External charring limits sugar yields obtained from flow-through subcritical water hydrolysis

Supporting Information for a manuscript submitted to *Sustainable Energy & Fuels*

Zijian Ma,[a] Patricia Guerra,[a] Maksim Tyufekchiev,[a] Azadeh Zaker,[a] Geoffrey A. Tompsett,[a] Paulo Cesar Torres Mayanga,[b] Tânia Forster-Carneiro,[b] Peng Wang,[c] Michael T. Timko*[a]

[a] Department of Chemical Engineering, Worcester Polytechnic Institute, 100 Institute Road, Worcester, MA 01609

[b] School of Food Engineering, University of Campinas (UNICAMP), Rua Monteiro Lobato, n.80, 13083-862 Campinas, SP, Brazil

[c] Bruker Optics, Bruker Corporation, Billerica, MA, USA

Summary. The Supporting Information provides a schematic representation of the batch and flow processes; raw data for TG analysis (thermal loss curves and differential thermograms), TG fitting and data quality assurance, Raman spectroscopy, and ATR infrared spectroscopy. The Supporting Information is divided into 4 sections: 1) experimental details, 2) TGA results obtained for flow-through treated samples, 3) IR results obtained from analysis of flow-through treated samples, 4) results obtained from analysis of batch-treated samples.

1. Experimental details. Green coffee powder was knife milled and used as a feed for flow-through and batch subcritical water hydrolysis processing. Figure SI-1 is a schematic representation of both processes.

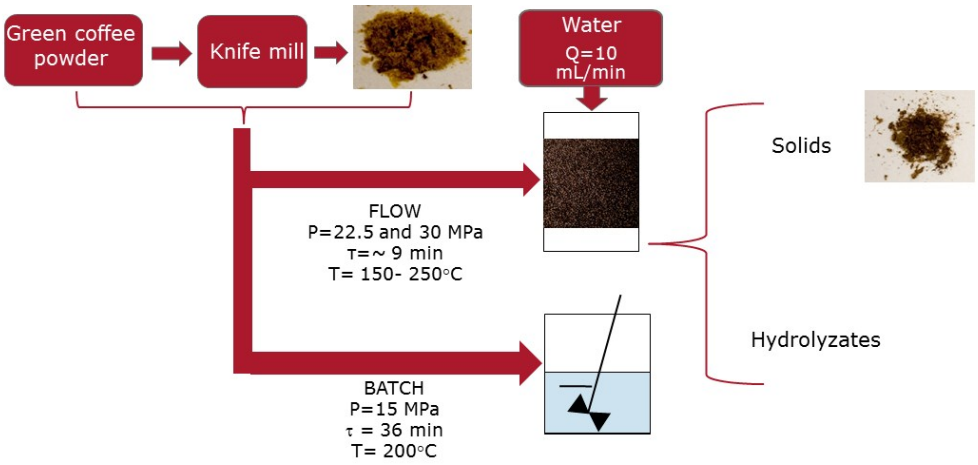

Figure SI-1. Schematic representation of the flow and batch processes.

2. Thermogravimetric Analysis of Flow-Through Samples. Figure SI-2 contains the raw thermal loss curves obtained for the feed biomass and for biomass treated at 150, 175, 200, and 250 °C. Figure SI-3 shows the raw DTG curves. Figure SI-4 shows representative results of DTG curve fitting. Figure SI-5 compares TGA compositional analysis to NREL analysis. Table SI-1 provides average temperatures and ranges (calculated as standard deviations) used to fit all raw DTG spectra.

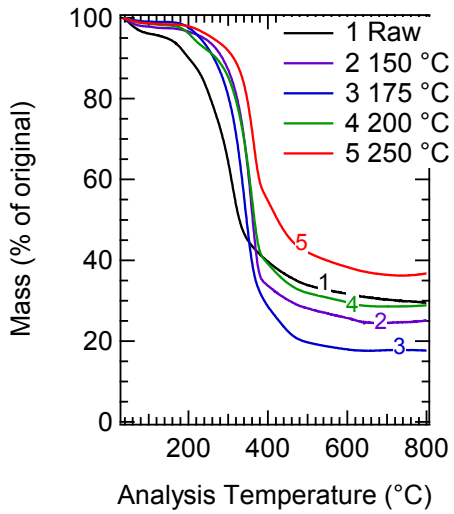

Figure SI-2. Raw TGA thermograms obtained for coffee powder and coffee powder treated under FT-SWH conditions (temperatures listed).

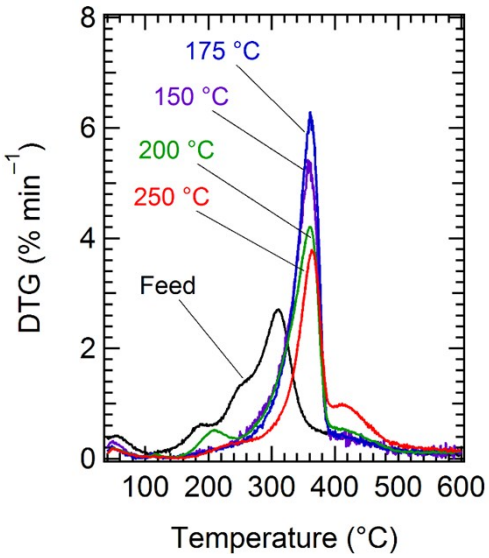

Figure SI-3. DTG data obtained from biomass treated under FT-SWH conditions.

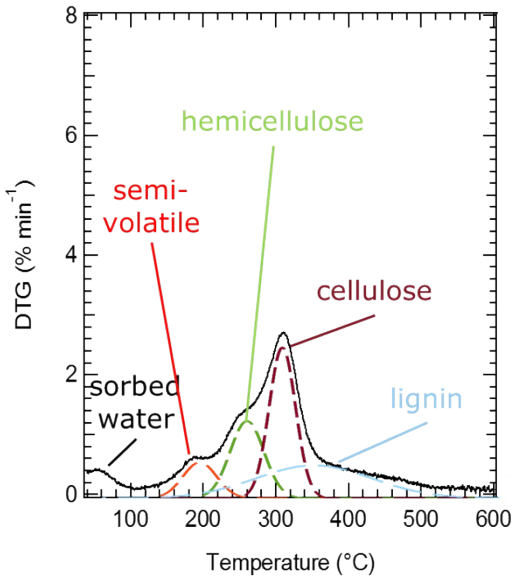

Figure SI-4. Raw DTG thermogram obtained for coffee powder showing curve fits for water, semi-volatile (SV1), hemicellulose, cellulose, and lignin.

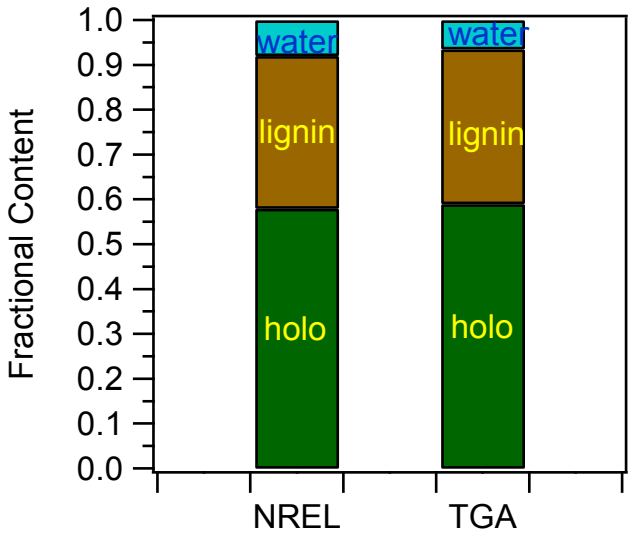

Figure SI-5. Comparison of holocellulose, lignin, and moisture content of green coffee powder obtained using TGA and the NREL analysis methods.

Table SI-1. Average peak temperatures and full-width half maxima (FWHM) used for peak fitting biomass and solid residue DTG curves.

Biomass/residue component	Average Peak Temperature (°C)	FWHM (°C)
SV1s	200±18	60
SV2	207±0	55
hemicellulose	262±28	60
cellulose	329±17	60
lignin	352±9	200
char	410±21	108

3. Spectroscopic Analysis of Flow-Through Samples. Table SI-2 provides Raman band assignments of all major bands observed in the powder samples. Table SI-3 provides the same for IR bands. Figure SI-6 provides raw ATR-FTIR spectra obtained from the feed biomass and for biomass treated at 150, 175, 200, and 250 °C. Figure SI-7 shows representative curve fits for specific C=C and C=O bands in the ATR-FTIR spectra.

Table SI-2. Raman band positions and assignments of the spectra at different temperatures for the green coffee powder and its hydrothermal treatment products

Green Powder (cm^{-1})	SWH 150 °C (cm^{-1})	SWH 175 °C (cm^{-1})	SWH 200 °C (cm^{-1})	SWH 250 °C (cm^{-1})	Assignment	Compound	Reference
1656					C=C	Lipids, Polyphenols and phenolic (chlorogenic) acids	Keidel et al.[1]
1596							Rubayiza and Meurens[2]
	1580	1580	1580	1580	G-band		Sadezky et al.[3]
1445					CH_3	Roasted coffee, Lipid fraction form arabica and robusta coffee	Rubayiza and Meurens[2]
	1435	1435	1426	1426	D3 band		Sadezky et al.[3]
1374sh					CH_2	Roasted coffee, Lipid fraction form arabica and robusta coffee	Rubayiza and Meurens[2]
1332							
1311sh							
1300sh							
1265					CH deformation	Roasted coffee, Lipid fraction form arabica and robusta coffee	Rubayiza and Meurens.[2]
	1317	1317		1317	D-band		Sadezky et al.[3]
1120					cyclohexane (cyc) CH	Chlorogenic acid	El-Abassy et al.[4]
1092	1096	1096	1096			carbohydrates	
	944	944				Unknown	
576	768	768				Unknown	
375	571	571	571			Unknown	

Table SI-3. IR band positions and assignments of the spectra at different temperatures for the green coffee powder and its hydrothermal carbonization residues.

Coffee powder (cm^{-1})	SWH 150 °C (cm^{-1})	SWH 175 °C (cm^{-1})	SWH 200 °C (cm^{-1})	SWH 250 °C (cm^{-1})	Assignment	Reference
670	668	674	664	664	Skeletal modes (starch)	Reis et al.[5]
	776	780	783	812	Skeletal modes (starch), α-linked D-galactopyranose units	Reis et al.[5], Ballesteros et al.[6]
894	895	899	894	851	Skeletal modes (starch), β–linked D-mannopyranose units	Reis et al.[5], Ballesteros et al.[6]
1029	1030	1028	1036	1031	C-O, C-O-H, glycosidic bands from carbohydrates	Reis et al.[5]
	1051	1050	1057	1057	C-O Chlorogenic acids, lignin aromatic C-H deformation	Mishra et al.[7], Agarwal and Atalla[8]
1102	1115	1105	1105	1113	Chlorogenic acids, carbohydrates	Mishra et al.[7], Hineno[9]
1147	1160	1152	1161	1157	Chlorogenic acids, carbohydrates	Mishra et al.[7], Hineno[9]
	1202	1205	1203	1213	carbohydrates	Hineno[9]
1240	1231	1232			Chlorogenic acids	Mishra et al.[7]
	1263	1269	1261	1266	Lignin, aryl ring breathing with C=O	Agarwal and Atalla[8]
1323	1318	1313	1319	1316	Unknown	
	1342	1337	1332	1337	C-O-C ester, lignin O-H bend	Pujol et al.[10], Craig et al.[11]
1374	1368	1366	1367	1361	Chlorogenic acids	Mishra et al.[7]
1422	1424	1424	1430	1430	Unknown	
1457	1456	1448	1457	1451	CH bending of CH_3, Chlorogenic acids, lignin O-CH_3 or CH_2 scissor	Agarwal and Atalla[8]
1508	1509	1504	1512	1509	C=C,	Pujol et al.[10]
1598	1615	1615	1610	1601	C=C, lignin ring C=C	Agarwal and Atalla[8]
1636	1649	1654	1658		C=C, lipids, fatty acids, chlorogenic acids, lignin C=C	Pujol et al.[10], Raba et al.[12], Agrawal and Atalla[8]
1729	1720	1715	1704	1705	C=O, triglycerides or esters	Reis et al. [5], Pujol et al.[10], Raba et al.[12]
2857 2918	2850	2853	2853	2848	C-H aliphatic	Reis et al.[5], Craig et al.[11]
2956	2930	2922	2922	2924	C-H aliphatic	Reis et al.[5], Craig et al.[11]
3322	3337	3337	3334	3339	O-H	Reis et al.[5]

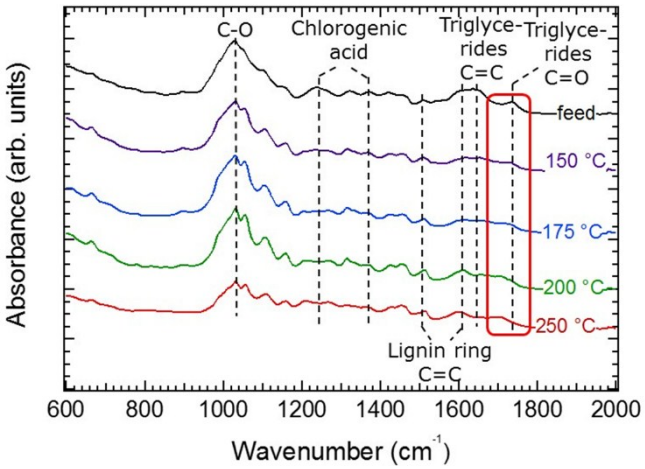

Figure SI-6. Raw ATR infrared spectra obtained for feed and feed treated at different FT-SWH temperatures (as indicated). Specific bands are highlighted for chemical content.

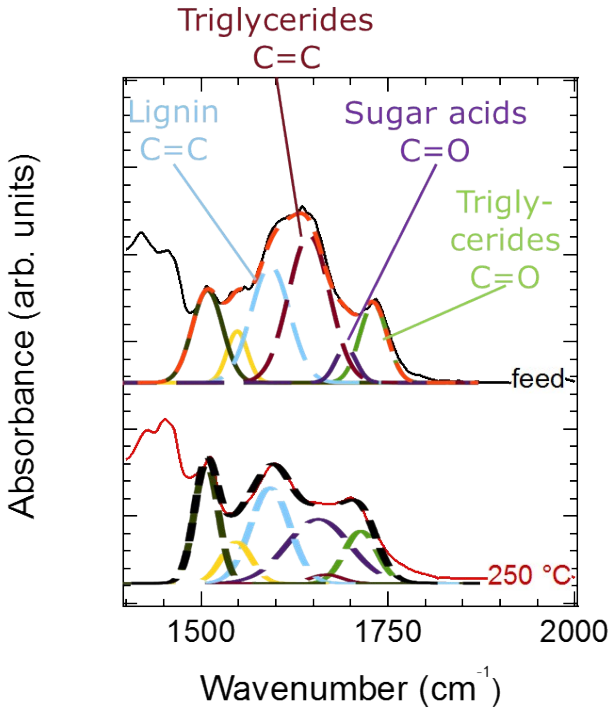

Figure SI-7. Curve fitting analysis of ATR infrared spectra for the feed and for biomass treated at 250 °C.

4. Analysis of Samples Obtained from Batch Experiments. Coffee powder was treated batch-wise at conditions comparable to those used for FT-SWH treatment (e.g., 175 and 200 °C). Figure SI-8 provides ATR-IR spectra obtained from batch-treated biomass at 175 °C showing retention of bands associated with semi-volatile content; in comparison, bands associated with semi-volatile content are not observed in the spectrum obtained from analysis of the sample treated under FT-SWH conditions. Figure SI-9 provides DTG data obtained from batch-treated samples and compares them to samples obtained from flow-through treatment. The char region is highlighted to show that the char content of samples treated under batch conditions is greater than that obtained under flow conditions.

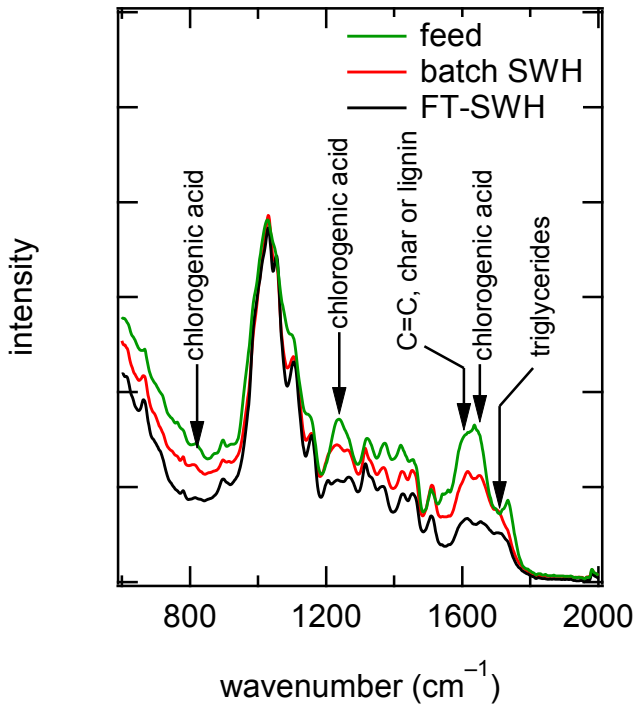

Figure SI-8. ATR-IR spectra obtained from analysis of the biomass feed, FT-treated biomass (175 °C), and batch-treated biomass (175 °C).

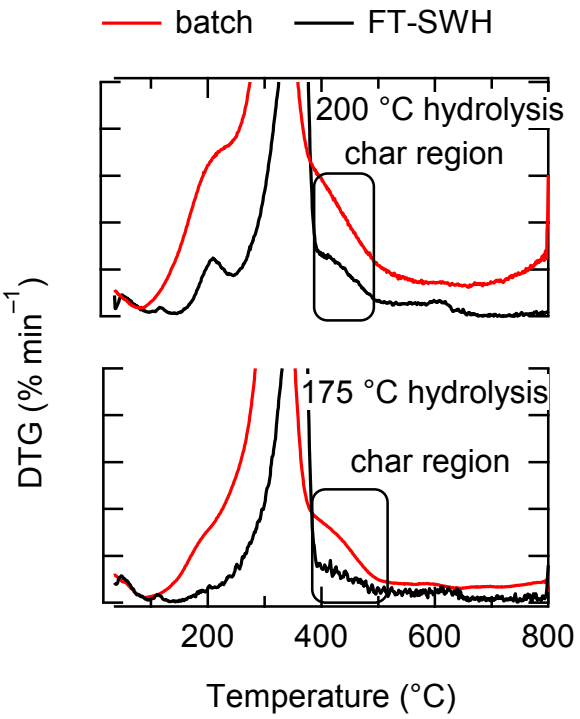

Figure SI-9. DTG data obtained from analysis of batch and FT-treated biomass at 175 and 200 °C.

References

1. A. Keidel, David von Stetten, Carla Rodrigues, Cristina Ma ´ Guas and P. Hilderbrandt, *J. Agric. Food Chem.*, 2010, 11187–11192.
2. A. B. Rubayiza and M. Meurens, *J. Agric. Food Chem.*, 2005, **53**, 4654-4659.
3. A. Sadezky, H. Muckenhuber, H. Grothe, R. Niessner and U. Poschl, *Carbon*, 2005, **43**, 1731–1742.
4. R. M. El-Abassy, Patrice Donfack and A. Materny, *Food Chemistry* 2011, **126**, 1443–1448.
5. N. Reis, Adriana S. Franca and L. S. Oliveira, *Talanta*, 2013, **115**, 563–568.
6. L. F. Ballesteros, J. A. Teixeira and S. I. Mussatto, *Food Bioprocess Technology*, 2014, **7**, 3493–3503.
7. S. Mishra, Poonam Tandon, Pinkie J. Eravuchira, Rasha M. El-Abassy and A. Materny, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2013, **104**, 358–367.
8. U. P. Agarwal and R. H. Atalla, in *Advances in Chemistry*, ed. D. D. Cyril Heitner, John Schmidt, CRC Press, 2010.
9. M. Hineno, *Carbohydrate Research*, 1977, **56**, 219-227.
10. D. Pujol, C. Liu, J. Gominho, M. A. Olivella, N. Fiol, I. Villaescusa and H. Pereira, *Industrial Crops and Products*, 2013, **50**, 423-429.

11. A. P. Craig, Adriana S. Franca and L. S. Oliveira, *LWT - Food Science and Technology*, 2012, **47**, 505-511.
12. D. N. Raba, M.-A. Poiana, A. B. Borozan, M. Stef, F. Radu and M.-V. Popa, *PloS one*, 2015, **10**, e0138080.