

Kinetics of thermal decomposition: calculating the activation energy

Introduction

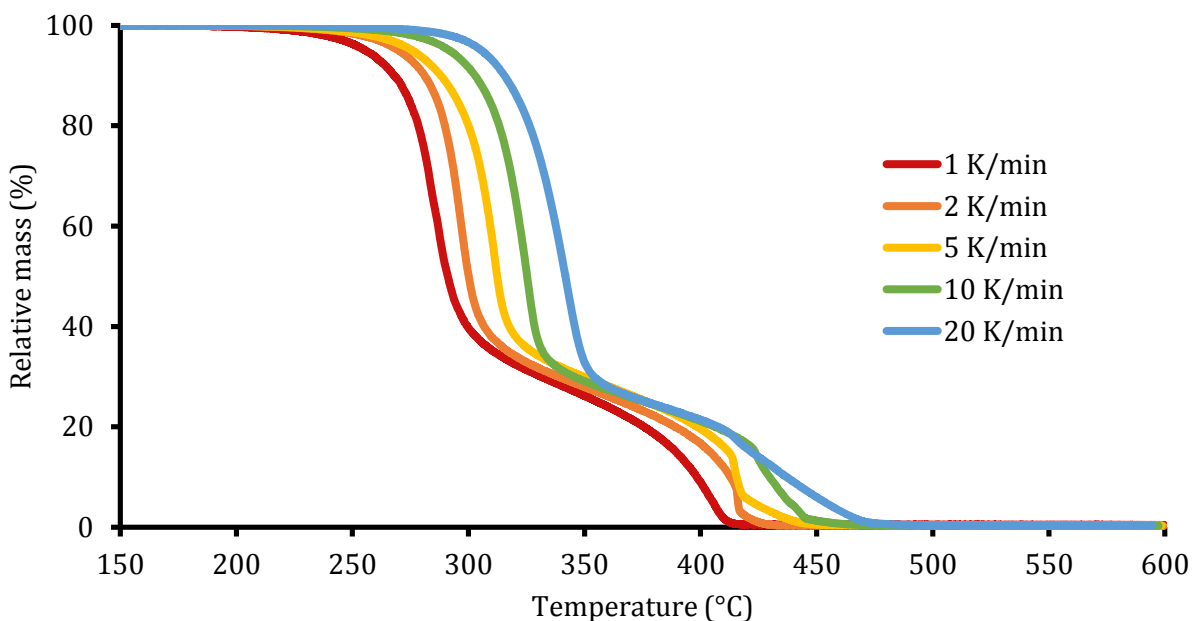
Thermal decomposition is characterised using thermogravimetric analysis (TGA), i.e. by monitoring the evolution of the system's mass with temperature. Usually the kinetics of the decomposition process are extracted from a series of experiments conducted at various heating rates. **The parameter of interest is the activation energy, which can be used in reaction engineering to model and**

optimise the process.

As the heating rate increases the temperature at which the thermal event occurs is shifted to higher temperatures. The measurement of this temperature shift at various heating rates is the basis of the present method. The corresponding activation energy is then calculated using the Arrhenius equation.

Experimental details

- Method: ISO 11358-2:2014(E) standard method for the determination of activation energies [1]
- Instrument: *Setaram Setsys Evo 16/18*, equipped with suspensions for TGA alone
- Thermal profile: heating ramp to 600 °C at various rates (1, 2, 5, 10 or 20 K/min)
- Atmosphere: dry air flow at 20 mL/min
- Sample: parchment paper Whatman B-2
- Amount of sample: around 17 mg
- Sample holder: open crucible of 170 μ L in alumina
- Sample preparation: drying at 150 °C for 20 min



Evolution of the relative mass with the temperature from 150 °C, at various heating rates. In all curves a first mass loss is observed between 300 °C and 350 °C but it is shifted toward high temperatures as the rate increases. N.B. The curve was corrected to remove the contribution of buoyancy effect, by subtracting the data from a identical run with the sample holder left empty.

Results

Kinetic models may be applied to the mass loss observed around 300 °C because it has the same shape and the same relative amplitude, i.e. 70 %, at all the heating rates tested. To do so the Ozawa-Flynn-Wall formula is employed, which considers that at a given degree of conversion, i.e. relative mass, the following term is constant: [1]

$$\ln \beta + \frac{E_a}{RT}$$

Where β is the heating rate, E_a the activation energy, R the gas constant and T the temperature reached at the given degree of conversion. That term being constant for all the couples of heating rate and temperature, the activation energy is calculated by a simple linear regression.

In the table on the right activation energies are presented at several relative mass thresholds, i.e. degrees of conversion according to the

theory. The standard deviation originating from the regression is also presented. The activation energy is similar through the entire mass loss step with values around 170 kJ/mol. Those values are similar to the ones obtained by the same approach on parchment paper, for small degrees of conversion [2].

Relative mass (%)	E_a (kJ/mol) with standard deviation
95	156 (18)
90	170 (17)
85	175 (13)
80	175 (10)
75	173 (9)
70	171 (8)
65	170 (9)
60	170 (10)
55	169 (11)
50	172 (13)
45	176 (16)

Conclusion

- Kinetics of thermal decomposition can be extracted from thermogravimetric curves, based on the fact that the temperature at which the thermal event occurs varies with the heating rate.
- That model may be applied only to thermogravimetric curves whose mass step shows the same shape and amplitude whatever the heating rate. At least three heating rates must be used and it is advised that the lowest and highest heating rates differ by a factor of 5.
- The experimental conditions must be rigorously kept the same for all the measurements. The buoyancy effect must be removed from each by subtracting a blank curve measured in the same condition, especially with the same heating rate.
- The calculation of activation energies relies on a linear regression, so the goodness of fit must be assessed and the calculated parameters must be presented with their standard deviation.

[1] Plastics — Thermogravimetry (TG) of polymers — Part 2: Determination of activation energy, ISO 11358-2:2014(E)

[2] Budrugač, P. J. Therm Anal Calorim (2009) 97: 443. <https://doi.org/10.1007/s10973-009-0081-9>