Supplementary Information

Optimising Supercritical Water Gasification of Biomass: Exploring Heating Strategy Through a Quantitative Kinetic Modelling Approach

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Appendix A - Supplementary Graphs

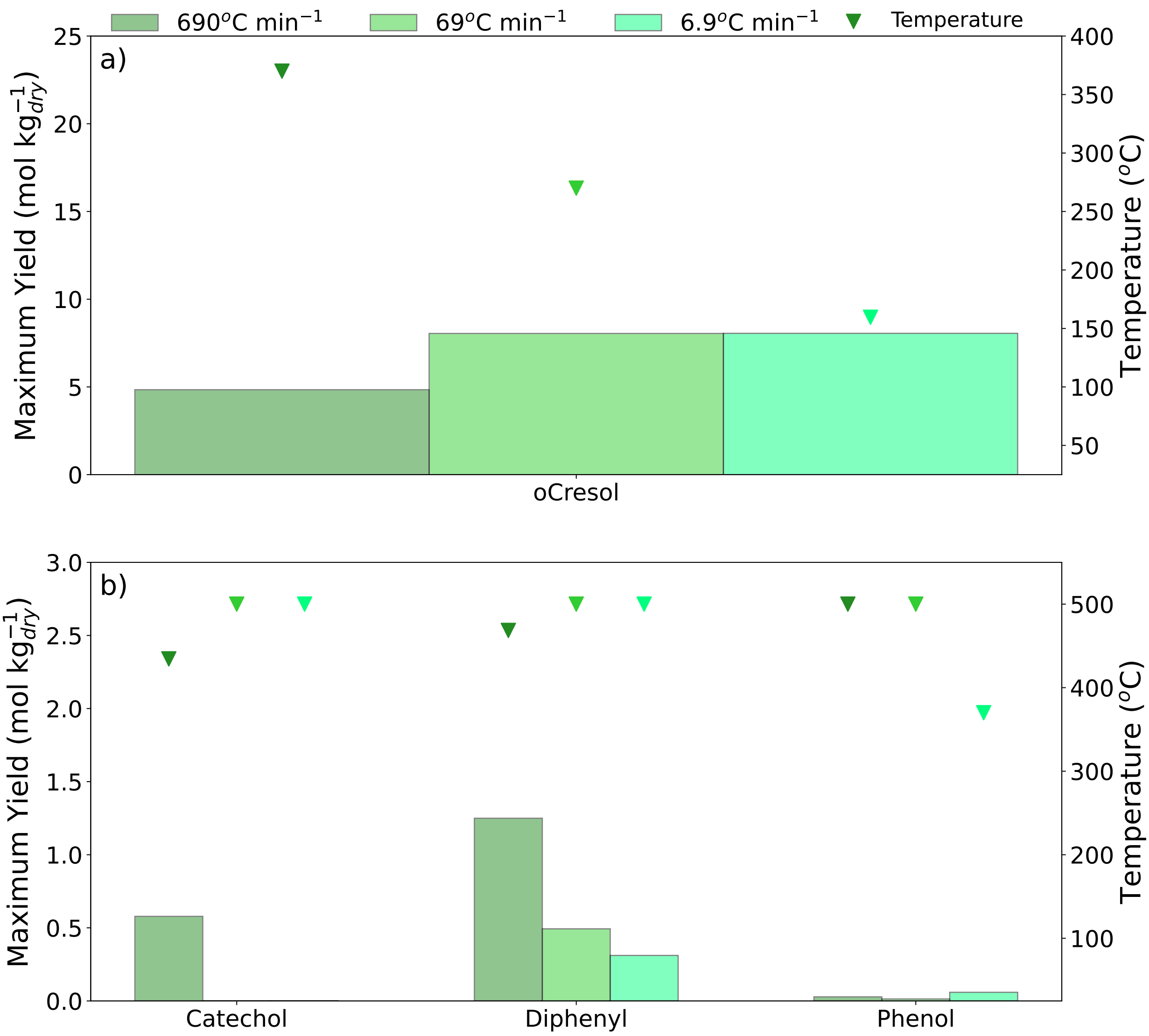

Figure A1: Maximum yields of intermediates formed during the SCWG of lignin with linear SUB-HEX heating rates of 690, 69, and 6.9 °C min^{-1}.

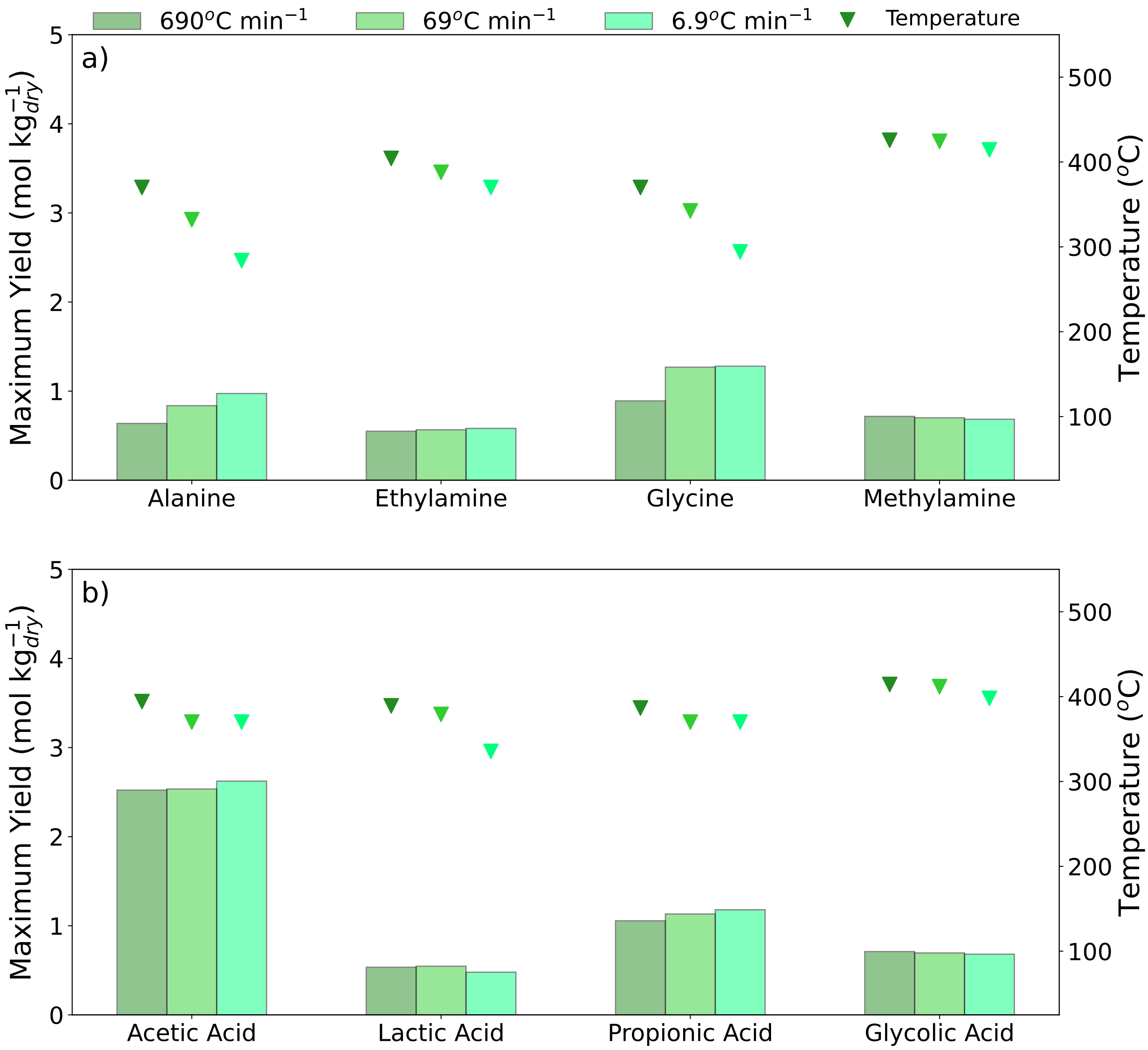

Figure A2: Maximum yields of intermediates formed during the SCWG of protein with linear SUB-HEX heating rates of 690, 69, and 6.9 °C min^{-1}.

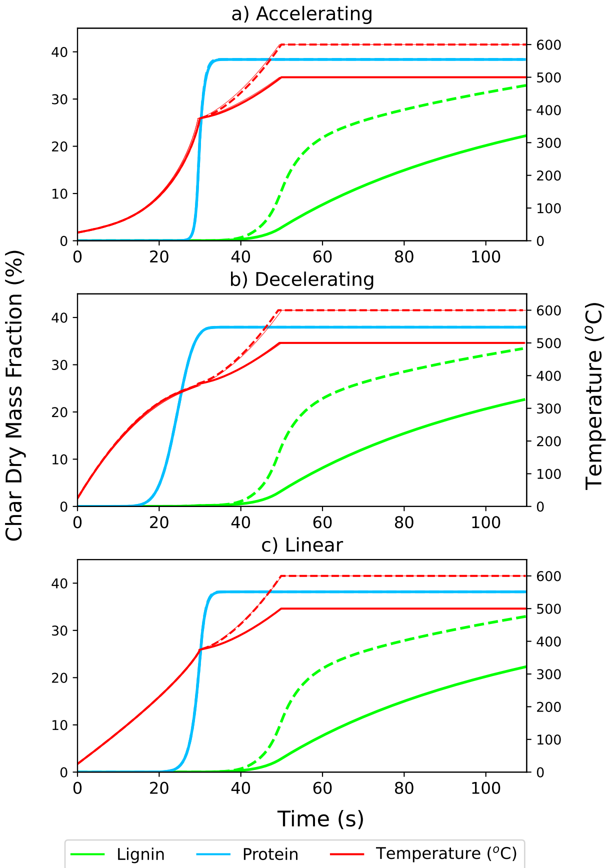

Figure A3: Total dry mass fraction of lignin and protein derived char, and temperature, versus reaction time at a accelerating, decelerating, and linear sub-critical heating rate 690 °C min^{-1}. Final reaction temperatures of 500°C (solid) and 600°C (dashed)

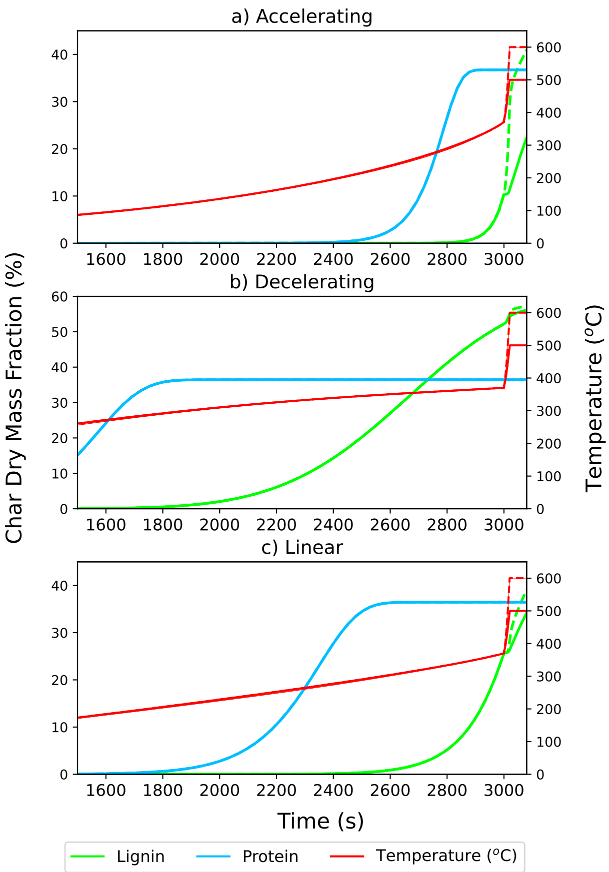

Figure A4: Total dry mass fraction of lignin and protein derived char, and temperature, versus reaction time at a accelerating, decelerating, and linear sub-critical heating rate 6.9 °C min^{-1}. Final reaction temperatures of 500°C (solid) and 600°C (dashed)

Appendix B - Kinetic Model

$$\frac{d\xi_r}{dt} = kc_A \tag{1}$$

where c_A is the concentration of the
The rate constant is assumed to

$$k(T) = Ae^{-E_a/(RT)} \tag{2}$$

where A is a constant prefactor, E_a is the activation energy of the reaction, and T is the absolute temperature of the system.

Table B1: Arrhenius parameters for reactions of cellulose in sub- and supercritical water

Name	A (s^{-1})	E_a ($kJ\,mol^{-1}$)	Reaction
1	3.1×10^4	6.69×10^4	Cellobiose $\longrightarrow$ GlyEryt + Glycolal
2	7.8×10^4	6.93×10^4	Cellobiose $\longrightarrow$ GlyGly + Erythrose
3	1.4×10^9	1.09×10^5	Cellobiose + H_2O $\longrightarrow$ Glucose + Glycolal + Erythrose
ge.g	3.6×10^8	1.06×10^5	GlyEryt + H_2O $\longrightarrow$ Glucose + Glycolal + 0.5Erythrose
gg.g	1.4×10^8	1.11×10^5	GlyGly + H_2O $\longrightarrow$ 0.5Glucose + 0.5Glycolal + Erythrose
g.f	3×10^9	1.13×10^5	Glucose $\longrightarrow$ Fructose
g.a	9×10^3	6.59×10^4	Glucose $\longrightarrow$ AnhyGlu + H_2O
g.5	1.48×10^8	1.14×10^5	Glucose $\longrightarrow$ HMF + $3H_2O$
f.5	1.15×10^3	4.23×10^4	Fructose $\longrightarrow$ HMF + $3H_2O$
g.e	1.2×10^{12}	1.41×10^5	Glucose $\longrightarrow$ Erythrose + Glycolal
f.e	$5.3\times^{11}$	1.4×10^5	Fructose $\longrightarrow$ Erythrose + Glycolal
g.gly	2.5×10^7	9.57×10^4	Glucose $\longrightarrow$ 2Glyceral
f.gly	1.2×10^{11}	1.33×10^5	Fructose $\longrightarrow$ 2Glyceral
gly.dih	1.5×10^{13}	1.54×10^5	Glyceral $\longrightarrow$ Dihydrox
dih.gly	4.6×10^5	7.73×10^4	Dihydrox $\longrightarrow$ Glyceral
gly.p	7.6×10^6	8.26×10^4	Glyceral $\longrightarrow$ Pyruval + H_2O
dih.p	1.8×10^7	8.87×10^4	Dihydrox $\longrightarrow$ Pyruval + H_2O
f.acid	7.4×10^{10}	1.29×10^5	Fructose $\longrightarrow$ 2LacticAcid
p.acid	6.59×10^7	9.4×10^4	Pyruval + H_2O $\longrightarrow$ LacticAcid
a.acid	8×10^7	1.09×10^5	AnhyGlu + $3H_2O$ $\longrightarrow$ 2AceticAcid + 2FormicAcid + 4H
e.acid	2.1×10^{10}	1.25×10^5	Erythrose + $2H_2O$ $\longrightarrow$ AceticAcid + 2FormicAcid + 4H
glyo.acid	2.1×10^{10}	1.25×10^5	Glycolal $\longrightarrow$ AceticAcid
5.lf	8×10^7	9.56×10^4	HMF + $2H_2O$ $\longrightarrow$ LevuAcid + FormicAcid
5.ff	7.1×10^9	1.15×10^5	HMF $\longrightarrow$ Furfural + Formalde

Table B2: Arrhenius parameters for reactions of hemicellulose in sub-critical water

Name	A (s^{-1})	E_a ($kJ\,mol^{-1}$)	Reaction
xy.fu	2.26×10^{10}	1.11×10^5	Xylose $\longrightarrow$ Furfural + $3H_2O$
fu.aa	1.19×10^5	5.88×10^4	Furfural + $2H_2O$ $\longrightarrow$ WSHS
xy.gm	5.03×10^{13}	1.43×10^5	Xylose $\longrightarrow$ Glyceral + MethForm

Table B3: Arrhenius parameters for reactions of hemicellulose in supercritical water

Name	A (s^{-1})	E_a ($kJ\,mol^{-1}$)	Reaction
xy.fu	1.3×10^{13}	1.48×10^{5}	$\text{Xylose} \longrightarrow \text{Furfural} + 3H_2O$
xy.wshs	6.6×10^{14}	1.55×10^{5}	$\text{Xylose} \longrightarrow \text{WSHS} + H_2O$
fu.wshs	1.7×10^{6}	1.01×10^{5}	$\text{Furfural} + 2H_2O \longrightarrow \text{WSHS}$
fu.ch	1.37×10^{4}	8.79×10^{4}	$\text{Furfural} \longrightarrow \text{CharFurf}$
wshs.gas	3.5×10^{8}	1.43×10^{5}	$\text{WSHS} + H_2O \longrightarrow 5CO + 5H_2$

Table B4: Arrhenius parameters for reactions of lignin in sub-critical water

Name	A (s^{-1})	E_a ($kJ\,mol^{-1}$)	Reaction
gu.oc	0.0311	0	$\text{Guaiacol} \longrightarrow \text{oCresol} + O$
gu.ga	6.7×10^{10}	1.69×10^{05}	$\text{Guaiacol} + 4.099H_2O \longrightarrow 0.198H_2 + 0.001CO + 3.049CO_2 + 3.95CH_4$
gu.c	6.83×10^{03}	8.24×10^{04}	$\text{Guaiacol} \longrightarrow \text{Catechol} + aCH_2$
gu.t	0.773	1.01×10^{05}	$\text{Guaiacol} \longrightarrow 0.5\text{Diphenyl} + CH_3O + O$
c.oc	0.005	8.48×10^{03}	$\text{Catechol} + aCH_2 \longrightarrow \text{oCresol} + O$
c.t	0.3	1.09×10^{04}	$\text{Catechol} \longrightarrow 0.5\text{Diphenyl} + OH + O$
t.ga	0.08	1.82×10^{04}	$\text{Diphenyl} + 9.637H_2O \longrightarrow 0.277H_2 + 0.002CO + 4.817CO_2 + 7.18CH_4$
t.p	1.8	3.75×10^{04}	$\text{Diphenyl} + 2OH \longrightarrow 2\text{Phenol}$
t.b	1.13×10^{03}	7.98×10^{04}	$\text{Diphenyl} + H_2 \longrightarrow 2\text{Benzene}$
t.ch	3.09×10^{04}	6.69×10^{04}	$\text{Diphenyl} \longrightarrow \text{CharDiph}$
gu.b	8.28×10^{03}	8.46×10^{04}	$\text{Guaiacol} \longrightarrow \text{Benzene} + \text{Formalde} + O$
b.ch	3.4×10^{22}	2.99×10^{05}	$\text{Benzene} \longrightarrow \text{CharBenz}$
oc.t	9.5×10^{10}	1.63×10^{05}	$\text{oCresol} \longrightarrow 0.5\text{Diphenyl} + CH_3 + O$

Table B5: Arrhenius parameters for reactions of lignin in supercritical water

Name	A (s^{-1})	E_a ($kJ\,mol^{-1}$)	Reaction
gu.ch	4.4×10^{17}	2.68×10^5	Guaiacol $\longrightarrow$ CharGuai
gu.ga*	1.58×10^5	9.68×10^4	Guaiacol + $4.648H_2O \longrightarrow 1.316H_2 + 0.021CO + 3.313CO_2 + 3.666CH_4$
gu.ga**	1.58×10^5	9.68×10^4	Guaiacol + $5.577H_2O \longrightarrow 3.253H_2 + 0.098CO + 3.74CO_2 + 3.162CH_4$
gu.oc	3.7×10^4	8.33×10^4	Guaiacol $\longrightarrow$ oCresol + O
gu.c	0.039	0	Guaiacol $\longrightarrow$ Catechol + aCH_2
gu.t	3.38×10^3	5.61×10^4	Guaiacol $\longrightarrow$ 0.5Diphenyl + CH_3O + O
c.oc	0.06	1.85×10^4	Catechol + $aCH_2 \longrightarrow$ oCresol + O
t.p	0.001	0	Diphenyl + 2OH $\longrightarrow$ 2Phenol
t.ch	8.15×10^5	1.1×10^5	Diphenyl $\longrightarrow$ CharDiph
t.ga*	3.3	3.78×10^4	Diphenyl + $10.324H_2O \longrightarrow 1.683H_2 + 0.035CO + 5.145CO_2 + 6.821CH_4$
t.ga**	3.3	3.78×10^4	Diphenyl + $11.51H_2O \longrightarrow 4.184H_2 + 0.164CO + 5.673CO_2 + 6.162CH_4$
c.t	44.4	4.78×10^4	Catechol $\longrightarrow$ 0.5Diphenyl + OH + O
p.c	1.41×10^3	8.92×10^4	Phenol + O $\longrightarrow$ Catechol
p.t	1.8	2.31×10^4	Phenol $\longrightarrow$ 0.5Diphenyl + OH
p.ga*	54.8	5.95×10^4	Phenol + $4.496H_2O \longrightarrow 1.009H_2 + 0.018CO + 2.739CO_2 + 3.243CH_4$
p.ga**	54.8	5.95×10^4	Phenol + $5.21H_2O \longrightarrow 2.503H_2 + 0.083CO + 3.063CO_2 + 2.853CH_4$
p.ch	1.37×10^4	8.79×10^4	Phenol $\longrightarrow$ CharPhen
b.t	3.5	5.08×10^4	Benzene $\longrightarrow$ 0.5Diphenyl + $0.5H_2$
b.p	15.6	5.81×10^4	Benzene + O $\longrightarrow$ Phenol
b.ga*	0.1	3.36×10^4	Benzene + $4.929H_2O \longrightarrow 0.875H_2 + 0.017CO + 2.456CO_2 + 3.527CH_4$
b.ga**	0.1	3.36×10^4	Benzene + $5.546H_2O \longrightarrow 2.172H_2 + 0.08CO + 2.733CO_2 + 3.186CH_4$
b.na	391	6.92×10^4	Benzene $\longrightarrow$ 0.5Naphtalene + $0.5C_2H_4$
na.ch	1.9	3.72×10^4	Naphtalene $\longrightarrow$ CharNaph
b.ch	50.9	6.27×10^4	Benzene $\longrightarrow$ 0.5Diphenyl + CH_3 + O
oc.t	0.0063	0	oCresol $\longrightarrow$ 0.5Diphenyl + CH_3 + O

*Gasification stoichiometry at 500°C
**Gasification stoichiometry at 600°C

Table B6: Arrhenius parameters for reactions of protein in sub-critical water

Name	**A** (s^{-1})	**Ea** ($kJ\,mol^{-1}$)	**Equation**
as.a	7.75e+09	1.28e+05	AspAcid + 0.667H_2O $\rightarrow$0.333AceticAcid + 0.333PropAcid + 0.333Alanine + 0.333H_2 + 1.333CO_2 + 0.667NH_3
as.g	1.75e+10	1.31e+05	AspAcid + 0.34H_2O $\rightarrow$0.34AceticAcid + 0.34Glycine + 0.681CharAspAcid
al.et	1.4e+12	1.56e+05	0.47Alanine + 0.235H_2O $\rightarrow$0.235LacticAcid + 0.235EthAmine + 0.235NH_3 + 0.235CO_2
g.met	3.6e+11	1.6e+05	0.78Glycine + 0.39H_2O $\rightarrow$0.39GlyAcid + 0.39MethAmine + 0.39NH_3 + 0.39CO_2

Table B7: Arrhenius parameters for reactions of protein in supercritical water

Name	**A** (s^{-1})	**Ea** ($kJ\,mol^{-1}$)	**Equation**
al.et	1.4e+12	1.56e+05	0.47Alanine + 0.235H_2O →0.235LacticAcid + 0.235EthAmine + 0.235NH_3 + 0.235CO_2
g.met	3.6e+11	1.6e+05	0.78Glycine + 0.39H_2O →0.39GlyAcid + 0.39MethAmine + 0.39NH_3 + 0.39CO_2
al.gas*	7.37e+05	1.31e+05	Alanine + 0.757H_2O →0.982H_2 + 0.008CO + 1.374CO_2 + 1.617CH_4 + 0.486N_2 + 0.028NH_3
al.gas**	7.37e+05	1.31e+05	Alanine + 1.421H_2O →2.341H_2 + 0.042CO + 1.69CO_2 + 1.268CH_4 + 0.485N_2 + 0.029NH_3
g.gas*	7.37e+05	1.31e+05	Glycine + 0.146H_2O →0.765H_2 + 0.006CO + 1.07CO_2 + 0.924CH_4 + 0.489N_2 + 0.023NH_3
g.gas**	7.37e+05	1.31e+05	Glycine + 0.648H_2O →1.79H_2 + 0.029CO + 1.309CO_2 + 0.661CH_4 + 0.488N_2 + 0.023NH_3
et.gas*	7.37e+05	1.31e+05	EthAmine + 0.646H_2O →0.745H_2 + 0.003CO + 0.322CO_2 + 1.675CH_4 + 0.483N_2 + 0.033NH_3
et.gas**	7.37e+05	1.31e+05	EthAmine + 1.097H_2O →1.665H_2 + 0.019CO + 0.539CO_2 + 1.442CH_4 + 0.484N_2 + 0.032NH_3
met.gas*	7.37e+05	1.31e+05	MethAmine + 0.123H_2O →0.684H_2 + 0.001CO + 0.061CO_2 + 0.938CH_4 + 0.479N_2 + 0.042NH_3
met.gas**	7.37e+05	1.31e+05	MethAmine + 0.412H_2O →1.284H_2 + 0.008CO + 0.202CO_2 + 0.79CH_4 + 0.484N_2 + 0.031NH_3

*Gasification stoichiometry at 500°C
**Gasification stoichiometry at 600°C

Table B8: Arrhenius parameters for reactions of intermediates in sub- and supercritical water

Name	**A** (s^{-1})	**Ea** ($kJ\,mol^{-1}$)	**Region***	**Equation**
f.ga1	1.6e+06	8.5e+04	sub	FormicAcid →CO_2 + H_2
f.ga2	0.004	0	sub	FormicAcid →CO + H_2O
levu.lacet	6.59e+07	9.4e+04	both	LevuAcid + H_2O →LacticAcid + Acetalde
la.lacet	2.37e+09	1.48e+05	both	LacticAcid →Acetalde + CO_2 + H_2
acet.aa	0.0325	0	both	Acetalde + H_2O →AceticAcid + H_2
la.acry	689	6.88e+04	both	LacticAcid →AcryAcid + H_2O
acry.la	0.2	3.54e+04	both	AcryAcid + H_2O →LacticAcid
acry.pa	0.6	3.49e+04	both	AcryAcid + H_2 →PropAcid
acry.hpa	4.13e+03	8.01e+04	both	AcryAcid + H_2O →HPA
hpa.acry	0.0265	0	both	HPA →AcryAcid + H_2O
hpa.glyco	0.00131	0	both	HPA + 2H_2O →GlyAcid + CO_2 + 3H_2
f.ga1	4.8e+12	1.68e+05	sup	FormicAcid →CO_2 + H_2
f.ga2	3.4e+17	2.44e+05	sup	FormicAcid →CO + H_2O
aa.ga	2.5e+04	9.4e+04	sup	AceticAcid →CO_2 + CH_4
pa.ga	1.4e+05	8.94e+04	sup	PropAcid + H_2O →3CO + 4H_2
glycol.ga	2.5e+04	9.4e+04	sup	GlyAcid + H_2O →2CO_2 + 3H_2
fal.ga	4.8e+12	1.68e+05	sup	Formalde →CO + H_2
mf.aa	7.5e+23	2.51e+05	sup	MethForm →AceticAcid
wgs	3.8e+05	1.16e+05	sup	CO + H_2O →CO_2 + H_2

*Reaction present in either sub-critical ('sub') or supercritical ('sup') region only, or both regions

Table B9: Nomenclature of Chemical Species in Kinetic Model

Shorthand	**Longhand**	**Formula**
Cellobiose	Cellobiose	$C_{12}H_{22}O_{11}$
GlyEryt	Glucosyl Erythrose	$C_{10}H_{18}O_9$
Glycolal	Glycolaldehyde	$C_2H_4O_2$
GlyGly	Glucosyl Glycolaldehyde	$C_8H_{14}O_7$
Erythrose	Erythrose	$C_4H_8O_4$
H_2O	Water	H_2O
Glucose	Glucose	$C_6H_{12}O_6$
Fructose	Fructose	$C_6H_{12}O_6$
AnhyGlu	Anhydroglucose	$C_6H_{10}O_5$
HMF	5-(Hydroxymethyl)furfural	$C_6H_6O_3$
Glyceral	Glyceraldehyde	$C_3H_6O_3$
Dihydrox	Dihydroxyacetone	$C_3H_6O_3$
Pyruval	Pyruvaldehyde	$C_3H_4O_2$
LacticAcid	Lactic Acid	$C_3H_6O_3$
AceticAcid	Acetic Acid	$C_2H_4O_2$
LevuAcid	Levulinic Acid	$C_5H_8O_3$
FormicAcid	Formic Acid	CH_2O_2
Furfural	Furfural	$C_5H_4O_2$
Formalde	Formaldehyde	CH_2O
Xylose	Xylose	$C_5H_{10}O_5$
WSHS	Water Soluble Humic Species	$C_2H_4O_2 + C_3H_4O_2$
AcryAcid	Acrylic Acid	$C_3H_4O_2$
PropAcid	Propionic Acid	$C_3H_6O_2$
GlyAcid	Glycolic Acid	$C_2H_4O_3$
Acetalde	Acetaldehyde	C_2H_4O
HPA	3-Hydroxypropionic Acid	$C_3H_6O_3$
MethForm	Methyl Formate	$C_2H_4O_2$
Guaiacol	Guaiacol	$C_7H_8O_2$
oCresol	oCresol	C_7H_8O
Catechol	Catechol	$C_6H_6O_2$
Diphenyl	Diphenyl	$C_{12}H_{10}$
Phenol	Phenol	C_6H_6O
Benzene	Benzene	C_6H_6
Naphtalene	Naphtalene	$C_{10}H_8$
AspAcid	Aspartic Acid	$C_4H_7NO_4$
Alanine	Alanine	$C_3H_7NO_2$
Glycine	Glycine	$C_2H_5NO_2$
EthAmine	Ethylamine	C_2H_7N
MethAmine	Methylamine	CH_5N
CO	Carbon Monoxide	CO
H_2	Hydrogen	H_2
CO_2	Carbon Dioxide	CO_2
CH_4	Methane	CH_4
C_2H_6	Ethane	C_2H_6
CharFurf	Char (Furfural)	$C_5H_4O_2$*
CharGuai	Char (Guaiacol)	$C_7H_8O_2$*
CharBenz	Char (Benzene)	C_6H_6*

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Table B9 – *Continued from previous page*

Shorthand	Longhand	Formula
CharDiph	Char (Diphenyl)	$C_{12}H_{10}$*
CharPhen	Char (Phenol)	C_6H_6O*
CharNaph	Char (Naphtalene)	$C_{10}H_8$*
CharAspAcid	Char (Aspartic Acid)	$C_4H_7NO_4$*

* *Solid char species*