Supporting Information for Article

Thermogravimetric study of biomass pyrolysis kinetics. A distributed activation energy model with prediction tests

Energy Fuels, **2011**, *25*, 24-32. *doi:* 10.1021/ef101079r

Gábor Várhegyi,[†,*] *Balázs Bobály,*[†] *Emma Jakab,*[†] *and Honggang Chen,*[‡]

[†] Institute of Materials and Environmental Chemistry, Chemical Research Center, Hungarian Academy of Sciences, P.O. Box 17, Budapest, Hungary 1525; and [‡] National Engineering Laboratory for Biomass Power Generation Equipment, School of Renewable Energy, North China Electric Power University, 2 Beinong Road, Beijing, China 102206.

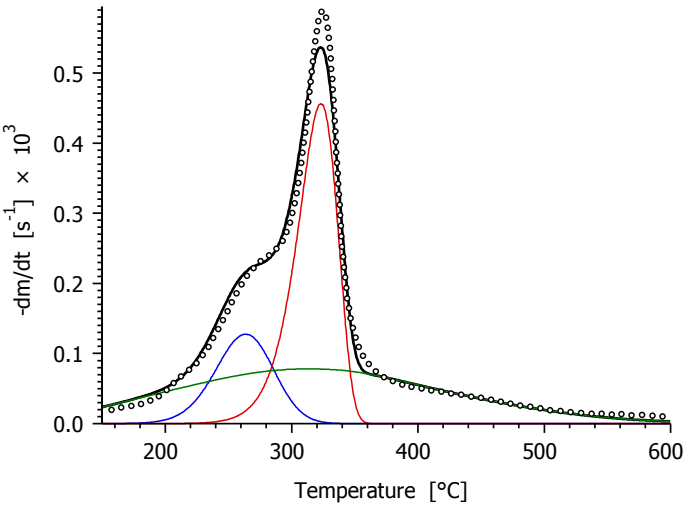
[*] To whom correspondence should be addressed.
Email: varhegyi.gabor@t-online.hu or gvarhegyi@gmail.com

Keywords: Corn stalk; rice husk; sorghum; wheat straw; thermal decomposition; kinetics; prediction.

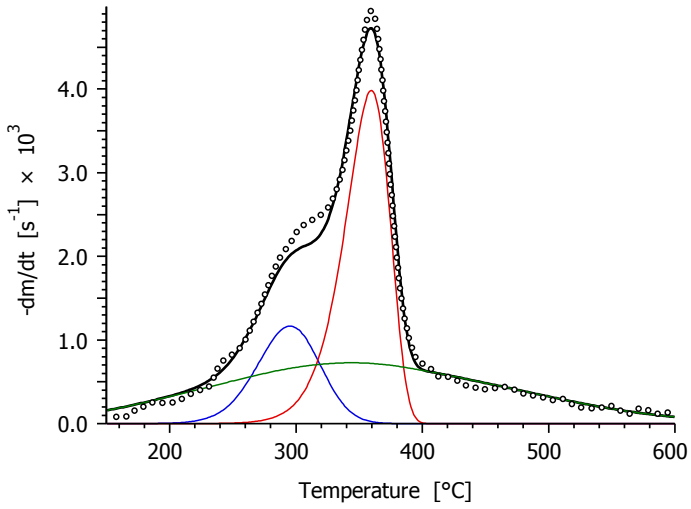
Scope of this document: The kinetic evaluation of the samples was illustrated by figures on the highest heating rate (40°C/min) in the corresponding paper. The present *Supporting Information* shows all the 16 experiments that were evaluated simultaneously. Figures S1 and S2 corresponds to model variants II and V in the article.

Notations: The first row below each figure contains the name of the sample and a brief description of the experimental conditions. The second row lists the fit quality for the given experiment (fit_1) and for the whole series (fit_{16}). The further rows display the parameters (E_0, $\log_{10} A$, σ and c) for the partial processes.

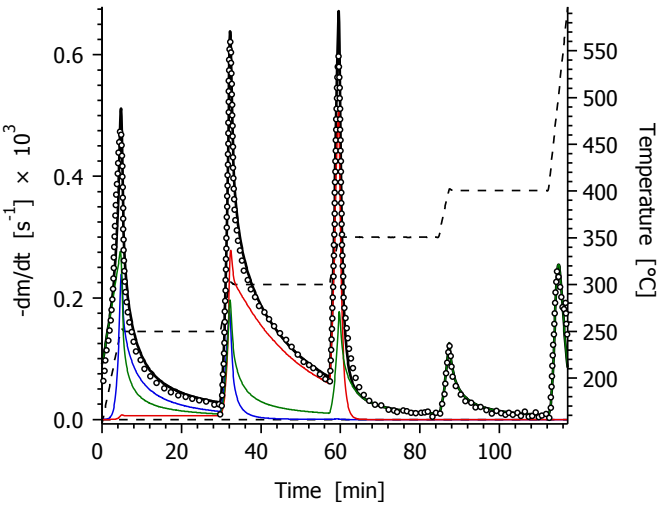
Colors: ***Blue color*** denotes a pseudocomponent due mainly to the thermal decomposition of hemicelluloses. ***Red color*** indicates the process associated to cellulose pyrolysis. ***Dark green*** represents a very wide partial peak that starts with the low temperature phenomena of the biomass pyrolysis; continues with lignin decomposition processes; and terminates with the formation and devolatilization reactions of charcoal. The connection between the very different chemical reactions in the dark green peak is that they can be described by the same kinetic equation by the same kinetic parameters.



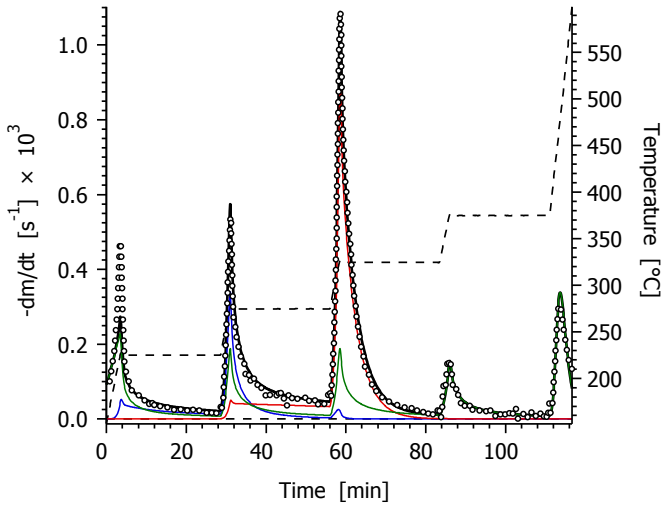
Corn stalk, 4mg, 4°C/min
fit_1=2.19%; fit_{16}=1.86%
1: E_0=175.6 $\log_{10}A$=14.64 σ(E)=5.8
2: E_0=185.4 $\log_{10}A$=13.86 σ(E)=0
3: E_0=195.4 $\log_{10}A$=14.68 σ(E)=36.6
C: 10.7 27.9 31.7



Corn stalk, 0.5mg, 40°C/min
fit_1=1.87%; fit_{16}=1.86%
1: E_0=175.6 $\log_{10}A$=14.64 σ(E)=5.8
2: E_0=185.4 $\log_{10}A$=13.86 σ(E)=0
3: E_0=195.4 $\log_{10}A$=14.68 σ(E)=36.6
C: 10.7 27.9 31.7

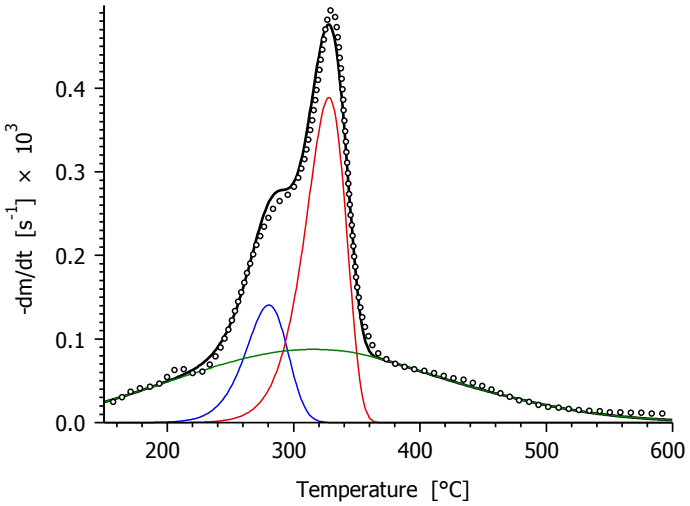


Corn stalk, 2mg, steps: 250 - 400°C
fit_1=2.39%; fit_{16}=1.86%
1: E_0=175.6 $\log_{10}A$=14.64 σ(E)=5.8
2: E_0=185.4 $\log_{10}A$=13.86 σ(E)=0
3: E_0=195.4 $\log_{10}A$=14.68 σ(E)=36.6
C: 10.7 27.9 31.7



Corn stalk, 2mg, steps: 225 - 375°C
fit_1=2.13%; fit_{16}=1.86%
1: E_0=175.6 $\log_{10}A$=14.64 σ(E)=5.8
2: E_0=185.4 $\log_{10}A$=13.86 σ(E)=0
3: E_0=195.4 $\log_{10}A$=14.68 σ(E)=36.6
C: 10.7 27.9 31.7

Figure S1. Simultaneous evaluation of 16 experiments assuming identical $E_{0,j}$ values for the four biomasses. The rest of the parameters, $\log_{10}A$, σ and c, depend on the kind of biomass in this approximation. The experimental data (○○○), their simulated counterparts (**—**) and the calculated partial curves (—, —, —) are displayed. The curves are plotted as functions of time in the figures with stepwise heating programs. In this case the experimental temperature values are also displayed (- - -).



Rice husk, 4mg, 4°C/min

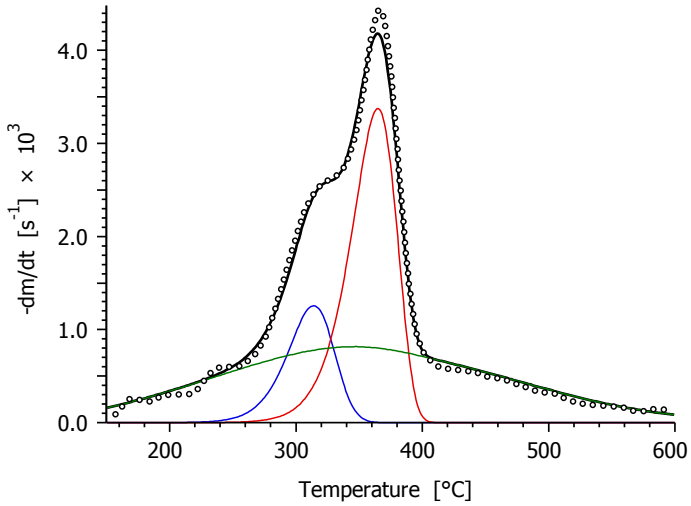
fit_1=1.68%; fit_{16}=1.86%

1: E_0=175.6 $\log_{10}A$=14.19 σ(E)=2.5

2: E_0=185.4 $\log_{10}A$=13.73 σ(E)=0

3: E_0=195.4 $\log_{10}A$=14.63 σ(E)=35.6

C: 8.8 24.1 34.7



Rice husk, 1mg, 40°C/min

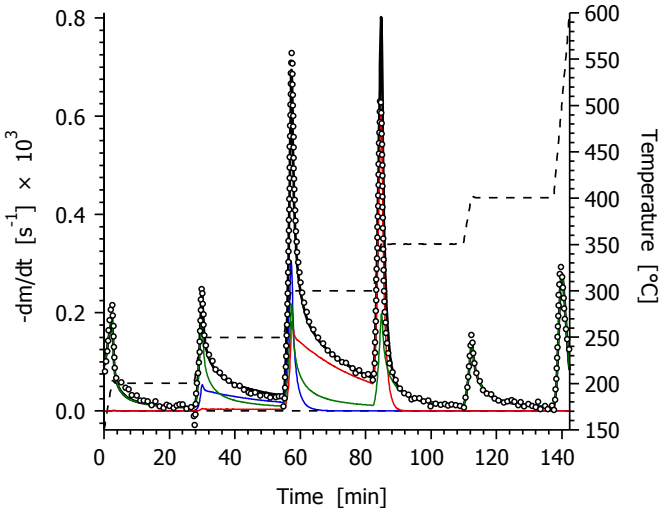
fit_1=1.73%; fit_{16}=1.86%

1: E_0=175.6 $\log_{10}A$=14.19 σ(E)=2.5

2: E_0=185.4 $\log_{10}A$=13.73 σ(E)=0

3: E_0=195.4 $\log_{10}A$=14.63 σ(E)=35.6

C: 8.8 24.1 34.7



Rice husk, 2mg, steps: 200 - 400°C

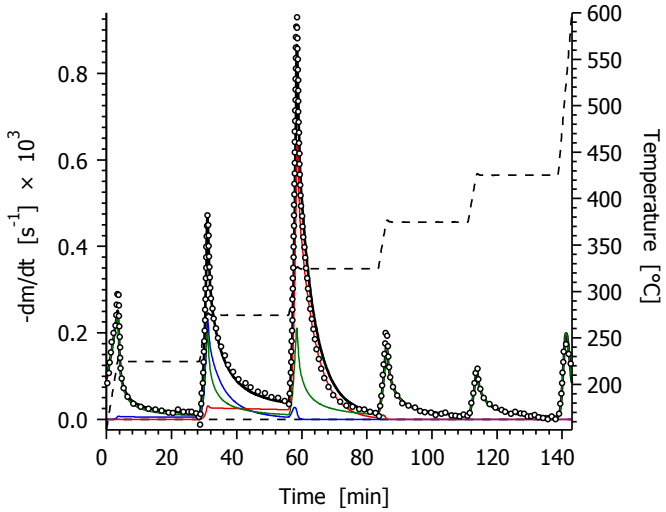
fit_1=2.64%; fit_{16}=1.86%

1: E_0=175.6 $\log_{10}A$=14.19 σ(E)=2.5

2: E_0=185.4 $\log_{10}A$=13.73 σ(E)=0

3: E_0=195.4 $\log_{10}A$=14.63 σ(E)=35.6

C: 8.8 24.1 34.7



Rice husk, 2mg, steps: 225 - 425°C

fit_1=1.67%; fit_{16}=1.86%

1: E_0=175.6 $\log_{10}A$=14.19 σ(E)=2.5

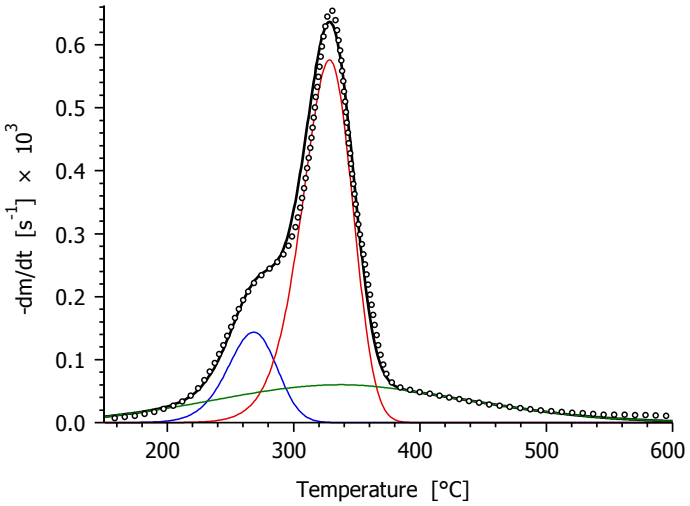
2: E_0=185.4 $\log_{10}A$=13.73 σ(E)=0

3: E_0=195.4 $\log_{10}A$=14.63 σ(E)=35.6

C: 8.8 24.1 34.7

Figure S1. *(Continued)*

Figure S1: Simultaneous evaluation of 16 experiments assuming identical $E_{0,j}$ values for the four biomasses



Sorghum, 4mg, 4°C/min

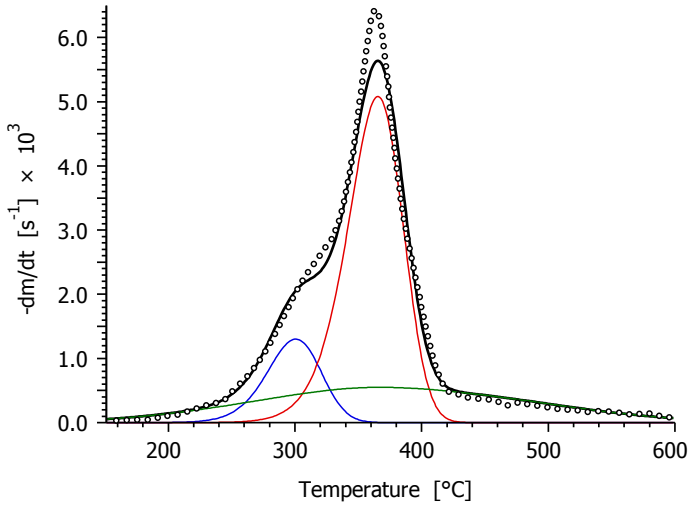
fit_1=2.26%; fit_{16}=1.86%

1: E_0=175.6 $\log_{10}A$=14.52 σ(E)=4.3

2: E_0=185.4 $\log_{10}A$=13.64 σ(E)=3.5

3: E_0=195.4 $\log_{10}A$=13.98 σ(E)=32.0

C: 10.4 43.7 22.5



Sorghum, 1mg, 40°C/min

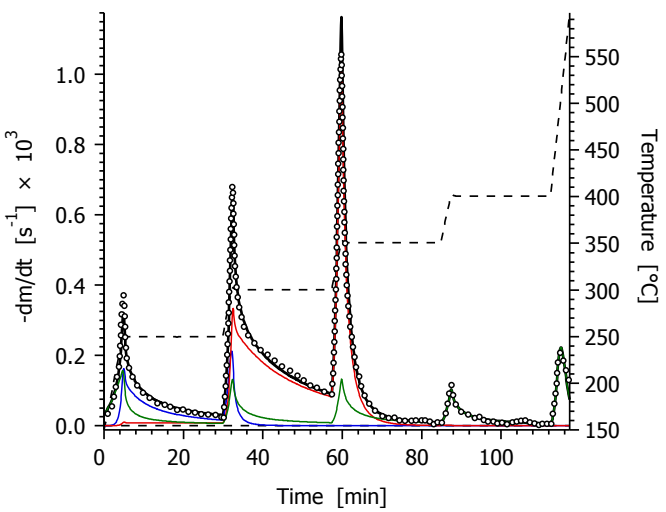
fit_1=2.66%; fit_{16}=1.86%

1: E_0=175.6 $\log_{10}A$=14.52 σ(E)=4.3

2: E_0=185.4 $\log_{10}A$=13.64 σ(E)=3.5

3: E_0=195.4 $\log_{10}A$=13.98 σ(E)=32.0

C: 10.4 43.7 22.5



Sorghum, 2mg, steps: 250 - 400°C

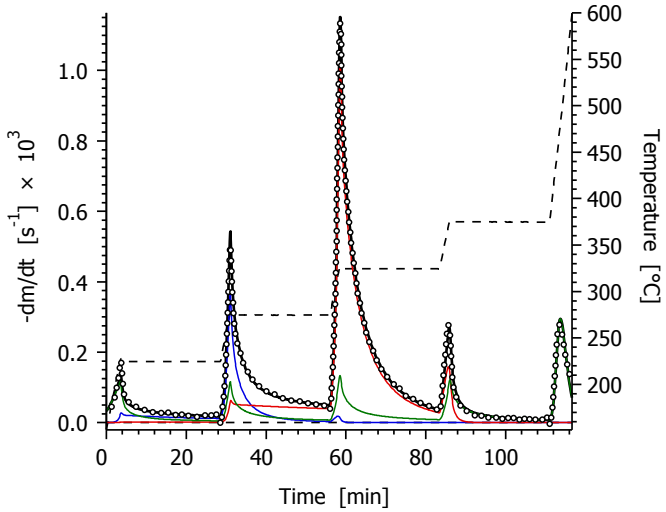
fit_1=1.29%; fit_{16}=1.86%

1: E_0=175.6 $\log_{10}A$=14.52 σ(E)=4.3

2: E_0=185.4 $\log_{10}A$=13.64 σ(E)=3.5

3: E_0=195.4 $\log_{10}A$=13.98 σ(E)=32.0

C: 10.4 43.7 22.5



Sorghum, G_0=2mg, Steps: 225-375°C

fit_1=0.77%; fit_{16}=1.86%

1: E_0=175.6 $\log_{10}A$=14.52 σ(E)=4.3

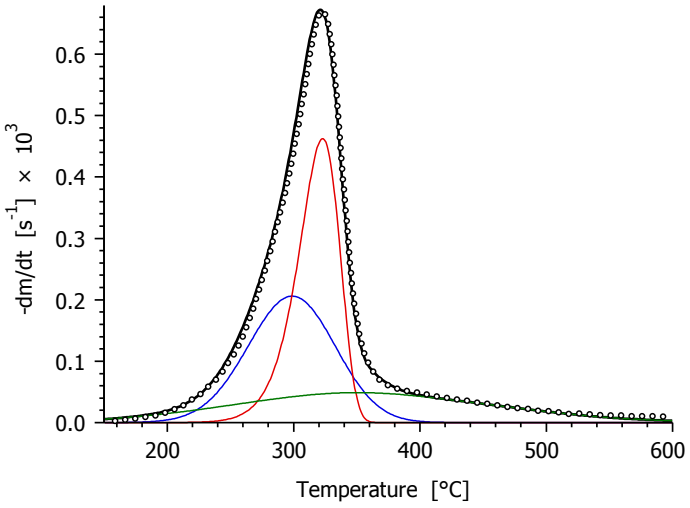
2: E_0=185.4 $\log_{10}A$=13.64 σ(E)=3.5

3: E_0=195.4 $\log_{10}A$=13.98 σ(E)=32.0

C: 10.4 43.7 22.5

Figure S1. *(Continued)*

Figure S1: Simultaneous evaluation of 16 experiments assuming identical $E_{0,j}$ values for the four biomasses



Wheat straw, 4mg, 4°C/min

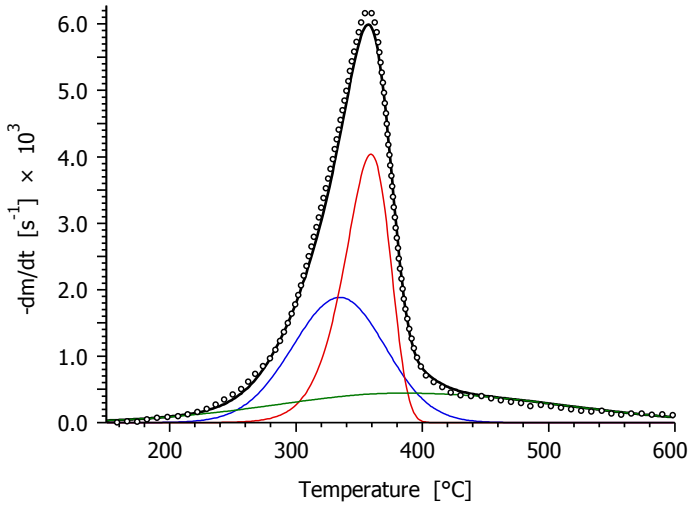
fit_1=1.45%; fit_{16}=1.86%

1: E_0=175.6 $\log_{10}A$=13.48 σ(E)=9.4

2: E_0=185.4 $\log_{10}A$=13.86 σ(E)=1.0

3: E_0=195.4 $\log_{10}A$=13.53 σ(E)=31.2

C: 26.2 28.8 18.5



Wheat straw, 1mg, 40°C/min

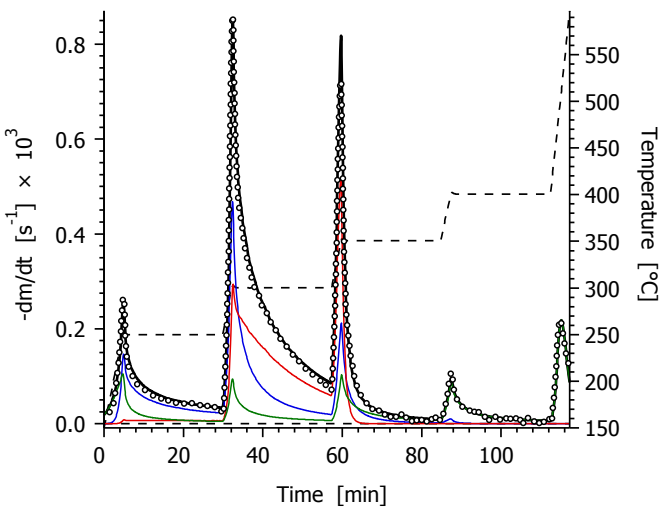
fit_1=1.22%; fit_{16}=1.86%

1: E_0=175.6 $\log_{10}A$=13.48 σ(E)=9.4

2: E_0=185.4 $\log_{10}A$=13.86 σ(E)=1.0

3: E_0=195.4 $\log_{10}A$=13.53 σ(E)=31.2

C: 26.2 28.8 18.5



Wheat straw, 2mg, steps: 250 - 400°C

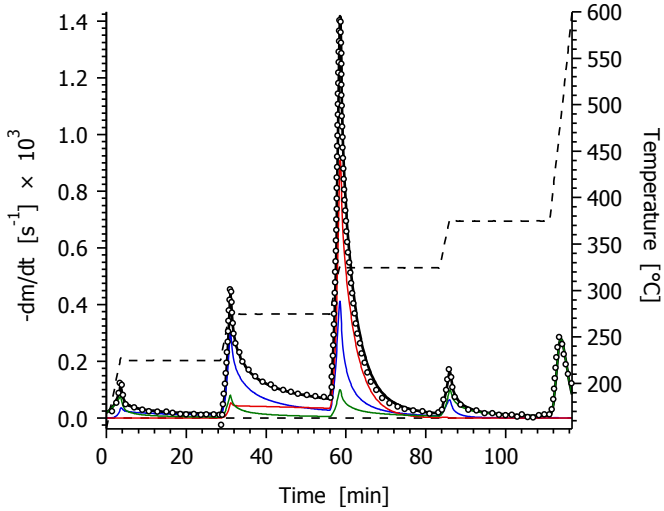
fit_1=1.37%; fit_{16}=1.86%

1: E_0=175.6 $\log_{10}A$=13.48 σ(E)=9.4

2: E_0=185.4 $\log_{10}A$=13.86 σ(E)=1.0

3: E_0=195.4 $\log_{10}A$=13.53 σ(E)=31.2

C: 26.2 28.8 18.5



Wheat straw, G_0=2 mg steps: 225 - 375°C

fit_1=1.06%; fit_{16}=1.86%

1: E_0=175.6 $\log_{10}A$=13.48 σ(E)=9.4

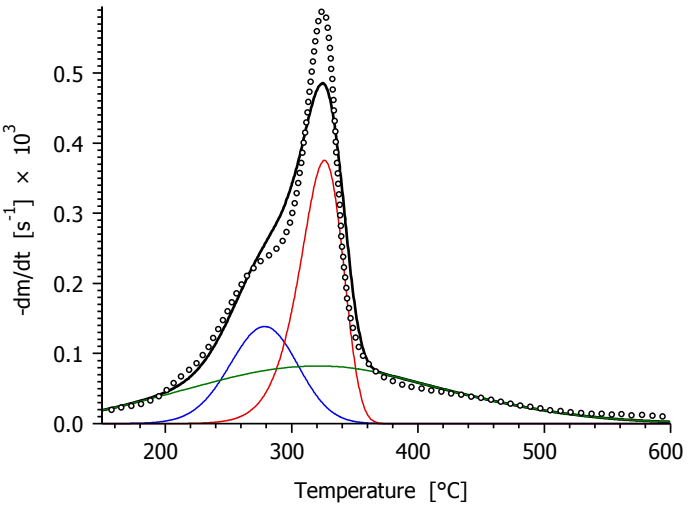
2: E_0=185.4 $\log_{10}A$=13.86 σ(E)=1.0

3: E_0=195.4 $\log_{10}A$=13.53 σ(E)=31.2

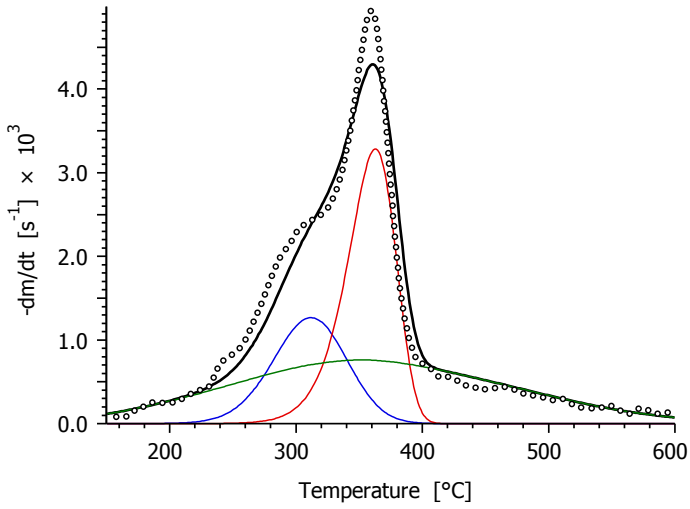
C: 26.2 28.8 18.5

Figure S1. *(Continued)*

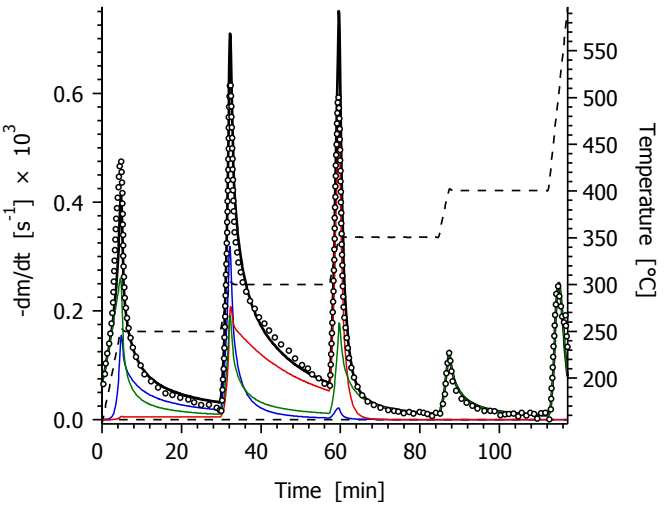
Figure S1: Simultaneous evaluation of 16 experiments assuming identical $E_{0,j}$ values for the four biomasses



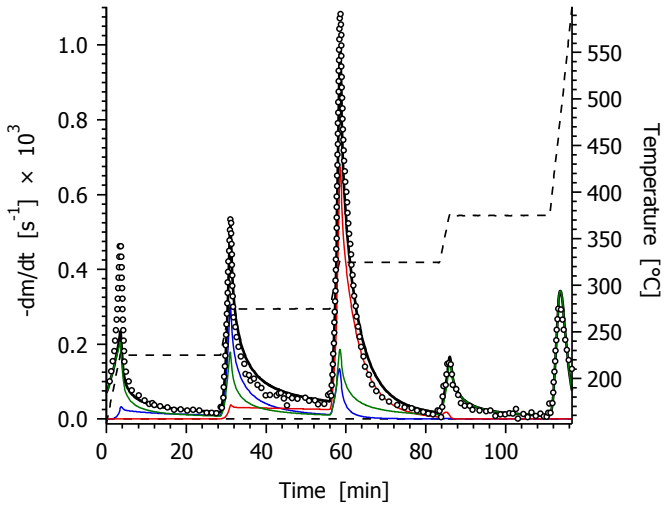
Corn stalk, 4mg, 4°C/min
fit_1=4.02%; fit_{16}=3.59%
1: E_0=175.5 $\log_{10}A$=14.13 σ(E)=7.1
2: E_0=184.9 $\log_{10}A$=13.71 σ(E)=1.7
3: E_0=188.9 $\log_{10}A$=13.90 σ(E)=32.7
C: 13.7 24.7 31.3



Corn stalk, 0.5mg, 40°C/min
fit_1=4.22%; fit_{16}=3.59%
1: E_0=175.5 $\log_{10}A$=14.13 σ(E)=7.1
2: E_0=184.9 $\log_{10}A$=13.71 σ(E)=1.7
3: E_0=188.9 $\log_{10}A$=13.90 σ(E)=32.7
C: 13.7 24.7 31.3

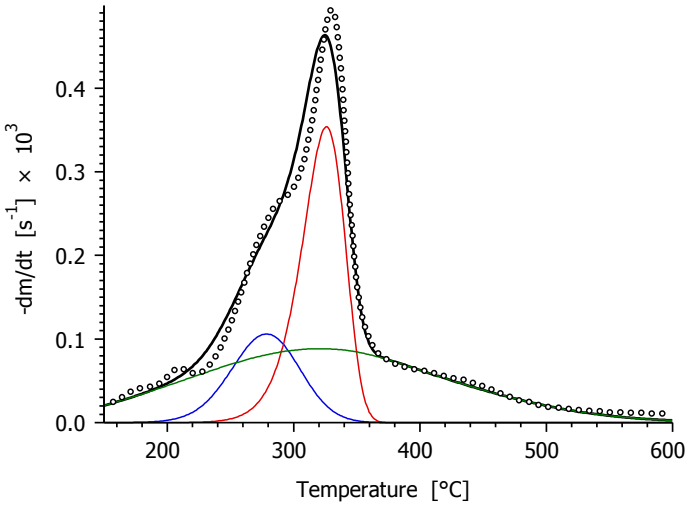


Corn stalk, 2mg, steps: 250 - 400°C
fit_1=3.92%; fit_{16}=3.59%
1: E_0=175.5 $\log_{10}A$=14.13 σ(E)=7.1
2: E_0=184.9 $\log_{10}A$=13.71 σ(E)=1.7
3: E_0=188.9 $\log_{10}A$=13.90 σ(E)=32.7
C: 13.7 24.7 31.3



Corn stalk, 2mg, steps: 225 - 375°C
fit_1=2.99%; fit_{16}=3.59%
1: E_0=175.5 $\log_{10}A$=14.13 σ(E)=7.1
2: E_0=184.9 $\log_{10}A$=13.71 σ(E)=1.7
3: E_0=188.9 $\log_{10}A$=13.90 σ(E)=32.7
C: 13.7 24.7 31.3

Figure S2. Simultaneous evaluation of 16 experiments assuming identical $E_{0,j}$, σ_j, and A_j for the four biomasses. In this approximation all structural and compositional differences are expressed by the c_j parameters. The experimental data (○○○), their simulated counterparts (—) and the calculated partial curves (—, —, —) are displayed. The curves are plotted as functions of time in the figures with stepwise heating programs. In this case the experimental temperature values are also displayed (- - -).



Rice husk, 4mg, 4°C/min

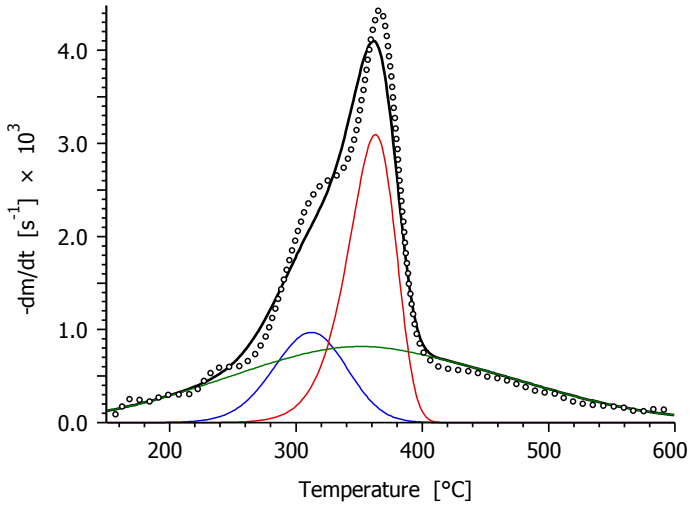
fit_1=3.42%; fit_{16}=3.59%

1: E_0=175.5 $\log_{10}A$=14.13 σ(E)=7.1

2: E_0=184.9 $\log_{10}A$=13.71 σ(E)=1.7

3: E_0=188.9 $\log_{10}A$=13.90 σ(E)=32.7

C: 10.5 23.2 33.6



Rice husk, 1mg, 40°C/min

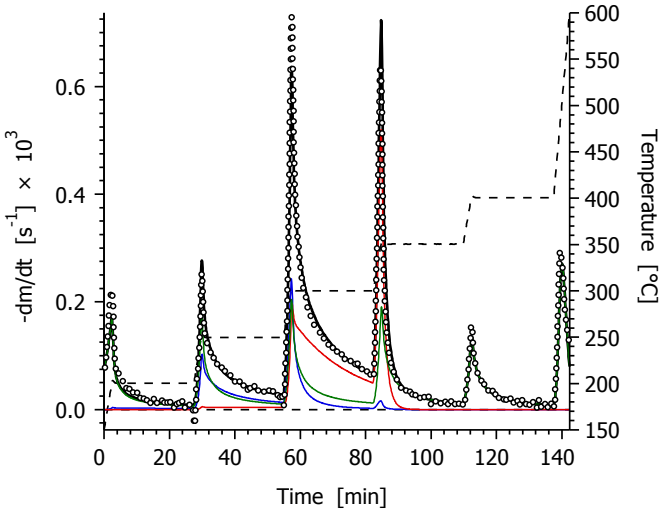
fit_1=3.60%; fit_{16}=3.59%

1: E_0=175.5 $\log_{10}A$=14.13 σ(E)=7.1

2: E_0=184.9 $\log_{10}A$=13.71 σ(E)=1.7

3: E_0=188.9 $\log_{10}A$=13.90 σ(E)=32.7

C: 10.5 23.2 33.6



Rice husk, 2mg, steps: 200 - 400°C

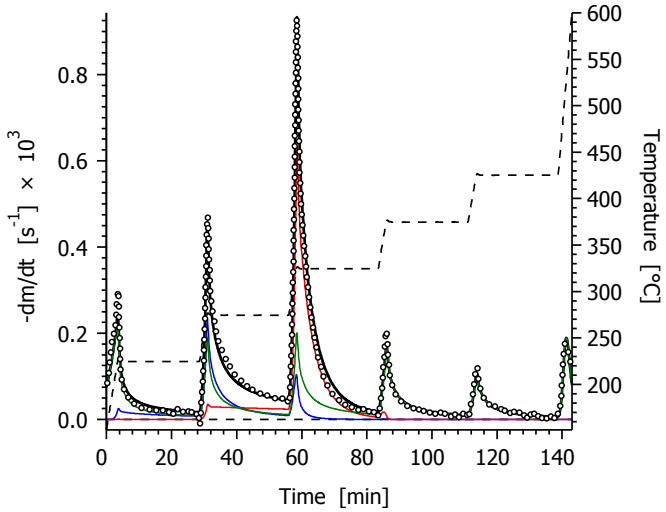
fit_1=2.39%; fit_{16}=3.59%

1: E_0=175.5 $\log_{10}A$=14.13 σ(E)=7.1

2: E_0=184.9 $\log_{10}A$=13.71 σ(E)=1.7

3: E_0=188.9 $\log_{10}A$=13.90 σ(E)=32.7

C: 10.5 23.2 33.6



Rice husk, 2mg, steps: 225 - 425°C

fit_1=1.46%; fit_{16}=3.59%

1: E_0=175.5 $\log_{10}A$=14.13 σ(E)=7.1

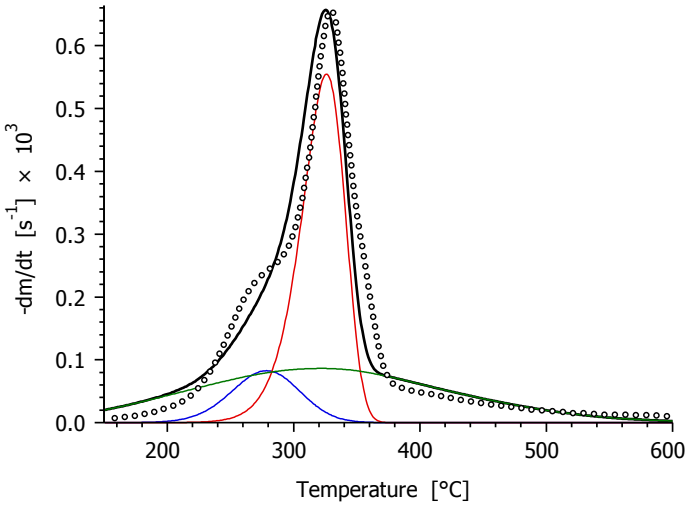
2: E_0=184.9 $\log_{10}A$=13.71 σ(E)=1.7

3: E_0=188.9 $\log_{10}A$=13.90 σ(E)=32.7

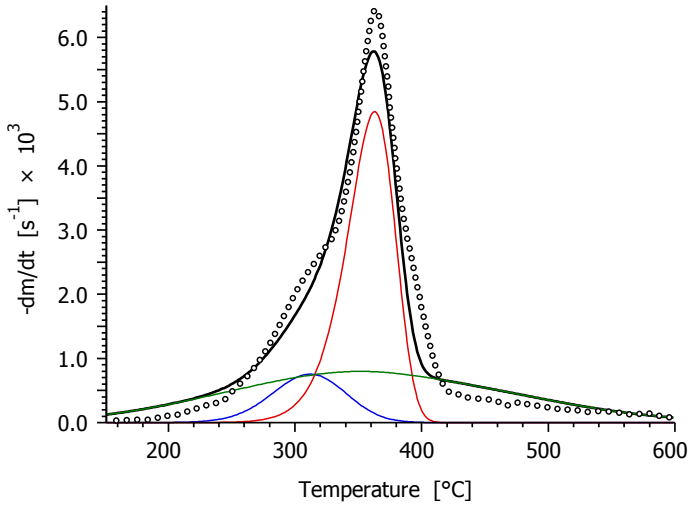
C: 10.5 23.2 33.6

Figure S2. *(Continued)*

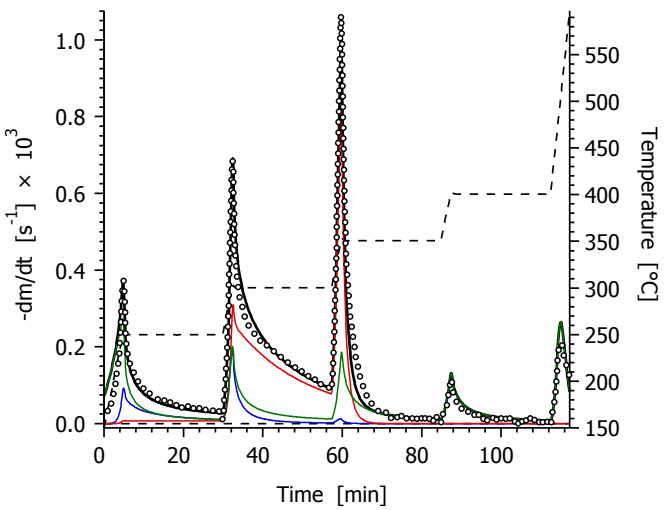
Figure S2: Simultaneous evaluation of 16 experiments assuming identical $E_{0,j}$, σ_j, and A_j for the four biomasses



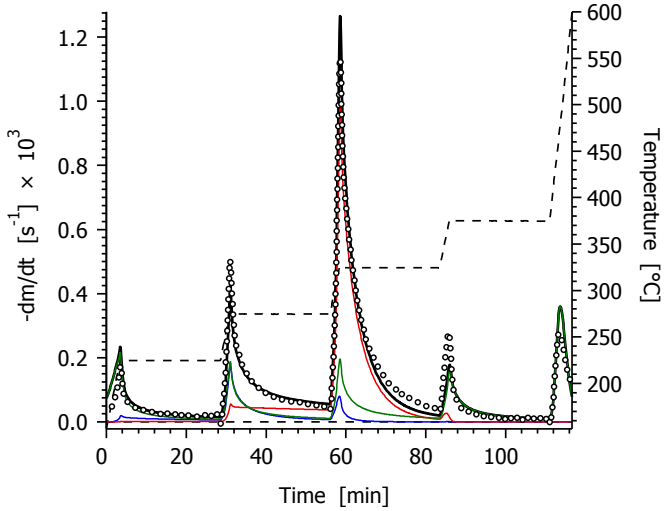
Sorghum, 4mg, 4°C/min
fit_1=6.03%; fit_{16}=3.59%
1: E_0=175.5 $\log_{10}A$=14.13 σ(E)=7.1
2: E_0=184.9 $\log_{10}A$=13.71 σ(E)=1.7
3: E_0=188.9 $\log_{10}A$=13.90 σ(E)=32.7
C: 8.2 36.4 32.9



Sorghum, 1mg, 40°C/min
fit_1=4.54%; fit_{16}=3.59%
1: E_0=175.5 $\log_{10}A$=14.13 σ(E)=7.1
2: E_0=184.9 $\log_{10}A$=13.71 σ(E)=1.7
3: E_0=188.9 $\log_{10}A$=13.90 σ(E)=32.7
C: 8.2 36.4 32.9



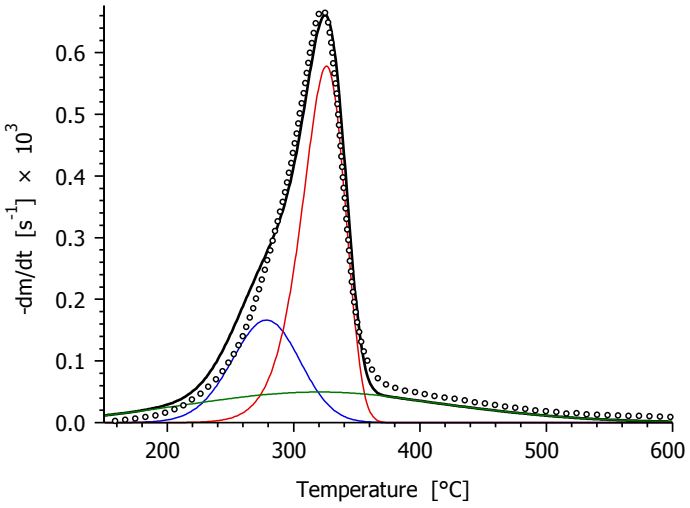
Sorghum, 2mg, steps: 250 - 400°C
fit_1=2.73%; fit_{16}=3.59%
1: E_0=175.5 $\log_{10}A$=14.13 σ(E)=7.1
2: E_0=184.9 $\log_{10}A$=13.71 σ(E)=1.7
3: E_0=188.9 $\log_{10}A$=13.90 σ(E)=32.7
C: 8.2 36.4 32.9



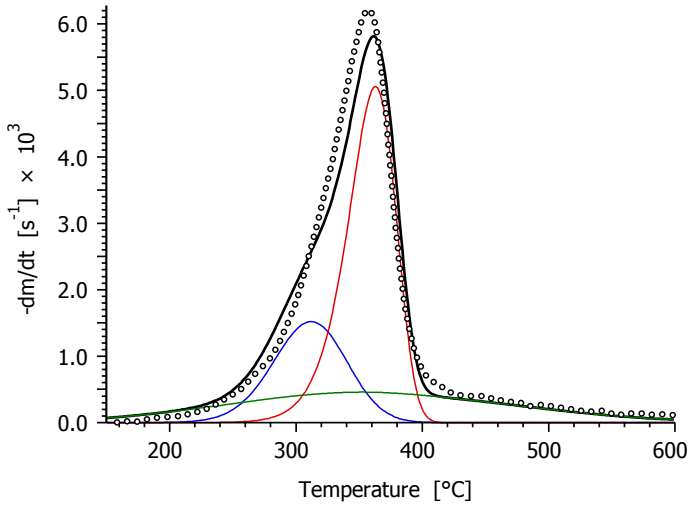
Sorghum, G_0=2mg, Steps: 225-375°C
fit_1=2.56%; fit_{16}=3.59%
1: E_0=175.5 $\log_{10}A$=14.13 σ(E)=7.1
2: E_0=184.9 $\log_{10}A$=13.71 σ(E)=1.7
3: E_0=188.9 $\log_{10}A$=13.90 σ(E)=32.7
C: 8.2 36.4 32.9

Figure S2. *(Continued)*

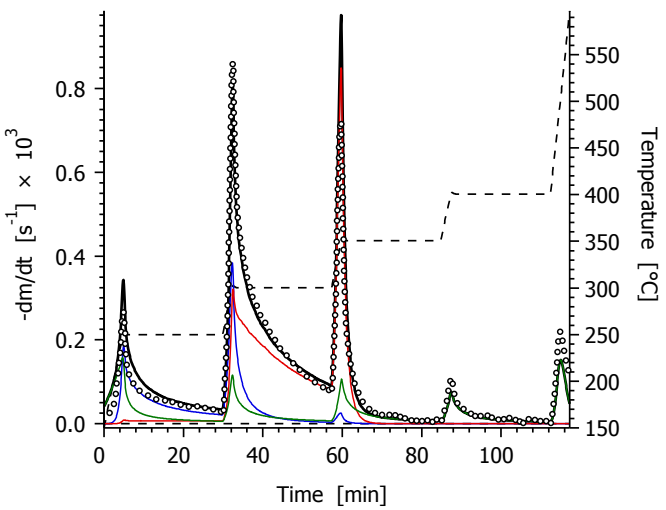
Figure S2: Simultaneous evaluation of 16 experiments assuming identical $E_{0,j}$, σ_j, and A_j for the four biomasses



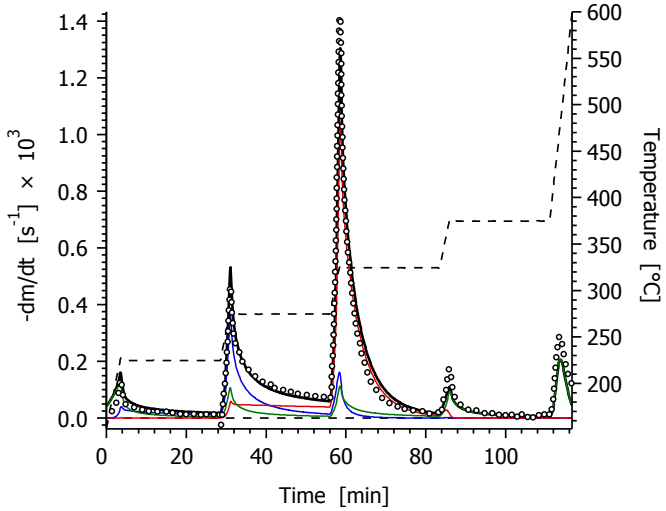
Wheat straw, 4mg, 4°C/min
fit_1=2.88%; fit_{16}=3.59%
1: E_0=175.5 $\log_{10}A$=14.13 σ(E)=7.1
2: E_0=184.9 $\log_{10}A$=13.71 σ(E)=1.7
3: E_0=188.9 $\log_{10}A$=13.90 σ(E)=32.7
C: 16.5 37.9 18.9



Wheat straw, 1mg, 40°C/min
fit_1=4.10%; fit_{16}=3.59%
1: E_0=175.5 $\log_{10}A$=14.13 σ(E)=7.1
2: E_0=184.9 $\log_{10}A$=13.71 σ(E)=1.7
3: E_0=188.9 $\log_{10}A$=13.90 σ(E)=32.7
C: 16.5 37.9 18.9



Wheat straw, 2mg, steps: 250 - 400°C
fit_1=3.73%; fit_{16}=3.59%
1: E_0=175.5 $\log_{10}A$=14.13 σ(E)=7.1
2: E_0=184.9 $\log_{10}A$=13.71 σ(E)=1.7
3: E_0=188.9 $\log_{10}A$=13.90 σ(E)=32.7
C: 16.5 37.9 18.9



Wheat straw, G_0=2 mg steps: 225 - 375°C
fit_1=2.23%; fit_{16}=3.59%
1: E_0=175.5 $\log_{10}A$=14.13 σ(E)=7.1
2: E_0=184.9 $\log_{10}A$=13.71 σ(E)=1.7
3: E_0=188.9 $\log_{10}A$=13.90 σ(E)=32.7
C: 16.5 37.9 18.9

Figure S2. *(Continued)*

Figure S2: Simultaneous evaluation of 16 experiments assuming identical $E_{0,j}$, σ_j, and A_j for the four biomasses