Supporting Information

Torrefaction of Pine Using A Pilot-Scale Rotary Reactor: Experimentation, Kinetics, and Process Simulation using Aspen Plus™

Suchandra Hazra[1,2], Prithvi Morampudi[2] , John C. Prindle[2], Dhan Lord B. Fortela[2,3], Rafael Hernandez[2,3], Mark E. Zappi[2,3], and Prashanth R. Buchireddy[2,3]*

Table S1. Condensable species recovered from the torrefaction of pinewood at various temperatures.

Process	Type of reactor	Method of analysis	Species analyzed	References
Torrefaction	3L Laboratory reactor	GC	Water, acetic acid, methanol, formic acid, and furfural.	[1]
Torrefaction	Batch reactor	HPLC with Chrompack organic acid column, with detection based on refraction index	Water, acetic acid, methanol, formic acid, lactic acid, furfural, 2-propanone, 1-hydroxy-, and phenol.	[2]
Torrefaction and pyrolysis	TGA	FTIR	Water, acetic acid, methanol, formic acid, lactic acid, and furfural.	[3]
Torrefaction	TGA	FTIR	Acetaldehyde, formaldehyde, acetic acid, formic acid, methanol, and methane.	[4]
Torrefaction	Batch reactor	Infrared gas analysis (Gasboard-5110)	Water, acetic acid and other oxygenates.	[5]
Torrefaction	TGA	GC-MS (Perkin Elmer Clarus 500)	Acetic acid, acetic anhydride, furfural, and 3-methylbutanol.	[4]
Torrefaction	Thermal desorption tube	GC-MS and TD (Perkin Elmer Turbomatrix)	Acetic acid, furfural, methylfurfural, hydroxymethylfurfural, phenol,2-methoxy-, phenol,2,6-dimethoxy-, vanillin, syringaldehyde, acetovanillin, and acetosyringon.	[6]
Torrefaction	Batch reactor	GC-MS (Agilent 6890 and 5973)	Phenol, pheno,2-methoxy, phenol,4-methyl-, eugenol, and vanillin.	[7]
Torrefaction	Batch reactor	GC-MS	Acetaldehyde, acetic acid, formaldehyde,	[4]

|			formic acid, 2-furanmethanol, furfural, glycolaldehyde dimer, 2-propanone,1-hydroxy-, and propanoic acid	
Torrefaction	TGA	TGA coupled with MS	Water, acetic acid, formic acid, formaldehyde, chloromethane, hydrogen sulphide, and carbonyl sulphide	[8]
Torrefaction and pyrolysis	Auger reactor	Karl Fischer titration (Metrohm, 787KF Titrino) for water; GC-FID (Agilent HP 4890)	Water, acetic acid, 2 cyclopenten-1-one, 2-propanone,1-hydroxy-, propanoic acid, 2-furanmethanol, phenol, phenol,4-ethyl- 2-methoxy-, phenol,2-methoxy-, eugenol, isoeugenol, and vanillin.	[9]
Torrefaction	Batch reactor	GC-MS and GC-FID	Formaldehyde, acetaldehyde, acetone, methanol, ethanol, glycolaldehyde, acetic acid, water, glyoxal, lactic acid, and formic acid.	[10]
Torrefaction	Batch reactor	Karl Fischer titration (Mettler Toledo V20), GC-MS (Agilent 6890 and 5975)	Acetic acid, formaldehyde, formic acid, 2-furanmethanol, furfural, glycolaldehyde dimer, 2-propanone,1-hydroxy-, and propanoic acid.	[11]
Torrefaction	Batch reactor	FTIR (Nicolet Magna-IR 550)	Water, acetic acid, formic acid, formaldehyde, furfural, and methanol.	[4]
Torrefaction	Laboratory-scale fixed-bed reactor	Micro-GC, Karl Fischer titrator and GC-MS	Water, acetic acid, 2-propanone,1-hydroxy-, methanol, glycoaldehyde dimer, 2-furanmethanol, formic acid, formaldehyde, 2-methoxy-4-vinylphenol, 2-butanone,1-hydroxy-, furfural, 1-acetyloxy-2-propanone, propanoic acid, levoglucosan, 3-methyl-1,2-cyclopentanedione, isoeugenol, 2,6-dimethoxyphenol, phenol-2-methoxy-, CO2, and CO.	[12]
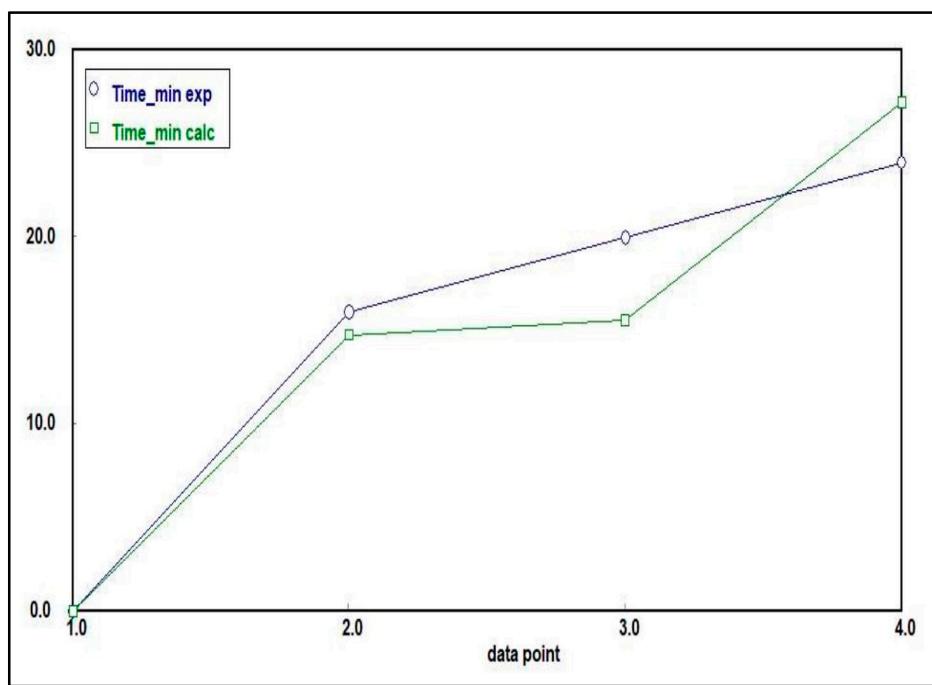
Figure S1. a. Polymath graphs showing the fitting of carbon data at 232°C (experiment vs. calculated).
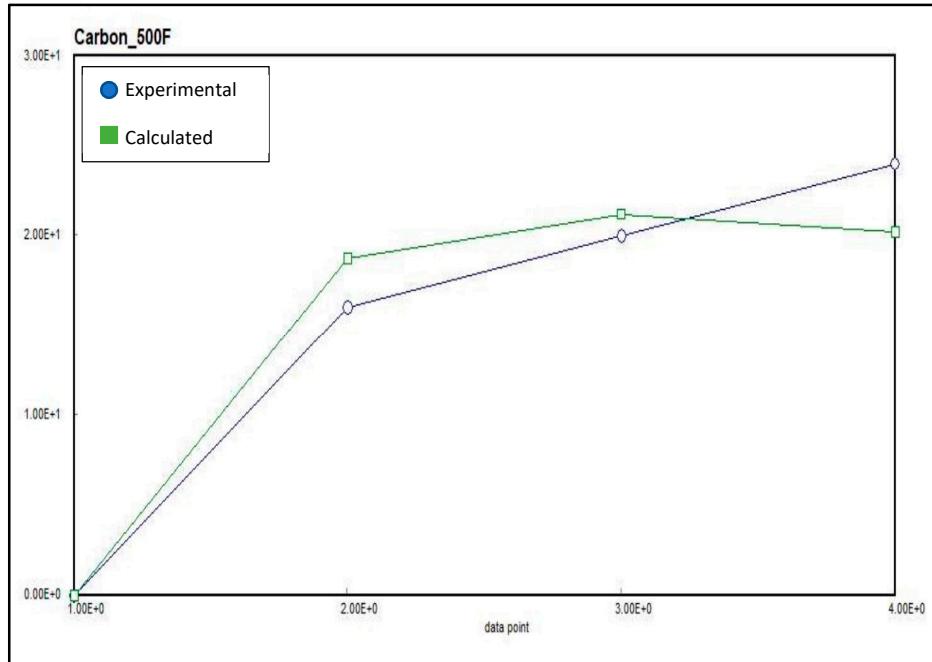

Figure S1. b. Polymath graphs showing the fitting of carbon data at 260°C (experiment vs. calculated).
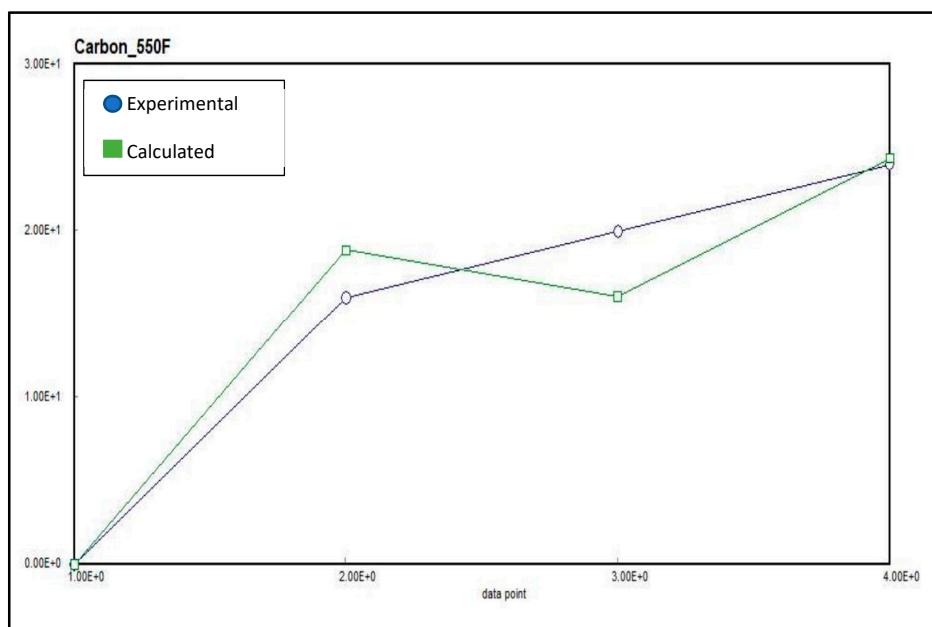
**Figure S1. c.** Polymath graphs showing the fitting of carbon data at 288°C (experiment vs. calculated).
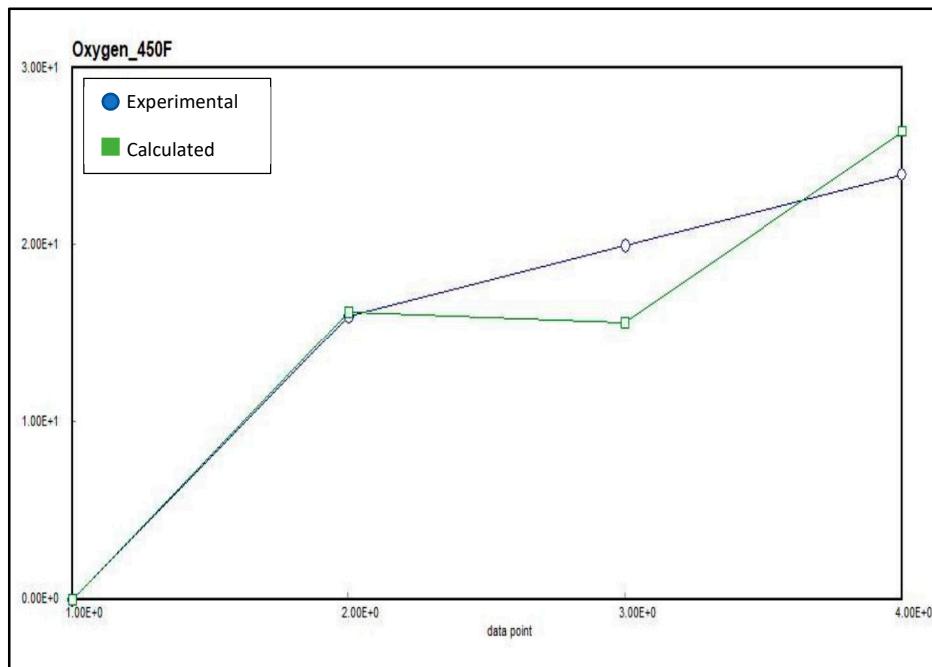
Figure S2. a. Polymath graphs showing the fitting of oxygen data at 232°C (experiment vs. calculated).
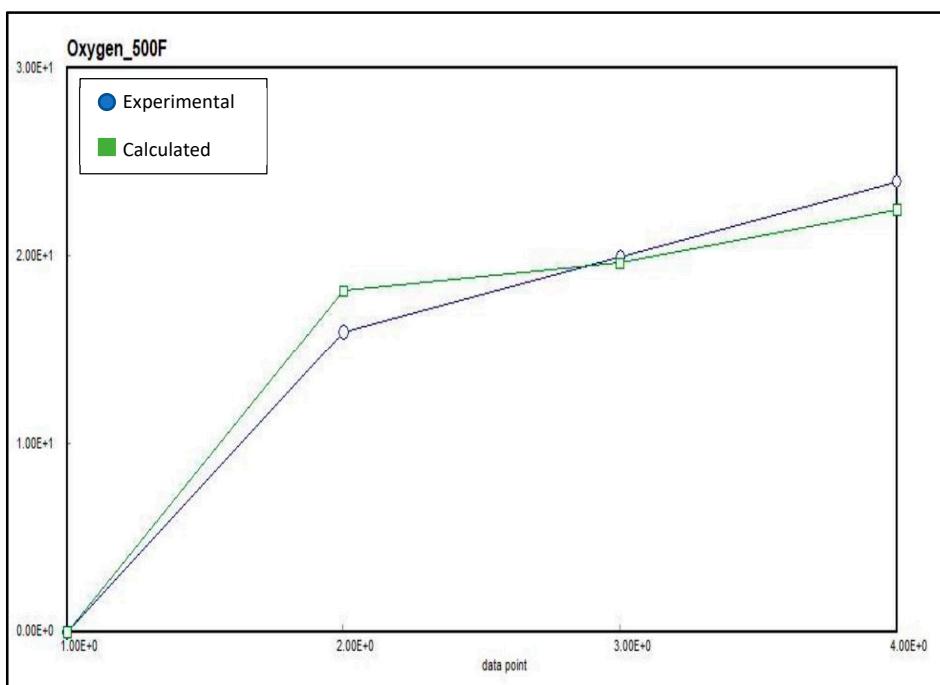
Figure S2. b. Polymath graphs showing the fitting of oxygen data at 260°C (experiment vs. calculated).
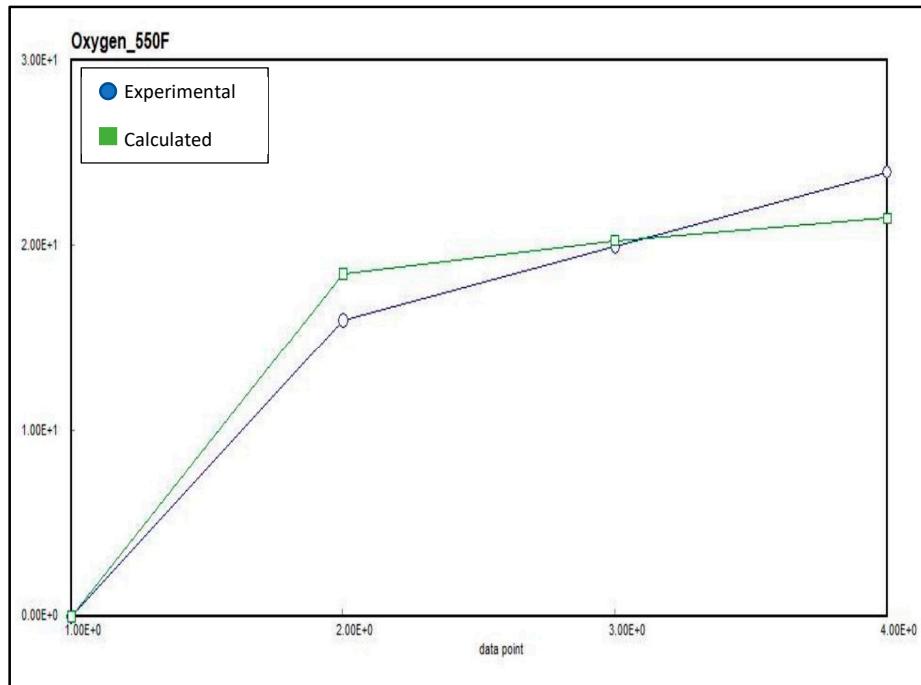

Figure S2. c. Polymath graphs showing the fitting of oxygen data at 288°C (experiment vs. calculated).
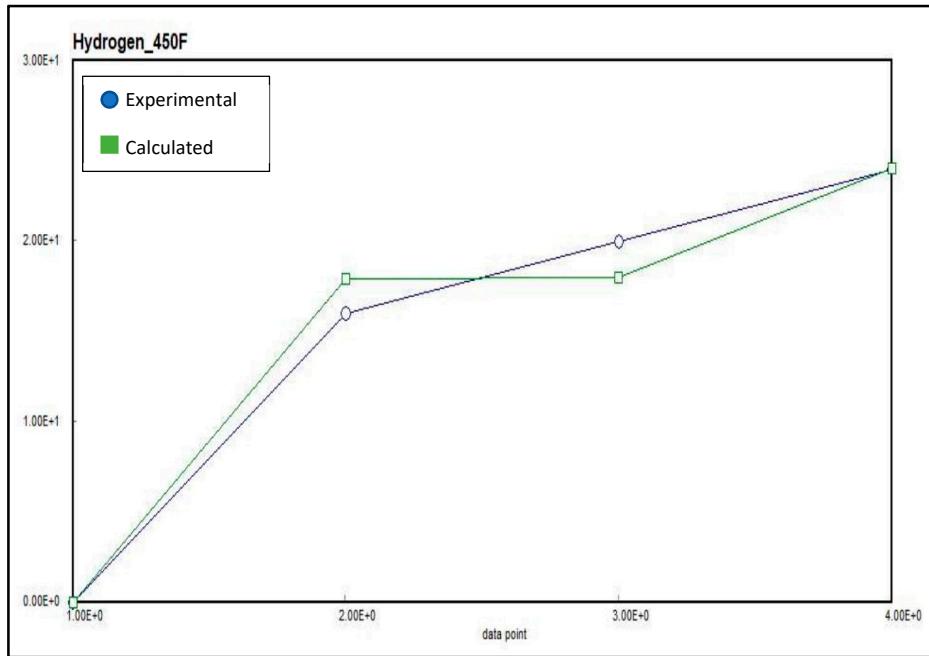
Figure S3. a. Polymath graphs showing the fitting of hydrogen data at 232°C (experiment vs. calculated).
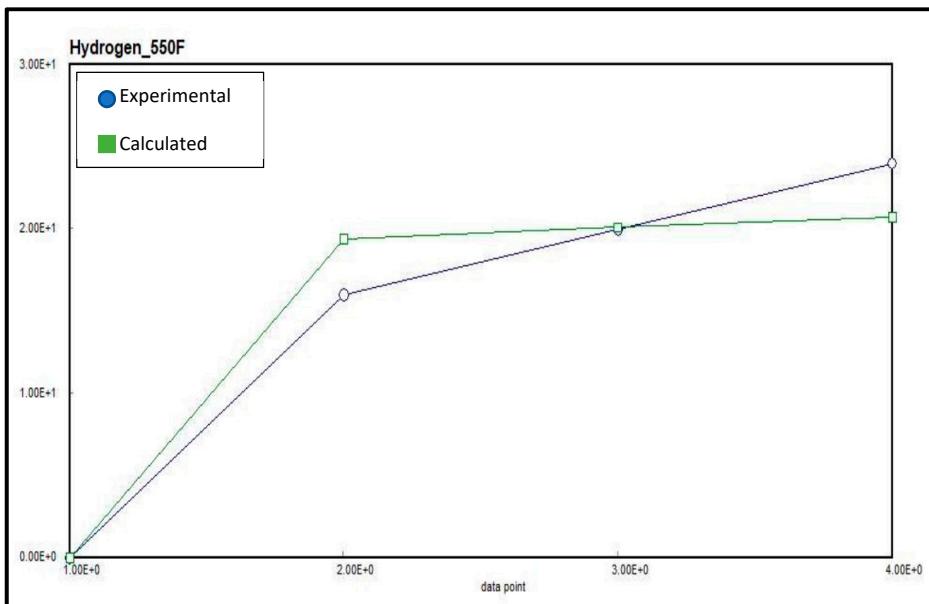

**Figure S3. b.** Polymath graphs showing the fitting of hydrogen data at 260°C (experiment vs. calculated).
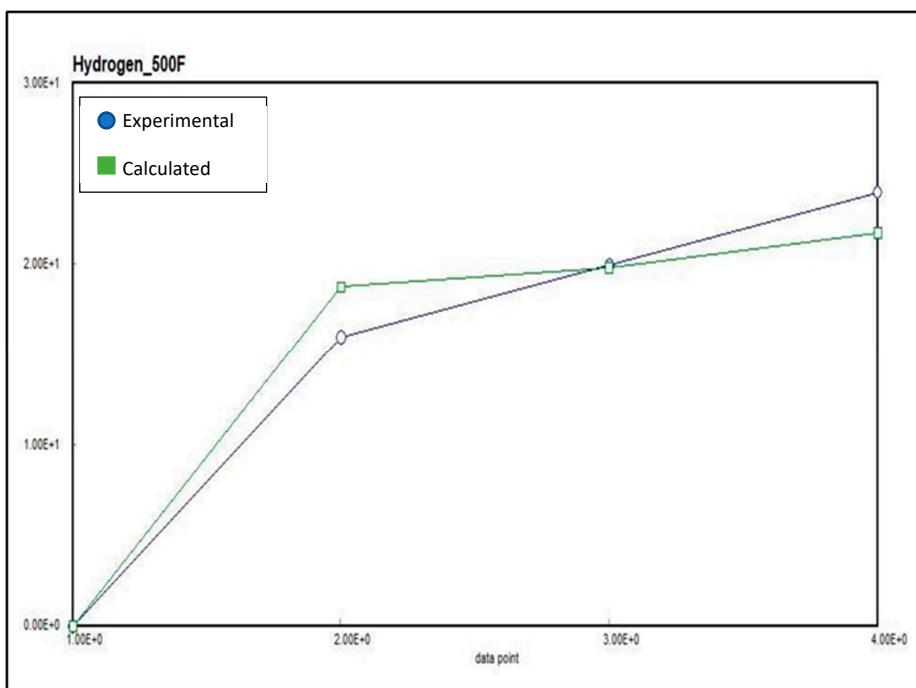
Figure S3. c. Polymath graphs showing the fitting of hydrogen data at 288°C (experiment vs. calculated).
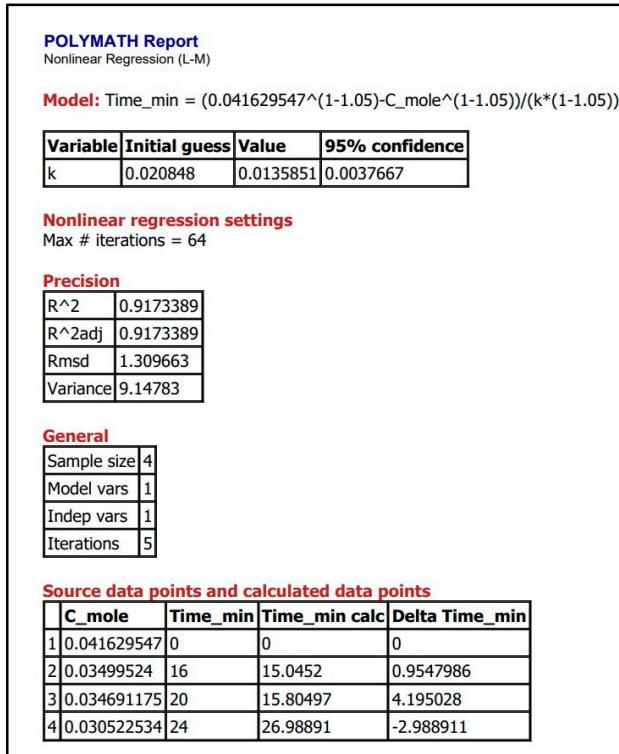
Figure S4. Polymath report for carbon data regression at 232°C (450F).

POLYMATH Report
Nonlinear Regression (L-M)

Model: Time_min = (0.027001688^(1-1.98)-O_mole_550F^(1-1.98))/(k*(1-1.98))

Variable	Initial guess	Value	95% confidence
k	0.01	1.819569	0.5266268

Nonlinear regression settings
Max # iterations = 64

Precision

R^2	0.9101124
R^2adj	0.9101124
Rmsd	1.365711
Variance	9.947561

General

Sample size	4
Model vars	1
Indep vars	1
Iterations	13

Source data points and calculated data points

	O_mole_550F	Time_min	Time_min calc	Delta Time_min
1	0.027001688	0	0	0
2	0.016440278	16	12.09903	3.900969
3	0.013852616	20	17.84088	2.159124
4	0.011025689	24	27.15647	-3.156471

Figure S5. Polymath report for oxygen data regression at 288°C (550F).

POLYMATH Report
Nonlinear Regression (L-M)

Model: Time_min = (0.065486585^(1-1.97)-H_mole_500F^(1-1.97))/(k*(1-1.97))

Variable	Initial guess	Value	95% confidence
k	0.01	0.5104119	0.045703

Nonlinear regression settings
Max # iterations = 64

Precision

R^2	0.9912037
R^2adj	0.9912037
Rmsd	0.4272265
Variance	0.9734532

General

Sample size	4
Model vars	1
Indep vars	1
Iterations	11

Source data points and calculated data points

	H_mole_500F	Time_min	Time_min calc	Delta Time_min
1	0.065486585	0	0	0
2	0.041286315	16	16.0396	-0.0395982
3	0.038955588	20	18.61762	1.382379
4	0.034164153	24	25.0039	-1.003902

Figure S6. Polymath report for hydrogen data regression at 260°C (500°F).

(a)

(b)

Carbon 2nd order Rxn

y = -442.19x - 0.222
R² = 0.3966
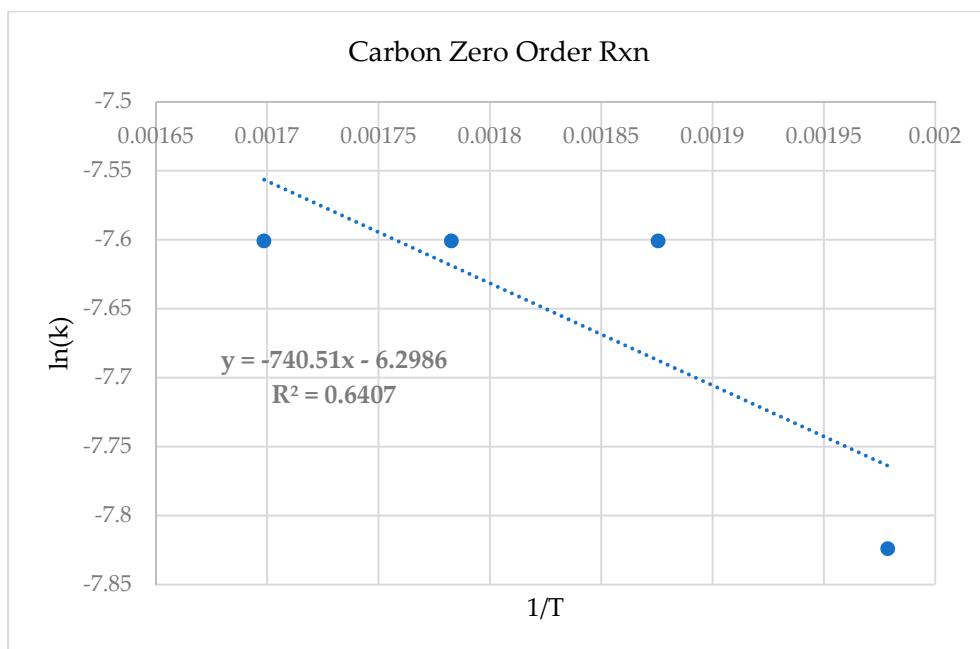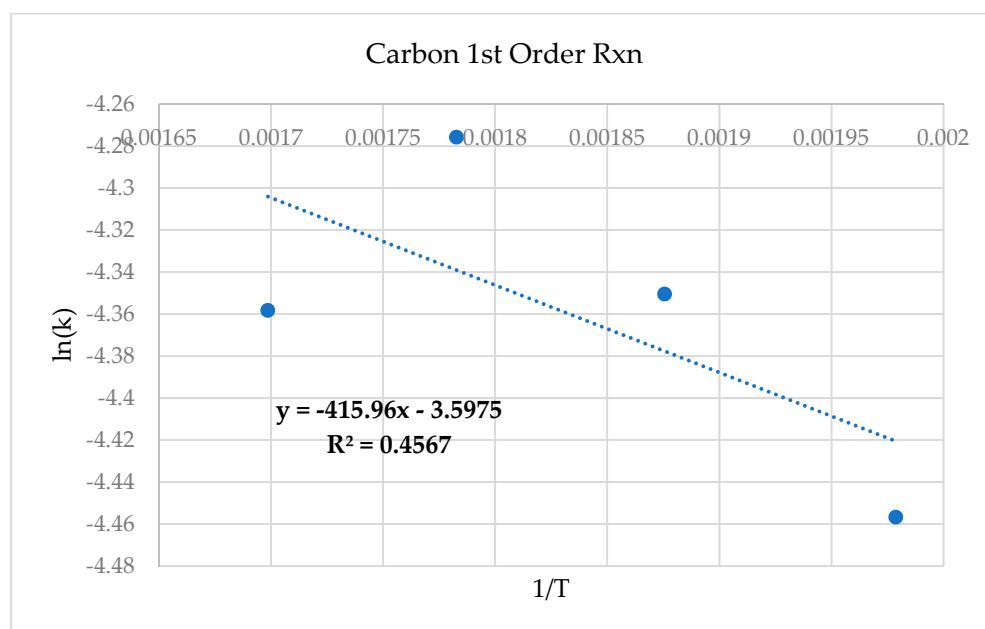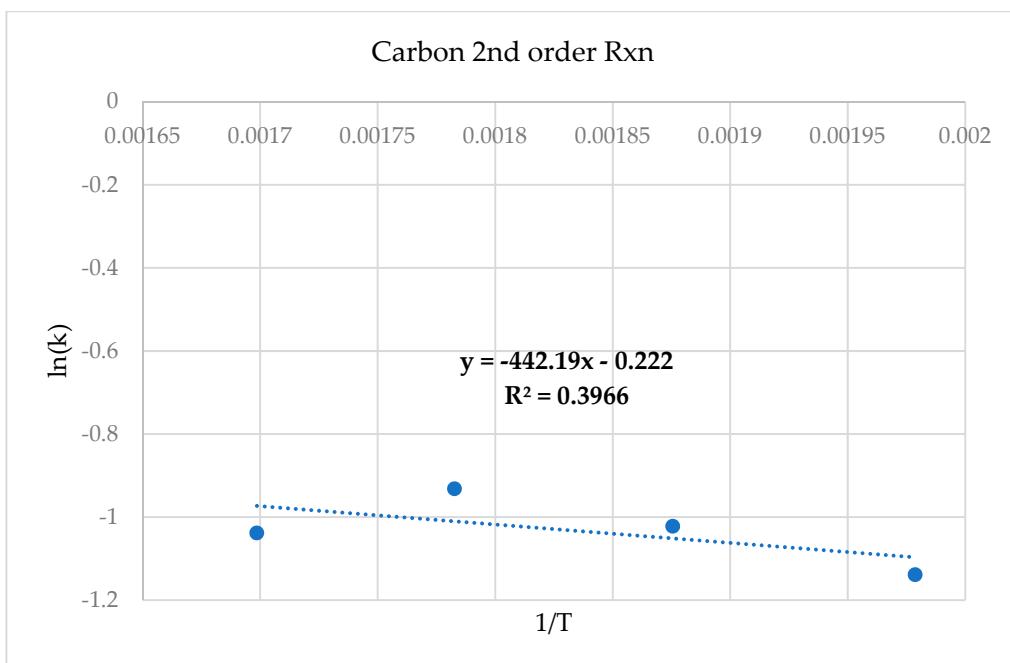
(c)

Figure S7. (a) Arrhenius plots for zero-order, (b) 1st order, and (c) 2nd order reactions of carbon obtained by the integral rate law method.

Oxygen Zero Order Rxn

y = -3912.7x - 0.3218
R² = 0.9868
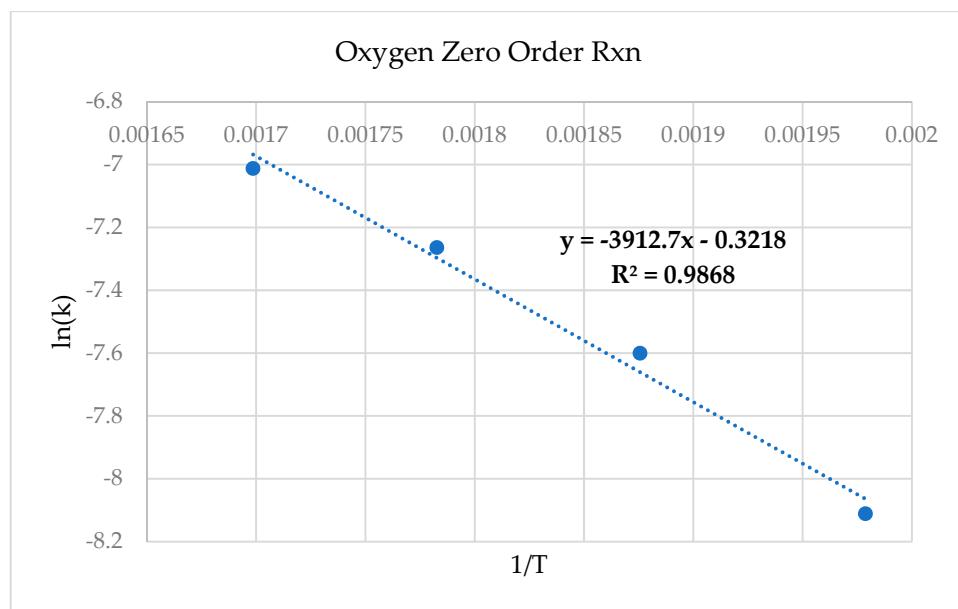
(a)
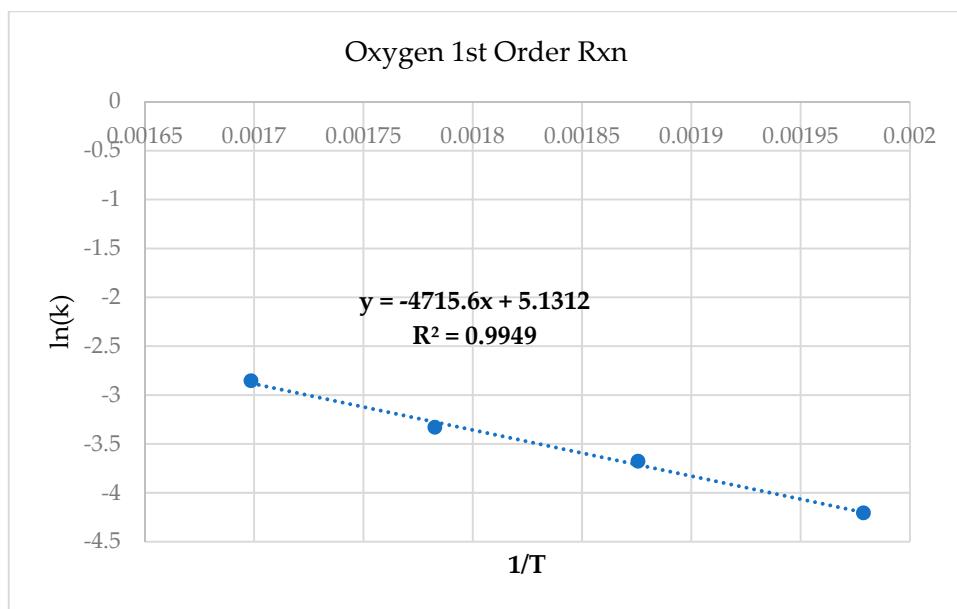
(b)
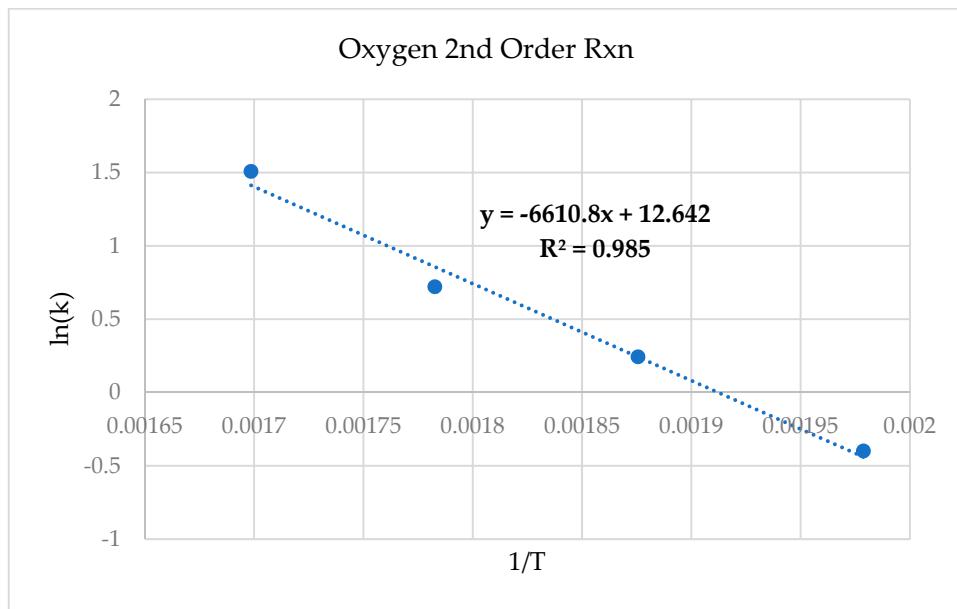
(c)

Figure S8. Arrhenius plots for (a) zero-order, (b) 1st order, and (c) 2nd order reactions of oxygen obtained by the integral rate law method.
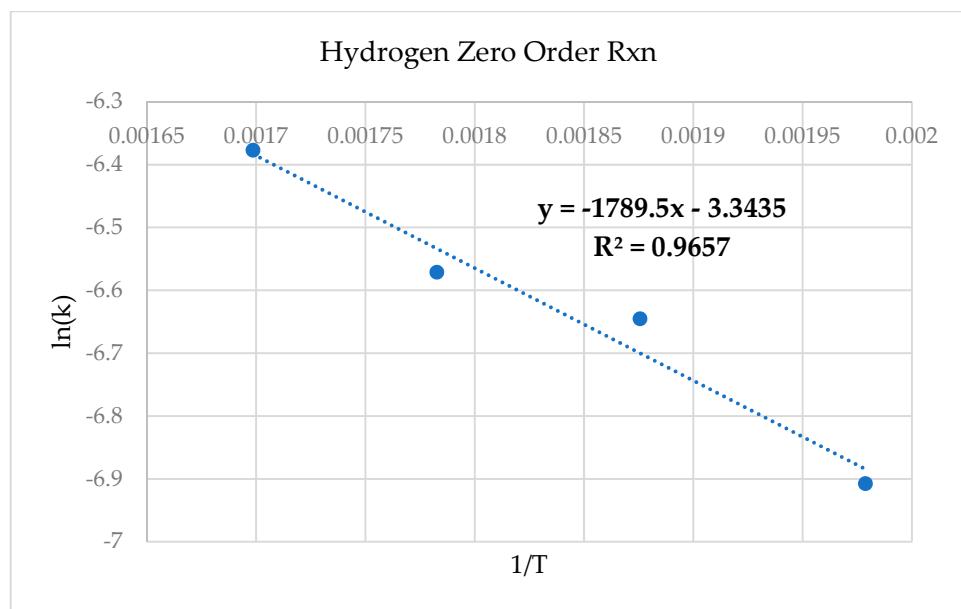
(a)
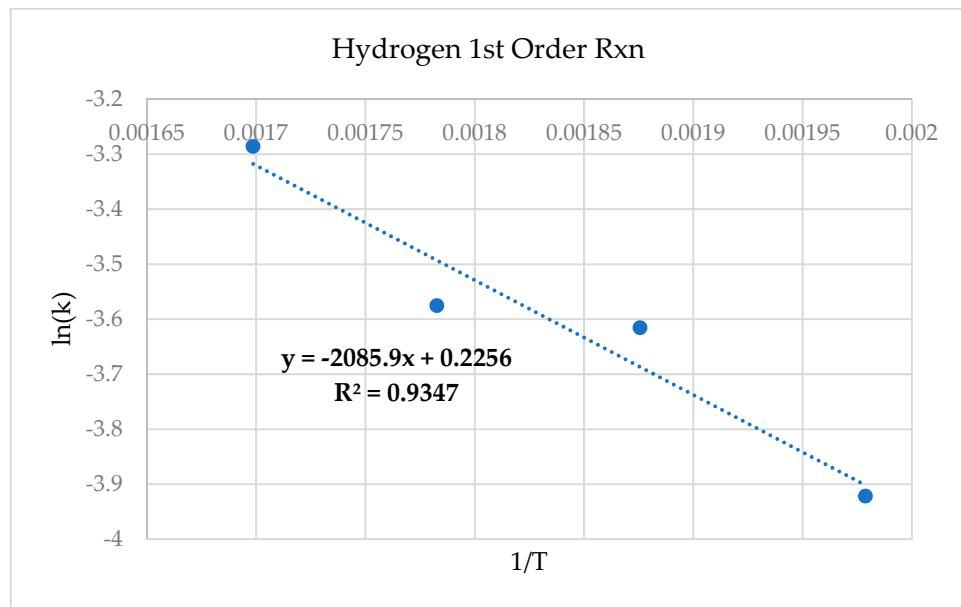
(b)
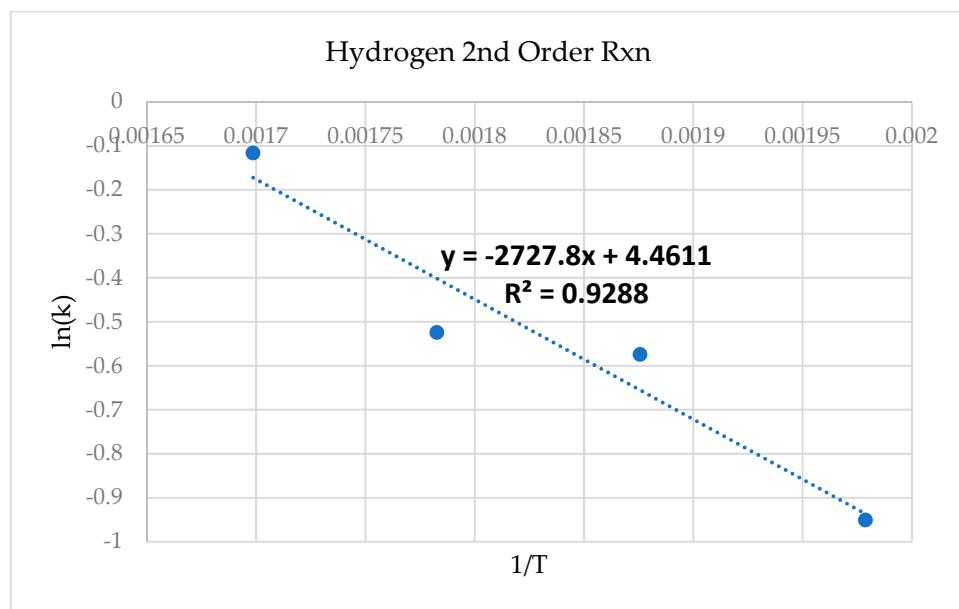
(c)

**Figure S9**. Arrhenius plots for (a) zero-order, (b) 1st order, and (c) 2nd order reactions of hydrogen obtained by the integral rate law method.

Table S2. Experimental results showing biomass composition after torrefaction at 232, 260, 288, and 316°C at 16 minutes residence time [13].

16mins	232°C	260°C	288°C	316°C
C	50.6	53.1	56.05	65.67
N	0.1	0.12	0.14	0.16
H	5.84	5.7	5.56	4.74
S	0.2	0.11	0.13	0.08
O	43.26	40.97	38.12	29.35
HHV, db	9014.7	9583	10143	12629
Ash	0.112	0.16	0.1472	0.16
Volatiles	76.28	74.87	68.75	49
Fixed carbon	19.108	21.12	26.6028	44.84

Table S3. Experimental results showing biomass composition after torrefaction at 232, 260, 288, and 316°C at 20 minutes residence time [13].

20mins	232°C	260°C	288°C	316°C
C	50.33	53.65	61.75	64.89
N	0.09	0.13	0.24	0.15
H	5.86	5.69	5.29	5.13
S	0.08	0.06	0.6	0.07
O	43.64	40.47	32.12	29.76
HHV. Db	9031	9499	10351	12303
Ash	0.155	0.4	0.33	0.1629
Volatiles	78	73	61.3	49.66
Fixed carbon	17.945	23.16	33.67	42.6471

Table S4. Experimental results showing biomass composition after torrefaction at 232, 260, 288, and 316°C at 24 minutes residence time [13].

24mins	232°C	260°C	288°C	316°C
C	53.13	58.94	61.9	75.5
N	0.21	0.22	0.03	0.6
H	5.65	5.38	6.2	5.5
S	0.322	0.24	0	0
O	40.688	35.22	31.5	18.4
HHV, db	9555	10557	12598	12874
Ash	0.1518	0.0967	0.28	0.17
Volatiles	74	63	45.36	46.82
Fixed carbon	22.0982	32.1033	53.76	52.94

References

1.	Bourgois, J.; Guyonnet, R. Characterization and Analysis of Torrefied Wood. *Wood Sci. Technol. 1988 222* **1988**, *22*, 143–155, doi:10.1007/BF00355850.

2.	Prins, M.J.; Ptasinski, K.J.; Janssen, F.J.J.G. Torrefaction of Wood. Part 2. Analysis of Products. *J. Anal. Appl. Pyrolysis* **2006**, *77*, 35–40, doi:10.1016/j.jaap.2006.01.001.

3.	Repellin, V.; Govin, A.; Rolland, M.; Guyonnet, R. Modelling Anhydrous Weight Loss of Wood Chips during Torrefaction in a Pilot Kiln. *Biomass and Bioenergy* **2010**, *34*, 602–609, doi:10.1016/J.BIOMBIOE.2010.01.002.

4.	Nocquet, T.; Dupont, C.; Commandre, J.M.; Grateau, M.; Thiery, S.; Salvador, S. Volatile Species Release during Torrefaction of Wood and Its Macromolecular Constituents: Part 1-Experimental Study. *Energy* **2014**, *72*, 180–187, doi:10.1016/J.ENERGY.2014.02.061.

5.	Deng, J.; Wang, G. jun; Kuang, J. hong; Zhang, Y. liang; Luo, Y. hao Pretreatment of Agricultural Residues for Co-Gasification via Torrefaction. *J. Anal. Appl. Pyrolysis* **2009**, *86*, 331–337, doi:10.1016/J.JAAP.2009.08.006.

6.	Candelier, K.; Chaouch, M.; Dumaray, S.; Pétrissans, A.; Pétrissans, M.; Gérardin, P. Utilization of Thermodesorption Coupled to GC–MS to Study Stability of Different Wood Species to Thermodegradation. *J. Anal. Appl. Pyrolysis* **2011**, *92*, 376–383, doi:10.1016/J.JAAP.2011.07.010.

7.	Chen, W.H.; Hsu, H.C.; Lu, K.M.; Lee, W.J.; Lin, T.C. Thermal Pretreatment of Wood (Lauan) Block by Torrefaction and Its Influence on the Properties of the Biomass. *Energy* **2011**, *36*, 3012–3021, doi:10.1016/J.ENERGY.2011.02.045.

8.	Shang, L.; Ahrenfeldt, J.; Holm, J.K.; Barsberg, S.; Zhang, R.Z.; Luo, Y.H.; Egsgaard, H.; Henriksen, U.B. Intrinsic Kinetics and Devolatilization of Wheat Straw during Torrefaction. *J. Anal. Appl. Pyrolysis* **2013**, *100*, 145–152, doi:10.1016/J.JAAP.2012.12.010.

9.	Portilho, G.R.; de Castro, V.R.; Carneiro, A. de C.O.; Zanuncio, J.C.; Zanuncio, A.J.V.; Surdi, P.G.; Gominho, J.; Araújo, S. de O. Potential of Briquette Produced with Torrefied Agroforestry Biomass to Generate Energy. *For. 2020, Vol. 11, Page 1272* **2020**, *11*, 1272, doi:10.3390/F11121272.

10.	Anca-Couce, A.; Mehrabian, R.; Scharler, R.; Obernberger, I. Kinetic Scheme to Predict Product Composition of Biomass Torrefaction. *Chem. Eng. Trans.* **2014**, *37*, 43–48, doi:10.3303/CET1437008.

11.	Commandré, J.M.; Leboeuf, A. Volatile Yields and Solid Grindability after Torrefaction of Various Biomass Types. *Environ. Prog. Sustain. Energy* **2015**, *34*, 1180–1186, doi:10.1002/EP.12073.

12.	Lê Thành, K.; Commandré, J.M.; Valette, J.; Volle, G.; Meyer, M. Detailed Identification and Quantification of the Condensable Species Released during Torrefaction of Lignocellulosic Biomasses. *Fuel Process. Technol.* **2015**, *139*, 226–235, doi:10.1016/J.FUPROC.2015.07.001.

13.	Prithvi Morampudi Pilot Scale Evaluation of Torrefaction Operating Process Parameters on Thermal Properties of Biomass, University of Louisiana at Lafayette, 2019.