

# **Microscale combustion calorimetry as a tool to develop kinetic models of polymer pyrolysis and volatile oxidation**

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Formal kinetics is still a matter of choice, instead of detailed mechanisms, for many practical fuels considered in engineering simulations of ignition, flame spread, and extinction. This is particularly relevant for fire modeling when the chemical composition of combustibles is complicated and often not fully prescribed, which is the case, for example, when flammable volatiles are produced in solid pyrolysis. In that case, kinetic models are required both for thermal decomposition of combustible materials and for volatile oxidation. In this work, we present methodology to derive both types of kinetic models from microscale combustion calorimetry (MCC) data, and demonstrate the results for a number of practical fuels.

First, the generalized approach [1] is applied to model pyrolysis of solid materials. Generalization implies use of conversion-dependent, rather than constant, formal kinetic parameters. Within this approach, two functions characterizing thermochemical stability of a material are evaluated: the apparent activation energy and the product of pre-exponential factor and conversion function. Both functions are obtained by the iso-conversional Friedman method and tabulated depending on the global conversion variable. Key advantage of this approach is application of a single global reaction to model pyrolysis with multi-step reaction mechanism of arbitrary complexity. The method is shown to provide excellent agreement with the MCC measurements in a range of heating rates from 0.25 to 1.5 °C/s.

Second, we present the MCC measurements performed in incomplete oxidation regime for combustible volatiles produced by pyrolysis of solid combustibles [2]. Based on these measurements, the kinetic parameters of volatile oxidation are derived for the simplified single-step formal kinetic model. It was found that the temperature range considered (500°C to 800°C) may or may not be adequately represented by the first order oxidation reaction with the single value of the apparent activation energy. In the latter case, different values could be suitable for lower and higher temperatures, which is an indication of complex oxidation chemistry.

The methodology developed in this work is expected to be useful in coupled CFD modeling of turbulent flames fed by thermal degradation of solid fuels.

- [1] A.Yu. Snegirev. Generalized approach to model pyrolysis of flammable materials. *Thermochimica Acta* 590 (2014) 242-250.
- [2] A.Yu. Snegirev, V.A. Talalov, V.V. Stepanov, A.S. Tsoy. Oxidation kinetics of pyrolysis volatiles and its implication to critical conditions of flame extinction. Proc. of ISHPMIE-X (Bergen, Norway, June 9–14, 2014), Edited by T. Skjold, R.K. Eckhoff, K. van Wingerden., 2014, pp. 71-84.