Thermal volatilisation is usually fitted with n-th order kinetics.

“Pyrolysis of lignocellulosic materials is usually explained as the sum of the thermal degradation of its main components: Hemicellulose (H), cellulose (C), and lignin (L).” Barneto et al 2009

broad pyrolysis profile makes it ok and possible to use regular nth order kinetics.

thermal analysis of biomass, mainly in the energy field, uses the Prout-Tompkin equation, an autocatalytic model, to estimate kinetic parameters, because it incorporates the nucleation order. This allows the model to depend on both reacted and not reacted fractions. The PT model estimates activation energies that are lower, and more realistic, than those estimated by nth order kinetics.

Burnham et al 1996

Prout-Tompkin 1944

However, recent analytical research ( Barneto et al 2009) has determined that, under N2 atmosphere and moderate heating rates, autocatalytic processes matter little to lignin, cellulose, and hemicellulose thermal degradation.

Nth order kinetics

Da/dt = k(1-a)n

K = k0\*exp(-E/RT)

Want to use symmetric Gaussian function for DTG curve deconvolution as part of the three parallel reaction model.

We would expect that

Tp(HC) < Tp(CL) < Tp(LG)

And

W(CL) < w(HC) < w(LG)

As in Yang et al 2007 and Chen et al 2017

Overlaps of curves gives rise to shoulder in curves (chen et al 2015, gronli et al 2002)

At each stage the kinetic analysis is performed to estimate the parameters and coefficients of a single stage problem. Then then are combined for the whole process using data from each stage. Sun et al 2015

Barneto et al 2009

Hu et al 2016

Capped their kinetic analysis between 105 and 675, the upper limit was to limit the effect of secondary char reactions with volatiles.

Orfao et al 1999

The characteristic shape of the DTG curve is characterised by the degradation of three main components. The cellulose is generally recognised as the main peak, at about 350C. Hemicellulose degrades at lower temperatures, and can be seen in the shoulder less than about 300C, and lignin degrades over a wider range of temperatures, from 150 all the way through 500.

Measurements were highly reproducible. Used linear temperature ramp of 5K/min.

Carrier et al 2011

Differences in chemical structures lead to different chemical reactivities – therefore composition of these three compounds crucial factor for desing in fuel projects in particular.

Concluded that TGA was useful for hemi and cell, but no possible for lignin.

Only tested on two materials: poplar wood and fern.

Tga has been proved to be useful as an alternative biomass measurement technique.

Orfao et al 1999

Three independent first-order reactions used for successful TGA determination. Using a priori pyrolysis of cellulose to inform model.

Term them ‘psedu-components’ because the three fractions are not exactly hemi, cell, and lignin. …

Barneto et al 2009

Thermal volatilization of biomass pseudo-component fitted suing nth order kinetics.

Dalpha/dt = k(1-alpha)^n

Where k = koe^-E/rt

Alpha is the conversion, n is the reaction order and k inetic constance. (according to Arrhenius law).

Using inert atmosphere (like mine – N) and moderate heatin grates (10C/min ok – source) nth order kinetics suitable for modelling degradation of biomass.

Autocatalytic processes not relevant for thermal degradation of extractives or pseudocomponents in inert atmosphere. Would be necessary for hmi and cell under air atmosphere. Mine is N2.