Challenges in kinetic parameter determination for wheat straw pyrolysis

Supplementary Information

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Table S1: TGA instrument characteristics (Netzsch STA-409). Source: #3, Table 3 at [4]

Sensitivity (µg)	Temperature accuracy (K)	Sample mass (mg)	Type	N_2 purge flow (ml/min)	Sample holder	Calibration
1	1	≈ 200	Vertical	70	Alumina	Melting point

Table S2: Fundamentals of the thermogravimetric data (TGA/DTG) for the Beech wood powder samples.

β (K/min)	T peak DTG (°C)	T shoulder DTG (°C)	Initial mass (mg)	Char yield @ 900 °C (wt. %)	$\Delta m/\Delta T_{max}$ (K^{-1})	Kissinger Kinetics R^2 = 0.99		# Curves
						E_a (kJ/mol)	$\log_{10}$(A [s^{-1}])	
1	322.9 ± 0.1	260.6 ± 0.5	99.7 ± 0.0	25.8 ± 1.1	1.12 ± 0.00	218.48 ± 12.63	16.15 ± 2.47	2
5	345.1 ± 0.7	294.3 ± 0.9	99.9 ± 1.3	25.1 ± 0.1	5.12 ± 0.00			2
10	354.9 ± 0.2	299.1 ± 0.6	99.9 ± 0.9	25.1 ± 0.1	10.17 ± 0.05			2
20	368.3	312.2	108.3	24.8	22.85			1

Table S3: Fundamentals of the thermogravimetric data (TGA/DTG) for the wheat straw powder (WS-P) samples.

β (K/min)	T peak DTG (°C)	Initial mass (mg)	Char yield @ 900 °C (wt. %)	$\Delta m/\Delta T_{max}$ (K^{-1})	Kissinger Kinetics R^2 = 0.93 *		# Curves
					E_a (kJ/mol)	$\log_{10}$(A [s^{-1}])	
1	288.6 ± 0.5	211.9 ± 33.3	25.6 ± 0.5	0.75 ± 0.00	220.21 ± 43.57	17.41 ± 5.73	2
5	310.9 ± 1.9	182.7 ± 1.0	26.9 ± 0.0	3.84 ± 0.02			2
10	321.4 ± 1.0	224.2 ± 11.0	26.9 ± 0.0	8.08 ± 0.02			5
20	334.6 ± 0.1	200.1 ± 14.3	26.3 ± 0.0	17.83 ± 0.15			2
50	338.5 ± 0.2	180.2 ± 4.0	25.2 ± 0.0	72.34 ± 0.31			2

* The values from the 1 K/min curve were not considered to improve fit. Removing the 50 K/min curve (while keeping the 1 K/min curve), the values obtained are E_a 121.78 ± 19.27, $\log_{10}$A: 8.51 ± 3.30, R^2: 0.95.

Table S4: Fundamentals of the thermogravimetric data (TGA/DTG) for the wheat straw hull (WS-H) samples.

β (K/min)	**T peak DTG (°C)**	**Initial mass (mg)**	**Char yield @ 900 °C (wt. %)**	**$\Delta m/\Delta T_{max}$ (K^{-1})**	**Kissinger Kinetics R^2 = 0.85 ***		**# Curves**
					Ea (kJ/mol)	$\log_{10}(A\ [s^{-1}])$	
1	287.9	195.6	25.7	0.70	222.04 ± 53.83	17.90 ± 6.85	1
5	300.7	216.8	26.7	2.63			1
10	319.5	183.7	26.7	7.62			1
20	326.7 ± 1.4	169.2 ± 5.4	25.8 ± 0.0	15.59 ± 0.14			2
50	321.5 ± 2.5	191.4 ± 4.9	24.7 ± 0.1	67.51 ± 2.36			2

* Removing the 50 K/min curve, the values obtained are E_a 187.81 ± 34.00, $\log_{10}A$: 14.67 ± 4.89, R^2: 0.94.

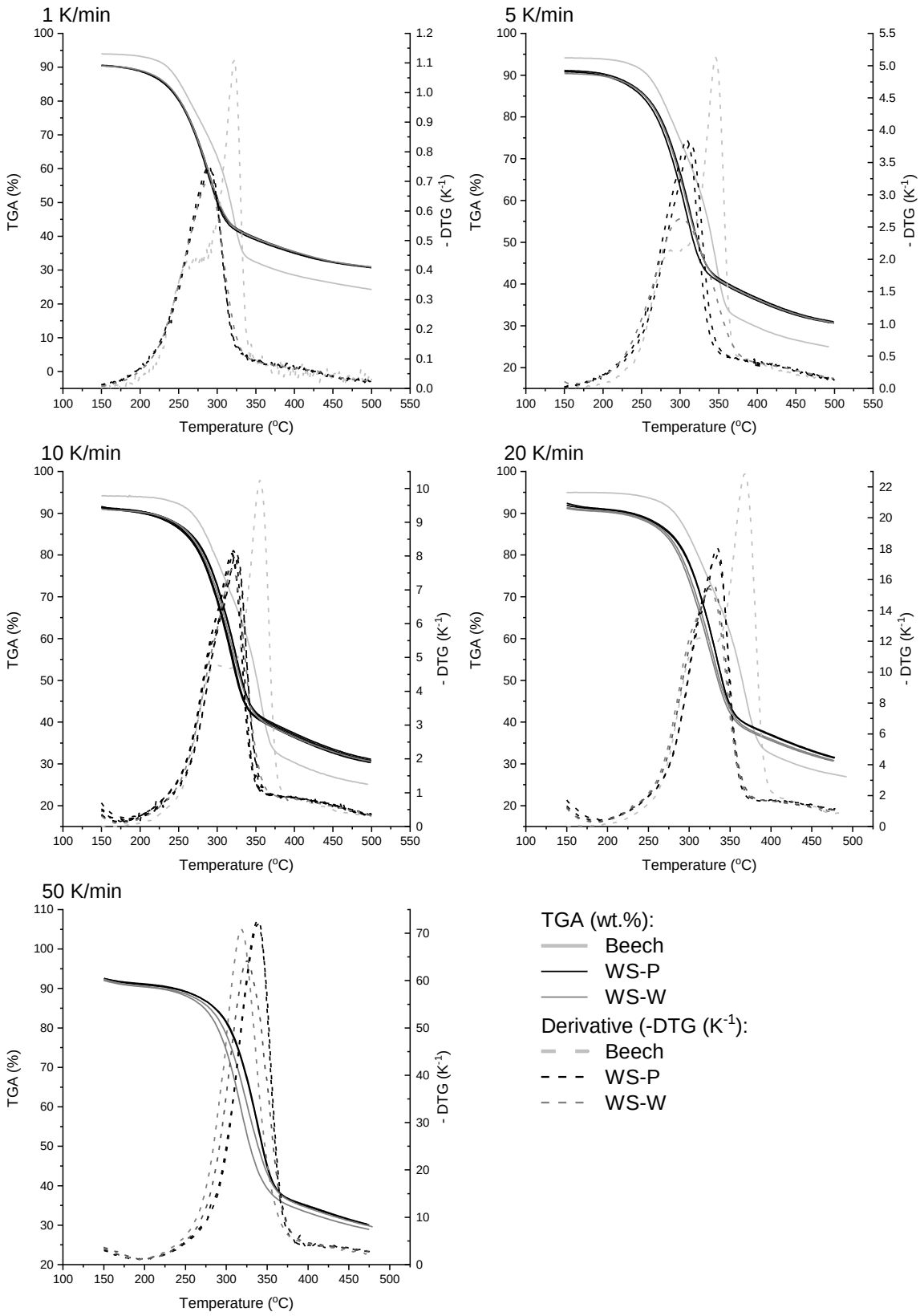


Figure S1: Comparison of the behavior of the mass loss profiles for the different samples at the different heating rates tested.

Deconvolution

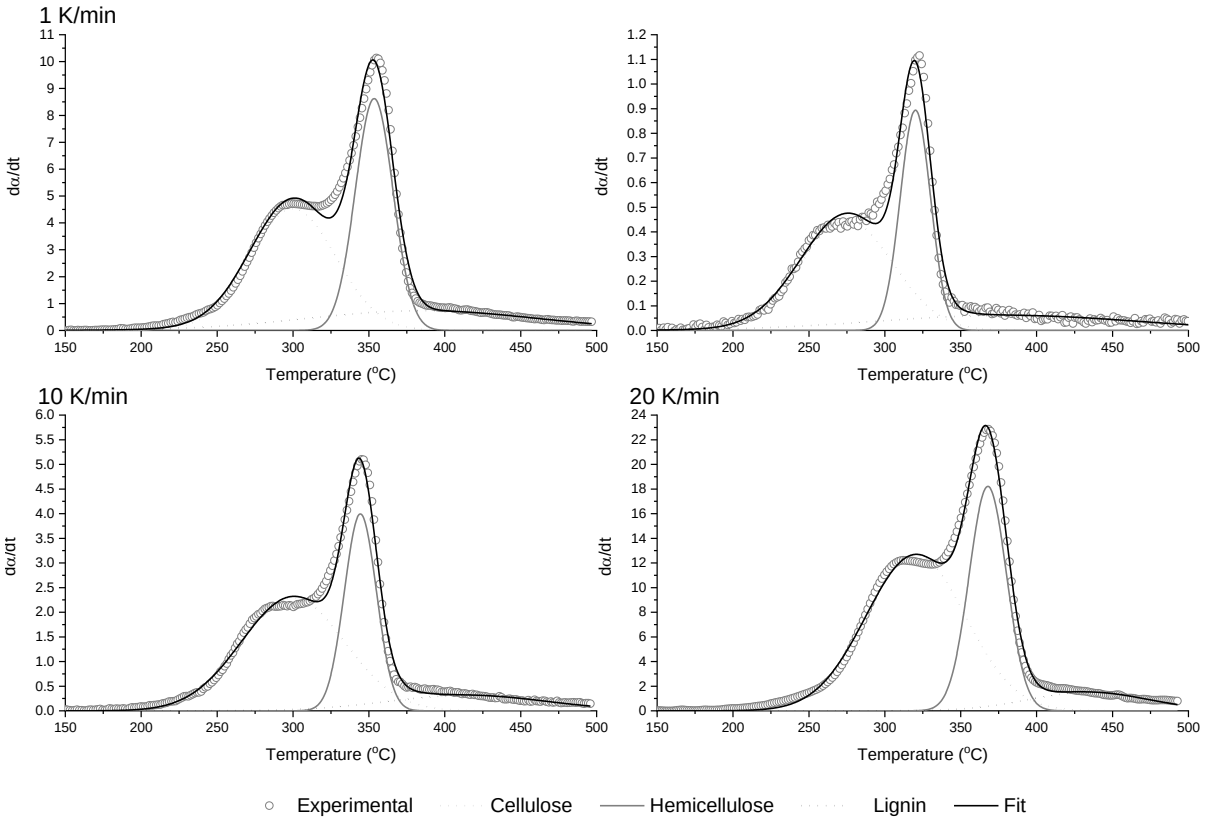


Figure S2: DTG Deconvolution for Beech.

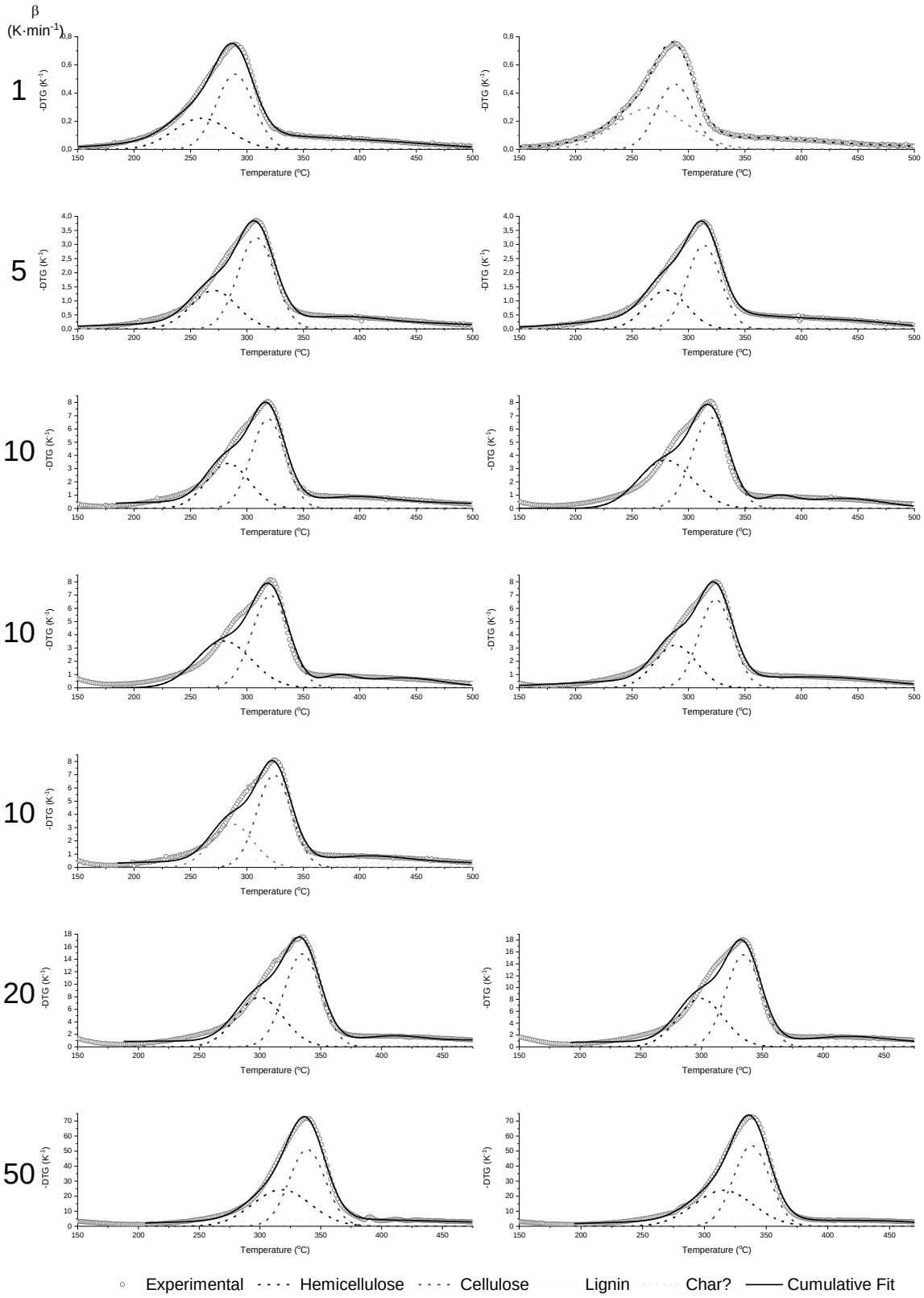


Figure S3: DTG Deconvolution for WS-P.

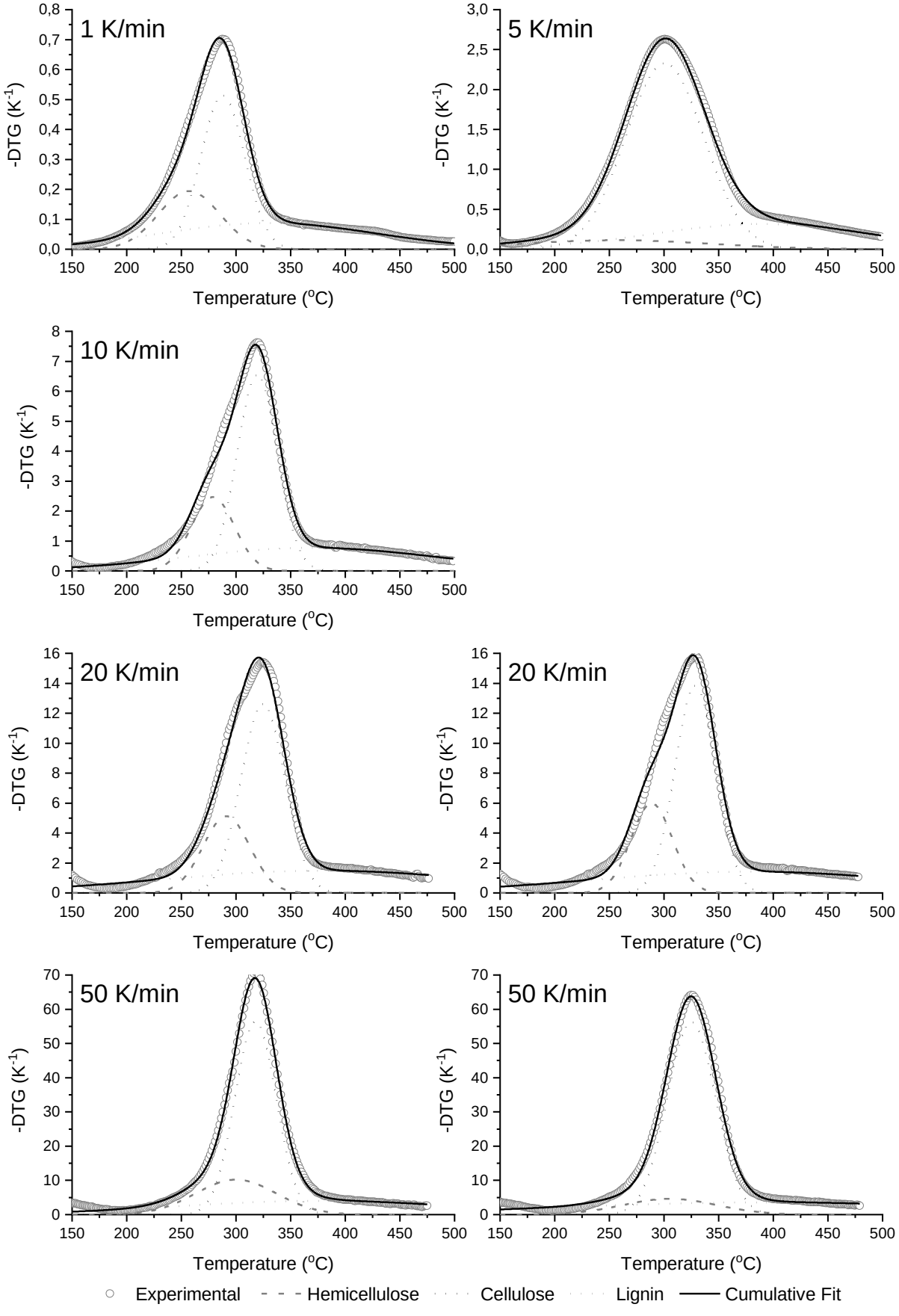


Figure S4: DTG Deconvolution for WS-H.

Table S5: Lignocellulosic composition of the different materials, obtained using Gaussian deconvolution procedures (wt.%, dab., extractives-free). Values disregarded to estimate the total average are in italic.

β (K/min)	Beech				WS-P				WS-H			
	Hemicellulose	**Cellulose**	**Lignin**	**R^2**	**Hemicellulose**	**Cellulose**	**Lignin**	**R^2**	**Hemicellulose**	**Cellulose**	**Lignin**	**R^2**
1	*44.7 ± 17.1*	*34.1 ± 2.2*	*21.2 ± 19.4*	*0.92*	31.0 ± 0.6	33.0 ± 0.5	36.0 ± 0.5	1.00 ± 0.00	22.4 ± 0.4	42.2 ± 0.4	35.0 ± 0.6	1.00
5	45.6 ± 2.5	33.3 ± 0.9	21.1 ± 2.5	0.99	23.5 ± 1.1	38.5 ± 1.7	38.0 ± 0.5	0.99 ± 0.00	*7.9 ± 0.8*	*67.0 ± 0.6*	*25.2 ± 0.8*	*1.00*
10	47.0 ± 3.9	36.0 ± 0.9	17.0 ± 4.7	0.99	24.1 ± 0.7	37.8 ± 0.6	38.1 ± 2.3	0.98 ± 0.00	18.9 ± 0.4	46.8 ± 0.4	34.3 ± 1.0	1.00
20	48.9 ± 1.3	36.4 ± 0.8	14.7 ± 1.8	0.99	24.0 ± 0.6	35.6 ± 0.5	40.4 ± 0.4	0.99 ± 0.00	19.3 ± 0.5	44.0 ± 0.5	36.8 ± 1.7	0.99 ± 0.00
50					29.3 ± 0.5	37.1 ± 0.4	33.6 ± 1.6	1.00 ± 0.00	*14.3 ± 0.8*	*56.6 ± 0.6*	*29.0 ± 1.5*	*1.00 ± 0.00*
Average	47.1 ± 2.8	35.3 ± 0.9	17.6 ± 3.3		26.4 ± 1.1	36.4 ± 1.3	37.2 ± 0.4		20.2 ± 0.4	44.3 ± 0.4	35.5 ± 0.7	
Reference [a]	34.3 ± 1.9	45.0 ± 5.4	20.7 ± 2.7		32.6 ± 0.7	45.5 ± 1.4	21.9 ± 1.0		32.6 ± 0.7	45.5 ± 1.4	21.9 ± 1.0	

a: Based on data obtained in the Phyllis2 database (www.phyllis.nl). Using 14 sources for wheat straw data and 3 for beech wood data.

Table S6: Comparison of replicas (WS-P, 10 K/min), obtained using Gaussian deconvolution procedures (wt.%, dab., extractives-free).

Replicas	Hemicellulose	Cellulose	Lignin	R^2
R1	24.4 ± 0.6	37.1 ± 0.5	38.4 ± 1.6	0.99
R2	26.1 ± 0.9	38.1 ± 0.8	35.7 ± 2.8	0.98
R3	23.9 ± 0.8	38.0 ± 0.7	38.1 ± 2.9	0.98
R4	23.7 ± 0.5	37.2 ± 0.5	39.2 ± 1.5	0.99
R5	22.5 ± 0.6	38.7 ± 0.6	38.8 ± 2.0	0.99
Average	24.1 ± 0.7	37.8 ± 0.6	38.1 ± 2.3	

Model-fitting

Table S7: Results of the model fitting for Beech, obtained by simultaneous fitting to all thermograms.

	First-order			**fit % ***
	Cellulose	Hemicellulose	Lignin	3.9% ± 2.0%
$\log_{10}$ (A [s^{-1}])	14.55	10.41	1.60	
E_a [kJ·mol^{-1}]	198.4	136.3	58.2	
c_i	54.7%	28.2%	17.1%	
T_p	318.70 - 366.20	257.07 - 314.69	324.31 - 492.14	
	n_{Lig}=3			**fit % ***
	Cellulose	Hemicellulose	Lignin	3.5% ± 1.4%
$\log_{10}$ (A [s^{-1}])	15.44	10.72	6.43	
E_a [kJ·mol^{-1}]	208.6	139.3	105.0	
c_i	46.9%	24.9%	28.2%	
T_p	320.10 - 366.20	257.07 - 312.92	292.18 - 374.53	
	Free-order			**fit % ***
	Cellulose	Hemicellulose	Lignin	2.9% ± 0.6%
$\log_{10}$ (A [s^{-1}])	15.61	12.55	18.09	
E_a [kJ·mol^{-1}]	211.0	156.2	222.6	
c_i	45.6%	19.3%	35.0%	
n_i	1.00	1.62	7.73	
T_p	321.48 - 366.20	251.49 - 301.84	278.20 - 316.21	

*: Confidence interval of 95%.

Table S8: Results of the model fitting for WS-P, averaged from all 5 heating rates, obtained by simultaneous fitting to all thermograms.

	First-order			**fit % ***
	Cellulose	Hemicellulose	Lignin	6.2% ± 5.9%
$\log_{10}$ (A [s^{-1}])	14.24	9.58	1.45	
E_a [kJ·mol^{-1}]	185.17	125.47	54.38	
c_i	47.2%	24.7%	28.1%	
T_p	289.29 - 354.49	245.83 - 331.31	301.97 – 500**	
	n_{Lig}=3			**fit % ***
	Cellulose	Hemicellulose	Lignin	5.8% ± 6.5%
$\log_{10}$ (A [s^{-1}])	14.49	8.96	7.20	
E_a [kJ·mol^{-1}]	188.21	119.76	119.94	
c_i	44.3%	31.4%	24.4%	
T_p	292.12 - 355.50	247.22 - 336.68	327.13 - 433.88	
	Free-order			**fit % ***
	Cellulose	Hemicellulose	Lignin	5.3% ± 5.6%
$\log_{10}$ (A [s^{-1}])	14.74	10.87	10.71	
E_a [kJ·mol^{-1}]	190.61	138.84	160.53	
c_i	42.5%	32.5%	25.0%	
n_i	1.00	1.74	4.93	
T_p	290.70 - 354.03	248.64 - 325.22	331.34 - 409.95	

*: Confidence interval of 95%.

**: Peak of curve outside of the temperature interval considered for this work.

Table S9: Results of the model fitting for WS-H, obtained by simultaneous fitting to all thermograms.

	First-order			**fit % ***
	Cellulose	Hemicellulose	Lignin	9.6% ± 8.9%
$\log_{10}$ (A [s^{-1}])	14.78	11.68	2.79	
E_a [kJ·mol^{-1}]	191.6	147.3	69.7	
c_i	43.2%	32.1%	24.6%	
T_p	292.12 - 355.66	251.48 - 325.06	314.49 – 500 **	
	n_{Lig}=3			**fit % ***
	Cellulose	Hemicellulose	Lignin	8.8% ± 9.3%
$\log_{10}$ (A [s^{-1}])	15.20	11.72	7.96	
E_a [kJ·mol^{-1}]	195.9	147.6	126.0	
c_i	41.7%	31.7%	26.7%	
T_p	292.12 - 354.17	251.48 - 324.10	315.87 - 415.28	
	Free-order			**fit % ***
	Cellulose	Hemicellulose	Lignin	8.1% ± 9.5%
$\log_{10}$ (A [s^{-1}])	15.71	14.14	13.26	
E_a [kJ·mol^{-1}]	201.36	172.50	185.86	
c_i	39.0%	31.5%	29.5%	
n_i	1.00	1.48	5.68	
T_p	292.12 - 352.68	254.28 - 316.63	320.06 - 388.24	

*: Confidence interval of 95%.

**: Peak of curve outside of the temperature interval considered for this work.

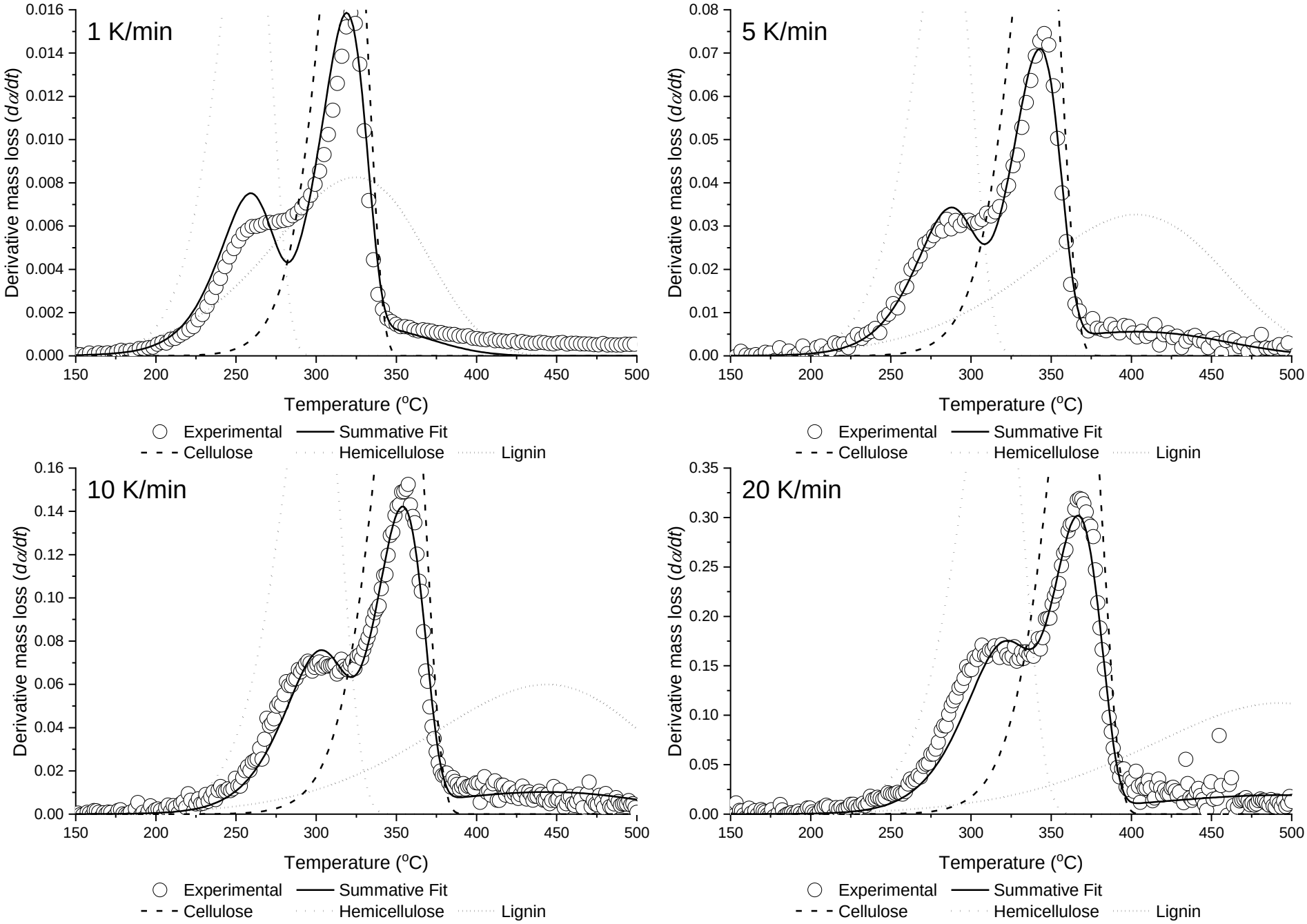


Figure S5: Model-fitting graphs for Beech, model first-order.

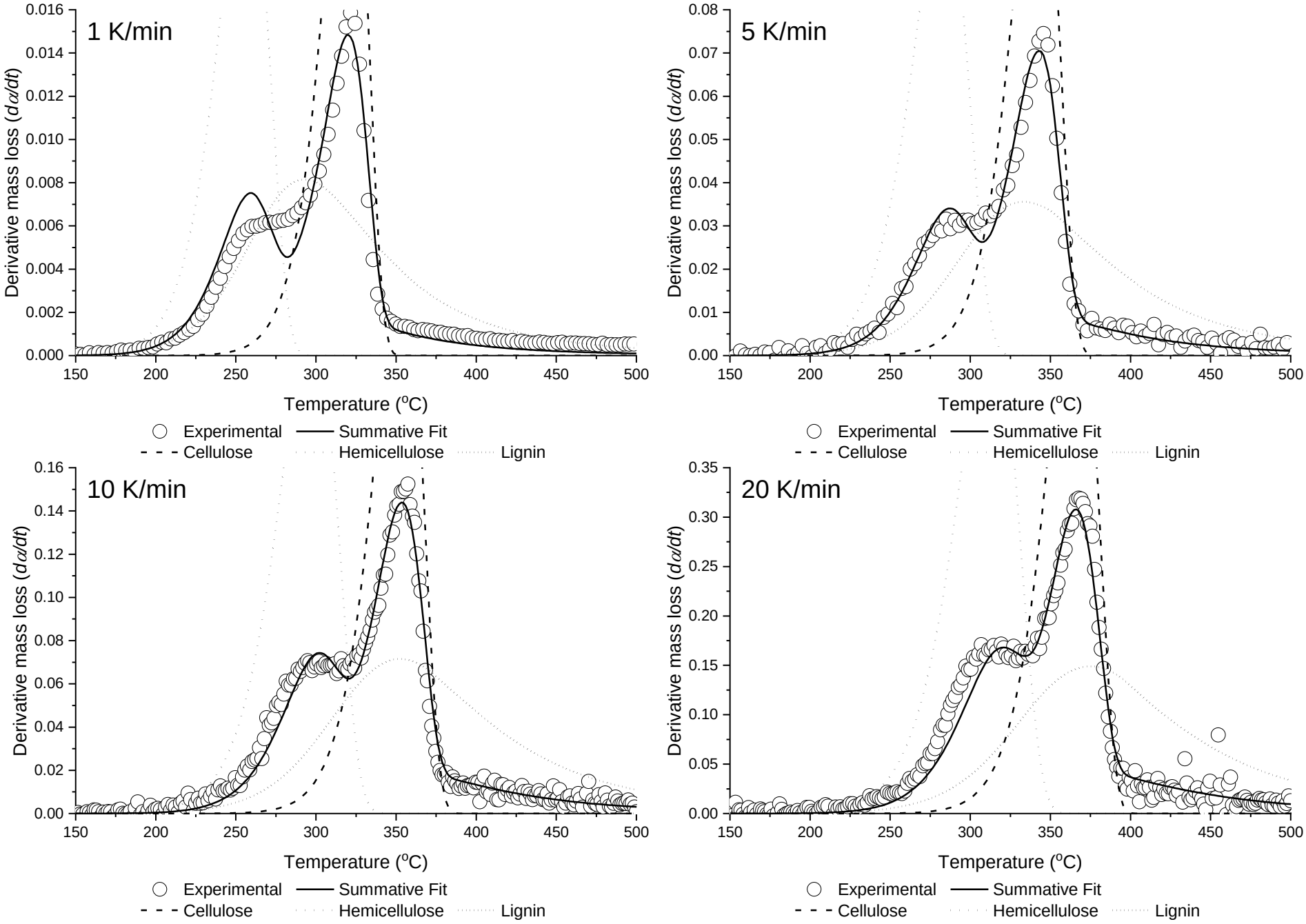


Figure S6: Model-fitting graphs for Beech, model third order to lignin.

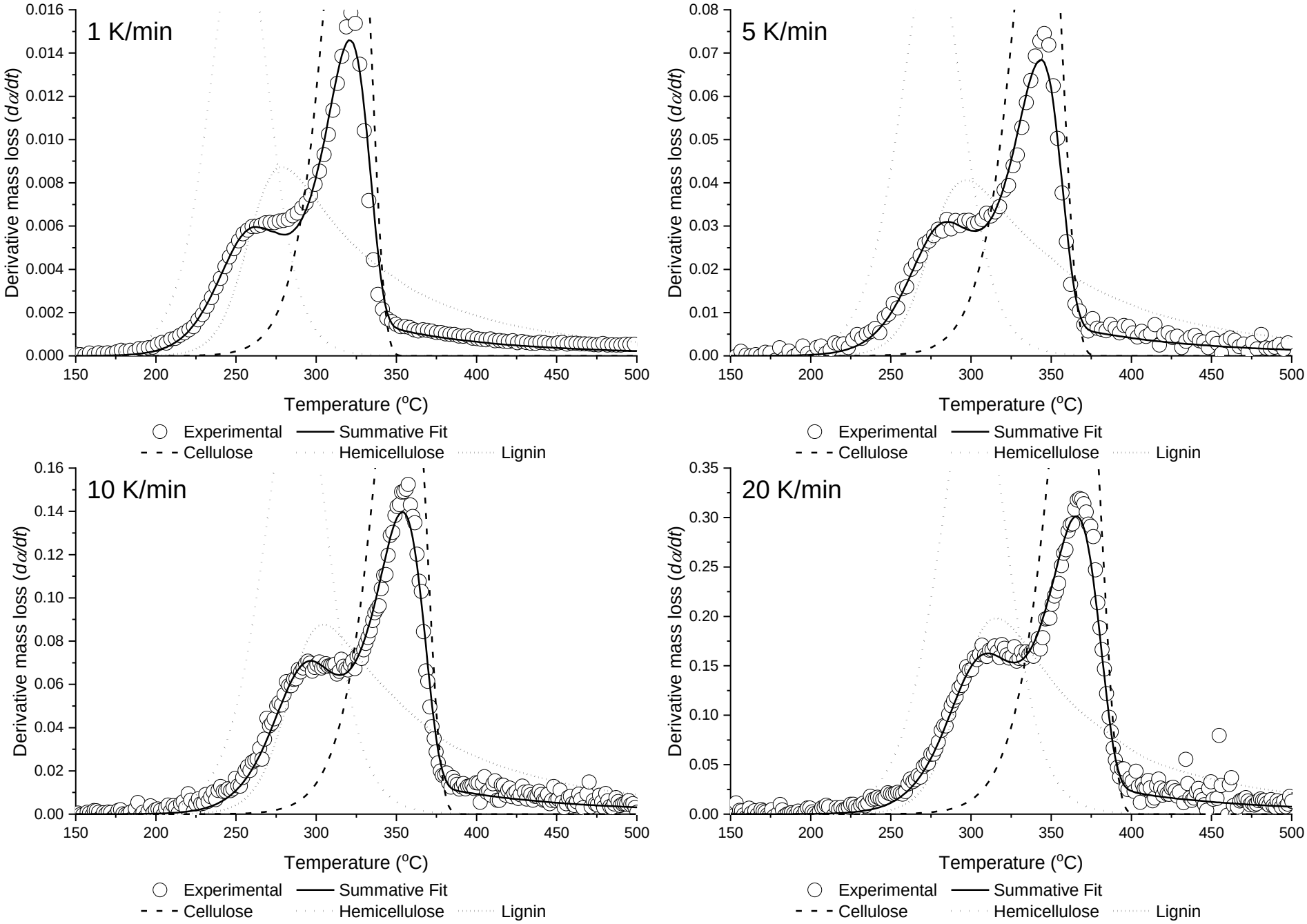


Figure S7: Model-fitting graphs for Beech, model free-order.

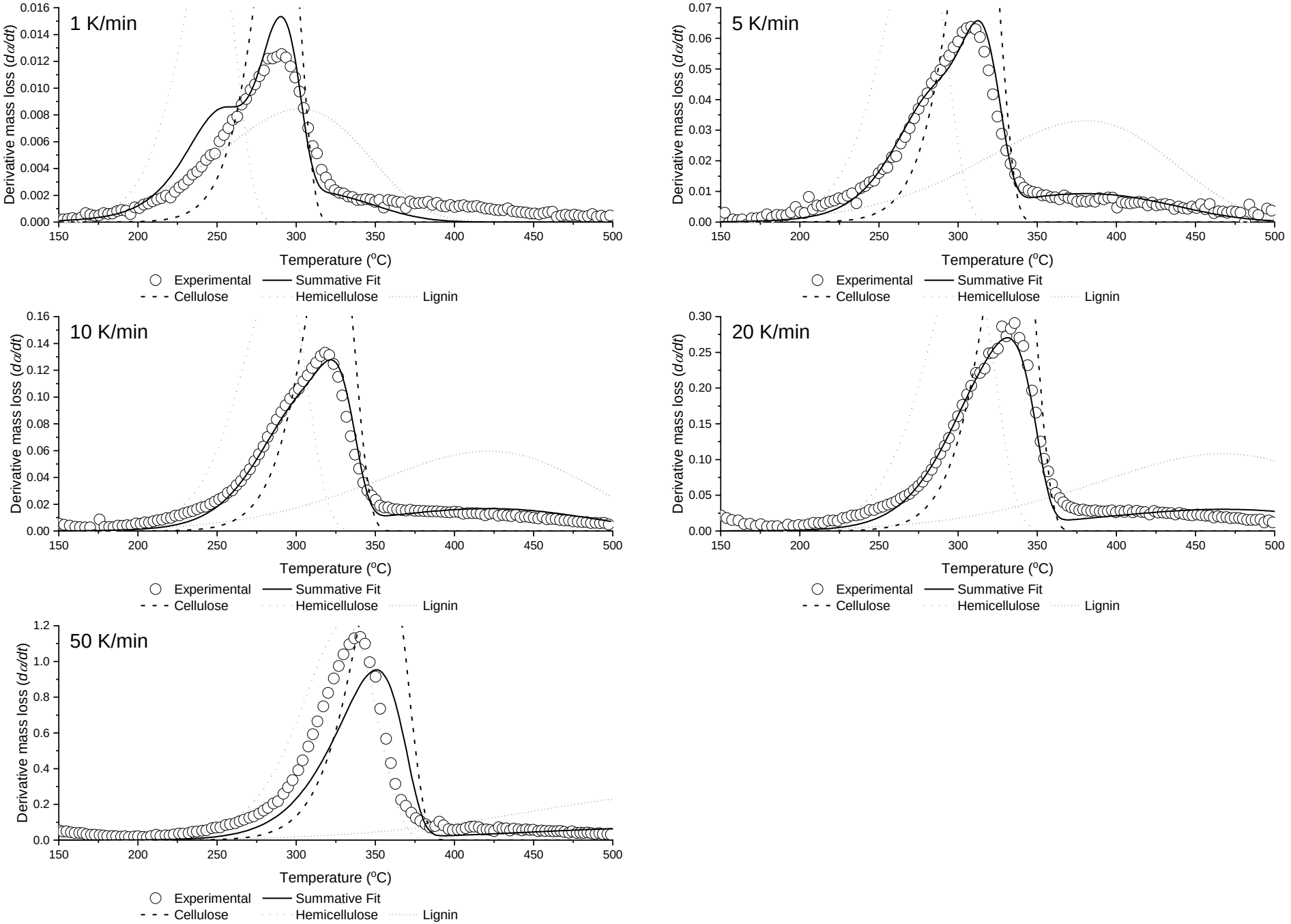


Figure S8: Model-fitting graphs for Wheat straw powder (WS-P), model first-order.

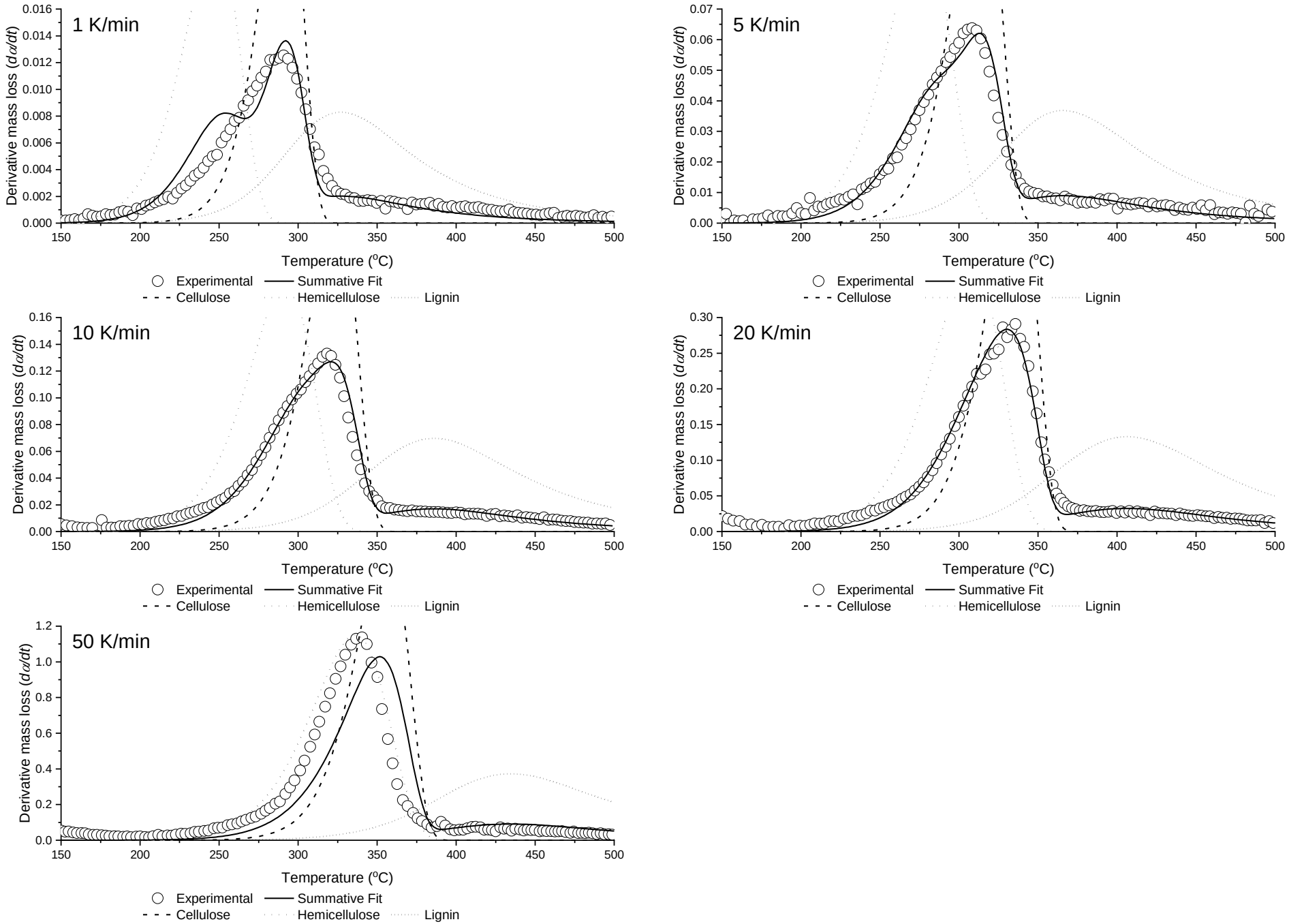


Figure S9: Model-fitting graphs for Wheat straw powder (WS-P), model third-order to lignin.

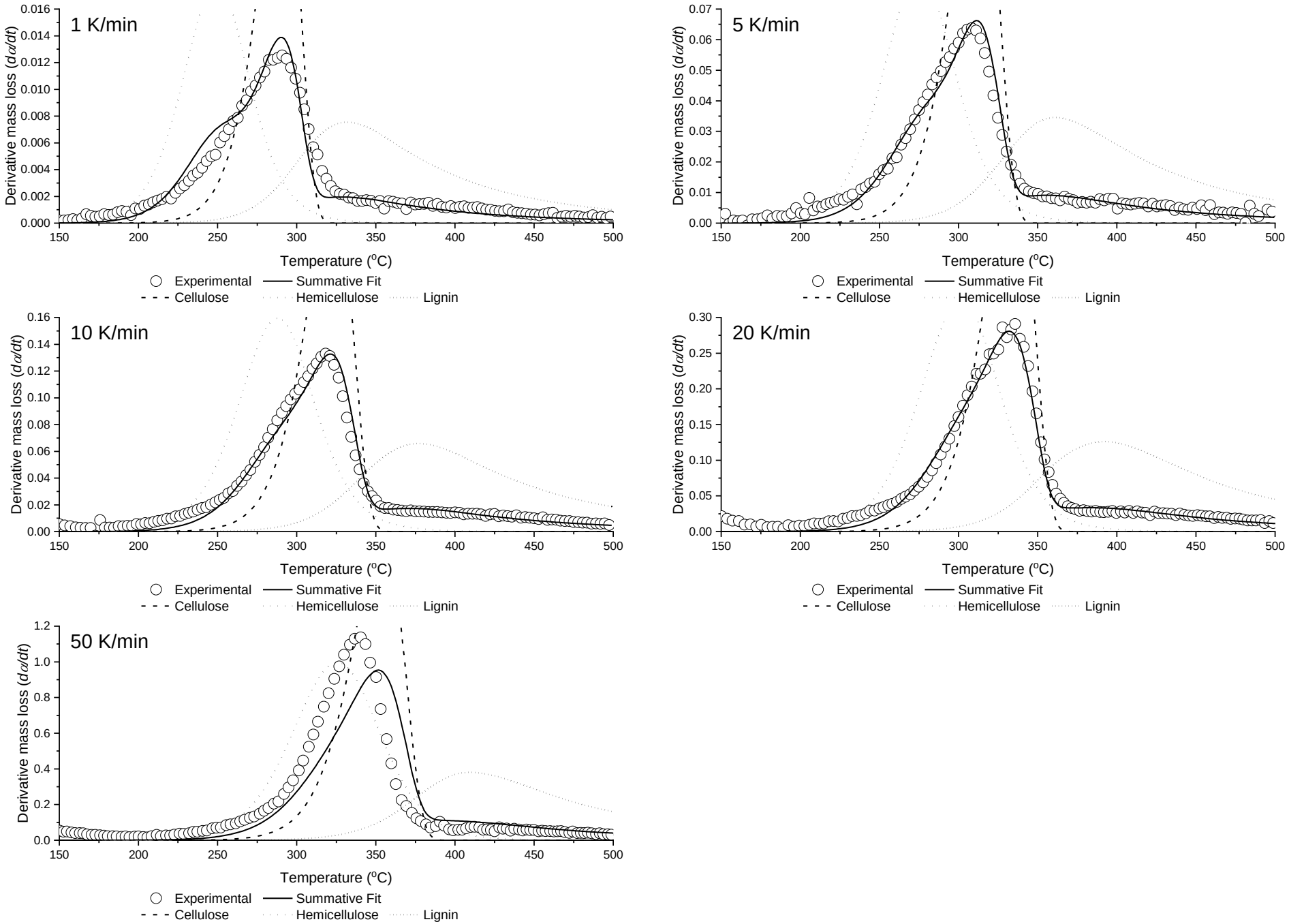


Figure S10: Model-fitting graphs for Wheat straw powder (WS-P), model free-order.

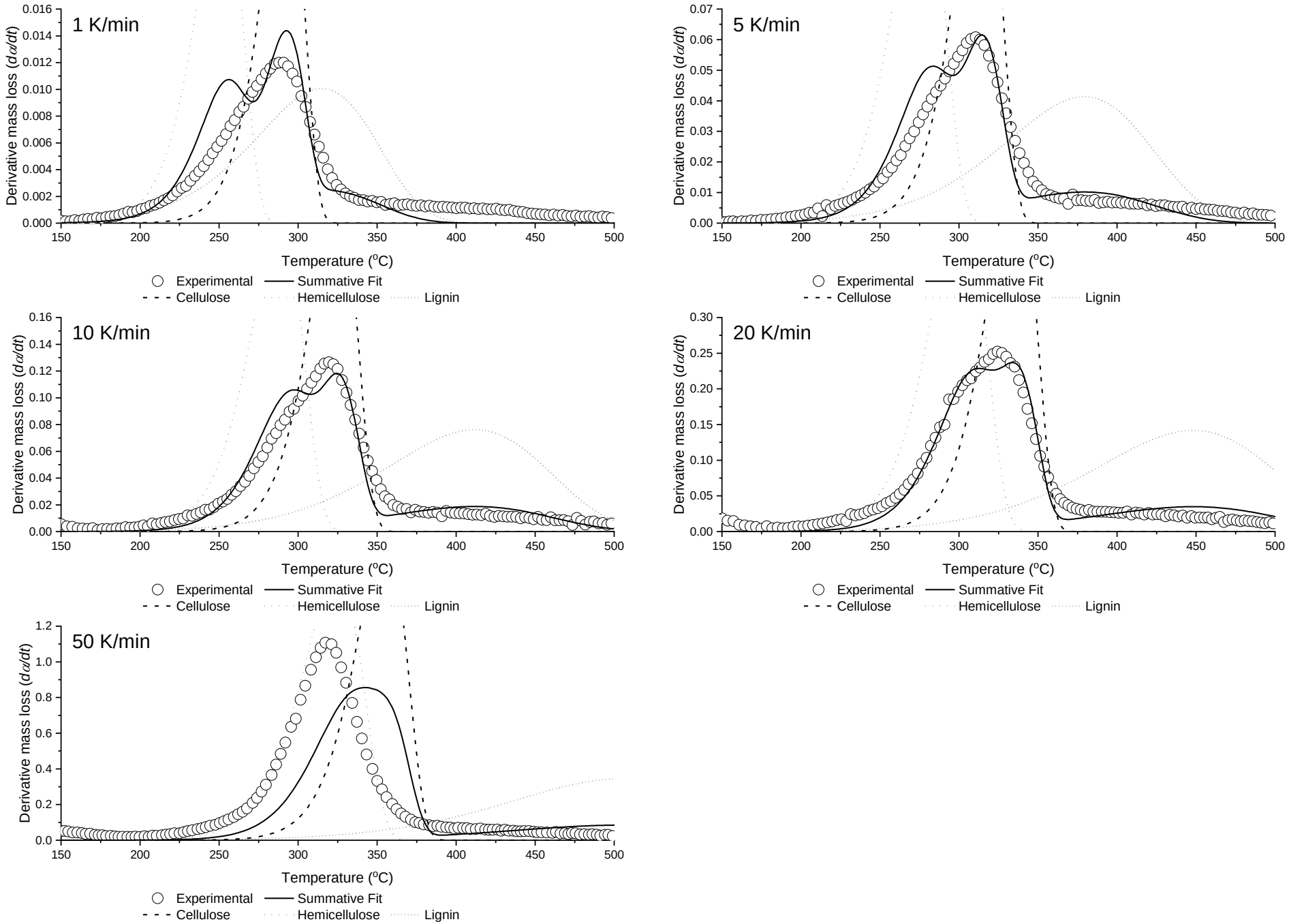


Figure S11: Model-fitting graphs for Wheat straw hull (WS-W), model first-order.

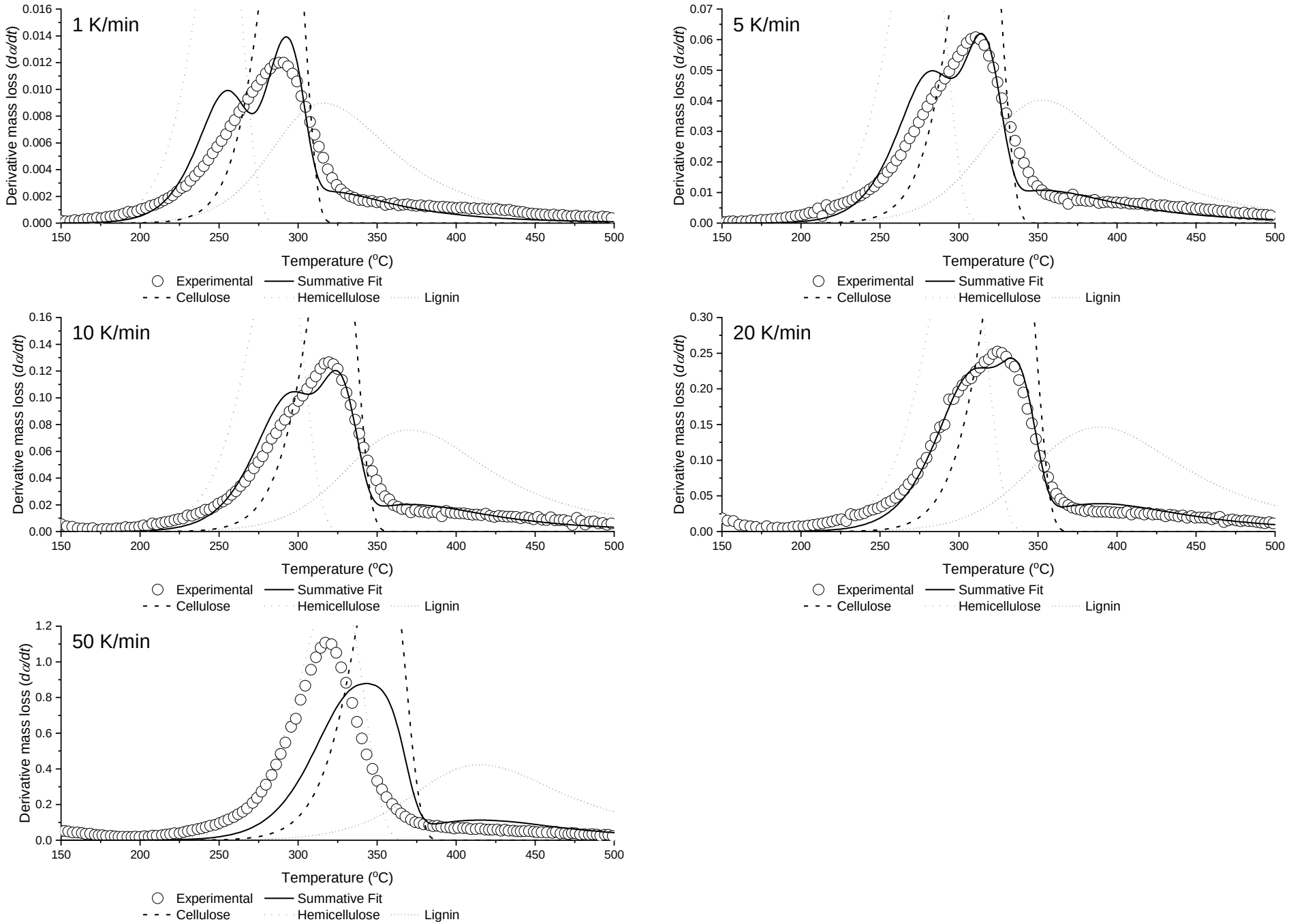


Figure S12: Model-fitting graphs for Wheat straw hull (WS-W), model third-order to lignin.

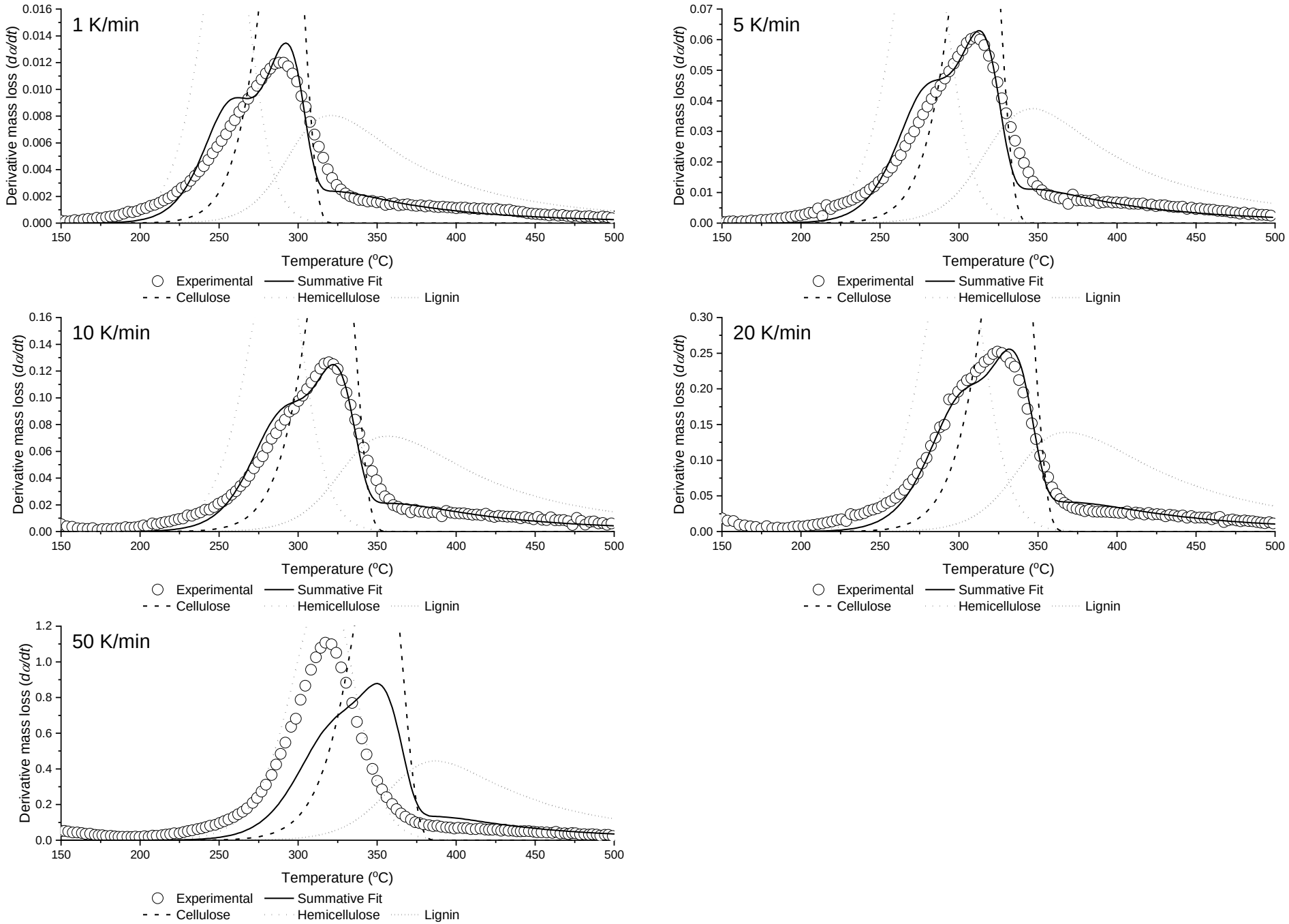


Figure S13: Model-fitting graphs for Wheat straw hull (WS-W), model free-order.

Isoconversional Methods

Numerical values

Table S10: Kinetic parameters obtained for Beech using the isoconversional methods.

α	KAS		FWO		Friedman	
	E_a (kJ/mol)	log10 (A [s^{-1}])	E_a (kJ/mol)	log10 (A [s^{-1}])	E_a (kJ/mol)	log10 (A [s^{-1}])
0.05	164.21 ± 6.71	12.68 ± 0.50	164.44 ± 6.31	10.41 ± 5.29	162.65 ± 3.56	12.42 ± 1.41
0.10	164.91 ± 4.50	12.61 ± 0.41	165.33 ± 4.21	10.35 ± 5.04	169.75 ± 3.38	12.95 ± 1.41
0.15	170.44 ± 5.65	13.05 ± 0.80	170.73 ± 5.32	10.78 ± 4.85	179.13 ± 5.41	13.67 ± 1.20
0.20	177.45 ± 3.64	13.61 ± 0.55	177.53 ± 3.40	11.31 ± 4.71	188.90 ± 1.56	14.38 ± 1.54
0.25	177.52 ± 5.11	13.47 ± 0.94	177.72 ± 4.79	11.19 ± 4.62	190.76 ± 5.54	14.34 ± 1.15
0.30	187.77 ± 8.19	14.28 ± 1.51	187.60 ± 7.73	11.97 ± 4.46	197.45 ± 6.64	14.74 ± 1.02
0.35	193.60 ± 6.30	14.67 ± 1.30	193.25 ± 5.93	12.33 ± 4.44	199.26 ± 4.42	14.72 ± 1.20
0.40	196.12 ± 3.23	14.74 ± 0.80	195.76 ± 3.00	12.41 ± 4.35	199.80 ± 2.53	14.62 ± 1.33
0.45	196.71 ± 3.54	14.66 ± 0.94	196.43 ± 3.30	12.33 ± 4.30	200.80 ± 2.37	14.62 ± 1.31
0.50	201.05 ± 3.93	14.94 ± 1.08	200.64 ± 3.70	12.60 ± 4.25	200.56 ± 0.81	14.55 ± 1.41
0.55	202.88 ± 1.61	15.03 ± 0.55	202.45 ± 1.48	12.69 ± 3.99	201.08 ± 1.03	14.58 ± 1.34
0.60	199.93 ± 4.02	14.70 ± 1.21	199.72 ± 3.75	12.38 ± 4.14	198.90 ± 4.25	14.38 ± 1.02
0.65	202.65 ± 4.59	14.90 ± 1.37	202.35 ± 4.36	12.58 ± 4.09	200.60 ± 6.70	14.53 ± 0.76
0.70	201.77 ± 3.63	14.78 ± 1.25	201.57 ± 3.39	12.46 ± 4.01	201.44 ± 4.93	14.56 ± 0.84
0.75	198.78 ± 5.00	14.49 ± 1.56	198.79 ± 4.71	12.19 ± 3.98	202.19 ± 6.36	14.56 ± 0.65
0.80	198.05 ± 4.67	14.39 ± 1.57	198.16 ± 4.38	12.09 ± 3.91	210.60 ± 6.68	15.14 ± 0.53
0.85	212.14 ± 5.77	15.51 ± 1.82	211.63 ± 5.43	13.16 ± 3.84	275.01 ± 6.18	20.15 ± 0.45
0.90	354.51 ± 23.26	26.72 ± 3.89	347.28 ± 22.06	23.97 ± 2.98	443.27 ± 11.50	32.66 ± 0.14
0.95	*1006.56 ± 234.32*	*74.53 ± 20.77*	*967.78 ± 222.73*	*70.93 ± 11.89*	*1101.33 ± 338.10*	*80.00 ± 24.94*

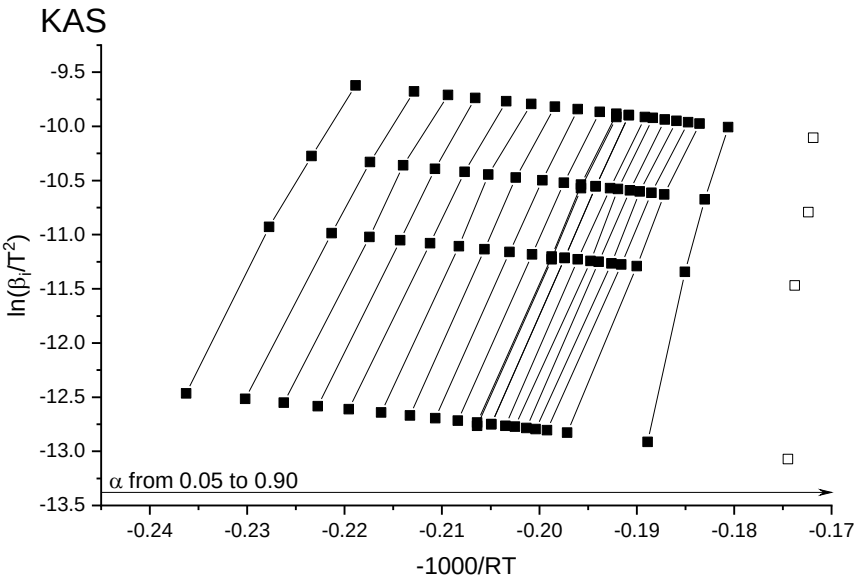
Table S11: Kinetic parameters obtained for WS-P using the isoconversional methods.

α	KAS		FWO		Friedman	
	E_a (kJ/mol)	log10 (A [s^{-1}])	E_a (kJ/mol)	log10 (A [s^{-1}])	E_a (kJ/mol)	log10 (A [s^{-1}])
0.05	222.51 ± 16.03	19.67 ± 1.87	241.08 ± 21.28	19.43 ± 4.18	195.54 ± 10.33	16.38 ± 0.70
0.10	186.63 ± 8.20	15.31 ± 1.05	193.57 ± 7.56	13.73 ± 4.94	168.14 ± 8.85	13.10 ± 0.87
0.15	176.54 ± 8.19	14.04 ± 1.21	185.59 ± 8.52	12.65 ± 4.72	170.23 ± 9.32	13.13 ± 0.82
0.20	182.34 ± 7.72	14.44 ± 1.27	190.19 ± 7.60	12.92 ± 4.64	181.17 ± 7.93	14.05 ± 0.94
0.25	181.98 ± 8.18	14.30 ± 1.44	190.24 ± 7.96	12.81 ± 4.52	186.86 ± 6.66	14.49 ± 1.04
0.30	184.47 ± 7.04	14.44 ± 1.35	193.45 ± 8.08	13.01 ± 4.43	192.84 ± 4.40	14.95 ± 1.22
0.35	193.29 ± 8.86	15.20 ± 1.70	201.51 ± 8.40	13.68 ± 4.34	200.59 ± 4.98	15.58 ± 1.14
0.40	197.54 ± 6.76	15.51 ± 1.45	210.33 ± 11.40	14.43 ± 4.12	209.08 ± 3.28	16.27 ± 1.26
0.45	205.68 ± 6.87	16.19 ± 1.54	216.54 ± 9.99	14.91 ± 4.14	216.00 ± 3.75	16.81 ± 1.18
0.50	200.96 ± 7.03	15.67 ± 1.62	217.55 ± 15.07	14.93 ± 3.79	219.58 ± 5.02	17.06 ± 1.03
0.55	201.21 ± 5.78	15.63 ± 1.48	220.11 ± 17.34	15.10 ± 3.58	224.17 ± 6.82	17.40 ± 0.83
0.60	210.75 ± 8.13	16.44 ± 1.89	225.84 ± 14.01	15.55 ± 3.75	233.26 ± 5.10	18.12 ± 0.93
0.65	218.34 ± 5.78	17.06 ± 1.59	234.34 ± 14.65	16.24 ± 3.66	246.28 ± 2.83	19.16 ± 1.08
0.70	233.13 ± 6.32	18.28 ± 1.73	251.05 ± 17.10	17.64 ± 3.45	276.96 ± 4.28	21.65 ± 0.88
0.75	244.29 ± 4.69	19.14 ± 1.52	266.04 ± 21.47	18.84 ± 3.11	308.74 ± 17.27	24.12 ± 0.31
0.80	293.39 ± 13.69	23.15 ± 2.81	323.86 ± 34.95	23.66 ± 2.08	410.51 ± 47.73	32.25 ± 2.97
0.85	399.75 ± 151.71	31.30 ± 15.28	389.93 ± 144.20	28.41 ± 6.77	509.70 ± 290.93	39.17 ± 23.13
0.90	*499.99 ± 334.65*	*37.73 ± 29.53*	*485.73 ± 318.10*	*34.70 ± 20.34*	*495.08 ± 345.33*	*35.97 ± 26.40*
0.95	*656.71 ± 600.22*	*47.35 ± 48.14*	*635.34 ± 570.53*	*44.13 ± 38.44*	*723.02 ± 653.27*	*50.93 ± 48.05*

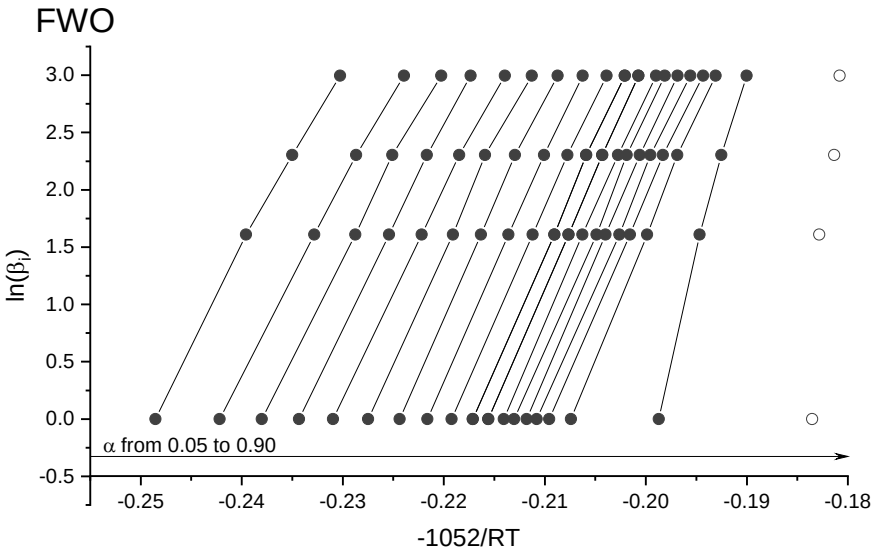
Table S12: Kinetic parameters obtained for WS-H using the isoconversional methods.

α	KAS		FWO		Friedman	
	E_a (kJ/mol)	$\log_{10}$ (A [s^{-1}])	E_a (kJ/mol)	log10 (A [s^{-1}])	E_a (kJ/mol)	log10 (A [s^{-1}])
0.05	219.08 ± 23.28	19.04 ± 2.76	216.27 ± 22.16	16.49 ± 4.11	191.55 ± 9.25	15.78 ± 0.81
0.10	192.54 ± 14.15	15.81 ± 1.86	191.36 ± 13.49	13.40 ± 4.57	189.51 ± 11.80	15.20 ± 0.57
0.15	198.97 ± 13.35	16.21 ± 1.92	197.65 ± 12.74	13.79 ± 4.46	205.13 ± 13.57	16.52 ± 0.40
0.20	204.35 ± 13.73	16.57 ± 2.09	202.90 ± 13.09	14.13 ± 4.32	212.06 ± 13.83	17.01 ± 0.37
0.25	204.04 ± 14.73	16.42 ± 2.31	202.71 ± 14.05	14.00 ± 4.16	215.23 ± 15.96	17.17 ± 0.16
0.30	209.52 ± 16.45	16.84 ± 2.60	208.00 ± 15.69	14.40 ± 3.97	219.03 ± 18.29	17.40 ± 0.07
0.35	215.63 ± 18.45	17.30 ± 2.90	213.89 ± 17.58	14.84 ± 3.77	221.32 ± 18.50	17.49 ± 0.11
0.40	215.69 ± 14.95	17.22 ± 2.55	214.02 ± 14.26	14.77 ± 3.94	224.49 ± 14.02	17.69 ± 0.28
0.45	226.86 ± 18.57	18.15 ± 3.02	224.72 ± 17.69	15.67 ± 3.65	235.21 ± 16.02	18.55 ± 0.07
0.50	229.45 ± 17.59	18.29 ± 2.97	227.25 ± 16.76	15.81 ± 3.66	240.52 ± 15.75	18.92 ± 0.06
0.55	225.04 ± 14.68	17.82 ± 2.68	223.11 ± 14.01	15.36 ± 3.79	238.31 ± 14.34	18.64 ± 0.15
0.60	230.22 ± 16.60	18.20 ± 2.95	228.10 ± 15.83	15.73 ± 3.62	246.08 ± 17.82	19.21 ± 0.20
0.65	244.68 ± 13.63	19.40 ± 2.65	241.92 ± 13.01	16.87 ± 3.75	269.20 ± 16.42	21.08 ± 0.12
0.70	241.81 ± 21.62	19.02 ± 3.60	239.26 ± 20.60	16.51 ± 3.20	267.03 ± 29.81	20.69 ± 1.34
0.75	262.39 ± 23.47	20.68 ± 3.84	258.92 ± 22.35	18.11 ± 3.04	300.05 ± 35.25	23.28 ± 1.86
0.80	275.57 ± 15.46	21.48 ± 3.02	271.57 ± 14.73	18.89 ± 3.50	326.19 ± 20.22	24.89 ± 0.65
0.85	363.52 ± 79.40	28.17 ± 9.05	355.49 ± 75.49	25.37 ± 1.11	375.81 ± 88.40	27.92 ± 6.36
0.90	*435.08 ± 75.05*	*32.36 ± 8.43*	*424.06 ± 71.36*	*31.76 ± 0.54*	*455.00 ± 76.93*	*32.61 ± 5.26*
0.95	*600.73 ± 67.29*	*42.79 ± 7.58*	*582.18 ± 63.98*	*41.97 ± 0.22*	*605.02 ± 58.80*	*41.80 ± 3.87*

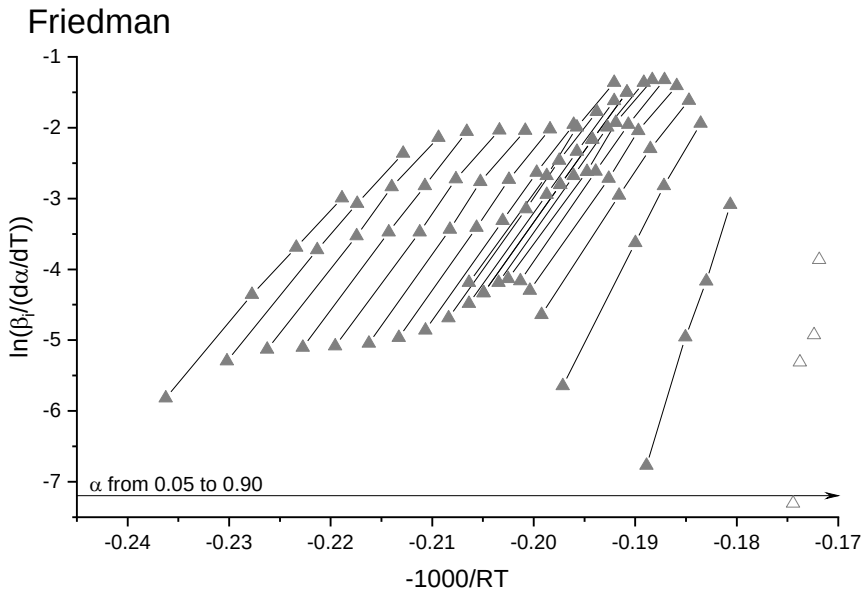
Arrhenius Plots



α	R2
0.05	1.00
0.10	1.00
0.15	1.00
0.20	1.00
0.25	1.00
0.30	1.00
0.35	1.00
0.40	1.00
0.45	1.00
0.50	1.00
0.55	1.00
0.60	1.00
0.65	1.00
0.70	1.00
0.75	1.00
0.80	1.00
0.85	1.00
0.90	0.99
0.95	0.90

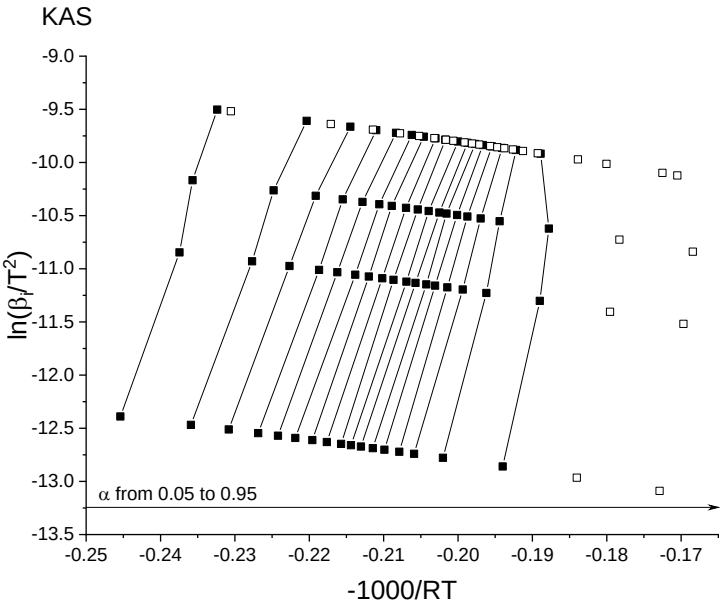


α	R2
0.05	1.00
0.10	1.00
0.15	1.00
0.20	1.00
0.25	1.00
0.30	1.00
0.35	1.00
0.40	1.00
0.45	1.00
0.50	1.00
0.55	1.00
0.60	1.00
0.65	1.00
0.70	1.00
0.75	1.00
0.80	1.00
0.85	1.00
0.90	0.99
0.95	0.90

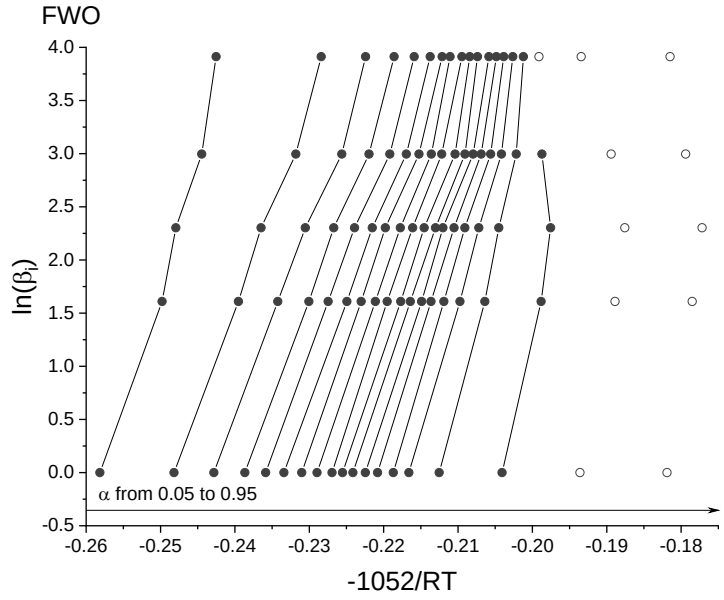


α	R2
0.05	1.00
0.10	1.00
0.15	1.00
0.20	1.00
0.25	1.00
0.30	1.00
0.35	1.00
0.40	1.00
0.45	1.00
0.50	1.00
0.55	1.00
0.60	1.00
0.65	1.00
0.70	1.00
0.75	1.00
0.80	1.00
0.85	1.00
0.90	1.00
0.95	0.84

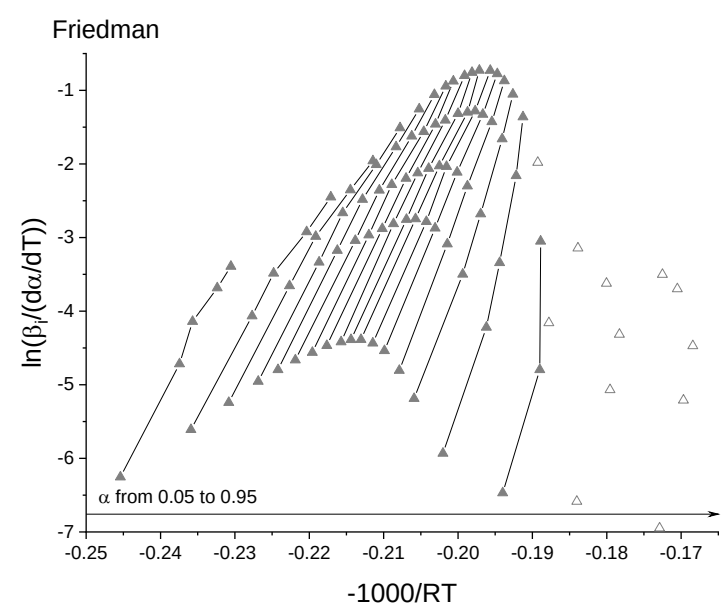
Figure S14: Arrhenius plots for the isoconversional methods for Beech.



α	R2
0.05	0.99
0.10	1.00
0.15	1.00
0.20	1.00
0.25	1.00
0.30	1.00
0.35	1.00
0.40	1.00
0.45	1.00
0.50	1.00
0.55	1.00
0.60	1.00
0.65	1.00
0.70	1.00
0.75	1.00
0.80	1.00
0.85	0.78
0.90	0.69
0.95	0.54

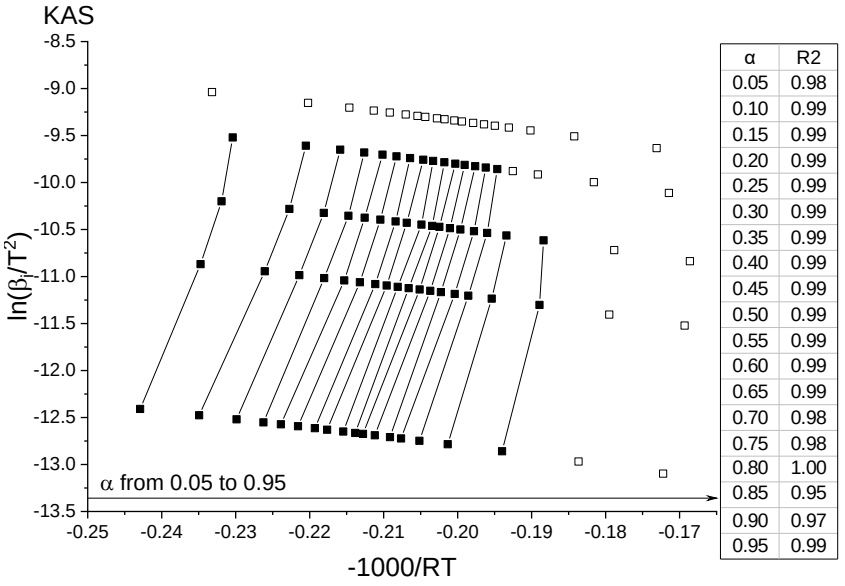


α	R2
0.05	0.98
0.10	1.00
0.15	0.99
0.20	1.00
0.25	0.99
0.30	0.99
0.35	0.99
0.40	0.99
0.45	0.99
0.50	0.99
0.55	0.98
0.60	0.99
0.65	0.99
0.70	0.99
0.75	0.98
0.80	0.97
0.85	0.79
0.90	0.70
0.95	0.55

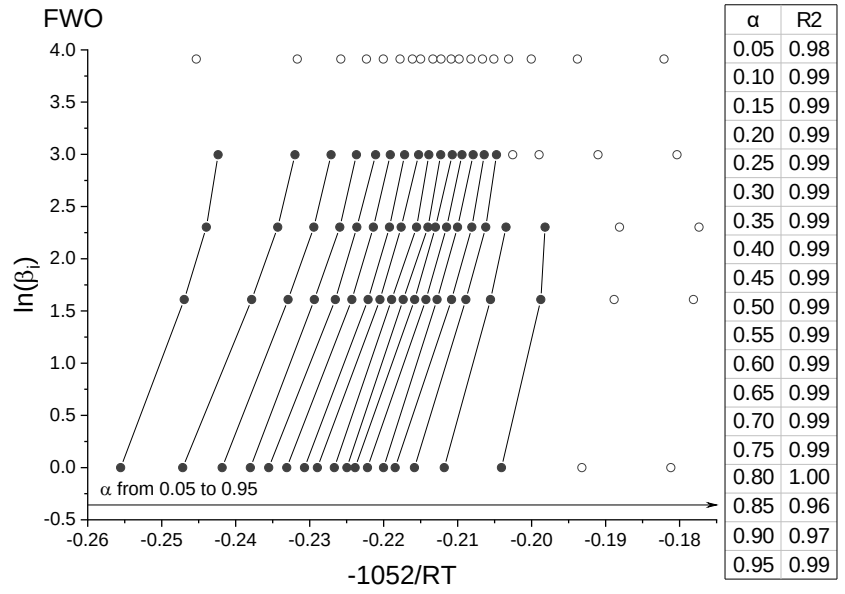


α	R2
0.05	0.99
0.10	0.99
0.15	0.99
0.20	0.99
0.25	1.00
0.30	1.00
0.35	1.00
0.40	1.00
0.45	1.00
0.50	1.00
0.55	1.00
0.60	1.00
0.65	1.00
0.70	1.00
0.75	0.99
0.80	0.96
0.85	0.75
0.90	0.67
0.95	0.55

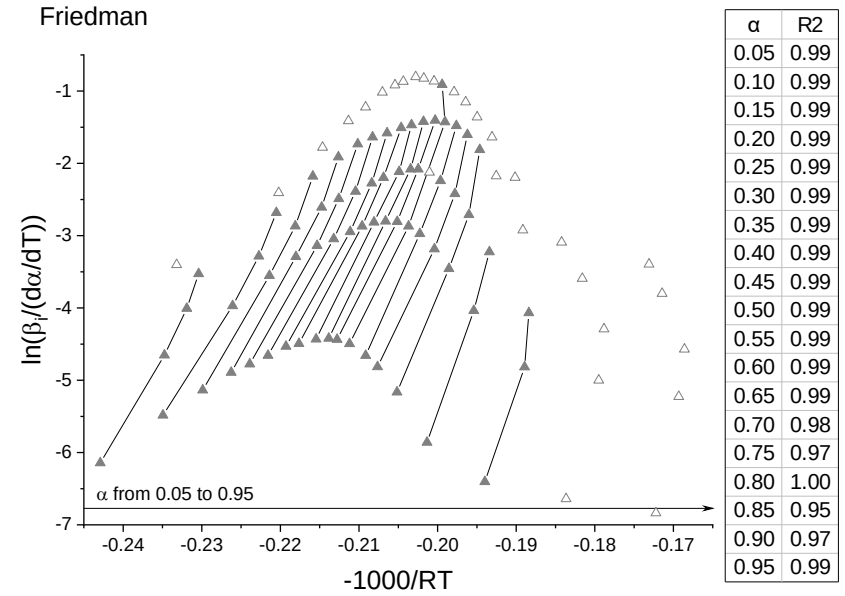
Figure S15: Arrhenius plots for the isoconversional methods for WS-P.



α	R2
0.05	0.98
0.10	0.99
0.15	0.99
0.20	0.99
0.25	0.99
0.30	0.99
0.35	0.99
0.40	0.99
0.45	0.99
0.50	0.99
0.55	0.99
0.60	0.99
0.65	0.99
0.70	0.98
0.75	0.98
0.80	1.00
0.85	0.95
0.90	0.97
0.95	0.99



α	R2
0.05	0.98
0.10	0.99
0.15	0.99
0.20	0.99
0.25	0.99
0.30	0.99
0.35	0.99
0.40	0.99
0.45	0.99
0.50	0.99
0.55	0.99
0.60	0.99
0.65	0.99
0.70	0.99
0.75	0.99
0.80	1.00
0.85	0.96
0.90	0.97
0.95	0.99



α	R2
0.05	0.99
0.10	0.99
0.15	0.99
0.20	0.99
0.25	0.99
0.30	0.99
0.35	0.99
0.40	0.99
0.45	0.99
0.50	0.99
0.55	0.99
0.60	0.99
0.65	0.99
0.70	0.98
0.75	0.97
0.80	1.00
0.85	0.95
0.90	0.97
0.95	0.99

Figure S16: Arrhenius plots for the isoconversional methods for WS-H.

Comparison of results – Isoconversional and Model-fitting

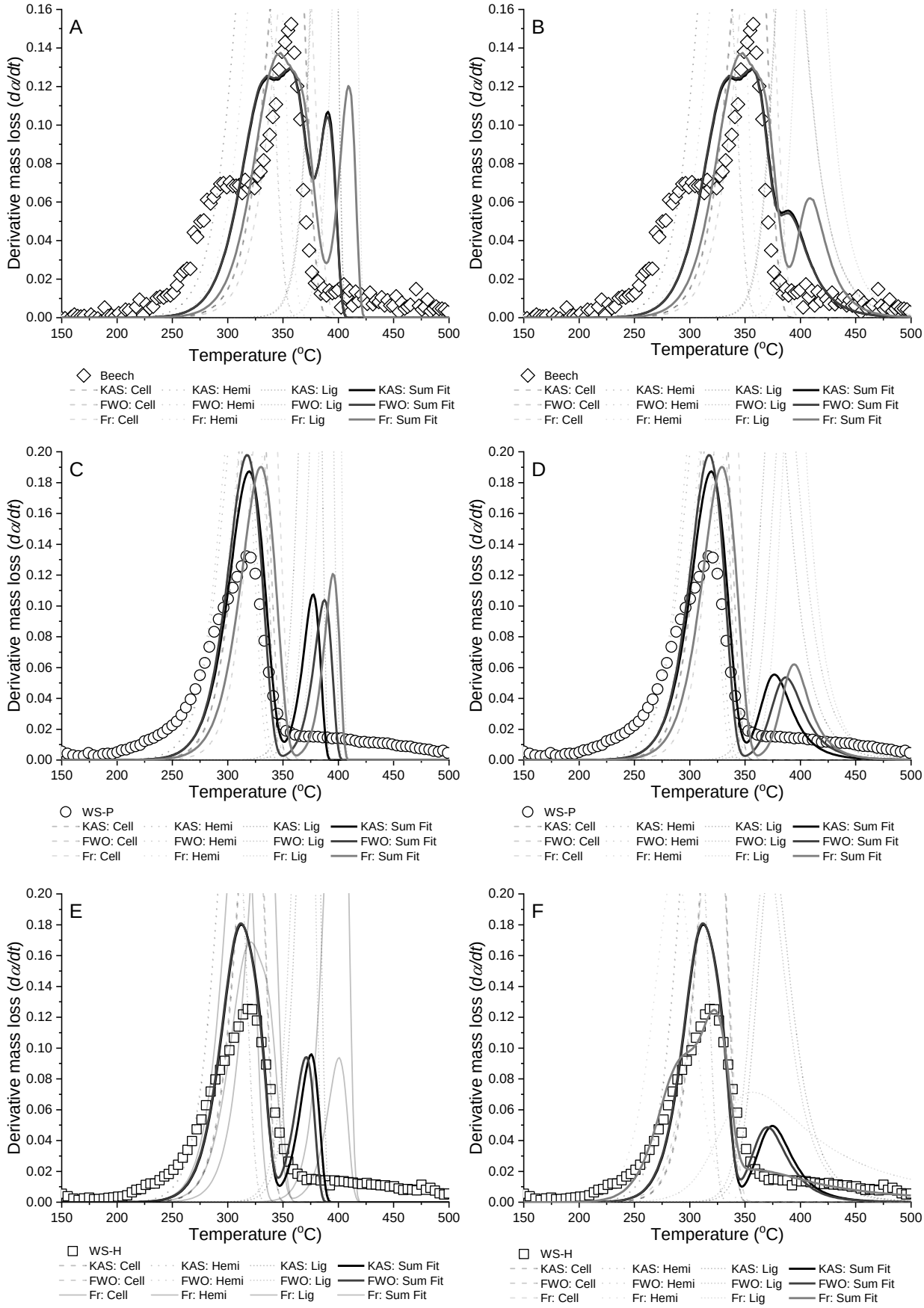


Figure S17: Comparison of degradation behavior using curves traced using the estimated isoconversional methods and the experimental data at 10 K/min. A: Beech, n_3=1; B: Beech, n_3=3; C: WS-P, n_3=1; D: WS-P, n_3=3; E: WS-W, n_3=1; E: WS-W, n_3=3. Fr = Friedman method.

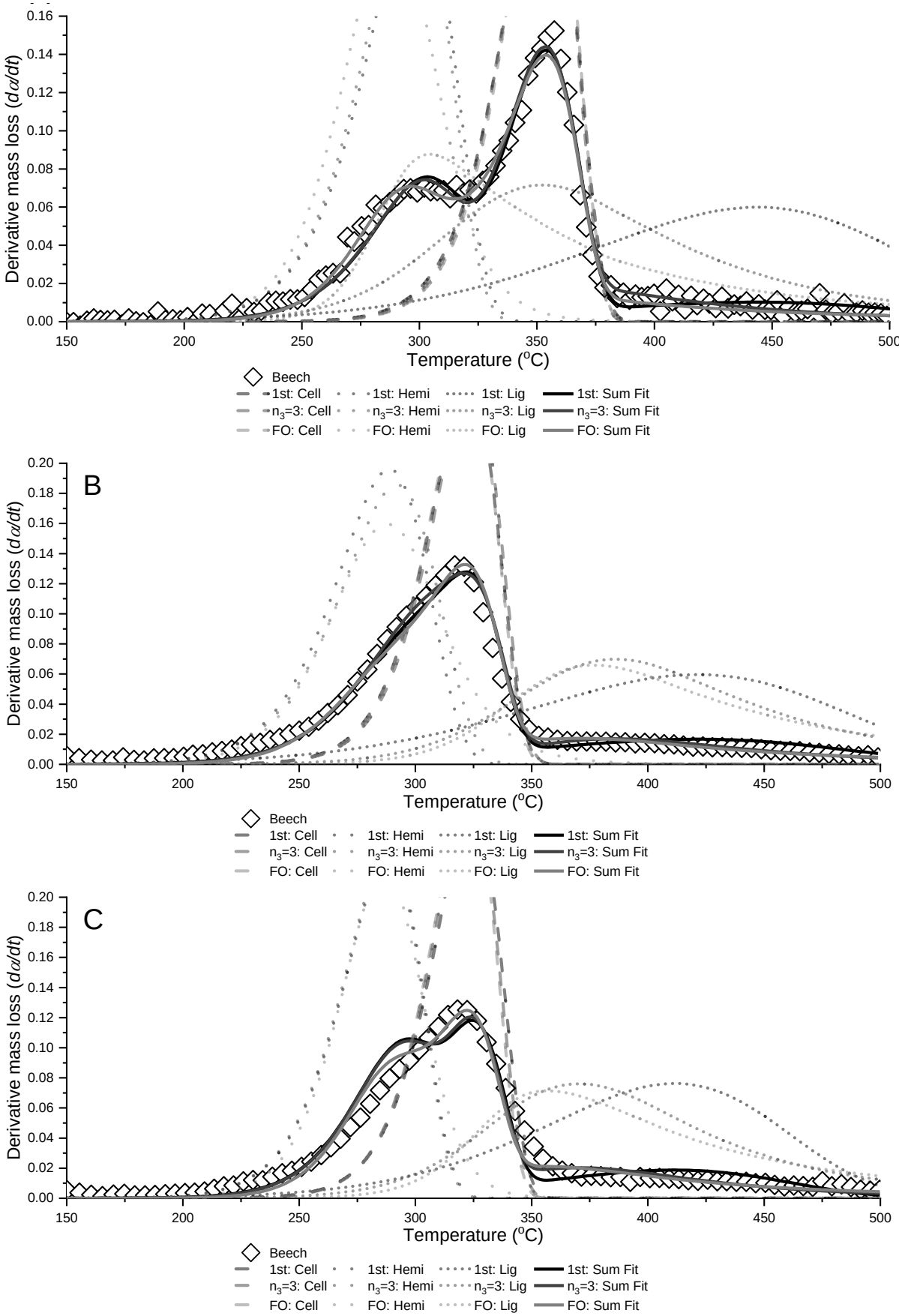


Figure S18: Comparison of degradation behavior using curves traced using the estimated curve-fitting methods and the experimental data at 10 K/min. A: Beech; B: WS-P; C: WS-W. FO = Free-order.

Reaction Networks

All the kinetics assume first-order (also called power law), which can vary with the operational temperature:

$$r = AT^n \exp\left(\frac{E_a}{RT}\right)$$

Table S13: Reaction network from Ranzi et al. [11].

Group	#		E_a (kJ/mol)	$\log_{10}[A\ (s^{-1})]$	T^n
Cellulose	1	*CELLULOS → CELL-ACT*	192.28	13.90	0
	2	*CELL-ACT → 0.95 HAA + 0.25 GLYOXAL + 0.2 ACETALDY + 0.25 HMF + 0.2 CO2 + 0.15 CO + 0.9 WATER + 0.65 C + 0.2 ACETONE + 0.1 H2 + 0.1 CH4*	125.40	9.00	0
	3	*CELL-ACT → LEVOGLUC*	41.80	0.60	1
	4	*CELLULOS → 5 WATER + 6 C*	133.76	7.90	0
Hemicellulose	1	*HEMICELL → 0.4 HEMCELL1 + 0.6 HEMCELL2*	129.58	10.00	0
	2	*HEMCELL1 → 2.5 H2 + 0.775 CO2 + CO + 0.5 FORMALDY + 0.25 METHANOL + 0.125 ETHANOL + 0.125 WATER + 2 C*	112.86	9.48	0
	3	*HEMCELL1 → XYLOSE*	45.98	0.48	1
	4	*HEMCELL2 → 0.2 CO2 + 1.5 H2 + 0.7 FORMALDY + 0.25 METHANOL + 0.125 ETHANOL + 0.125 WATER + 2 C + 0.8 GCO2 + 0.8 GCOH2*	137.94	10.00	0
Lignin	1	*LIGNIN-C → 0.35 LIGN-CC + 0.1 CMRYLALC + 0.08 PHENOL + 1.49 H2 + WATER + 7.05 C + 1.32 GCOH2*	202.73	15.60	0
	2	*LIGNIN-H → LIGN-OH + ACETONE*	156.75	13.30	0
	3	*LIGNIN-O → LIGN-OH + CO2*	106.59	9.00	0
	4	*LIGN-CC → 0.3 CMRYLALC + 0.2 PHENOL + 0.35 PROPDIAL + 1.2 H2 + 0.7 WATER + 0.25 CH4 + 0.25 ETHENE + 7.5 C + 0.5 GCO + 1.3 GCOH2*	131.67	6.70	0
	5	*LIGN-OH → LIG + 0.5 H2 + WATER + METHANOL + 5 C + GCO + GCOH2*	206.91	13.00	0
	6	*LIG → SYNAPALD*	50.16	1.90	1
	7	*LIG → WATER + 0.5 CO + 0.4 CH4 + 0.4 FORMALDY + 0.5 ETHENE + 6 C + 0.7 H2 + 0.4 METHANOL + 0.2 ACETALDY + 0.2 PROPDIAL + GCO + 0.5 GCOH2*	125.40	9.08	0

Table S14: Reaction network from Ranzi et al. [11] *and Faravelli et al.* [13]*, and modified by Peters et al.* [54].

Group	#		E_a (kJ/mol)	$\log_{10}[A (s^{-1})]$	T^n
Cellulose	1	*CELLULOS → CELL-ACT*	221.12	13.90	0
	2	*CELL-ACT → 0.95 HAA + 0.25 GLYOXAL + 0.2 ACETALDY + 0.25 HMF + 0.2 CO2 + 0.15 CO + 0.9 WATER + 0.65 C + 0.2 ACETONE + 0.1 H2 + 0.1 CH4*	125.40	9.00	0
	3	*CELL-ACT → LEVOGLUC*	41.80	0.60	1
	4	*CELLULOS → 5 WATER + 6 C*	153.82	7.90	0
Hemicellulose	1	*HEMICELL → 0.4 HEMCELL1 + 0.6 HEMCELL2*	129.58	10.00	0
	2	*HEMCELL1 → 2.5 H2 + 0.775 CO2 + CO + 0.5 FORMALDY + 0.25 METHANOL + 0.125 ETHANOL + 0.125 WATER + 2 C*	11.29	9.48	0
	3	*HEMCELL1 → XYLOSE*	45.98	0.48	1
	4	*HEMCELL2 → 0.2 CO2 + 1.5 H2 + 0.7 FORMALDY + 0.25 METHANOL + 0.125 ETHANOL + 0.125 WATER + 2 C + 0.8 GCO2 + 0.8 GCOH2*	137.94	9.90	0
Lignin	1	*1LIGH → PROPENE + 1ROH + 1RLIGM2A*	163.25	13.00	0
	2	*LIGNIN-H → 1PRLIGH + 1RH*	163.25	13.00	0
	3	*1LIGM2 → 1RPHOXM2 + 1RADIOM2*	163.25	13.00	0
	4	*LIGN-OH → 1PRLGM2A + 1RH*	163.25	13.00	0
	5	*LIGN-OH + 1RH → 1RPHOXM2 + 1RADIOM2*	163.25	13.00	0
	6	*1LIG → 1RPHENOX + 1RADIO*	184.18	13.00	0
	7	*LIGNIN-C → 1PRLIG-A + 1RH*	184.18	13.00	0
	8	*LIGNIN-C → 1RPHENOX + 1PRADIO*	188.37	13.00	0
	9	*1PADIOM2 → 1RADIOM2*	171.63	13.00	0
	10	*1PADIO → 1PRADIO + 1RH*	180.00	13.00	0
	11	*1PKETM2 → 1PRKETM2 + 1RH*	167.44	13.00	0
	12	*1PLIGC → LIGNIN-C + KETEN-01*	121.39	8.00	0
	13	*LIGNIN-O → LIGN-OH + CO2*	108.84	9.00	0

Table S15: Reaction network from Corbetta et al. [19]. *Hemicellulose assumed to be xylan-rich based on the conclusions of Peng and Wu* [52].

Group	#		E_a (kJ/mol)	$\log_{10}[A (s^{-1})]$	T^n
Cellulose	1	*CELL → CELLA*	188.10	13.60	0
	2	*CELLA → 0.8 HAA + 0.2 GLYOXAL + 0.1 ACETALDY + 0.25 HMF + 0.3 ACETONE + 0.21 CO2 + 0.1 H2 + 0.4 FORMALDY + 0.16 CO + 0.1 CH4 + 0.83 WATER + 0.02 FORMICAC + 0.61 C*	121.22	8.70	0
	3	*CELLA → LEVOGLUC*	41.80	0.26	1
	4	*CELL → 5 WATER + 6 C*	163.02	7.60	0
Hemicellulose	1	*XYHW → 0.4 HEM1 + 0.6 HEM2*	129.58	9.52	0
	2	*HEM1 → 0.025 WATER + 0.5 CO2 + 0.025 FORMICAC + 0.5 CO + 0.8 FORMALDY + 0.125 ETHANOL + 0.1 METHANOL + 0.25 C2H4 + 0.125 GH2 + 0.275 GCO2 + 0.4 GCOH2 + 0.45 GCH3OH + 0.325 GCH4 + 0.875 C*	133.76	9.00	0
	3	*HEM1 → 0.25 WATER + 0.5 CO2 + 0.05 FORMICAC + 0.3 CO + 0.15 GCO + 0.25 GCO2 + 1.7 GCOH2 + 0.625 GCH4 + 0.375 GC2H4 + 0.875 C*	45.98	-0.05	1
	4	*HEM1 → XYLOSAN*	33.44	-1.30	1
	5	*HEM2 → 0.2 WATER + 0.175 CO + 0.275 CO2 + 0.5 FORMALDY + 0.1 ETHANOL + 0.2 HAA + 0.025 FORMICAC + 0.25 GCH4 + 0.3 GCH3OH + 0.275 GC2H4 + 0.4 GCO2 + 0.925 GCOH2 + C*	137.94	9.52	0
Lignin	1	*LIGC → 0.35 LIGCC + 0.1 CMRYLALC + 0.08 PHENOL + 0.41 C2H4 + WATER + 0.3 FORMALDY + 0.32 CO + 0.7 GCOH2 + 0.495 GCH4 + 5.735 C*	202.73	15.12	0
	2	*LIGH → LIGOH + ACETONE*	156.75	12.83	0
	3	*LIGO → LIGOH + GCO2*	106.59	8.52	0
	4	*LIGCC → 0.3 CMRYLALC + 0.2 PHENOL + 0.35 HAA + 0.7 WATER + 0.4 CO + 0.65 GCH4 + 0.6 GC2H4 + GCOH2 + 0.4 GCO + 6.75 C*	131.67	6.20	0
	5	*LIGOH → LIG + 0.15 GH2 + 0.9 WATER + 0.1 CH4 + 0.5 METHANOL + 0.5 GCH3OH + 0.05 CO2 + 0.3 CO + GCO + 0.05 FORMICAC + 0.6 GCOH2 + 0.35 GCH4 + 0.2 GC2H4 + 4.15 C*	125.40	7.70	0
	6	*LIGOH → 1.5 WATER + 0.5 CO + 0.1 CH4 + 0.5 GH2 + 1.6 GCO + 3.9 GCOH2 + 1.65 GCH4 + 0.3 GC2H4 + 0.5 GCH3OH + 10.15 C*	62.70	1.52	1
	7	*LIG → SYNAPALD*	50.16	0.38	1
	8	*LIG → 0.95 WATER + 0.2 FORMALDY + 0.4 METHANOL + CO + 0.2 CH4 + 0.05 FORMICAC + 0.45 GCO + 0.5 GCOH2 + 0.4 GCH4 + 0.65 GC2H4 + 0.2 ACETALDY + 0.2 ACETONE + 5.5 C*	125.40	8.60	0
	9	*LIG → 0.6 WATER + 0.4 CO + 0.2 CH4 + 0.4 FORMALDY + 0.2 GCO + 0.4 GCH4 + 0.5 GC2H4 + 0.4 GCH3OH + 2 GCOH2 + 6 C*	33.44	-1.08	1

Table S16: Reaction network from Anca-Couce and Scharler [12]*, assuming low charring conditions as reported by Pecha et al.* [23].

Group	#		E_a (kJ/mol)	$\log_{10}[A (s^{-1})]$	T^n
Cellulose	1	*CELLULOS → CELL-ACT*	188.37	13.60	0
	2	*CELL-ACT → 0.43875 HAA + 0.195 GLYOXAL + 0.2925 ACETONE + 0.24375 HMF + 0.07375 H2 + 0.30225 CO + 0.41225 CO2 + 0.39 FORMALDY + 0.14625 METHANOL + 0.0975 ACETALDY + 0.90925 WATER + 0.0195 FORMICAC + 0.04875 GH2 + 0.195 GCH4 + 0.73225 C*	80.00	6.30	0
	3	*CELL-ACT → 0.975 LEVOGLUC + 0.1375 C + 0.1 WATER + 0.0125 CO2 + 0.025 H2*	41.86	0.60	1
Hemicellulose	1	*HEMICELL → 0.58 HEMCELL1 + 0.42 HEMCELL2 + 0.4 ACETICAC*	129.77	10.00	0
	2	*HEMCELL1 → 0.475 CO + 0.5 CO2 + 0.30875 CH4 + 0.76 FORMALDY + 0.095 METHANOL + 0.2375 C2H4 + 0.11875 ETHANOL + 0.17375 WATER + 0.02375 FORMICAC + 0.26125 GCO2 + 0.38 GCOH2 + 0.11875 GH2 + 0.4275 GCH3OH + 1.05625 C + 0.05 H2*	125.58	9.08	0
	3	*HEMCELL1 → 0.095 CO + 0.785 CO2 + 0.285 FORMALDY + 0.3875 WATER + 0.0475 FORMICAC + 0.1425 GCO2 + 0.1425 GCO + 1.14 GCOH2 + 0.19 GH2 + 0.59375 GCH4 + 0.35625 GC2H4 + 1.05625 C + 0.05 H2*	33.50	-0.82	1
	4	*HEMCELL1 → 0.95 XYLOSAN + 0.225 C + 0.15 WATER + 0.025 CO2 + 0.05 H2*	46.05	0.48	1
	5	*HEMCELL2 → 0.19 HAA + 0.16625 CO + 0.29 CO2 + 0.475 FORMALDY + 0.095 ETHANOL + 0.34 WATER + 0.02375 FORMICAC + 0.38 GCO2 + 0.87875 GCOH2 + 0.2375 GCH4 + 0.285 GCH3OH + 0.26125 GC2H4 + 1.18 C + 0.05 H2*	138.14	9.70	0
Lignin	1	*LIGNIN-C → 0.35 LIGN-CC + 0.1 CMRYLALC + 0.08 PHENOL + 0.32 CO + 0.3 FORMALDY + WATER + 0.7 GCOH2 + 0.495 GCH4 + 0.41 GC2H4 + 5.735 C*	203.02	15.12	0
	2	*LIGNIN-H → LIGN-OH + 0.25 HAA + 0.5 ACETONE + 5 GC2H4*	156.97	12.83	0
	3	*LIGNIN-O → LIGN-OH + CO2*	106.74	8.52	0
	4	*LIGN-CC → 0.315 HAA + 0.27 CMRYLALC + 0.18 PHENOL + 0.36 CO + 0.585 CH4 + 0.54 C2H4 + 1.03 WATER + 0.36 GCO + 0.9 GCOH2 + 7.575 C + 0.3 H2*	131.86	7.48	0
	5	*LIGN-OH → LIG + 0.55 CO + 0.05 CO2 + 0.1 CH4 + 0.6 METHANOL + 0.9 WATER + 0.05 FORMICAC + 0.6 GCO + 0.85 GCOH2 + 0.1 GH2 + 0.35 GCH4 + 0.3 GCH3OH + 0.2 GC2H4 + 4.15 C*	125.58	8.00	0
	6	*LIG → 0.9 SYNAPALD + 1.1 C + 0.3 WATER + 0.1 CO2 + 0.3 H2*	50.20	0.60	1
	7	*LIG → 0.18 ACETONE + 0.9 CO + 0.18 CH4 + 0.18 FORMALDY + 0.36 METHANOL + 0.18 ACETALDY + 1.155 WATER + 0.045 FORMICAC + 0.405 GCO + 0.45 GCOH2 + 0.36 GCH4 + 0.585 GC2H4 + 6 C + 0.05 CO2 + 0.3 H2*	125.58	8.60	0
	8	*LIG → 0.36 CO + 0.18 CH4 + 0.36 FORMALDY + 0.84 WATER + 0.18 GCO + 1.8 GCOH2 + 0.36 GCH4 + 0.36 GCH3OH + 0.45 GC2H4 + 6.45 C + 0.05 CO2 + 0.3 H2*	33.50	-1.08	1
Extractives	1	*TANN → PHENOL + ITANN*	46.02	1.70	0
	2	*ITANN → 5 C + 3 CO + GCOH2 + 2 WATER*	25.52	3.79	0
	3	*TGL → ACROLEIN + 3 FFA*	191.20	12.85	0

Table S17: Reaction network from Anca-Couce and Scharler [12]*, assuming high charring conditions as reported by Pecha et al.* [23].

Group	#		E_a (kJ/mol)	$\log_{10}[A (s^{-1})]$	T^n
Cellulose	1	*CELLULOS → CELL-ACT*	188.37	13.60	0
	2	*CELL-ACT → 0.405 HAA + 0.18 GLYOXAL + 0.27 ACETONE + 0.225 HMF + 0.145 H2 + 0.279 CO + 0.419 CO2 + 0.36 FORMALDY + 0.135 METHANOL + 0.09 ACETALDY + 1.147 WATER + 0.018 FORMICAC + 0.045 GH2 + 0.18 GCH4 + 1.099 C*	80.00	6.30	0
	3	*CELL-ACT → 0.405 HAA + 0.18 GLYOXAL + 0.27 ACETONE + 0.225 HMF + 0.145 H2 + 0.279 CO + 0.419 CO2 + 0.36 FORMALDY + 0.135 METHANOL + 0.09 ACETALDY + 1.147 WATER + 0.018 FORMICAC + 0.045 GH2 + 0.18 GCH4 + 1.099 C*	41.86	0.60	1
Hemicellulose	1	*HEMICELL → 0.58 HEMCELL1 + 0.42 HEMCELL2 + 0.4 ACETICAC*	129.77	10.00	0
	2	*HEMCELL1 → 0.4 CO + 0.5 CO2 + 0.26 CH4 + 0.64 FORMALDY + 0.08 METHANOL + 0.2 C2H4 + 0.1 ETHANOL + 0.62 WATER + 0.02 FORMICAC + 0.22 GCO2 + 0.32 GCOH2 + 0.1 GH2 + 0.36 GCH3OH + 1.6 C + 0.2 H2*	125.58	9.08	0
	3	*HEMCELL1 → 0.08 CO + 0.74 CO2 + 0.24 FORMALDY + 0.8 WATER + 0.04 FORMICAC + 0.12 GCO2 + 0.12 GCO + 0.96 GCOH2 + 0.16 GH2 + 0.5 GCH4 + 0.3 GC2H4 + 1.6 C + 0.2 H2*	33.50	-0.82	1
	4	*HEMCELL1 → 0.08 CO + 0.74 CO2 + 0.24 FORMALDY + 0.8 WATER + 0.04 FORMICAC + 0.12 GCO2 + 0.12 GCO + 0.96 GCOH2 + 0.16 GH2 + 0.5 GCH4 + 0.3 GC2H4 + 1.6 C + 0.2 H2*	46.05	0.48	1
	5	*HEMCELL2 → 0.16 HAA + 0.14 CO + 0.32 CO2 + 0.4 FORMALDY + 0.08 ETHANOL + 0.76 WATER + 0.02 FORMICAC + 0.32 GCO2 + 0.74 GCOH2 + 0.2 GCH4 + 0.24 GCH3OH + 0.22 GC2H4 + 1.7 C + 0.2 H2*	138.14	9.70	0
Lignin	1	*LIGNIN-C → 0.35 LIGN-CC + 0.1 CMRYLALC + 0.08 PHENOL + 0.32 CO + 0.3 FORMALDY + WATER + 0.7 GCOH2 + 0.495 GCH4 + 0.41 GC2H4 + 5.735 C*	203.02	15.12	0
	2	*LIGNIN-H → LIGN-OH + 0.25 HAA + 0.5 ACETONE + 5 GC2H4*	156.97	12.83	0
	3	*LIGNIN-O → LIGN-OH + CO2*	106.74	8.52	0
	4	*LIGN-CC → 0.21 HAA + 0.18 CMRYLALC + 0.12 PHENOL + 0.24 CO + 0.39 CH4 + 0.36 C2H4 + 2.02 WATER + 0.24 GCO + 0.6 GCOH2 + 10.05 C + 1.2 H2*	131.86	7.48	0
	5	*LIGN-OH → LIG + 0.55 CO + 0.05 CO2 + 0.1 CH4 + 0.6 METHANOL + 0.9 WATER + 0.05 FORMICAC + 0.6 GCO + 0.85 GCOH2 + 0.1 GH2 + 0.35 GCH4 + 0.3 GCH3OH + 0.2 GC2H4 + 4.15 C*	125.58	8.00	0
	6	*LIG → 0.6 SYNAPALD + 4.2 C + 1.2 WATER + 0.2 CO2 + 1.2 H2*	50.20	0.60	1
	7	*LIG → 0.12 ACETONE + 0.6 CO + 0.12 CH4 + 0.12 FORMALDY + 0.24 METHANOL + 0.12 ACETALDY + 1.77 WATER + 0.03 FORMICAC + 0.27 GCO + 0.3 GCOH2 + 0.24 GCH4 + 0.39 GC2H4 + 8 C + 0.2 CO2 + 1.2 H2*	125.58	8.60	0
	8	*LIG → 0.24 CO + 0.12 CH4 + 0.24 FORMALDY + 1.56 WATER + 0.12 GCO + 1.2 GCOH2 + 0.24 GCH4 + 0.24 GCH3OH + 0.3 GC2H4 + 7.8 C + 0.2 CO2 + 1.2 H2*	33.50	-1.08	1
Extractives	1	*TANN → PHENOL + ITANN*	46.02	1.70	0
	2	*ITANN → 5 C + 3 CO + GCOH2 + 2 WATER*	25.52	3.79	0
	3	*TGL → ACROLEIN + 3 FFA*	191.20	12.85	0

Table S18: Reaction network from Ranzi et al. [20]. *Hemicellulose assumed to be xylan-rich based on the conclusions of Peng and Wu* [52].

Group	#		E_a (kJ/mol)	$\log_{10}[A (s^{-1})]$	T^n
Cellulose	1	*CELL → CELLA*	196.46	14.18	0
	2	*CELLA → 0.45 HAA + 0.2 GLYOXAL + 0.1 ACETALDY + 0.25 HMF + 0.3 NPROPALD + 0.15 METHANOL + 0.4 FORMALDY + 0.31 CO + 0.41 CO2 + 0.05 H2 + 0.83 WATER + 0.02 FORMICAC + 0.2 GCH4 + 0.05 GH2 + 0.61 C*	79.84	6.30	0
	3	*CELLA → LEVOGLUC*	41.80	0.60	1
	4	*CELL → 5 WATER + 6 C*	129.58	7.81	0
Hemicellulose	1	*XYHW → 0.58 HEM1 + 0.42 HEM2*	129.58	10.00	0
	2	*HEM1 → 0.025 WATER + 0.5 CO2 + 0.025 FORMICAC + 0.5 CO + 0.8 FORMALDY + 0.125 ETHANOL + 0.1 METHANOL + 0.25 C2H4 + 0.125 GH2 + 0.275 GCO2 + 0.4 GCOH2 + 0.45 GCH3OH + 0.325 GCH4 + 0.875 C*	125.40	9.08	0
	3	*HEM1 → 0.25 WATER + 0.8 CO2 + 0.05 FORMICAC + 0.1 CO + 0.15 GCO + 0.15 GCO2 + 0.2 GH2 + 0.3 FORMALDY + 1.2 GCOH2 + 0.625 GCH4 + 0.375 GC2H4 + 0.875 C*	33.44	-0.82	1
	4	*HEM1 → XYLOSAN*	45.98	0.48	1
	5	*HEM2 → 0.2 WATER + 0.175 CO + 0.275 CO2 + 0.5 FORMALDY + 0.1 ETHANOL + 0.2 HAA + 0.025 FORMICAC + 0.25 GCH4 + 0.3 GCH3OH + 0.275 GC2H4 + 0.4 GCO2 + 0.925 GCOH2 + C*	137.94	9.70	0
Lignin	1	*LIGC → 0.35 LIGCC + 0.1 CMRYLALC + 0.08 PHENOL + 0.41 C2H4 + WATER + 0.7 GCOH2 + 0.3 FORMALDY + 0.32 CO + 0.495 GCH4 + 5.735 C*	202.73	15.12	0
	2	*LIGH → LIGOH + 0.5 NPROPALD + 0.5 C2H4 + 0.25 HAA*	156.75	12.83	0
	3	*LIGO → LIGOH + CO2*	106.59	8.52	0
	4	*LIGCC → 0.3 CMRYLALC + 0.2 PHENOL + 0.35 HAA + 0.7 WATER + 0.65 GCH4 + 0.6 GC2H4 + GCOH2 + 0.4 CO + 0.4 GCO + 6.75 C*	131.67	6.22	0
	5	*LIGOH → LIG + 0.9 WATER + 0.1 CH4 + 0.6 METHANOL + 0.1 GH2 + 0.3 GCH3OH + 0.05 CO2 + 0.55 CO + 0.6 GCO + 0.05 FORMICAC + 0.85 GCOH2 + 0.35 GCH4 + 0.2 GC2H4 + 4.15 C*	125.40	8.00	0
	6	*LIG → 0.7 SYNAPALD + 0.3 ANISOLE + 0.3 CO + 0.3 GCO + 0.3 ACETALDY*	50.16	0.60	1
	7	*LIG → 0.95 WATER + 0.2 FORMALDY + 0.4 METHANOL + CO + 0.2 CH4 + 0.05 FORMICAC + 0.45 GCO + 0.5 GCOH2 + 0.4 GCH4 + 0.65 GC2H4 + 0.2 ACETALDY + 0.2 NPROPALD + 5.5 C*	125.40	8.60	0
	8	*LIG → 0.6 WATER + 0.4 CO + 0.2 CH4 + 0.4 FORMALDY + 0.2 GCO + 0.4 GCH4 + 0.5 GC2H4 + 0.4 GCH3OH + 2 GCOH2 + 6 C*	33.44	-1.08	1
Extractives	1	*TGL → ACROLEIN + 3 FFA*	191.03	12.85	0
	2	*TANN → PHENOL + ITANN*	45.98	1.70	0
	3	*ITANN → 6 C + 3 CO + 3 WATER*	25.50	-1.82	0

Table S19: Reaction network from Ranzi et al. [21]. *Hemicellulose assumed to be xylan-rich based on the conclusions of Peng and Wu* [52].

Group	#		E_a (kJ/mol)	$\log_{10}[A (s^{-1})]$	T^n
Cellulose	1	*CELL → CELLA*	196.46	14.18	0
	2	*CELLA → 0.4 HAA + 0.05 GLYOXAL + 0.15 ACETALDY + 0.25 HMF + 0.35 NPROPALD + 0.15 METHANOL + 0.3 FORMALDY + 0.61 CO + 0.36 CO2 + 0.05 H2 + 0.93 WATER + 0.02 FORMICAC + 0.05 GCH4 + 0.05 GH2 + 0.61 C*	79.84	6.41	0
	3	*CELLA → LEVOGLUC*	41.80	0.52	1
	4	*CELL → 5 WATER + 6 C*	129.58	7.78	0
Hemicellulose	1	*XYHW → 0.35 HEM1 + 0.65 HEM2*	119.13	10.00	0
	2	*HEM1 → 0.6 XYLOSAN + 0.2 ACETOL + 0.12 GLYOXAL + 0.2 FURFURAL + 0.4 WATER + 0.08 GH2 + 0.16 CO*	45.98	0.48	1
	3	*HEM1 → 0.4 WATER + 0.79 CO2 + 0.05 FORMICAC + 0.69 CO + 0.01 GCO + 0.01 GCO2 + 0.35 GH2 + 0.3 FORMALDY + 0.9 GCOH2 + 0.625 GCH4 + 0.375 GC2H4 + 0.875 C*	12.54	-2.74	1
	4	*HEM2 → 0.2 WATER + 0.275 CO + 0.275 CO2 + 0.5 FORMALDY + 0.1 ETHANOL + 0.05 HAA + 0.35 ACETICAC + 0.025 FORMICAC + 0.25 GCH4 + 0.3 GCH3OH + 0.225 GC2H4 + 0.4 GCO2 + 0.725 GCOH2 + C*	131.67	9.70	0
Lignin	1	*LIGNIN-C → 0.35 LIGN-CC + 0.1 CMRYLALC + 0.08 PHENOL + 0.41 C2H4 + WATER + 0.7 GCOH2 + 0.3 FORMALDY + 0.32 CO + 0.495 GCH4 + 5.735 C*	155.50	11.00	0
	2	*LIGNIN-H → LIGN-OH + 0.5 NPROPALD + 0.5 C2H4 + 0.25 HAA*	156.75	12.83	0
	3	*LIGNIN-O → LIGN-OH + CO2*	106.59	8.52	0
	4	*LIGN-CC → 0.3 CMRYLALC + 0.2 PHENOL + 0.35 HAA + 0.7 WATER + 0.65 GCH4 + 0.6 GC2H4 + GCOH2 + 0.4 CO + 0.4 GCO + 6.75 C*	103.66	4.00	0
	5	*LIGN-OH → LIG + 0.9 WATER + 0.1 CH4 + 0.6 METHANOL + 0.1 GH2 + 0.3 GCH3OH + 0.05 CO2 + 0.55 CO + 0.6 GCO + 0.05 FORMICAC + 0.85 GCOH2 + 0.35 GCH4 + 0.2 GC2H4 + 4.15 C*	125.40	8.00	0
	6	*LIG → 0.7 SYNAPALD + 0.3 ANISOLE + 0.3 CO + 0.3 GCO + 0.3 ACETALDY*	50.16	0.60	1
	7	*LIG → 0.6 WATER + 0.4 CO + 0.2 CH4 + 0.4 FORMALDY + 0.2 GCO + 0.4 GCH4 + 0.5 GC2H4 + 0.4 GCH3OH + 2 GCOH2 + 6 C*	33.44	-1.08	1
	8	*LIG → 0.6 WATER + 2.6 CO + 1.1 CH4 + 0.4 FORMALDY + C2H4 + 0.4 METHANOL*	101.57	7.00	0
Extractives	1	*TGL → ACROLEIN + 3 FFA*	191.03	12.85	0
	2	*TANN → PHENOL + ITANN*	41.80	1.30	0
	3	*ITANN → 6 C + 3 CO + 3 WATER*	104.50	3.00	0

Table S20: Reaction network from Debiagi et al. [22]. In reaction 1 of hemicellulose, first set of values assumes xylan-rich hemicellulose, based on the conclusions of Peng and Wu [52]*, while second set assumes cereal structure.*

Group	#		E_a (kJ/mol)	$\log_{10}[A (s^{-1})]$	T^n
Cellulose	1	*CELL → CELLA*	196.46	14.18	0
	2	*CELLA → 0.05 3HYDPROP + 0.4 HAA + 0.03 GLYOXAL + 0.17 ACETALDY + 0.25 HMF + 0.35 NPROPALD + 0.2 METHANOL + 0.15 FORMALDY + 0.49CO + 0.43CO2 + 0.13H2 + 0.93 WATER + 0.02 FORMICAC + 0.05 CH4 + 0.66 C + 0.05 GCO + 0.05 GCOH2L + 0.1 GH2*	79.84	6.40	0
	3	*CELLA → LEVOGLUC*	41.80	0.52	1
	4	*CELL → 0.125 H2 + 4.45 WATER + 5.45 C + 0.12 GCOH2S + 0.25 GCO + 0.18 GCOH2L + 0.125 GH2*	129.58	7.95	0
Hemicellulose	1	*XYHW → 0.35/0.12 HEM1 + 0.65/0.88 HEM2*	131.25	11.10	0
	2	*HEM1 → 0.06 3HYDPROP + 0.16 FURFURAL + 0.1 GLYOXAL + 0.13 HMF + 0.09 CO2 + 0.02 H2 + 0.54 WATER + 0.25 LEVOGLUC + 0.1 CH4 + 0.25 XYLOSAN + 0.1 C*	53.92	1.20	1
	3	*HEM1 → 0.4 FORMALDY + 0.49 CO + 0.39 CO2 + 0.1 H2 + 0.4 WATER + 0.05 FORMICAC + 0.1 C2H4 + 0.3 CH4 + 0.975 C + 0.37GCOH2S + 0.51 GCO2 + 0.01 GCO + 0.325 GCH4 + 0.075 GC2H4 + 0.43 GCOH2L + 0.05 GH2 + 0.2 GC2H6*	15.05	-2.52	1
	4	*HEM2 → 0.145 FURFURAL + 0.105 ACETICAC + 0.035 HAA + 0.3 CO + 0.5125 CO2 + 0.5505 H2 + 0.056 WATER + 0.0175 FORMICAC + 0.049 ETHANOL + 0.1895 CH4 + 0.7125 C + 0.78 GCOH2S + 0.45 GCO2 + 0.105 GCH3OH + 0.05 GCH4 + 0.1GC2H4 + 0.18 GCOH2L + 0.21 GH2 + 0.2 GC2H6*	127.49	9.85	0
Lignin	1	*LIGC → 0.1 ANISOLE + 0.22 FORMALDY + 0.21 CO + 0.1 CO2 + WATER + 0.27 C2H4 + 0.1 VANILLIN + 0.35 LIGCC + 5.85 C + 0.4 GCOH2S + 0.36 GCH4 + 0.17 GCOH2L + 0.1 GH2 + 0.2 GC2H6*	155.50	11.00	0
	2	*LIGH → 0.2 HAA + 0.5 NPROPALD + 0.1 CO + 0.4 C2H4 + 0.1 C2H6 + LIGOH*	156.75	12.83	0
	3	*LIGO → LIGOH + CO2*	106.59	8.52	0
	4	*LIGCC → 0.15 ANISOLE + 0.35 HAA + 1.15 CO + 0.7 H2 + 0.7 WATER + 0.3 C2H4 + 0.45 CH4 + 0.25 VANILLIN + 0.15 CRESOL + 0.4 C2H6 + 6.8 C + 0.4 GCO*	103.66	4.00	0
	5	*LIGOH → 0.025 HMWL + 0.1 ACROLEIN + 0.6 CH3OH + 0.65 CO + 0.05 CO2 + WATER + 0.05 FORMICAC + 0.1 CH4 + 0.9 LIG + 4.25 C + 0.4 GCOH2S + 0.6 GCO + 0.3 GCH3OH + 0.25 GCH4 + 0.1 GC2H4 + 0.45 GCOH2L + 0.15 GC2H6*	125.40	8.00	0
	6	*LIG →0.1 ANISOLE + 0.3 ACETALDY + 0.6 CO + 0.5 C2H4 + VANILLIN + 0.1 C*	50.16	0.60	1
	7	*LIG → 0.4 METHANOL + 0.4 FORMALDY + 2.6 CO + 0.6 WATER + 0.75 C2H4 + 0.6 CH4 + 0.5 C2H6 + 4.5 C*	131.67	9.18	0
	8	*LIG → 0.4 FORMALDY + 0.3 CO + 0.1 CO2 + 0.6 WATER + 0.2 CH4 + 6.1 C + 0.65 GCOH2L + 0.2 GCO + 0.4 GCH3OH + 0.4 GCH4 + 0.5 GC2H4 + 1.25 GCOH2L + 0.1 GH2*	33.44	-1.08	1
Extractives	1	*TGL → ACROLEIN + 0.5 U2ME12 + 2.5 MLINO*	191.03	12.85	0
	2	*TANN → WATER + 0.85 PHENOL + ITANN + GCO + 0.15 GC6H5OH*	41.80	1.30	0
	3	*ITANN → 2 CO + WATER + 5 C + 0.45 GCOH2S + 0.55 GCOH2L*	104.50	3.00	0

When considering the modifications by Trendewicz et al. [25], replace the cellulose portion of the aforementioned reaction networks with the following shown in Table . Only the energies of activation change, all other parameters stay the same.

Table S21: Reaction network from Trendewicz et al. [25] for the degradation of cellulose. 'Beech' represents a potassium content of 0.13 wt.% and 'Wheat Straw' represents a potassium content of 1.21 wt.%.

Group	#		Beech	Wheat Straw	$\log_{10}[A (s^{-1})]$	T^n
			E_a (kJ/mol)	E_a (kJ/mol)		
Cellulose	1	Stays from original network				
	2	*CELLA → 0.05 3HYDPROP + 0.4 HAA + 0.03 GLYOXAL + 0.17 ACETALDY + 0.25 HMF + 0.35 NPROPALD + 0.2 METHANOL + 0.15 FORMALDY + 0.49CO + 0.43CO2 + 0.13H2 + 0.93 WATER + 0.02 FORMICAC + 0.05 CH4 + 0.66 C + 0.05 GCO + 0.05 GCOH2L + 0.1 GH2*	96.80	100.48	9.58	0
	3	*CELLA → LEVOGLUC*	106.20	120.27	9.42	0
	4	*CELL → 0.125 H2 + 4.45 WATER + 5.45 C + 0.12 GCOH2S + 0.25 GCO + 0.18 GCOH2L + 0.125 GH2*	132.34	123.81	9.30	0

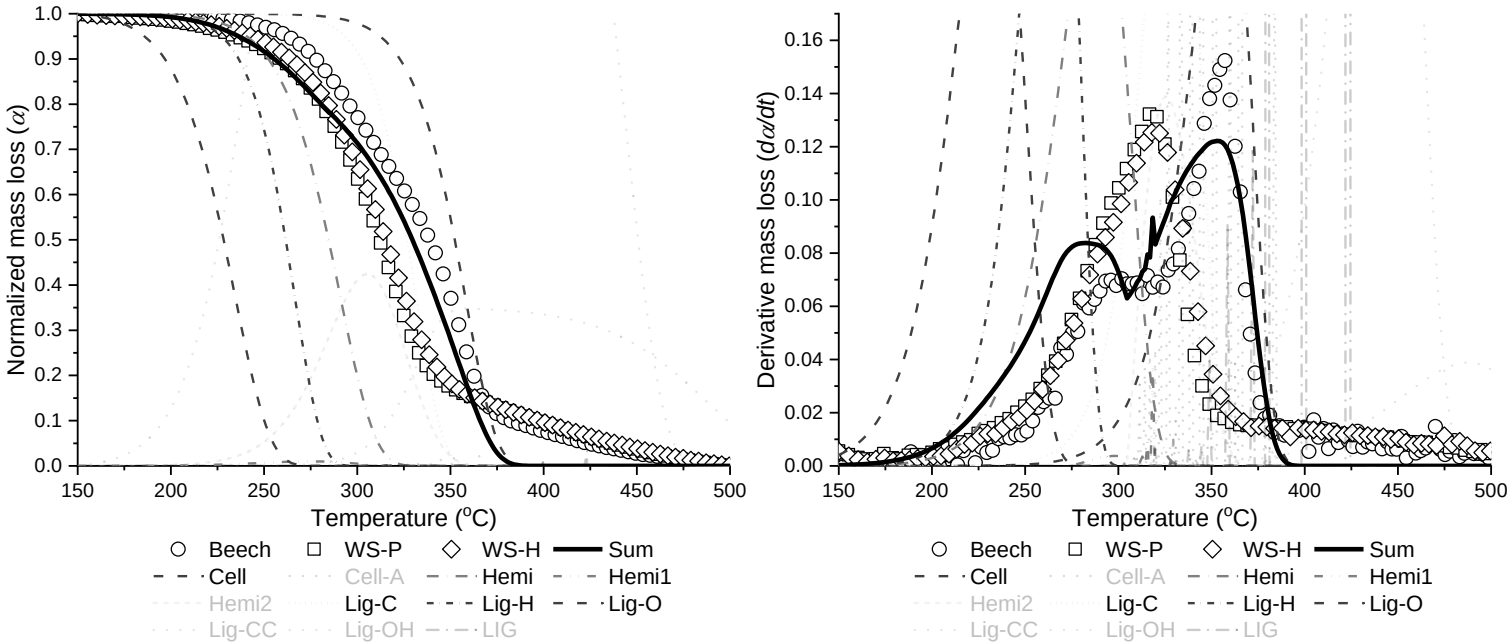


Figure S19: Comparison of the degradation profiles of the feedstocks (10 K/min) with the decomposition patterns by Ranzi et al. (2008) [11]*: mass loss (left) and derivative mass loss (right).*

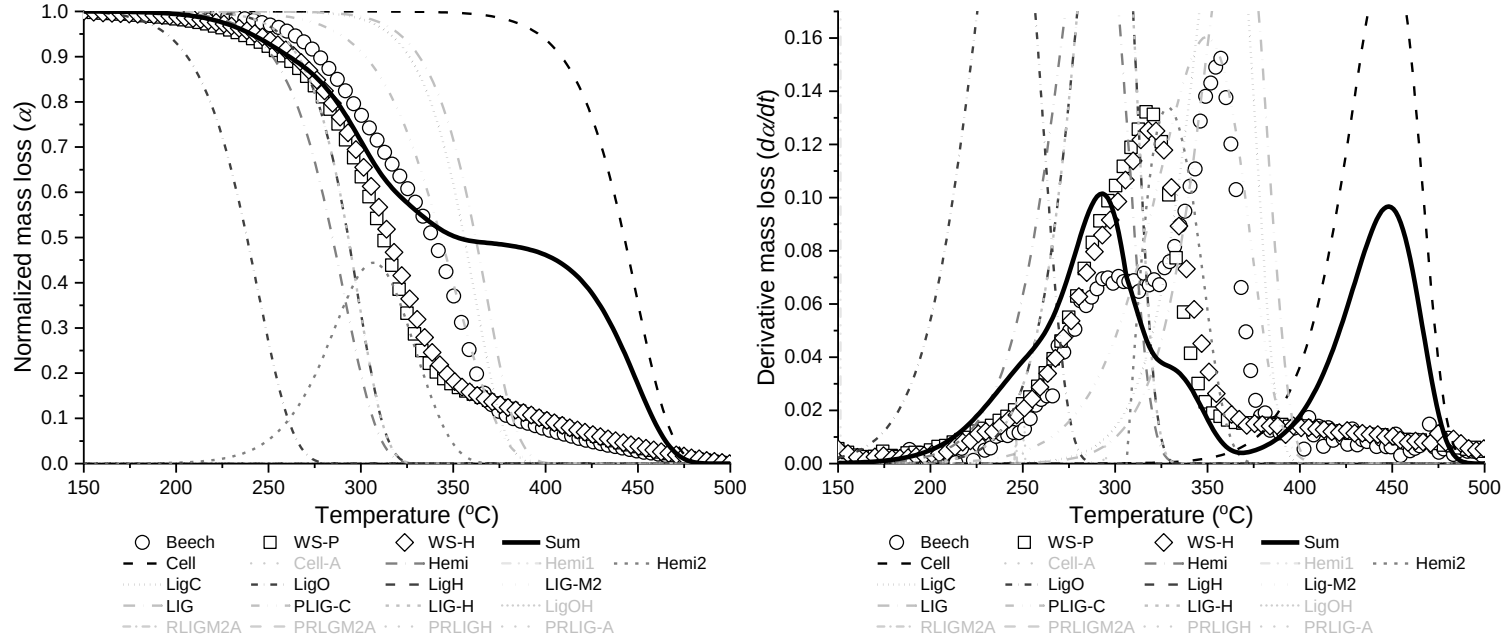


Figure S20: Comparison of the degradation profiles of the feedstocks (10 K/min) with the holocellulosic decomposition patterns by Ranzi et al. (2008) [11]*, and the lignin degradation patterns by Faravelli et al.* [13]*, modified by Peters et al.* [54]*: mass loss (left) and derivative mass loss (right).*

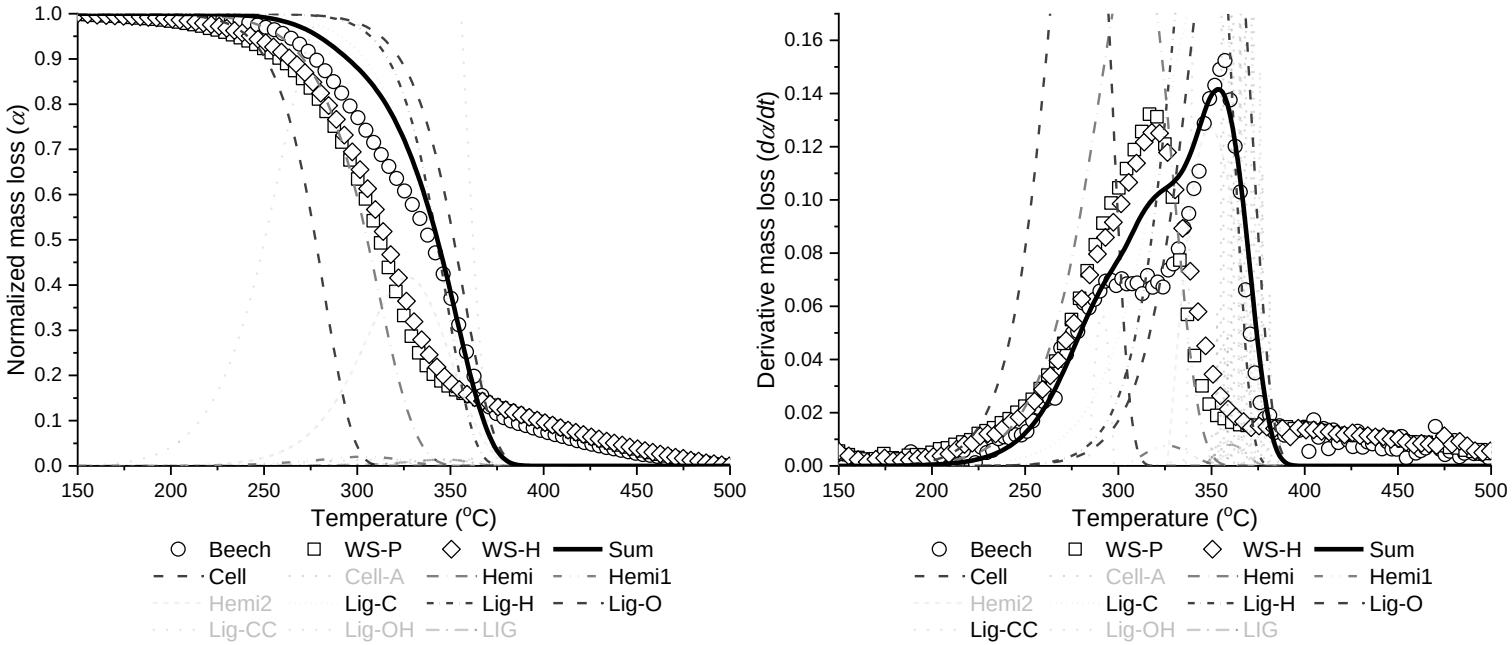


Figure S21: Comparison of the degradation profiles of the feedstocks (10 K/min) with the decomposition patterns by Corbetta et al. [19]*: mass loss (left) and derivative mass loss (right).*

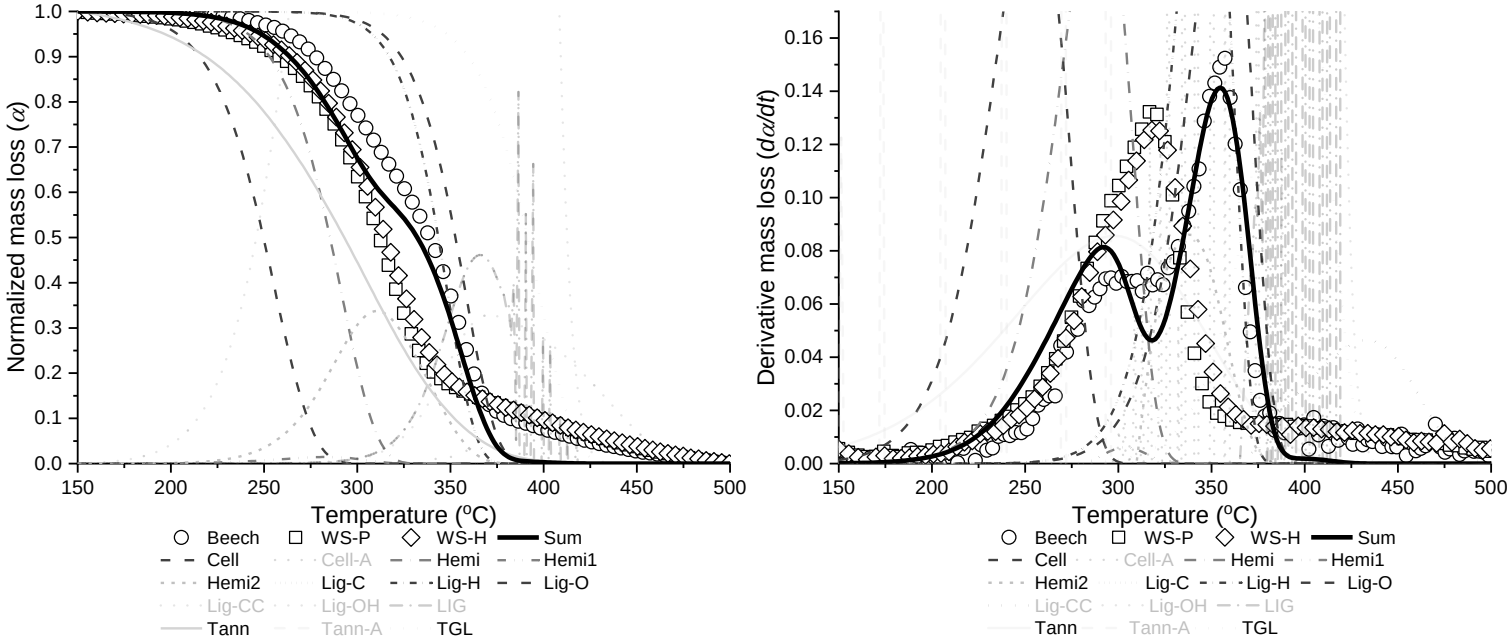


Figure S22: Comparison of the degradation profiles of the feedstocks (10 K/min) with the decomposition patterns by Anca-Couce and Scharler [12]*: mass loss (left) and derivative mass loss (right).*

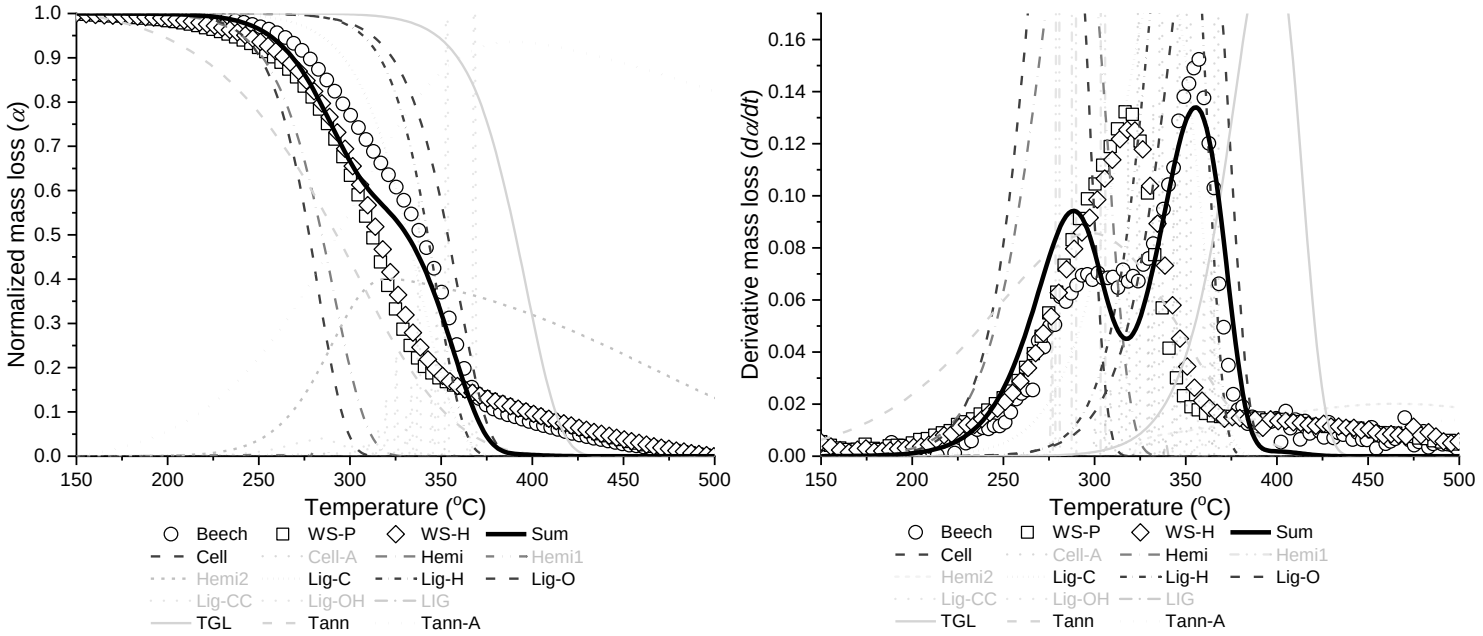


Figure S23: Comparison of the degradation profiles of the feedstocks (10 K/min) with the decomposition patterns by Ranzi et al. (2017a) [20]*: mass loss (left) and derivative mass loss (right). Hemicellulose assumed to be xylan-rich based on the conclusions of Peng and Wu* [52].

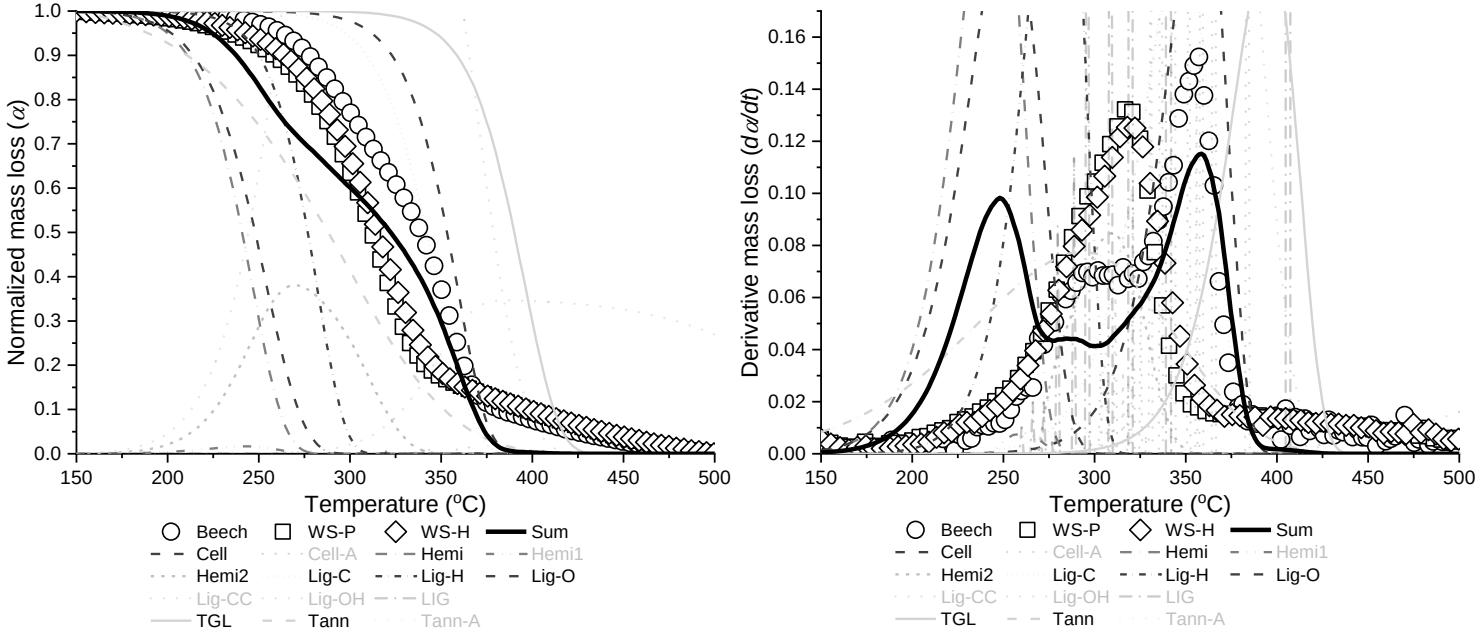


Figure S24: Comparison of the degradation profiles of the feedstocks (10 K/min) with the decomposition patterns by Ranzi et al. (2017b) [21]*: mass loss (left) and derivative mass loss (right). Hemicellulose assumed to be xylan-rich based on the conclusions of Peng and Wu* [52].

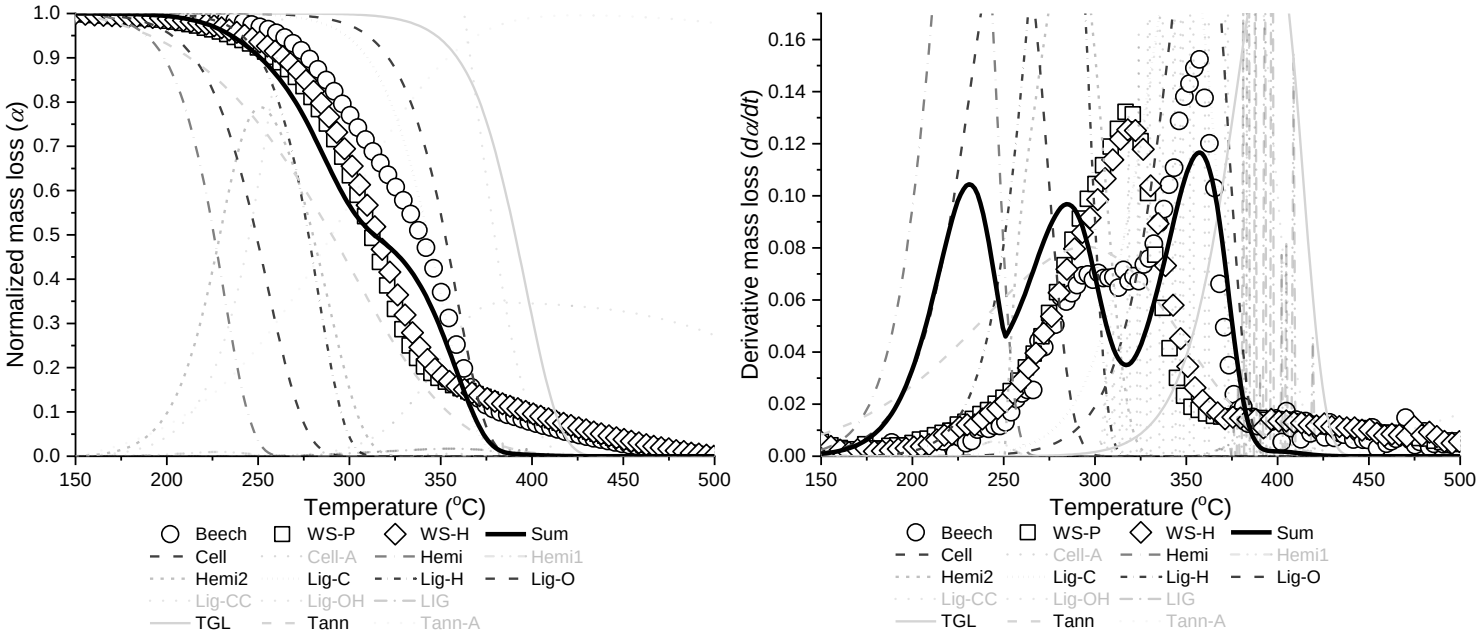


Figure S25: Comparison of the degradation profiles of the feedstocks (10 K/min) with the decomposition patterns by Debiagi et al. [22]*: mass loss (left) and derivative mass loss (right). Hemicellulose assumed to be xylan-rich based on the conclusions of Peng and Wu* [52]*.*

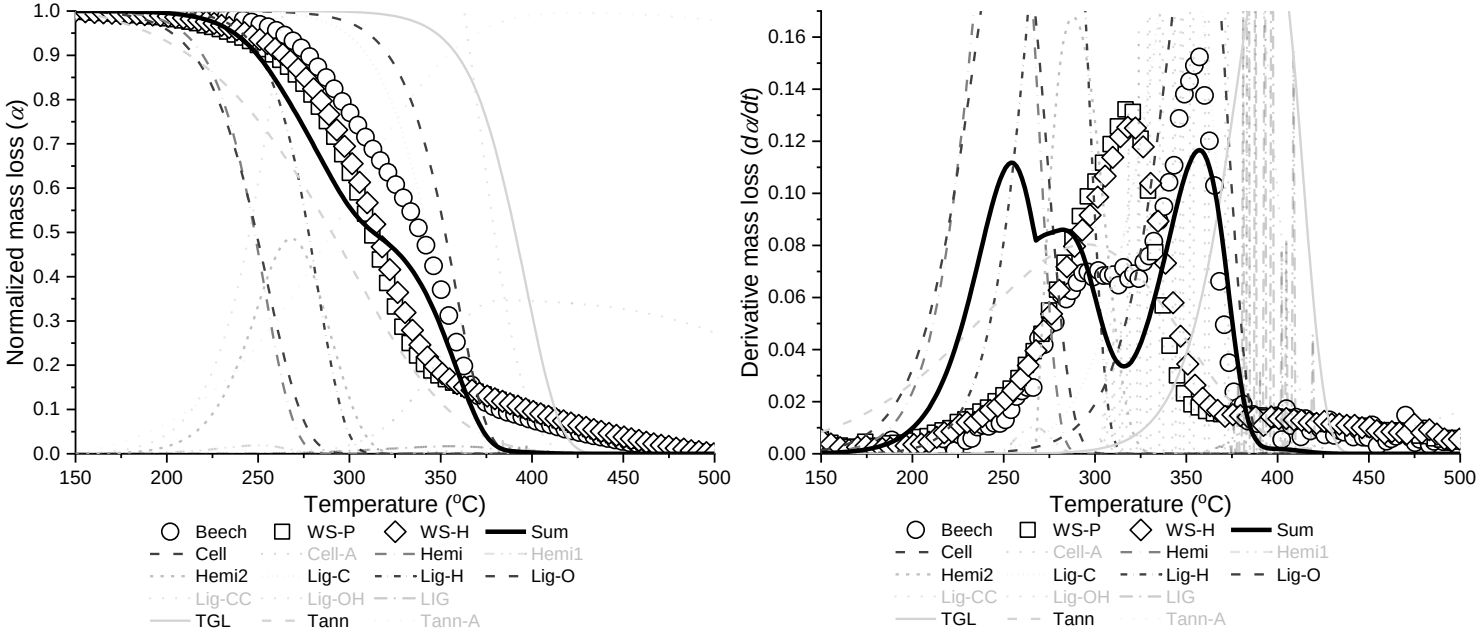


Figure S26: Comparison of the degradation profiles of the feedstocks (10 K/min) with the decomposition patterns by Debiagi et al. [22] *: mass loss (left) and derivative mass loss (right). Hemicellulose assumed to be cereal-type.*