temperature profiles because $H$ is affected by the thermal properties of the insulation (e.g., $C_p$ and $k$) and the convection conditions just outside of the column, which are both temperature-dependant. For 0.03 kg$_{GAC}$/kg$_{sand}$, $H$ values between 2 to 14 W/m$^2$K were explored, where the best match with the experimental results was achieved using $H = 7$ W/m$^2$K with an overall error equal to 6%. Note that a higher $H$ indicates poor insulation quality and higher radial heat losses. The numerical model predicts the peak and cooling zone
temperatures near the wall were cooler than those near the centreline due to radial heat losses, which agrees with the experimental results and similar studies, e.g., [7]. In addition, by increasing $H$ from 2 to 14 W/m$^2$ K, $T_p$ at the centerline and wall dropped from 723 to 708 °C and 550 to 405 °C, respectively.

Figure B.4. Various smouldering simulations with a concentration of 0.03 kg$_{GAC}$/kg$_{sand}$. The shaded region represents three repeats of experimental results; the dashed-dot, solid, and dashed lines represent numerical model predictions with $H$ equal to 2, 7, and 14 W/m$^2$ K, respectively, along the a) centerline and b) wall.

Like Fig. B.4, Fig. B.5 further illustrates the model’s reliability in reproducing key smouldering metrics (e.g., temperatures and front velocities). By exploring $H$ between 1 to 5 W/m$^2$ K, the best match with experimental results was achieved for $H=3.2$ W/m$^2$ K (with the error equal to 5 and 6.1 % at the centerline and wall, respectively). As highlighted above, the increased $H$ from 3 to 7 W/m$^2$ K with increasing GAC concentration from 0.02 to 0.03 is associated with higher temperatures that foster a greater rate of heat losses. The main reasons are associated with the temperature dependencies in: (i) the thermophysical properties of insulation that is embedded in $H$ (e.g., the thermal conductivity increases with temperature and leads to a higher $H$ value) and (ii) free-convection heat transfer dynamics between the column wall and ambient air (e.g., free-convection increases with increasing surface temperature, which also leads to a higher $H$ value [8]).
Figure B.5. Various smouldering simulations with a concentration of 0.02 kgGAC/kg sand. The shaded region and dashed line represents three and one repeats of experimental results; the dashed-dot, solid, and solid-dot lines represent numerical model predictions with $H$ equal to 1, 3.18, and 5 W/m$^2$ K, respectively, along the a) centerline and b) wall.
3. Appendix C. GAC kinetic Analysis

3.1 TG/DTG/DSC Experiments

Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) experiments (Fig. C.1) were performed in a Simultaneous Thermal analyzer (NETZSCH STA 449 F3 Jupiter) under air and N\textsubscript{2} atmospheres from 30 to 900 °C at four different heating rates (\(\beta = 5, 10, 15, 20 \) °C/min) and a gas flow of 100 ml/min. A small sample mass (5.55 ± 3.5 mg) was used to avoid thermal gradients in the sample. Under air, the TG data shows two steps in the mass loss (Fig. C.1a) followed by two peaks in the DTG (Fig. C.1c), which correspond to water evaporation and char oxidation, respectively. However, only one exothermic peak for the char oxidation is observed in the DSC (Fig. C.1e). Complete fuel consumption was achieved at all heating rates, except for \(\beta=5\) °C/min, which shows some residue (Fig. C.1a). Under N\textsubscript{2}, only one peak is observed in the DTG, which represents water evaporation (Fig. C.1d). As found by other researchers, these TGA/DSC results indicate that GAC does not undergo significant pyrolysis reactions [3, 7]. Thus, a one-step oxidation mechanism was defined as the simplest mechanism for GAC combustion:

\[
GAC + \left( \frac{Fr_{CO}}{2} + (1 - Fr_{CO}) \right) O_2 \xrightarrow{R_{GAC}} Fr_{CO} CO + (1 - Fr_{CO}) CO_2 \tag{C.1}
\]

where \(Fr_{CO}\) is the mole fraction of produced CO and is equal to 0.27, following previous experimental studies [9]. \(Fr_{CO}\) strongly affects \(\Delta H_{GAC}\), e.g., as \(Fr_{CO}\) decreases from 1 to 0, \(\Delta H_{GAC}\) increases from 110.5 to 393.5 kJ/mol [9]. While pure carbon with \(Fr_{CO}=0.27\) results in \(\Delta H_{GAC}=26.4\) MJ/kg, this value was corrected for the 2.2% unreactive and 3.2% water content measured in the GAC (which lowered \(\Delta H_{GAC}\) by 1.5 MJ/kg); therefore, \(\Delta H_{GAC}=24.9\) MJ/kg was used in the numerical model, agreeing with [9]. By considering the molar mass of GAC (12 kg/kmol), \(O_2\) (32 kg/kmol), CO (28 kg/kmol), and CO\textsubscript{2} (44 kg/kmol) Eq. (C.1) was converted to a mass fraction:
$GAC + ν_{O_2}O_2 \overset{R_{GAC}}{\rightarrow} ν_{CO}CO + ν_{CO_2}CO_2$ (C.2)

where $ν_{O_2}$, $ν_{CO}$, $ν_{CO_2}$ are the mass yields of oxygen (i.e., consumption of oxygen mass per mass of the GAC), carbon monoxide, and carbon dioxide and are equal to 2.304, 0.63, and 2.67, respectively. Eq. (C.2) was used as the governing equation for GAC oxidation.

Figure C.1. a, c, e) GAC Normalized TG, DTG, and DSC under air at four different heating rates; b, d, f) GAC Normalized TG, DTG, and DSC under $N_2$ at three different heating rates.
3.2 Inverse Modelling

The kinetic parameters (log (A) and E) in the Arrhenius equation were determined by inverse modelling via a Genetic Algorithm (GA) optimization method and TG experiments [10]. A GA code was developed in MATLAB and used in this study with a population size of 100 and maximum generations of 300. The best solution was determined by maximizing the fitness function ($\phi$), which was defined as the inverse of the error between calculations (“calc”, i.e., the solution proposed by Arrhenius equation) and experimental measurement (“exp”, i.e., TG and DTG experiments), via considering all heating rates at the same time:

$$\phi = \left( \int |\dot{Y}_{\text{calc}} - \dot{Y}_{\text{exp}}|dT \right)^{-1} + \gamma \left( \int |Y_{\text{calc}} - Y_{\text{exp}}|dT \right)^{-1}$$

where $\dot{Y}$ and $Y$ represent normalized mass loss rate (DTG) and mass loss (TG) considering the effect of both at the same time. The constant $\gamma$ was equal to 100 to scale the relative impact on the fitness of the TG over the DTG. The algorithm stopped when $\phi$ reached its maximum value or limit number of generations. Figure C.2 shows the comparison of experimental TG and DTG with the predictions. Note that the differences between experiments and predictions are primarily because water evaporation was not captured by the one-step oxidation reaction (Eq. (C.2)).
Figure C.2. Genetic Algorithm (GA) optimization for a one-step oxidation reaction. Dashed line shows the experimental data for TG and DTG, and shaded region shows the prediction of Arrhenius equation using the range of optimized kinetic parameters (see Table 2).

Table C.1 shows the optimized range of log (A) (1/s) and E (kJ/mol) that fits all heating rates at the same time. Within this range, log (A)=3.79 1/s) and E=72.9 kJ/mol were implemented in the numerical model.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Units</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating Rate (β)</td>
<td>°C/min</td>
<td>5-20</td>
</tr>
<tr>
<td>log (A)</td>
<td>(1/s)</td>
<td>3.21-3.80</td>
</tr>
<tr>
<td>E</td>
<td>kJ/mol</td>
<td>72.90-80.18</td>
</tr>
</tbody>
</table>
4. Appendix D. Sensitivity Analysis

Figure D represents a sensitivity analysis of GAC concentration and Darcy air flux on peak temperature ($T_p$) and smouldering front velocity ($v_f$). Figure D.a shows that increasing GAC concentration from 0.01 to 0.05 increased $T_p$ from 255 to 1145 °C, respectively, because of the increased oxidation energy rate, agreeing with [11-14]. With low GAC concentration ($C_c < 0.01$), radial heat losses dominated over the oxidation energy rate, which resulted in a negative global net energy rate and global quenching. With a high GAC concentration ($0.04 \leq C_c \leq 0.05$), $v_f$ decreased from 0.54 to 0.50 cm/min, respectively, because, the increased GAC concentration shifted the process toward oxygen-limited conditions, i.e., all of the oxygen mass fraction ($Y_{O_2}$) was consumed by the smouldering front [14].

Figure D.b shows that increasing the Darcy air flux from 0.01 to 0.09 m/s increased $v_f$ linearly from 0.13 to 0.84 cm/min, associated with increasing the convective heat transfer and oxygen mass flux to the reaction zone, agreeing with [11, 14-17]. By increasing $v_f$, the oxidation energy rate also increased, but $T_p$ reached a plateau (740 °C) at high Darcy air flux ($u_g > 0.07$ m/s). This result indicates that the released oxidation energy accumulated in the cooling zone length (which grew from 11 to 26 cm with applied air fluxes increasing from 0.01 to 0.09 m/s, respectively, at DT = 0.5) and did not affect the peak temperatures.
Figure D.1 Sensitivity analysis on (a) GAC concentration (\( - \)), and (b) Darcy air flux (m/s)

5. Appendix E. Permeability Heterogeneity

Figure E1 represents the computational domain with the inclusion of a second region perpendicular to the airflow direction (i.e., an outer concentric cylinder) that represented a separate porous medium with a different intrinsic permeability \( (k_p) \). \( R_1 \) and \( R_2 \) are 3.81 and 1.58 cm, respectively, which each provide the same cross-section area of \( 4.58 \times 10^{-3} \) m\(^2\). A sensitivity analysis on the position of layers and the ratio of intrinsic permeabilities were performed to provide insight into the effects of permeability heterogeneity on smouldering system performance, e.g., peak temperature, smouldering velocity, front curvature, and global quenching.
Figure E.1 Schematic view of the computational domain with two porous media regions with differing intrinsic permeabilities, which approximately reflect fine and coarse sand properties.

Table E1 shows a list of simulations with Regions 1 and 2 in different permeability heterogeneity scenarios. For simulations # 1-3, Region 1 represents coarse sand with high permeability and Region 2 represents fine sand with low permeability, and both contain a GAC concentration of 0.03. For simulations # 4-6, these conditions are reversed. $\dot{m}_{(1)}$ and $\dot{m}_{(2)}$ represent the air mass flow rate at DT = 0.5 that passed through Regions 1 and 2, respectively.
Table E1. Applied Smouldering Characteristics in Different Permeability Heterogeneity Scenarios

<table>
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<tr>
<th>Sim #</th>
<th>( u_g )</th>
<th>( C_c )</th>
<th>( k_p(1) )</th>
<th>( k_p(2) )</th>
<th>( \frac{k_p(1)}{k_p(2)} )</th>
<th>( T_p(1) )</th>
<th>( T_p(2) )</th>
<th>( \dot{m}_1 )</th>
<th>( \dot{m}_2 )</th>
<th>( v_f(1) )</th>
<th>( v_f(2) )</th>
<th>Self-Sustained</th>
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<td>( 1.4 \times 10^{-9} )</td>
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<td>645</td>
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<td>660</td>
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\[ \dot{m}_1 = \int_0^{R(1)} (\rho g u_g) 2\pi r dr \times 10^{-4} \text{ kg/s} \]

\[ \dot{m}_2 = \int_{R(1)}^{R(2)} (\rho g u_g) 2\pi r dr \times 10^{-4} \text{ kg/s} \]
6. References