Kinetic parameters for biomass at self-ignition conditions: low-temperature oxidation and pyrolysis

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Supporting Information

Reproduction of published experiments

Some published experiments were reproduced to ensure the validity of the thermogravimetric measurements. Grønli et al.¹ published a round-robin study on pyrolysis of cellulose. The experiment at 5 K/min was reproduced and compared to the model published in.¹ The measured peak decomposition rate temperature in this experiment was on the higher end (605 K) of the range reported in the original study (600 K ± 5 K), Figure 1. Instead of Avicel cellulose, cellulose from Sigma-Aldrich was used. Total gas flow rate was 150 mL/min of nitrogen.



Figure 1: Reproduction of a round-robin study on cellulose pyrolysis kinetics. Model data:,¹ experimental data: cellulose, 5 K/min heating rate, 150 mL/min nitrogen

Two experiments for pyrolysis of pine published by Grønli et al.² and Anca-Couce et al.³ were also reproduced. Results are summarized in Figure 2. Of the models presented by Grønli et al.,² the biomass named "pine A" showed a better agreement with the measured data in this work. The model consists of four components, extractives, hemicellulose, cellulose and lignin.² Anca-Couce et al.³ consider only hemicellulose, cellulose and lignin as components. The experimental in this work was measured at a constant heating rate of 5 K/min and a nitrogen flow rate of 150 mL/min. The measured data shows slightly higher conversion rates than either model below 523 K. Between 550-650 K, experimental data of this work falls between the two models.^{2,3}

A comparison between the kinetic models^{2,3} and experiments carried out at 423–523 K is shown in Figure 3. The experiment consisted of six isothermal holding stages (423 K, 443 K, 463 K, 483 K, 503 K and 523 K) held for one hour each, with rapid heating of 10 K/minbetween stages and to reach the first iosthermal stage. Gas flow rates were 150 mL/min of nitrogen. Experiments reported by Grønli et al.² were originally carried out at 383–773 K,



Figure 2: Reproduction of published TGA experiments on pine pyrolysis kinetics. Model data from² refers to species "pine A", model data from³ is the model with three components hemicellulose, cellulose and lignin. Experimental data: pine, 5 K/min heating rate, 150 mL/min nitrogen



Figure 3: Extrapolation of published pine pyrolysis kinetics. Model data from² refers to species "pine A", model data from³ is the model with three components hemicellulose, cellulose, lignin. Experimental data: pine, 150 mL/min nitrogen, six isothermal stages at 423 K, 443 K, 463 K, 483 K, 503 K and 523 K held for one hour each.

5 K/min heating rate and 150 mL/min nitrogen flow. Anca-Couce et al.³ report data for 473–723 K and heating rates 2.5-10 K/min, so that the models presented in^{2,3} are strictly only valid under those conditions. The comparison shows that the models do not extrapolate very well to low temperatures and low heating rates or isothermal conditions. The model of Grønli et al.² predicts mass loss well during the first three isothermal stages 423–463 K, but overpredicts mass loss for higher temperatures. The model by Anca-Couce et al.³ predicts lower mass loss rates than measured between 423–463 K, and higher rates than measured for 483–523 K.

Kinetic control

Experiments under transient heating conditions can become limited by heat transfer, if heat transfer to and within the particle are not significantly faster than reaction rates.⁴ Heat transfer limitations in the pyrolysis experiments were checked against criteria presented by Hayhurst.⁵ Following that work, experiments with transient heating need to satisfy:

$$\mathrm{Bi} = 0.6 \,\frac{\mathrm{Nu}}{2} \,\frac{\lambda_{\mathrm{g}}}{\lambda_{\mathrm{s}}} < 0.1 \tag{1}$$

where Bi is the Biot number, Nu the Nusselt number and λ_g and λ_s the thermal conductivities of gas and solid, respectively. Approximating Nu = 2 for spherical particles in near stagnant flow,⁵ as well as biomass solid thermal conductivities $\lambda_s = 0.12-0.18 \text{ W/(m K)}^6$ and thermal conductivity of air or nitrogen 0.04 W/(m K) at 523 K,⁶ Bi = 0.13-0.2. This value is slightly higher than that used in the literature,⁵ yet still smaller than unity (equal timescales of external and internal heat transfer). As discussed in,⁵ the above expression does not depend on particle size, if gas velocities are low enough that size influences on Nu are negligible.

The Biot number was also estimated for the entire sample, i.e. the crucible with the particle bed. The crucible is approximated as a spherical object in near-stagnant flow, so that Nu = 2. Thermal conductivity of the crucible material (alumina) is one order of magnitude

higher than that of wood ($\lambda \approx 2 \text{ W/(m K)}$), so that it does not limit heat transfer through the bed. Thermal conductivity of the particle bed depends on the thermal conductivities of solid particles and interstitial gas, as well as the porosity ϕ of the bed. Assuming loosely packed beds, $\phi = 0.5-0.8$, and an effective thermal conductivity⁷ of

$$\lambda_{\text{eff}} = \phi \,\lambda_{\text{g}} + (1 - \phi) \,\lambda_{\text{s}} \tag{2}$$

Biot-numbers for the *sample* evaluate to 0.2-0.4. Temperature in the sample bed is therfore mainly, but not exclusively controlled by external heat transfer. Approximate kinetic control was nevertheless assumed, as Bi < 0.1 is difficult to achieve in practice.⁵

As internal heat transfer is faster than external heat transfer, the external Pyrolysis number Py, i.e. the rate of external heat transfer to reaction rate,⁴ was evaluated. To assume kinetic control, in addidition to Bi $\ll 1$, the timescale of reactions must be much larger than that of heat transfer, Py = $\tau_{\rm kin}/\tau_{\rm heat} \gg 1$, where $\tau_{\rm kin}$ is the kinetic timescale and $\tau_{\rm ht}$ the heat transfer timescale. The criterion gives a maximum value for the particle radius $r:^5$

$$\frac{2\rho c_{\rm p} r^2}{3\,{\rm Nu}\,\lambda_{\rm g}} < 0.1\cdot\tau_{\rm kin} \tag{3}$$

where ρ is the density of the solid and c_p its specific heat capacity. The kinetic timescale is estimated as $\tau_{\rm kin} = 1/k$, where k are the modelled reaction rates. Reaction rates are below $1 \times 10^{-3} \,{\rm s}^{-1}$ for temperatures below 523 K. Assuming $\rho = 600 \,{\rm kg/m^3}$,⁶ and $c_p = 2000 \,{\rm J/(kg \, K)}$,⁷ this allows for particle sizes up to 6 mm diameter. The above expression was also used to calculate the critical rate for 250 µm particles (the largest particle size used) results in $k = 0.6 \,{\rm s}^{-1}$. Such rates were only predicted above 700 K for pyrolysis and above 625 K for the oxidation models. The same calculation was carried out for the entire bed of particles, i.e. for lower densities (bulk density instead of solid density). Again assuming Nu = 2 and using the bed depth $(1/3 \cdot 4 \,{\rm mm})$ instead of the particle radius, critical reaction rates would be reached at temperatures of 555 K (20 % oxygen, $\phi = 0.5$), 570 K (20 % oxygen, $\phi = 0.8$), 590 K (pyrolysis, $\phi = 0.5$) and 620 K (pyrolysis, $\phi = 0.8$). Critical temperatures are lower for the oxidation experiments as total reaction rates are higher when oxygen is present.

In the oxidation experiments, lack of oxygen can inhibit kinetic control in addition to possible heat transfer limitations. For the loosely packed sample in the crucible, diffusion through the bed is the main mode of mass transfer. The ratio of oxygen consumption to oxygen diffusion can be expressed by a Damköhler number Da. In this work, it was estimated by:

$$Da = \frac{k(T) \cdot f(p_{O_2}) C_{O_2,\text{stoich}} L^2}{D C_{O_2,\text{amb}}}$$

$$\tag{4}$$

where $k(T) \cdot f(p_{O_2})$ is the reaction rate including oxygen partial-pressure dependency, $C_{O_2,\text{stoich}}$ the concentration of oxygen required for complete conversion (i.e., molar amount of oxygen per unit volume occupied by the sample), $C_{O_2,\text{amb}}$ the concentration of oxygen in the surroundings and D the diffusion coefficient. L is a characteristic length, in this case, the sample depth, 1.3 mm (one third of the crucible height). Kinetic control is given for Da \ll 1. The kinetic expression was evaluated for wheat, using the rate of oxidation model I. The diffusion coefficient was estimated by

$$D = 1.5 \times 10^{-5} \left(\frac{T}{T_{\rm ref}}\right)^{1.75}; \qquad T_{\rm ref} = 300 \,\mathrm{K}$$
 (5)

Stoichiometric oxygen demand can be calculated from the elemental composition. Ambient oxygen concentrations were calculated assuming a pressure of 101 325 Pa, 20 % oxygen, and by assuming sample and surroundings in thermal equilibrium. Based on these values, diffusion is much faster than consumption of oxygen (Da < 0.1) for T < 570 K.

Thermal runaway of samples can occur when heat is (locally) released faster than it can be dissipated by internal heat transfer. Such possible self-ignition of the sample was evaluating the dimensionless Frank-Kamenetskii parameter⁸ δ :

$$\delta = \frac{h_{\rm R} \rho}{\lambda_{\rm eff}} \frac{E_{\rm a}}{R T^2} L^2 \cdot k(T) \cdot f(p_{\rm O_2}) \tag{6}$$

where the mass-specific enthalpy of reaction $h_{\rm R}$ was set equal to the lower heating value of wheat (18.2 MJ/kg), the bulk density of the sample was $\rho = 97 \,\rm kg/m^3$, the effective thermal conductivity of the sample $\lambda_{\rm eff} = 0.07 \,\rm W/(m \,\rm K)$. The sample depth was used as characteristic length L. According to the theory of thermal explosions, samples are stable, i.e., do not self-ignite, when $\delta < \delta_{\rm crit}$. The critical values $\delta_{\rm crit}$ depend only on geometry, and are given as 0.88 for infinite slabs, 2.00 for infinite cylinders and 3.23 for spheres.⁸ In the worst-case assumption, the sample was treated as an infinite layer. Evaluating δ as a function of temperature T gave a critical temperature of 530 K. Assuming the sample can be represented by a sphere resulted in $T_{\rm crit} = 555 \,\rm K$. Repeating this calculation for 80 % oxygen, i.e. higher reaction rates, gave critical temperatures of 520 K and 540 K, respectively. Heat release kinetics are likely overestimated in the above calculation, as the smoldering conversion typical of the temperature range investigated leads to highly incomplete conversion⁹ (and thus lower heat release). Additionally, thermal runaway should be fairly easy to observe if it occured at low heating rates or during the isothermal stages – however, no excessive (uncompensated) self-heating was measured in any of the experiments.

In conclusion, which transport limitation is most critical with respect to assuming kinetic control depends on the type of experiment. The largest concern in experiments with constant heating rate was the Biot-number. For the stepwise isothermal experiment, this can be neglected, as the transient phases are short compared to the isothermal holding periods. As discussed by Hayhurst,⁵ the Biot-number depends largely on material properties, and values 1 < Bi < 0.1 are difficult to avoid for biomass. Possible self-ignition of the sample could be a concern in experiments with oxygen present. By conservative estimate, samples may come close to thermal runaway during the TG-experiments. Thermal runaway was

however not observed experimentally. Diffusion limitations were found to be negligible in the temperature range of interest. All estimations of critical parameters were carried out by neglecting the influence of conversion on reaction rates. Measured conversion rates were much lower ($< 0.0015 \,\mathrm{s}^{-1}$) than the reaction rates (compare the Arrhenius plots) used in the above calculations, so that the critical parameters include a considerable safety margin. The stepwise isothermal experiments are expected to be free from transport limitations, even if the above strict criteria are applied.

Kinetic data for cellulose, lignin, xylan and rapeseed oil

Kinetic parameters for the model components extractives, hemicellulose, lignin and cellulose were determined by thermogravimetric analysis and using the same time-temperature programs as for the six biomass samples. Rapeseed oil was used as a model compound for extractives. To simulate extractives bound in a matrix (i.e. as opposed to a bulk liquid), the oil was mixed in a ratio of 1:1 by weight with SiO_2 as an inert substrate. The consistency of the mixture was that of a thin paste. Alternative mixtures of rapessed oil and cellulose, and of linseed oil and either SiO_2 or cellulose were also investigated, but gave qualitatively similar results. As a model compound for hemicellulose, xylan (from cornstalk; abcr Chemie AB143294) was used. Lignin and cellulose were also acquired from a commercial supplier (alkali lignin: Sigma-Aldrich 471003, and cellulose powder: Sigma-Aldrich C6288).

Char yields of the model components were measured by heating in inert atmosphere at 5 K/min to 773 K, holding that temperature for 30 minutes, followed by a burnoff under 10% oxygen and 10 K/min heating rate to 973 K. Results of the heating in inert atmosphere are summarized in Figure 4 for xylan, lignin and cellulose. Extractives were assumed to be completely volatilizable, either by pyrolytic decomposition or by evaporation. The residues at 773 K were approximately 9% for cellulose, 25% for xylan and 65% for lignin. On burnout, cellulose and xylan left no residue, while the lignin sample left around 5% ash residue. Char ratios of the three components were therefore 9:25:60 (cellulose:xylan:lignin),



Figure 4: Experiments at 5 K/min heating rate under 0% oxygen to determine the volatilizable fractions of hemicellulose, cellulose and lignin. Xylan was used as a hemicellulose model component.

which was rounded to 10:30:60 in the model.

Activation energies of extractives, hemicellulose, lignin and cellulose were determined by the same stepwise isothermal heating program used for the six biomasses: holding for one hour each at 423 K, 443 K, 463 K, 483 K, 503 K and 523 K, with rapid heating (10 K/min) to reach the first isothermal period and in between isothermal stages. Experiments were carried out under 0%, 20% and 80% oxygen. Kinetic parameters were then obtained by the same model as for the six biomasses, i.e. total conversion rate is the sum of pyrolysis and oxidation rate

$$\frac{dX_i}{dt} = k_{\text{pyr, i}} \cdot (1 - X_i(t))^{n_{\text{pyr, i}}} + k_{\text{ox, i}} \cdot (1 - X_i(t))^{n_{\text{ox i}}} \cdot \left(\frac{p_{O_2}}{p_{\text{ref}}}\right)^{n_{O_2,i}}$$
(7)

for each component i. Reactions were assumed to be n-order and reaction rates k were modelled by an Arrhenius-expression as outlined above. Kinetic parameters were found by a least-square fit of the reaction model to the measured data. This was carried out in two steps: the parameters of the pyrolysis reaction $\{E_a, k_0, n_{pyr}\}$ were determined first from experimental data under 0% oxygen. These parameters were then kept fixed, while those of the oxidation reaction $\{E_a, k_0, n_{ox}, n_{O_2}\}$ were fitted. The numeric results are summarized in Table 1, and modelled and experimental data are compared in Figures 5 through 8. The value of the kinetic parameters depended to some degree on the final mass $m_{f,i}$ that was assumed in their fitting. For xylan, lignin and cellulose, the remaining mass fraction for pyrolysis up to 500 °C (Figure 4) was used. For the rapeseed-oil-SiO₂ mixture, it was assumed that all oil is reacted or evaporated and only the inert substrate remains.

Over the temperature range 423-523 K, xylan showed the highest mass loss. However, lignin and the rapeseed-oil-SiO₂ mixture have high 'baselines' of inert material (65% and 50%, respectively), so that the relative loss of reactive material is also considerable in the temperature range investigated. Cellulose showed very little mass loss during the lower temperature stages of the experiment, but reactions were found to rapidly accelerate beyond 503 K.

The overall behavior of lignin interestingly resembled that of native biomasses from a qualitative point of view. Similar to the native biomasses, its behavior is only approximated by the combination of two n-order reactions for pyrolysis and oxidation. Rapeseed oil, xylan

Table 1: Kinetic parameters for volatilizable fractions of extractives, hemicellulose, lignin and cellulose. Rapeseed oil mixed (50 % by weight) with SiO_2 as inert substrate was used as a model compound for extractives in a matrix. Xylan was used as a model compound for hemicellulose.

| | | Rapeseed $oil+SiO_2$ | Xylan | Lignin | Cellulose |
|----------------------|------------|----------------------|-----------------------|--------------------|-----------------------|
| $m_{ m f}/m_0$ | [kg/kg] | 0.5 | 0.25 | 0.65 | 0.09 |
| $E_{\rm a, \ pyr}$ | [kJ/mol] | 58.9 | 118 | 126 | 184 |
| $k_{0, \text{ pyr}}$ | $[s^{-1}]$ | 2.02×10^1 | 2.85×10^9 | 5.63×10^8 | 1.56×10^{13} |
| $n_{ m pyr}$ | [—] | 1 | 6.98 | 7.51 | 1 |
| $E_{\rm a, \ ox}$ | [kJ/mol] | 72.8 | 150 | 117 | 226 |
| $k_{0, \text{ ox}}$ | $[s^{-1}]$ | $8.85 	imes 10^2$ | 3.64×10^{-5} | 2.41×10^4 | 1.31×10^{15} |
| n_{ox} | [—] | 14.3 | 1 | 1.42 | 1 |
| n_{O_2} | [] | 0.40 | 1 | 0.76 | 0.67 |



Figure 5: Modelled and measured mass loss of rapeseed oil on SiO_2 powder, mixed 1:1 by weight. Six isothermal stages at 423 K, 443 K, 463 K, 483 K, 503 K and 523 K held for one hour each, different oxygen concentrations.



Figure 6: Modelled and measured mass loss of xylan. Six isothermal stages at 423 K, 443 K, 463 K, 483 K, 503 K and 523 K held for one hour each, different oxygen concentrations.



Figure 7: Modelled and measured mass loss of lignin. Six isothermal stages at 423 K, 443 K, 463 K, 483 K, 503 K and 523 K held for one hour each, different oxygen concentrations.



Figure 8: Modelled and measured mass loss of cellulose. Six isothermal stages at 423 K, 443 K, 463 K, 483 K, 503 K and 523 K held for one hour each, different oxygen concentrations.

and cellulose on the other hand showed very specific trends. The decomposition of xylan did not appear to be affected by the concentration or presence of oxygen. The modelled oxidation reaction has very low rates, so that the three model curves for 0%, 20% and 80% oxygen collapse onto the pyrolysis curve. Two explanations are possible: either oxidation of xylan is very slow compared to its pyrolysis, or the experiment was not kinetically controlled. Several researchers working in temperature ranges from ambient temperature to 800 K or higher consider 5 mg sufficiently small to avoid diffusion limitations, $^{2,10-15}$ while some allow up to 10 mg. $^{16-19}$ Sample masses were 6.8 mg, 6.5 mg and 7.1 mg in the experiments show in Figure 6, while final temperatures and heating rates were lower in our experiments (implying lower reaction rates) than those reported in the literature. $^{2,10-19}$

It was also noted that the xylan powder was very hygroscopic and would immediately absorb humidity from the surrounding air when preparing the samples, forming sticky agglomerates in the process. This may have led to additional transport limitations. Ultimately, the reasons for the observed behavior of xylan could not be resolved. The activation energy reported for xylan in Table 1 was initially used to model the hemicellulose component of the biomass, but replaced with higher values for reasons described in the results section of this work.

Pyrolysis reactions of both the rapeseed oil mixture and cellulose could be equally well represented by a first or zero-order reaction in the temperature range 423–523 K. The reaction order did not appear to affect the respective values determined for the activation energies.

Comparing the kinetic parameters for the pure coponents in Table 1 with those for the components as they appear in the biomasses (see main text) shows rather large differences in the pre-exponential factors k_0 and reaction orders n. This behavior is expected, owing to physical and chemical changes introduced during separation procedures, neglecting interactions among components and absence of catalytic effects of inorganic matter when studying the isolated components.²⁰

Comparison of oxidation models I and II

Oxidation models I and II showed only minor differences in the temperature region of interest, 423–523 K. A comparison of model I and measured data can be seen in the main body of the text. The corresponding plots for model II are found in Figure 9. Differences between the models become apparent at temperatures above ca. 520-550 K for a heating rate of 5 K/min.

Table 2 lists the scaled root-mean-square deviations of both oxidation models compared to measured data. Both models represent measured data with similar accuracy.



Figure 9: Oxidation model II: comparison of isothermal experiment and model, assuming separate oxidation kinetics of hemicellulose, cellulose, lignin and extractives. Kinetic parameters are listed in the main text

| Biomass | Model | $\delta_{ m S}(m/m_0)$ | | $\delta_{ m S}(dX/dt)$ | |
|-----------------|-------|------------------------|------------|------------------------|------------|
| Isothermal | | $20\% O_2$ | $80\% O_2$ | $20\% O_2$ | $80\% O_2$ |
| | | [%] | [%] | [%] | [%] |
| Beech | Ι | 1.25 | 1.53 | 11.0 | 12.3 |
| | II | 1.84 | 0.91 | 10.3 | 12.4 |
| Pine | Ι | 5.55 | 4.27 | 12.3 | 10.6 |
| | II | 0.72 | 1.25 | 14.4 | 11.9 |
| Sunflower | Ι | 1.15 | 0.80 | 12.5 | 13.2 |
| | II | 0.73 | 0.81 | 12.2 | 12.4 |
| Wheat | Ι | 3.79 | 1.76 | 11.4 | 9.2 |
| | II | 1.87 | 1.29 | 13.1 | 12.0 |
| Wood pellets I1 | Ι | 2.40 | 2.15 | 11.2 | 11.1 |
| | II | 0.88 | 1.32 | 10.4 | 12.5 |
| Wood pellets I2 | Ι | 2.79 | 2.80 | 11.1 | 11.2 |
| | II | 2.46 | 1.53 | 15.8 | 10.4 |
| 5 K/ min ramp | | $10\% O_2$ | $20\% O_2$ | $10\% O_2$ | $20\% O_2$ |
| | | [%] | [%] | [%] | [%] |
| Beech | Ι | 2.65 | 2.77 | 7.35 | 7.00 |
| | II | 1.73 | 1.46 | 6.29 | 5.90 |
| Pine | Ι | 5.09 | 5.53 | 10.4 | 10.8 |
| | II | 3.03 | 3.26 | 5.29 | 6.11 |
| Sunflower | Ι | 3.43 | 3.84 | 9.69 | 9.52 |
| | II | 3.13 | 3.40 | 10.6 | 9.31 |
| Wheat | Ι | 2.89 | 2.80 | 6.30 | 6.04 |
| | II | 2.18 | 2.59 | 11.2 | 13.8 |
| Wood pellets I1 | Ι | 3.97 | 3.91 | 9.79 | 9.70 |
| | II | 3.04 | 2.68 | 5.77 | 6.16 |
| Wood pellets I2 | Ι | 4.29 | 4.55 | 11.0 | 11.1 |
| | II | 4.89 | 4.72 | 8.43 | 8.99 |

Table 2: Scaled root-mean-square deviations $(\delta_{S,\varphi})$ between modelled and measured data in oxidative atmosphere. "Isothermal" refers to the stepwise isothermal experiments, "ramp" to those at constant heating rate 5 K/min.

Use of K-content to determine cellulose pyrolysis kinetics

Inorganic elements are well-known to catalyze the pyrolysis of biomass.^{20–22} Catalytic effects of potassium have been reported for cellulose^{22–26} and hemicellulose components.^{24,26} Our experiments were consistent with the literature, in that the temperature of peak pyrolytic decomposition rate scaled with the potassium content of the samples, Figure 10. The peak in pyrolysis decomposition rate is typically associated with the cellulose component.²⁰ A linear correlation can be found for the pre-exponential factor for celullose pyrolysis $k_{0,pyr,CELL}$ to reproduce these temperatures ($E_{a,pyr,CELL} = 185 \text{ kJ/mol}$) as a function of the cellulose mass fraction $w_{\rm K}$ [kg kg⁻¹]:

$$k_{0,\text{pvr,CELL}} = (9.34 \times 10^{15} \cdot w_{\text{K}} + 2.37 \times 10^{12} \pm 2.29 \times 10^{12}) \cdot \text{s}^{-1}$$
(8)

The correlation and the actual values used in the pyrolysis model are seen on the right side of Figure 10. Comparing the model predictions for the cellulose components with measured data for pure cellulose (Figure 11), it can be seen that the models predict a broader range



Figure 10: Peak pyrolysis rates and potassium content: The temperature of peak conversion rates T_{peak} correlates with biomass potassium content (left). This correlation can be used to estimate the interval of $k_{0,\text{pyr,CELL}}$ (right, dashed lines), for an apparent activation energy of 185 kJ/mol. Points represent the values used in the pyrolysis models of the six biomasses.

of decomposition than that seen for isolated cellulose. The peaks for sunflower and wheat cellulose components appear at lower temperatures than that of pure cellulose, those of pine and the two wood pellet samples are delayed.

Modelled conversion of biomass components

Figures 12 through 17 show the cumulated conversion of extractives, hemicellulose, lignin, cellulose and char as predicted by the pyrolysis model (left), oxidation model I at 20% oxygen (center) and oxidation model II at 20% oxygen (right), as predicted for the stepwise isothermal experiments 423-523 K (compare main text)

The figures illustrate how the different components of the biomasses are gradually consumed in the isothermal experiments, starting with the most reactive fractions (extractives and hemicellulose). No consumption of char is predicted. Conversion of cellulose is weak for the pyrolysis cases, and only occurs in the final isothermal stages. The main difference



Figure 11: Pyrolysis models of the cellulose components for six biomasses, compared to measured data for pure cellulose pyrolysis



Figure 12: Beech: cumulated conversion of components during stepwise isothermal TGA experiments (423–523 K). Unlabeled fractions are ash (bottom) and extractives (top). Labels (I) and (II) refer to oxidation models I and II, respectively.



Figure 13: Pine: cumulated conversion of components during stepwise isothermal TGA experiments (423–523 K). Unlabeled top fraction is extractives, ash content is < 0.01. Labels (I) and (II) refer to oxidation models I and II, respectively.



Figure 14: Sunflower: cumulated conversion of components during stepwise isothermal TGA experiments (423–523 K). Unlabeled fractions are ash (bottom) and extractives (top). Labels (I) and (II) refer to oxidation models I and II, respectively.



Figure 15: Wheat: cumulated conversion of components during stepwise isothermal TGA experiments (423–523 K). Unlabeled fractions are ash (bottom) and extractives (top). Labels (I) and (II) refer to oxidation models I and II, respectively.



Figure 16: Wood pellets I1: cumulated conversion of components during stepwise isothermal TGA experiments (423–523 K). Unlabeled top fraction is extractives, ash content is < 0.01. Labels (I) and (II) refer to oxidation models I and II, respectively.

Figure 17: Wood pellets I2: cumulated conversion of components during stepwise isothermal TGA experiments (423–523 K). Unlabeled top fraction is extractives, ash content is < 0.01. Labels (I) and (II) refer to oxidation models I and II, respectively.

between oxidation model I and II is in the relative conversion of cellulose and hemicellulose. Model II predicts very little cellulose conversion (in agreement with the pure cellulose experiments the model is based on). Lignin conversion does not differ much between the two oxidation models, as the global oxidation kinetic parameters (model I) and those of the lignin component (model II) are very similar.

References

- Grønli, M.; Antal, M. J.; Várhegyi, G. A Round-Robin Study of Cellulose Pyrolysis Kinetics by Thermogravimetry. *Industrial & Engineering Chemistry Research* 1999, 38, 2238–2244.
- (2) Grønli, M. G.; Várhegyi, G.; Blasi, C. D. Thermogravimetric Analysis and Devolatilization Kinetics of Wood. Industrial and Engineering Chemistry Research 2002, 41, 4201– 4208.
- (3) Anca-Couce, A.; Zobel, N.; Berger, A.; Behrendt, F. Smouldering of pine wood: Kinetics and reaction heats. *Combustion and Flame* 2012, 159, 1708–1719.
- (4) Pyle, D. L.; Zaror, C. A. Heat transfer and kinetics in the low temperature pyrolysis of solids. *Chemical Engineering Science* 1984, 39, 147–158.
- (5) Hayhurst, A. N. The kinetics of the pyrolysis or devolatilisation of sewage sludge and other solid fuels. *Combustion and Flame* **2013**, *160*, 138–144.
- (6) Verein Deutscher Ingenieure VDI-Gesellschaft Verfahrenstechnik und Chemieingenieurwesen (GVC),, Ed. VDI-Wärmeatlas, 10th ed.; Springer Berlin Heidelberg, 2006.
- (7) Sjöström, J.; Blomqvist, P. Direct measurements of thermal properties of wood pellets:
 Elevated temperatures, fine fractions and moisture content. *Fuel* 2014, 134, 460–466.

- (8) Frank-Kamenetskii, D. A. Diffusion and Heat Transfer in Chemical Kinetics, 2nd ed.;
 Plenum Press, 1969; English translation by J. P. Appleton.
- (9) Perzon, M. Emissions of organic compounds from the combustion of oats a comparison with softwood pellets. *Biomass and Bioenergy* 2010, 34, 828–837.
- (10) Branca, C.; Di Blasi, C. Global interinsic kinetics of wood oxidation. *Fuel* 2004, *83*, 81–87.
- (11) Font, R.; Conesa, J. A.; Moltó, J.; Muñoz, M. Kinetics of pyrolysis and combustion of pine needles and cones. *Journal of Analytical and Applied Pyrolysis* 2009, 85, 276–286.
- (12) Shen, D. K.; Gu, S.; Luo, K. H.; Bridgwater, A. V.; Fang, M. X. Kinetic study on thermal decomposition of woods in oxidative environment. *Fuel* **2009**, *88*, 1024–1030.
- (13) Conesa, J. A.; Domene, A. Biomasses pyrolysis and combustion kinetics through n-th order parallel reactions. *Thermochimica Acta* 2011, 523, 176–181.
- (14) Branca, C.; Di Blasi, C. A unified mechanism of the combustion reactions of lignocellulosic fuels. *Thermochimica Acta* 2013, 565, 58–64.
- (15) Benkorichi, S.; Fateh, T.; Richard, F.; Consalvi, J.-L.; Nadjai, A. Investigation of thermal degradation of pine needles using multi-step reaction mechanisms. *Fire Safety Journal* 2017, *91*, 811–819.
- (16) Safi, M. J.; Mishra, I. M.; Prasad, B. Global degradation kinetics of pine needles in air. *Thermochimica Acta* 2004, 412, 155–162.
- (17) Amutio, M.; Lopez, G.; Aguado, R.; Artetxe, M.; Bilbao, J.; Olazar, M. Kinetic study of lignocellulosic biomass oxidative pyrolysis. *Fuel* **2012**, *95*, 305–311.
- (18) Abreu Naranjo, R.; Conesa, J.; Foppa Pedretti, E.; Romero Romero, O. Kinetic analysis: Simultaneous modelling of pyrolysis and combustion processes of dichrostachys cinerea. *Biomass and Bioenergy* **2012**, *36*, 170–175.

- (19) Niu, H.; Liu, N. Thermal decomposition of pine branch: Unified kinetic model on pyrolytic reactions in pyrolysis and combustion. *Fuel* **2015**, *160*, 339–345.
- (20) Di Blasi, C. Modeling chemical and physical processes of wood and biomass pyrolysis. Progress in Energy and Combustion Science 2008, 34, 47–90.
- (21) Anca-Couce, A. Reaction mechanisms and multi-scale modelling of lignocellulosic biomass pyrolysis. Progress in Energy and Combustion Science 2016, 53, 41–79.
- (22) Saddawi, A.; Jones, J. M.; Williams, A. Influence of alkali metals on the kinetics of the thermal decomposition of biomass. *Fuel Processing Technology* **2012**, *104*, 189–197.
- (23) Antal, M. J.; Varhegyi, G. Cellulose Pyrolysis Kinetics: The Current State of Knowledge. Industrial & Engineering Chemistry Research 1995, 34, 703–717.
- (24) Jensen, A.; Dam-Johansen, K.; Wójtowicz, M. A.; Serio, M. A. TG-FTIR Study of the Influence of Potassium Chloride on Wheat Straw Pyrolysis. *Energy & Fuels* 1998, 12, 929–938.
- (25) Eom, I.-Y.; Kim, J.-Y.; Kim, T.-S.; Lee, S.-M.; Choi, D.; Choi, I.-G.; Choi, J.-W. Effect of essential inorganic metals on primary thermal degradation of lignocellulosic biomass. *Bioresource Technology* **2012**, *104*, 687–694.
- (26) Khazraie Shoulaifar, T.; DeMartini, N.; Karlström, O.; Hupa, M. Impact of organically bonded potassium on torrefaction: Part 1. Experimental. *Fuel* **2016**, *165*, 544–552.