From molecular structure to predicted thermal stability:

Molecular-based approaches for DSC Simulations

Baati Nadia, Nanchen Annik, Stoessel Francis, Meyer Thierry
EPFL, ISIC-GSCP, Group of Physical and Chemical Safety, Lausanne, Switzerland
Swissi Process Safety, Basel, Switzerland.
Corresponding author: thierry.meyer@epfl.ch

Thermal risks are potentially present in many steps of industrial chemical processes as most reactions carried out are exothermic, chemicals are often thermally unstable, and operating conditions set to favor high conversion and throughput. Therefore, it is crucial to perform an efficient risk assessment and to implement the proper risk mitigation measures to avoid accidents and their potentially disastrous consequences.

A rigorous thermal risk assessment is part of any appropriate safety system design. This requires answering crucial questions such as: would the chemical decompose? if so, at which temperature? how much heat would be released and at which rate? This information is deduced either from own data, literature, expertise, or experiments. In particular, Differential Scanning Calorimetry (DSC) allows to determine thermal decompositions characteristics such as its potential energy release, triggering temperature, and kinetic data. DSC experiments are not the most resources demanding thermal analysis, as an experiment can be conducted in a couple of hours on a sample of just few milligrams. However, when an intermediate cannot be isolated, is extremely toxic or is physically unavailable, it becomes simply impossible to perform a measurement. Additionally, when several tests have to be performed, the required resources accumulate. Hence, in the absence of practically feasible experiments and considering how important this information is, simulated estimations would be an appropriate substitute: they do not require samples, and could allow to analyze simultaneously numerous alternatives and determine the least hazardous one or highlight the one who demands further investigations.

This works aims at developing predictive models of the thermogram resulting from a DSC experiment on a pure compound only using its molecular structure. There are mainly two structure-based approaches of data prediction: Group Contribution (GC) models and Quantitative Structure-Property Relationships (QSPR). Within QSPR framework, each molecule is considered as an entity which structure can be encoded with numerical descriptors. The modelled property value is then estimated as a function of these descriptors. With GC methods, the molecules are divided into their constituting functional groups and each substructure is assigned a fraction of the compound's property. To estimate the property of a compound, the contributions of simple and complex groups are summed according to their occurrence in the molecular structure.

Within this study, 100 thermally reactive and structurally diverse chemicals are analyzed by DSC. Usually, only the onset temperature and the enthalpy are considered when modelling DSC-derived data, without regard that more comprehensive information regarding the thermal behavior is enclosed in the curve's shape as for instance the decomposition kinetics. Therefore, each experimental DSC measurement is characterized with five key properties that are modelled independently, and recombined to reconstruct the complete thermal trail. Predictive models are developed for each one of these five key properties

based on both QSPR and Marrero-Gani Group Contribution, and are evaluated relatively to the experimental data and compared to each other.

In summary, we propose a method relying on molecular-based approaches to predict the thermal stability and how it could be used to identify thermal threats without necessarily facing them. It is important to stress that predictive models should be handled with precaution when applied to sensitive data such as safety related information; they are not intended to replace proper experimental investigations, but rather be a helpful tool that delivers thermal stability estimations. This could, firstly, deliver estimated values in the absence of measurements and secondly, enable more efficient design of inherently safe processes by pointing early on at eventual substitutions with less hazardous chemicals. Finally, it could reduce the needed resources of experimental tests by narrowing the investigations focus and therefore enables better resources allocation.