**1. Second pyrolysis model (Model II) of Aalto University for MaCFP phase III**

**1.1. Model description**

The first part of this report presents numerical reproductions of PMMA gasification experiments performed by NIST [1] using the presented model by Alinejad et al. [2] at Aalto University. For completeness, Equations 1 to 3 show the reaction model for PMMA degradation through parallel reactions of three individual components, and Table 1 shows the previously estimated model parameters. The composition of PMMA is assumed as 0.013, 0.027, and 0.96 of humidity, , and by mass fraction, respectively.

|  |  |
| --- | --- |
|  | (1) |
|  | (2) |
|  | (3) |

The main difference of model II of Aalto university with the original one is in the modeling in-depth radiation transfer. In model II, the applied absorption coefficient is assumed as a function of source (flame) temperature () and depth from the material surface ():

|  |  |
| --- | --- |
|  | (4) |
|  | (5) |
|  | (6) |

Same value of was applied for different heat fluxes due to negligible sensitivity of mass loss rate results to this parameter. For the reflectivity at the air () and black PMMA () sides of the interface, following equation are applied in model II:

|  |  |
| --- | --- |
|  | (7) |
|  | (8) |
|  | (9) |

We assume a convective heat transfer coefficient of 10 W/(m2K) based on [3].

Table 1. Kinetic parameters for PMMA degradation and its thermophysical properties estimated for the model II of Aalto University.

|  |  |  |  |
| --- | --- | --- | --- |
| Parameter | Value | |  |
| Degradation kinetics | | |  |
|  | Component 1  (mass fraction = 0.013) | Component 2  (mass fraction = 0.027) | Component 3  (mass fraction = 0.96) |
| *A* (1/s) |  |  |  |
| *E* (J/mol) |  |  |  |
| *n* (-) | 1 | 1 | 1 |
| *v* (-)  *starting component*  *final product* | 1  1 | 1  1 | 1  1 |
| Thermophysical properties (for three components) | | | |
| *hr* (kJ/kg) |  |  |  |
| *cp* (J/(kg∙K)) |  | | |
| *k* (W/(m∙K)) |  | | |
| *D* (kg/m3) | 1210 | | |
|  | 1073 | | |
| *ε* (-) (upper surf., air-to-PMMA) | 0.914 | | |
| *ε* (-) (bottom surf., PMMA-to-Kaowool) | 0.01\* | | |
| Heat transfer | | | |
| *h* (W/(m2K)) | 10 | | |

**\* This value was selected in [2] to reach good agreement for MLR peak.**

**1.2. Simulation of experiments in NIST gasification apparatus**

The original experiments by NIST in gasification apparatus were performed on circular PMMA specimens nominally of 7 cm in diameter and 5.8 mm in thickness, exposed to external radiative heat fluxes of 25 and 50 kW/m2 in a nitrogen atmosphere [1]. As FDS mesh consists of rectangular cells, accurately creating a circular object would be impractical. Hence, the specimen is represented by a square of 6.2 cm by edge, that has approximately the same area as a circle 7 cm in diameter. The specimen thickness in simulation is equal to the reported real specimen nominal value, and its back side temperature is measured by a thermocouple.

The exposed side boundary condition is assumed as nominal incident heat flux from the heater (25 or 50 kW/m2). A Kaowool insulation assembly of 2.85 cm in total thickness, located below the specimen, is modelled as the unexposed side boundary. Its thermal properties are assumed as given [1]: density of 256 kg/m3, specific heat capacity of 1070 J/(kg∙K) and thermal conductivity according to Table 2. The reported specific heat is at 980 °C, but it is assumed to hold over all temperatures. Thermal conductivity was reported at temperatures of 260 °C and higher. A third-degree polynomial was fitted to the reported thermal conductivity data, which was used to extrapolate conductivity at 20 °C, presented also in Table 2.

Table 2. Thermal conductivity of Kaowool insulation below the PMMA specimen. In the model, a linear increase is assumed between conductivities at reported temperatures.

|  |  |
| --- | --- |
| Temperature (°C) | Thermal conductivity (W/(m∙K)) |
| 20 | 0.0397 |
| 260 | 0.0576 |
| 538 | 0.085 |
| 816 | 0.125 |
| 1093 | 0.183 |

The modified version of FDS 6.8.0 was used in generating numerical outputs. This applied version can be accessed from this address:

<https://github.com/FaridAlinejad/fds/tree/aaltofds>

Computational fluid dynamics modelling of gaseous phase was neglected in order to significantly reduce computational cost, the ambient gaseous phase temperature being assumed as constant 20 °C. In the presented simulations, CELL\_SIZE\_FACTOR was set at and N\_LAYER\_CELLS\_MAX at 1000. This enforces the layer to be divided in 1000 cells, i.e. cell size of 0.0058 mm. Similar results can be obtained with CELL\_SIZE\_FACTOR = 0.5.

Figures 1 to 4 compare experimentally measured temperatures and mass loss rates [1] in PMMA specimens to corresponding numerical predictions under heat flux levels of 25 and 50 kW/m2. The figures present the variation between all available experimental data as shaded grey area, and the simulations as a solid line. As an exception, Figure 2 presents only simulated mass loss rate under 25 kW/m2, as the corresponding experimental data was not available at the time of writing. In Figures 1 and 3, simulated temperature extends in time past the available experimental data.



Figure 1. Experimental variation (shaded grey area) and simulated (continuous line) temperatures at the back side of a PMMA specimen under 25 kW/m2 heat flux.



Figure 2. Simulated mass loss rate (MLR) of a PMMA specimen under 25 kW/m2 heat flux.



Figure 3. Experimental variation (shaded grey area) and simulated (continuous line) temperatures at the back side of a PMMA specimen under 50 kW/m2 heat flux.



Figure 4. Experimental variation (shaded grey area) and simulated (continuous line) mass loss rates of a PMMA specimen under 50 kW/m2 heat flux.

**Nomenclature**

*A* Frequency factor

*cp*  Specific heat capacity

D Density

*E* Activation energy

*h* Convective heat transfer coefficient

*hr* Heat of reaction

*k* Thermal conductivity

*n* Reaction order

Refraction index

*v* Stoichiometric coefficient

*α*  Effective absorption coefficient

*ε*  Emissivity

*ρ* Reflectivity

**References**

1. Leventon, I.T., De Lannoye, K. (2023), Experimental Measurements for Pyrolysis Model Validation - Anaerobic Gasification of PMMA Under External Thermal Radiation, National Institute of Standards and Technology, <https://doi.org/10.18434/mds2-2940> (Accessed May 16, 2023).
2. Alinejad, F., Bordbar, H., & Hostikka, S. (2023). On the importance and modeling of in-depth spectral radiation absorption in the pyrolysis of black PMMA. *Fire Safety Journal*, *135*, 103706.
3. Lautenberger, C., & Fernandez-Pello, C. (2009). Generalized pyrolysis model for combustible solids. Fire Safety Journal, 44(6), 819-839.