Supplementary material

One step catalytic conversion of polysaccharides in *Ulva prolifera* to Lactic Acid and value-added chemicals

*Mingyu Li, Yingdong Zhou, Changwei Hu**

Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu, Sichuan 610064, China

2. Materials and methods

2.3 Liquid products analysis

The liquid products in the aqueous phase filtrate were quantitatively analyzed by HPLC (waters e2695), equipped with an aminex column (Bio-Rad, HPX-87H, 300 mm × 7.8 mm) and a Refractive Index detector (Shodex, RI-101).

The molecular weight distribution of liquid products was analyzed using a gel permeation chromatography (GPC, Agilent, 1260 Infinity) equipped with a RI detector and a PL aquagel-OH column (Agilent).

ESI-MS (Shimadzu, LCMS-IT-TOF) analysis of liquid products was performed to determine the possible chemical structure of monomeric compounds and the oligomeric.

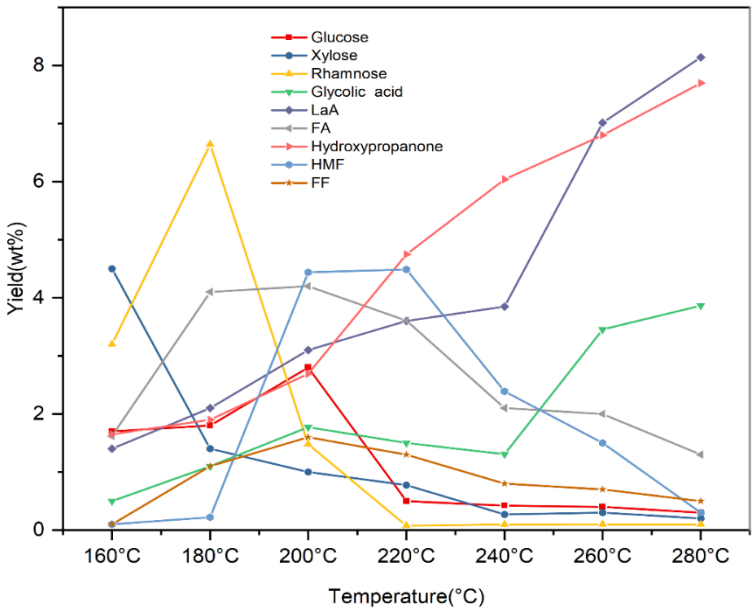

Figure S1. Yields of small molecular products from hydrothermal conversion of *U. prolifera* at different temperatures without YCl_3. Reaction conditions: 1.0 g of *U. prolifera*, 100 mL water, 2 MPa N_2, 1 h

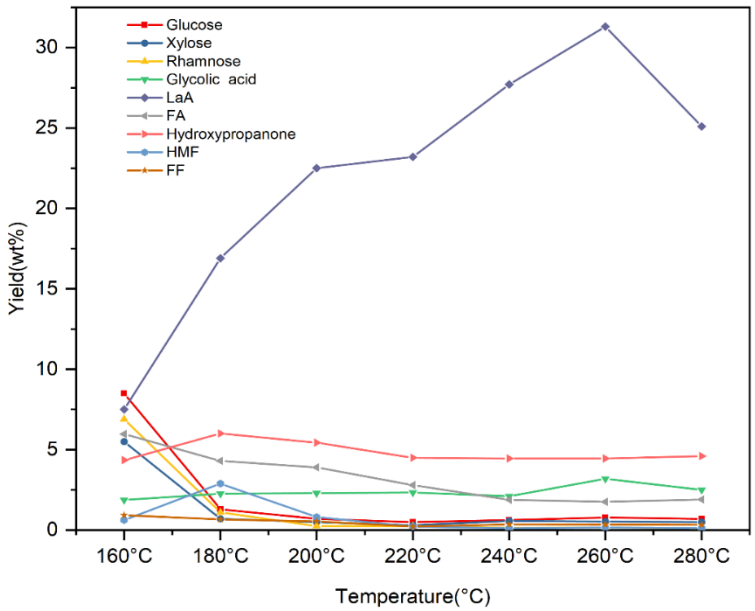

Figure S2. Yields of small molecular products from hydrothermal conversion of *U. prolifera* at different temperatures with YCl_3. Reaction conditions: 1.0 g of *U. prolifera*, 100 mL water, 13 mmol/L YCl_3 if used, 2 MPa N_2, 1 h

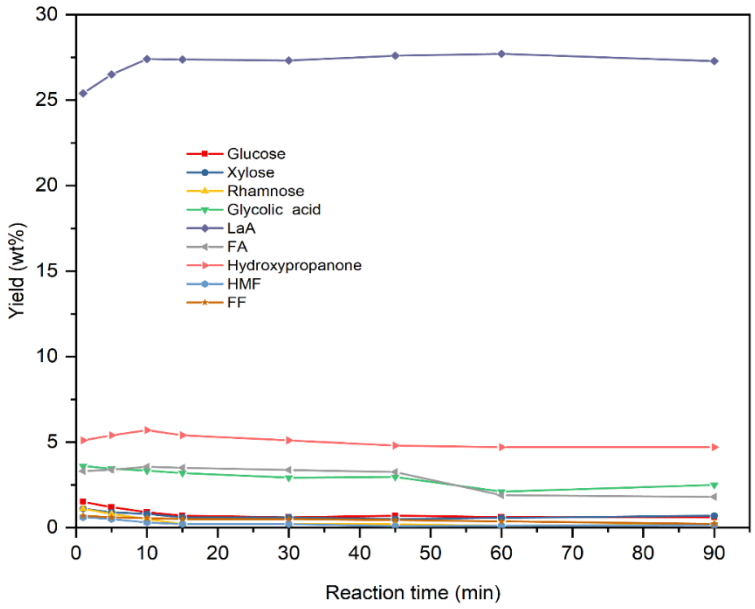

Figure S3. Yields of small molecular products from hydrothermal conversion of *U. prolifera* at different reaction time with YCl_3. Reaction conditions: 1.0 g of *U. prolifera*, 100 mL water, 13 mmol/L YCl_3 if used, 2 MPa N_2, 240 °C

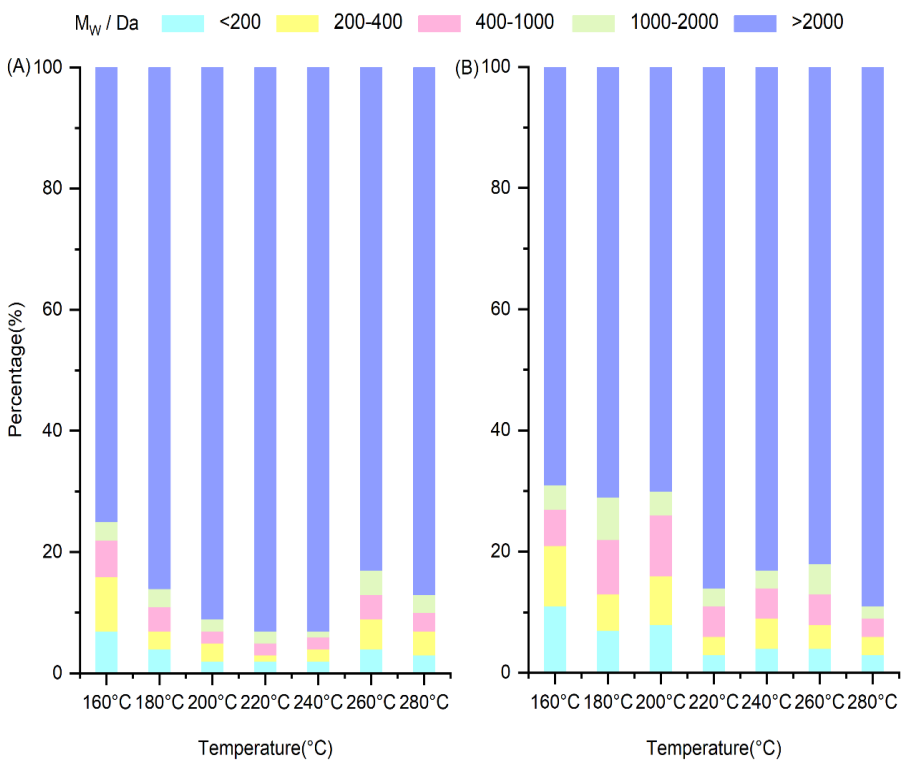

Figure S4. (A) Molecular weight distribution of liquid products from the conversion of *U. prolifera* at different temperatures with YCl_3. Reaction conditions: 1.0 g of *U. prolifera*, 100 mL water, 13 mmol/L YCl_3 if used, 2 MPa N_2, 1 h. (B) Molecular weight distribution of liquid products from the conversion of *U. prolifera* at different temperatures without YCl_3

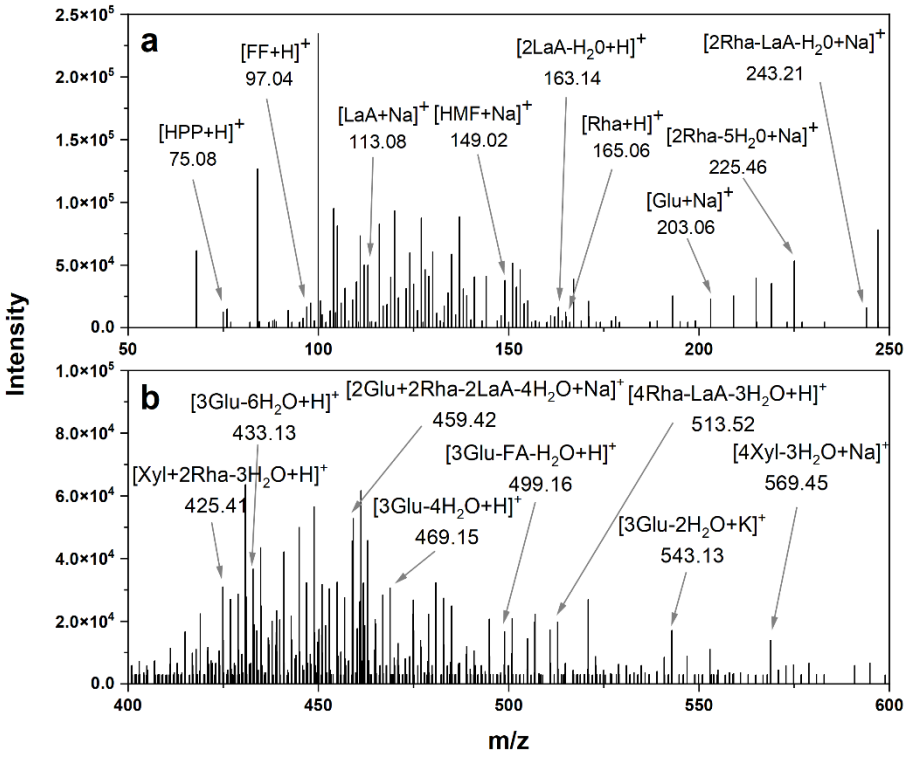

Figure S5. ESI-MS spectra (cation positive mode) of liquid products phase from the conversion of *U. prolifera* in the presence of 13mmol/L YCl_3 at 240 °C

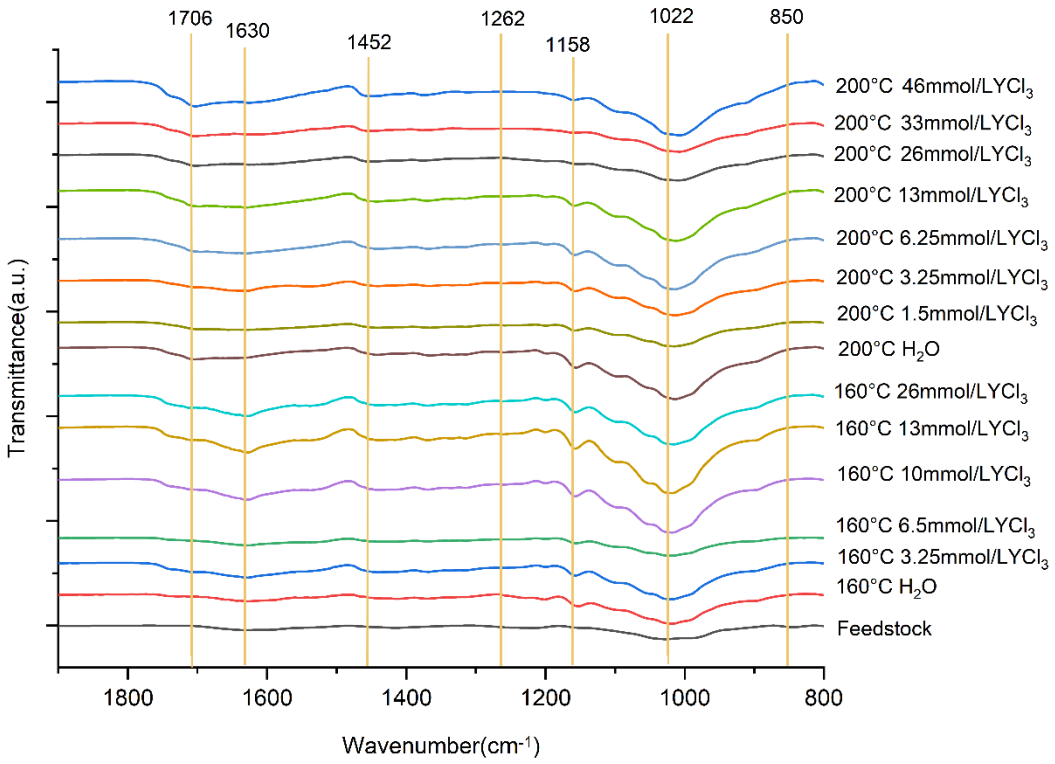

Figure S6. FT-IR spectra of *U. prolifera* feedstock and solid residue. Dry at 80 °C for 12 hours.

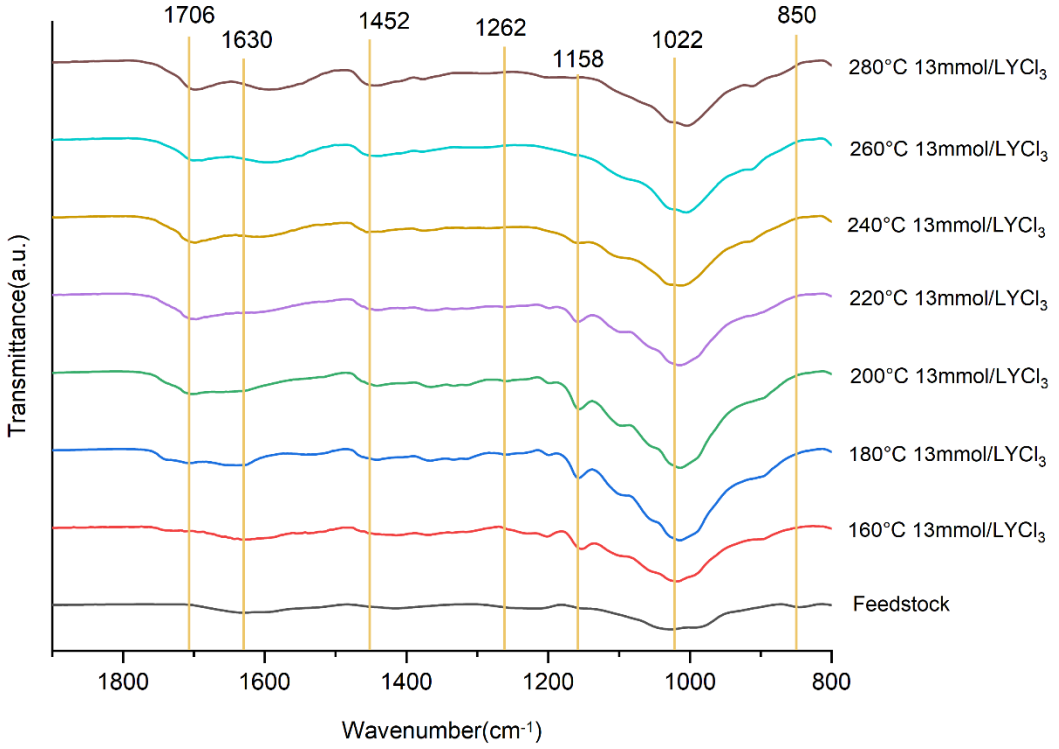

Figure S7. FT-IR spectra of *U. prolifera* feedstock and solid residue at different temperatures with 13 mmol/L YCl_3. Dry at 80 °C for 12 hours.

Table S1. Comparison of advantages and disadvantages of lactic acid prepared by different hydrothermal catalytic methods

Raw material	Catalyst	Time	Space time yield(%/min)	Advantages	Disadvantages	Reference
microcrystalline cellulose	400ppm-Ni	2 min	3.1	High space time yield, fast, reuse	Pure cellulose, complex process	[1]
xylan	ZrO_2	40 min	0.8	Low cost, simple operation, reuse	Pure xylan, low space time yield	[2]
rice straw	NiO, NaOH	2 h	0.5	Real biomass, high yield, simultaneous fractionation and conversion, low cost	Strong alkali, long time	[3]
corn stover	YCl_3	1 h	1.1	Real biomass, high selectivity, simultaneous fractionation and conversion, widely application	Difficult to reuse and separate	[4]
Ulva prolifera	YCl_3	10 min	3.1	Real biomass, simultaneous fractionation and conversion, high space time yield, low cost	Difficult to reuse and separate	This work

References

[1] L. Kong, G. Li, H. Wang, W. He, F. Ling, Hydrothermal catalytic conversion of biomass for lactic acid production, Journal of Chemical Technology & Biotechnology, 83 (2008) 383-388. https://doi.org/10.1002/jctb.1797

[2] L. Yang, J. Su, S. Carl, J.G. Lynam, X. Yang, H. Lin, Catalytic conversion of hemicellulosic biomass to lactic acid in pH neutral aqueous phase media, Applied Catalysis B: Environmental, 162 (2015) 149-157. https://doi.org/10.1016/j.apcatb.2014.06.025

[3] R. Younas, S. Zhang, L. Zhang, G. Luo, K. Chen, L. Cao, Y. Liu, S. Hao, Lactic acid production from rice straw in alkaline hydrothermal conditions in presence of NiO nanoplates, Catalysis Today, 274 (2016) 40-48. https://doi.org/10.1016/j.cattod.2016.03.052

[4] S. Xu, Y. Wu, J. Li, T. He, Y. Xiao, C. Zhou, C. Hu, Directing the Simultaneous Conversion of Hemicellulose and Cellulose in Raw Biomass to Lactic Acid, ACS Sustainable Chemistry & Engineering, 8 (2020) 4244-4255. https://doi.org/10.1021/acssuschemeng.9b07552

Table S2. The content of main metallic elements in ash

content（wt%）	Ca	K	Na	Mg	Fe
Ash	7.8	3.0	4.1	1.9	0.7

Table S3. The assignment of FT-IR peaks of *U. prolifera*

Wavenumber (cm^{-1})	Functional group	Vibration type of relative bond
1706	C=O	Amino bonds in proteins
1630	C=O	Uronic acid in sulfated polysaccharides
~1452	C-O	Uronic acid in sulfated polysaccharides
~1262	S=O	Sulfate ester group in sulfated polysaccharides
~1158	C-O-C	Cellulose and hemicellulose
~1022	C-O-C	lignin
850	C-O-S	Sulfate group in sulfated polysaccharides

Table S4. The content of main metallic elements in *Ulva prolifera* and Solid residue

content（wt%）	Ca	K	Na	Mg	Fe
Ulva prolifera	2.1	0.8	1.1	0.5	0.2
Solid residue (200 °C, 26mmol/L YCl_3)	4.3	0.7	0.8	1.2	0.4

Table S5. Yields of LaA (wt%) from separate hydrothermal conversion of xylose or rhamnose at different temperature with YCl_3

Temperature	rhamnose	xylose
140 °C	9.8	-[a]
160 °C	38.2	8.3
180 °C	38.3	16.3
200 °C	37.5	28.7
220 °C	-[a]	36.5
240 °C	-[a]	35.2

-[a]: not tested

Reaction conditions: 1.0 g of rhamnose/ xylose, 100 mL water, 26 mmol/L YCl_3, 2 MPa N_2, 1h

Table S6-1. The average of the data in Figure 1

Amount(mmol/L)	Glucose	Xylose	Rhamnose	Glycolic acid	LaA	FA	Hydroxypropanone	HMF	FF
0.0	0.9	4.5	3.2	0.5	1.4	1.6	1.7	0.1	0.1
3.3	1.5	4.8	11.2	0.9	1.7	3.2	1.9	0.1	0.4
6.5	2.1	5.1	10.9	1.2	3.1	3.9	3.0	0.3	0.8
10.0	7.1	5.4	7.7	1.4	6.7	4.6	4.4	0.5	0.9
13.0	8.5	5.5	6.9	1.9	7.5	4.7	4.3	0.6	0.9
26.0	9.2	4.8	2.0	2.1	11.8	4.8	4.9	1.5	1.0

Table S6-2. The standard deviation of the data in Figure 1

Amount(mmol/L)	Glucose	Xylose	Rhamnose	Glycolic acid	LaA	FA	Hydroxypropanone	HMF	FF
0.0	0.058	0.058	0.100	0.058	0.058	0.090	0.175	0.000	0.000
3.3	0.058	0.058	0.104	0.101	0.058	0.114	0.079	0.053	0.102
6.5	0.058	0.100	0.078	0.053	0.058	0.058	0.102	0.068	0.051
10.0	0.058	0.058	0.028	0.058	0.058	0.158	0.056	0.050	0.069
13.0	0.058	0.058	0.106	0.111	0.058	0.153	0.030	0.017	0.067
26.0	0.100	0.058	0.102	0.102	0.153	0.058	0.100	0.044	0.061

Table S7-1. The average of the data in Figure 2

Amount(mmol/L)	Glucose	Xylose	Rhamnose	Glycolic acid	LaA	FA	Hydroxypropanone	HMF	FF
0.0	0.5	0.3	1.5	1.8	3.1	3.3	2.7	5.6	1.6
1.5	0.7	0.5	0.8	1.9	6.2	3.6	4.8	5.6	1.6
3.3	1.1	0.8	0.6	2.0	6.8	3.7	4.9	2.6	1.2
6.5	1.3	0.8	0.3	2.6	17.8	3.8	5.2	2.2	0.8
13.0	1.5	0.9	0.2	2.7	22.5	3.9	5.4	0.8	0.5
26.0	1.6	0.9	0.2	2.7	30.4	5.0	5.4	0.3	0.3
33.0	1.6	0.9	0.2	4.2	27.7	4.9	5.5	0.4	0.4
46.0	1.7	1.0	0.2	4.1	27.6	4.7	5.6	0.5	0.6

Table S7-2. The standard deviation of the data in Figure 2

Amount(mmol/L)	Glucose	Xylose	Rhamnose	Glycolic acid	LaA	FA	Hydroxypropanone	HMF	FF
0.0	0.058	0.058	0.101	0.067	0.153	0.058	0.056	0.159	0.153
1.5	0.058	0.076	0.158	0.074	0.100	0.058	0.065	0.161	0.103
3.3	0.058	0.100	0.100	0.100	0.153	0.058	0.085	0.153	0.070
6.5	0.058	0.150	0.052	0.158	0.153	0.101	0.149	0.799	0.158
13.0	0.058	0.076	0.031	0.074	0.058	0.058	0.082	0.094	0.050
26.0	0.100	0.100	0.027	0.050	0.058	0.057	0.055	0.115	0.068
33.0	0.058	0.061	0.050	0.102	0.058	0.050	0.070	0.020	0.020
46.0	0.058	0.035	0.050	0.051	0.100	0.055	0.137	0.050	0.002

Table S8-1. The average of the data in Figure 3

T(°C)	Glucose	Xylose	Rhamnose	Glycolic acid	LaA	FA	Hydroxypropanone	HMF	FF
160°C	9.2	4.8	2.0	2.1	11.8	4.8	4.9	1.5	1.0
180°C	1.8	1.1	0.5	2.5	22.5	4.9	5.1	1.1	0.6
200°C	1.6	0.9	0.2	2.7	30.4	5.0	5.4	0.3	0.3
220°C	0.8	0.9	0.2	3.7	31.4	5.1	5.8	0.3	0.2
240°C	0.8	0.7	0.1	3.2	28.9	4.5	5.5	0.2	0.1
260°C	0.7	0.6	0.1	2.9	28.3	4.4	5.6	0.2	0.1
280°C	0.6	0.6	0.1	2.5	25.3	4.8	6.2	0.2	0.1

Table S8-2. The standard deviation of the data in Figure 3

T(°C)	Glucose	Xylose	Rhamnose	Glycolic acid	LaA	FA	Hydroxypropanone	HMF	FF
160°C	0.058	0.058	0.076	0.051	0.058	0.058	0.100	0.052	0.058
180°C	0.076	0.100	0.058	0.100	0.100	0.058	0.058	0.058	0.058
200°C	0.068	0.058	0.031	0.072	0.058	0.057	0.055	0.068	0.068
220°C	0.058	0.058	0.000	0.058	0.058	0.000	0.058	0.058	0.058
240°C	0.000	0.058	0.000	0.058	0.100	0.000	0.100	0.012	0.000
260°C	0.058	0.000	0.000	0.058	0.100	0.058	0.058	0.000	0.000
280°C	0.000	0.000	0.000	0.100	0.058	0.058	0.058	0.000	0.000

Table S9-1. The average of the data in Figure 4

T(°C)	Glucose	Xylose	Rhamnose	Glycolic acid	LaA	FA	Hydroxypropanone	HMF	FF
1.0	2.4	1.9	1.7	3.1	18.6	3.3	5.8	2.8	0.9
5.0	1.9	1.3	1.0	2.8	21.8	3.5	6.6	2.6	0.8
10.0	1.2	0.9	0.3	2.7	23.2	4.1	7.1	2.5	0.8
15.0	1.0	0.4	0.2	2.6	23.1	4.0	6.9	2.3	0.6
30.0	0.9	0.4	0.2	2.6	23.0	3.9	6.6	2.3	0.6
45.0	0.8	0.4	0.2	2.5	22.6	3.8	6.0	1.3	0.5
60.0	0.7	0.5	0.2	2.3	22.8	3.5	5.4	0.8	0.5
90.0	0.6	0.5	0.1	2.4	22.5	2.8	4.9	0.5	0.4

Table S9-2. The standard deviation of the data in Figure 4

T(°C)	Glucose	Xylose	Rhamnose	Glycolic acid	LaA	FA	Hydroxypropanone	HMF	FF
1.0	0.104	0.061	0.126	0.058	0.058	0.058	0.100	0.058	0.076
5.0	0.075	0.068	0.055	0.058	0.100	0.058	0.100	0.100	0.061
10.0	0.040	0.072	0.046	0.058	0.100	0.058	0.100	0.104	0.050
15.0	0.056	0.050	0.069	0.056	0.100	0.075	0.065	0.040	0.051
30.0	0.030	0.059	0.058	0.070	0.100	0.102	0.102	0.002	0.074
45.0	0.074	0.052	0.057	0.102	0.000	0.034	0.103	0.096	0.057
60.0	0.058	0.000	0.027	0.058	0.058	0.100	0.102	0.062	0.034
90.0	0.067	0.069	0.058	0.064	0.100	0.050	0.058	0.050	0.058

Table S10-1. The average of the data in Figure S1

T(°C)	Glucose	Xylose	Rhamnose	Glycolic acid	LaA	FA	Hydroxypropanone	HMF	FF
160°C	1.7	4.5	3.2	0.5	1.4	1.6	1.7	0.1	0.1
180°C	1.8	1.4	6.6	1.1	2.1	4.1	1.9	0.2	1.1
200°C	2.8	1.0	1.5	1.8	3.1	4.2	2.7	4.4	1.6
220°C	0.5	0.8	0.1	1.5	3.6	3.6	4.7	4.5	1.3
240°C	0.4	0.3	0.1	1.3	3.8	2.1	6.0	2.4	0.8
260°C	0.4	0.3	0.1	3.5	7.0	2.0	6.8	1.5	0.7
280°C	0.3	0.2	0.1	3.9	8.1	1.3	7.7	0.3	0.5

Table S10-2. The standard deviation of the data in Figure S1

T(°C)	Glucose	Xylose	Rhamnose	Glycolic acid	LaA	FA	Hydroxypropanone	HMF	FF
160°C	0.058	0.100	0.057	0.058	0.058	0.053	0.076	0.058	0.058
180°C	0.058	0.058	0.033	0.058	0.058	0.058	0.058	0.013	0.058
200°C	0.058	0.058	0.072	0.074	0.100	0.000	0.062	0.035	0.100
220°C	0.058	0.066	1.076	0.100	0.058	0.061	0.050	0.007	0.058
240°C	0.011	0.068	0.002	0.056	0.085	0.058	0.102	0.055	0.058
260°C	0.000	0.058	0.000	0.104	0.100	0.058	0.058	0.058	0.058
280°C	0.058	0.000	0.000	0.069	0.050	0.058	0.059	0.058	0.058

Table S11-1. The average of the data in Figure S2

T(°C)	Glucose	Xylose	Rhamnose	Glycolic acid	LaA	FA	Hydroxypropanone	HMF	FF
160°C	8.5	5.5	6.9	1.9	7.5	6.0	4.3	0.6	0.9
180°C	1.3	0.7	1.1	2.3	16.9	4.3	6.0	2.9	0.7
200°C	0.7	0.5	0.2	2.3	22.5	3.9	5.4	0.8	0.5
220°C	0.5	0.3	0.2	2.3	23.2	2.8	4.5	0.2	0.2
240°C	0.6	0.6	0.1	2.1	27.7	1.9	4.4	0.1	0.4
260°C	0.8	0.5	0.2	3.2	31.3	1.8	4.5	0.2	0.3
280°C	0.7	0.5	0.1	2.5	25.1	1.9	4.6	0.1	0.3

Table S11-2. The standard deviation of the data in Figure S2

T(°C)	Glucose	Xylose	Rhamnose	Glycolic acid	LaA	FA	Hydroxypropanone	HMF	FF
160°C	0.058	0.058	0.061	0.070	0.058	0.067	0.104	0.051	0.052
180°C	0.100	0.058	0.104	0.073	0.100	0.058	0.102	0.107	0.070
200°C	0.058	0.058	0.050	0.059	0.100	0.100	0.036	0.054	0.050
220°C	0.100	0.058	0.050	0.051	0.100	0.058	0.058	0.065	0.045
240°C	0.053	0.068	0.021	0.057	0.056	0.061	0.050	0.053	0.051
260°C	0.062	0.051	0.050	0.059	0.100	0.123	0.103	0.024	0.050
280°C	0.058	0.058	0.058	0.058	0.100	0.000	0.058	0.053	0.040

Table S12-1. The average of the data in Figure S3

Time(min)	Glucose	Xylose	Rhamnose	Glycolic acid	LaA	FA	Hydroxypropanone	HMF	FF
1.0	1.5	1.1	1.1	3.6	25.4	3.3	5.1	0.6	0.7
5.0	1.2	0.9	0.8	3.5	26.5	3.4	5.4	0.5	0.6
10.0	0.9	0.8	0.5	3.3	27.4	3.6	5.7	0.3	0.6
15.0	0.7	0.6	0.2	3.2	27.4	3.5	5.4	0.2	0.5
30.0	0.6	0.6	0.2	2.9	27.3	3.4	5.1	0.2	0.5
45.0	0.7	0.5	0.2	3.0	27.6	3.2	4.8	0.1	0.4
60.0	0.6	0.6	0.1	2.1	27.7	1.9	4.7	0.1	0.4
90.0	0.6	0.7	0.2	2.5	27.3	1.8	4.7	0.1	0.2

Table S12-2. The standard deviation of the data in Figure S3

Time(min)	Glucose	Xylose	Rhamnose	Glycolic acid	LaA	FA	Hydroxypropanone	HMF	FF
1.0	0.100	0.058	0.100	0.000	0.100	0.058	0.100	0.058	0.058
5.0	0.058	0.058	0.115	0.076	0.058	0.052	0.100	0.058	0.058
10.0	0.058	0.058	0.058	0.040	0.058	0.072	0.058	0.058	0.050
15.0	0.100	0.058	0.058	0.062	0.053	0.058	0.058	0.058	0.058
30.0	0.058	0.058	0.000	0.101	0.151	0.067	0.058	0.000	0.000
45.0	0.058	0.058	0.058	0.035	0.058	0.030	0.100	0.011	0.073
60.0	0.045	0.040	0.058	0.060	0.100	0.100	0.058	0.005	0.021
90.0	0.058	0.100	0.058	0.057	0.062	0.058	0.000	0.027	0.012