

Supplementary Material for Article

Non-Isothermal Kinetics: Best Fitting Empirical Models Instead of Model Free Methods

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Keywords: Non-isothermal kinetics • Least squares evaluation • Isoconversional methods • Model-free methods • Biomass • Wood • Spruce.

Scope of this document: The least squares evaluation of experimental $\alpha(t)$ curves and experimental $d\alpha(t)/dt$ curves are presented for five TGA experiments on a wood sample. An empirical model was used:

$$d\alpha/dt = A(\alpha)f(\alpha) \exp\left(-\frac{E}{RT}\right)$$

Note that E is constant here; the variation of the reactivity is expressed by function $A(\alpha)f(\alpha)$.

See more info in the paper.

The five TGA experiments were taken from the following work:

- Barta-Rajnai, E.; Várhegyi, G.; Wang, L.; Skreiberg, Ø.; Grønli, M.; Czégény, Zs. Thermal decomposition kinetics of wood and bark and their torrefied products. *Energy Fuels* **2017**, *31*, 4024-4034. doi: [10.1021/acs.energyfuels.6b03419](https://doi.org/10.1021/acs.energyfuels.6b03419) [Supporting info](#) [Repository](#)

Notation in the Figures:

Experimental curves: ○○○○;

Curves calculated from the model: — ;

Temperature (when present): - - - .

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S1. Evaluation of the experimental $\alpha(t)$ curves

Model: $d\alpha/dt = \tilde{A}(\alpha) \exp(-E/RT) (1-\alpha)$

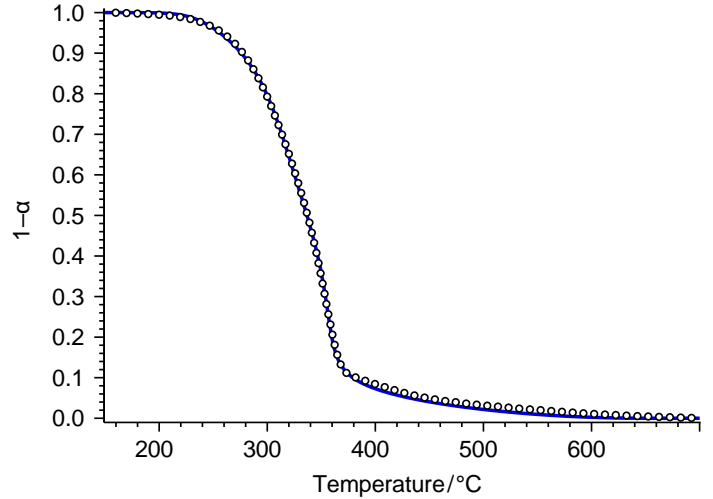
$E = 179.29911$

$x = 2\alpha - 1$

$\log_{10} \tilde{A}(x) = 12.241749 - .66597x + 2.01255x^2 + 2.242752x^3 - 3.154896x^4 - 4.881232x^5$

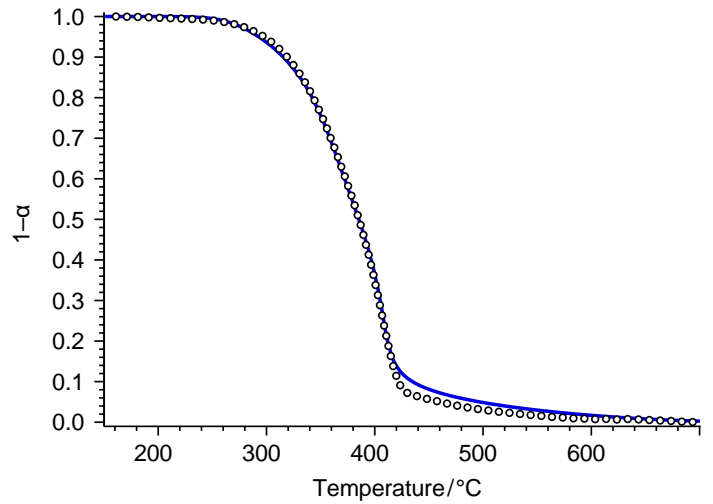
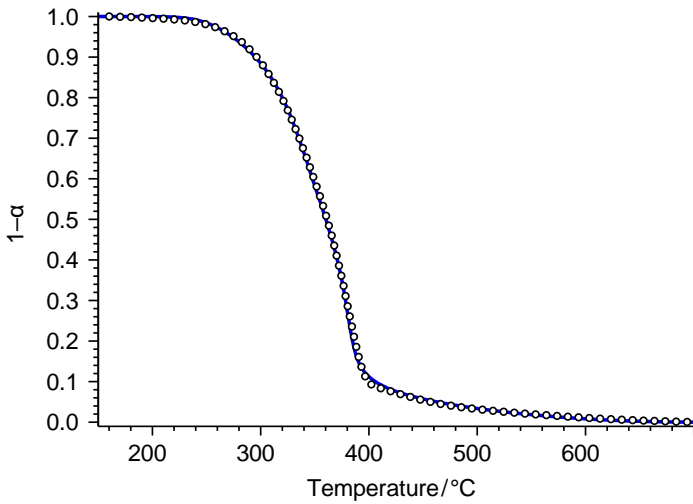
Expressed by Chebyshev polynomials of the first kind:

$\log_{10} \tilde{A}(x) = 12.064938T_0(x) - 2.034676T_1(x) - 0.571173T_2(x) - .964697T_3(x) - 0.394362T_4(x) - 0.305077T_5(x)$



Wood 2.5°C/min 4mg

Relative deviation: 0.72%, Deviation: 23. μg

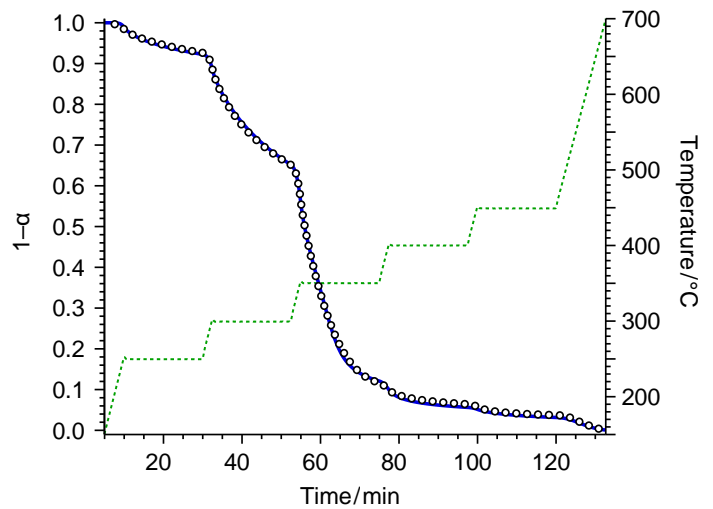
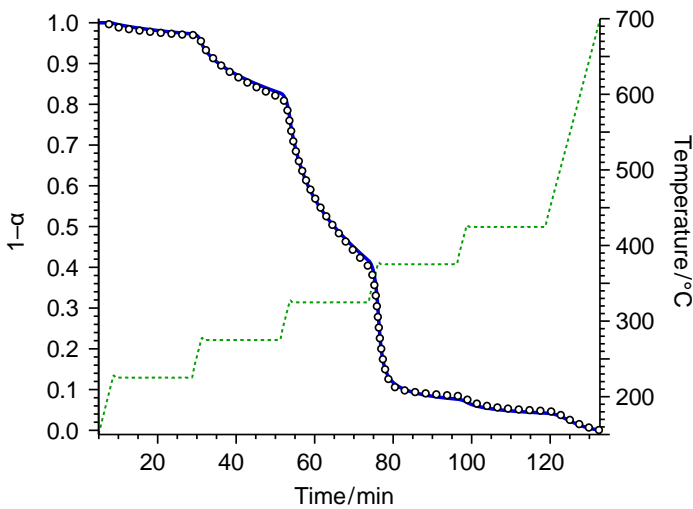


Wood 10°C/min 2mg

Relative deviation: 0.56 (0.56) %, Deviation: 9.3 μg

Wood 40°C/min 0.5mg

Relative deviation: 1.26 (1.26) %, Deviation: 5.1 μg



Wood stepwise T(t) A, 4mg

Relative deviation: 0.61 (0.61) %, Deviation: 20. μg

Wood stepwise T(t) B, 4mg

Relative deviation: 0.51 (0.51) %, Deviation: 19. μg

S2. Evaluation of the experimental $d\alpha/dt$ curves

Model: $d\alpha/dt = \tilde{A}(\alpha) \exp(-E/RT) (1-\alpha)$

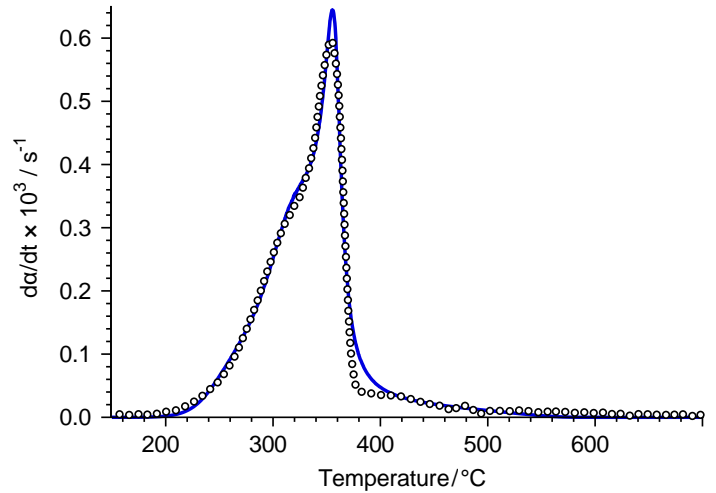
$E = 171.81292$

$x = 2\alpha - 1$

$\log_{10} \tilde{A}(x) = 11.613439 - 0.442952x + 1.448896x^2 + 0.847084x^3 - 2.244368x^4 - 2.849616x^5$

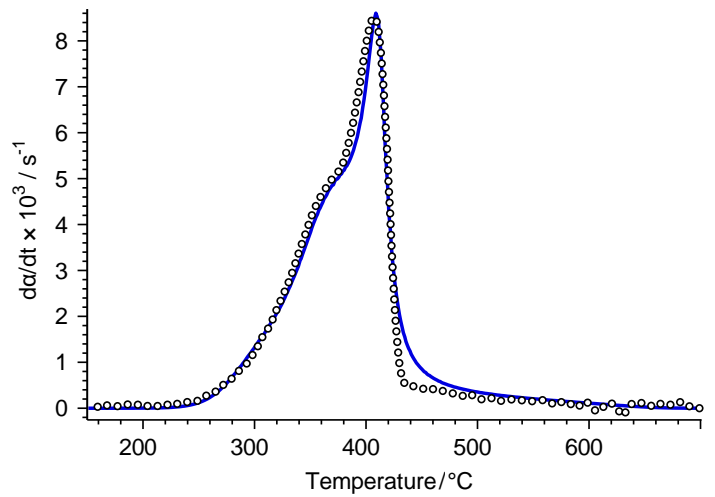
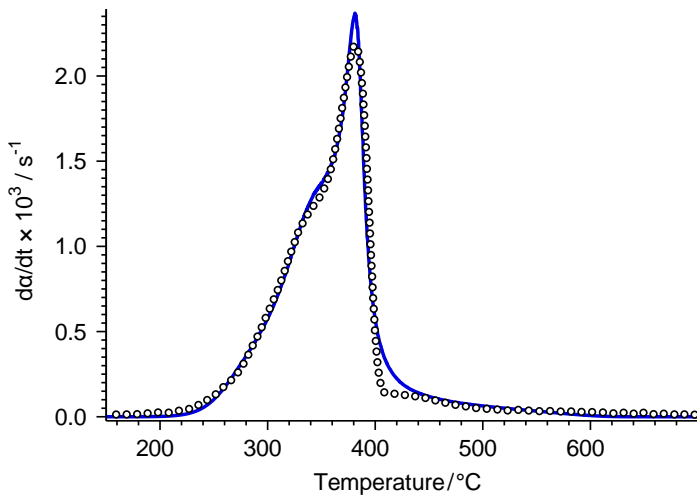
Expressed by Chebyshev polynomials of the first kind:

$\log_{10} \tilde{A}(x) = 11.496249T_0(x) - 1.588649T_1(x) - 0.397736T_2(x) - 0.678734T_3(x) - 0.280546T_4(x) - 0.178101T_5(x)$



Wood 2.5°C/min 4mg

Relative deviation: 2.29%, Deviation: 0.044 $\mu\text{g/s}$

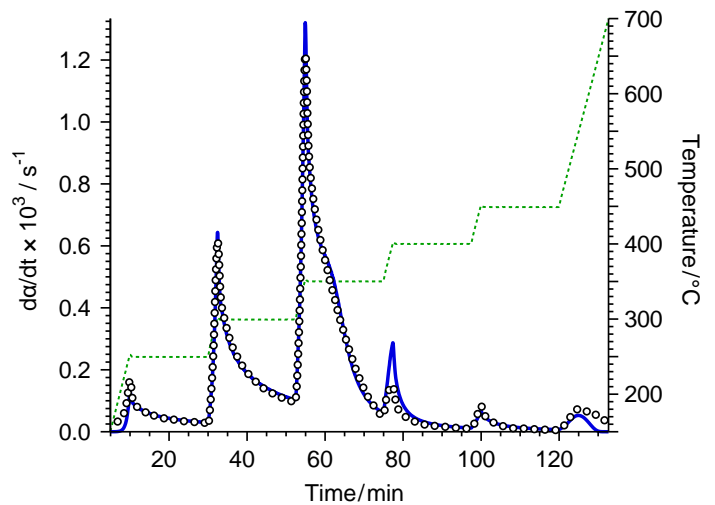
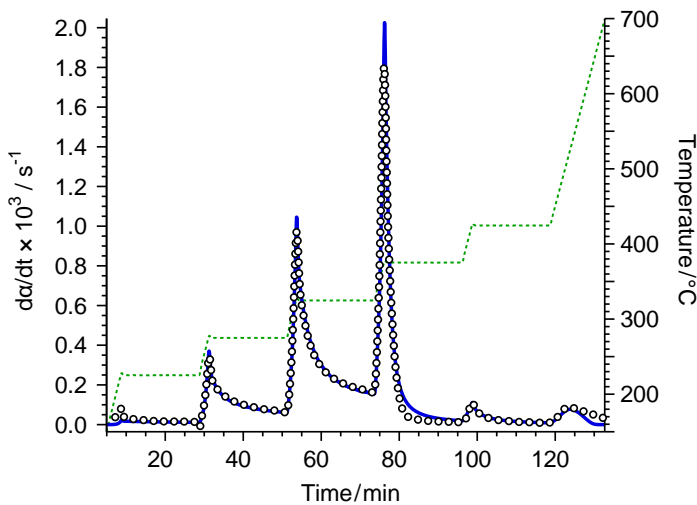


Wood 10°C/min 2mg

Relative deviation: 2.79%, Deviation: 0.10 $\mu\text{g/s}$

Wood 40°C/min 0.5mg

Relative deviation: 3.01%, Deviation: 0.10 $\mu\text{g/s}$



Wood stepwise T(t) A, 4mg

Relative deviation: 1.39%, Deviation: 0.082 $\mu\text{g/s}$

Wood stepwise T(t) B, 4mg

Relative deviation: 1.90%, Deviation: 0.085 $\mu\text{g/s}$