A New Adaptation of the Method of Invariant Kinetic Parameters and its Application to a Flame Retardant System

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Abstract

This thesis treats a particular flame retardant (FR) system with a new kinetic analysis method derived from the method of Invariant Kinetic Parameters (IKP). The IKP method is one of many techniques available that extract a kinetic triplet (activation energy, pre-exponential factor and function of conversion) from non-isothermal, constant heating rate thermogravimetric (TG) data. The principles and advantages of the IKP method are discussed within a broad context, as are its limitations that are shared by most other methods. Such a consolidated and critical literature review is uncommon and is designed to help the novice researcher navigate through the kinetic analysis “minefield”. Each and every step for all solid-state mechanism derivations are explained for the same purpose: To encourage the adoption of an informed and circumspect approach to often complex heterogenous kinetic analysis.

The new method improves kinetic analysis outcomes and reliability by, in part, refining the IKP. Its approach is described in such detail that the inherent complexity of this undertaking can be fully appreciated, and if possible, managed in better ways. Subroutines written in Visual Basic for Applications in Excel to realise the method are validated with synthetic data up to a complexity of two overlapped independent models. Output from the method that pertains to water evaporation and the decomposition of calcium carbonate compares favourably with expectation. Statistical analyses are integrated into the method and allow for the proper treatment of uncertainty in all applications.

Motivation for this study originated from a desire to characterise the commercial FR system, polypropylene/ tetrabromobisphenol A bis(2,3-dibromopropyl ether)/ antimony trioxide. No thorough analyses of this FR system previously existed. TG data nominally for input into the new method is correlated with differential scanning calorimetry and Fourier transform infrared spectroscopy, and the implications of these small-scale analytical techniques are illustrated with larger-scale cone calorimetry.

Benson’s Group Additivity Method applied to a characteristic exothermic weight loss during the thermal decomposition of the pure FR complements the results of the new kinetic analysis method. A proposed degradation pathway is affiliated with the nucleation and nucleus growth model of statistical significance implied as the first of three overlapped independent processes that match the pyrolysis behaviour of the FR. The synergistic effect of antimony trioxide derives from its ability to make bromine from the FR overcome the diffusive resistance of the polypropylene substrate and enter the gas phase prior to ignition. It is concluded that the FR system behaves as might have been expected from a careful interpretation of the literature.
Declaration

I certify that this work contains no material which has been accepted for the award of any other degree or diploma in my name in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. In addition, I certify that no part of this work will, in the future, be used in a submission in my name for any other degree or diploma in any university or other tertiary institution without the prior approval of the University of Adelaide.

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