Supplementary information

Catalytic sugarcane bagasse transformation into a proper biocrude for hydrocarbons production in typical refinery processes

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Supplementary Section 1 - Material and methods

Chemicals, reagents, and standard compounds

Acetonitrile (HPLC grade), ammonium formate and sulfuric acid was purchased from Sigma-Aldrich (Brazil). Acetone was purchased from Isofar (Brazil). Ultrapure water was prepared by a Milli-Q water purification system. Glucose diacetal (DG; 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose) was purchased from Sigma-Aldrich (Brazil). Xylose diacetal (DX; 1,2:3,5-di-*O*-isopropylidene-α-D-xylofuranose) was synthesized as described previously.[1] Glucose monoacetal (MG; 1,2-*O*-isopropylidene-α-D-glucofuranose) and xylose monoacetal (MX; 1,2-*O*-isopropylidene-α-D-xylofuranose) were obtained from the hydrolysis of DG and DX, respectively.[1]

Sample preparation and analysis

The sugarcane bagasse SC1 and SC2 was washed with distilled water to remove residues of solid particles and sugarcane juice, dried at room temperature for 24 h and then in a drying oven under a temperature of 135 °C for a period of 2 h. The dried fibers were milled in a knife mill and separated to a particle size of 20-80 mesh (0.841 - 0.177 mm) for SC1 and 6-20 mesh (3.36 - 0.841 mm) for SC2. Then, 50 g of the sugarcane bagasse was washed with distilled water at 50 °C until no residual free saccharide was observed by direct-infusion in the mass spectrometer model API2000. Lastly, the sugarcane bagasse was dried in a drying oven at 100 °C until constant weight. The following conditions were used in the direct-infusion in the mass spectrometer: curtain gas (CUR) =

20 psi; spray voltage (IS) = 5000 V; source gas 1 (GS1) = 20 psi; source gas 2 (GS2) = 5 psi; potential of decluster (DP) = 100 V; input potential (EP) = 10 V; focusing potential (PF) = 400 V.

Bromatological analysis - humidity procedure

Approximately 1 g of the material was weighed into a capsule containing washed sand, and then both were homogenized. The set was taken into a drying oven at 105 °C for 2 h, then cooled in a desiccator for 20 min and weighed. The heating and cooling operation were repeated until the weight showed a change of less than 0.05%. In this procedure, the capsule together with the washed sand was previously dried at 105 °C for 2 h, then cooled in a desiccator for 20 min and weighed. The humidity percentage in the sample was obtained by the following Equation (1):

$$Humidity\ (\%) = \frac{(P_1 - P_2)\ x\ 100}{P_m} \quad (1)$$

P_1: Weight of the capsule with washed sand + Weight of the material;

P_2: Weight of the capsule with washed sand + Weight of the dry material;

P_m: Weight of the material.

Bromatological analysis - ashes procedure

1 g of material was weighed in porcelain crucible and it was placed in muffle at 450 °C until clear ashes was obtained. After the calcination, the set was cooled to room temperature for 15 min and then oven dried at 105 °C for 30 min. Lastly, it was cooled in a desiccator for 20 min and weighed. Initially, the crucible used was oven dried at 105 °C for 2 h, cooled in a desiccator for 20 min and weighed. The ashes percentage in the material was obtained by the following Equation (2):

$$Ashes\ (\%) = \frac{(P_1 - P_2)\ x\ 100}{P_m} \quad (2)$$

P_1: Weight of the porcelain crucible + Ashes;

P_2: Weight of the porcelain crucible;

P_m: Weight of the material.

Analysis of pretreated and residual sugarcane bagasse

Besides the bromatological analysis, the pretreated sugarcane bagasse SC1 and SC2 was also analyzed by thermogravimetry, performed on a TG209 F1 Iris Instrument equipment from Netzsch, with a temperature programming of 35 to 800 °C at a rate of heating of 10 °C min^{-1}. The analysis was carried out under a nitrogen balance protection flow of the 10 mL min^{-1}. The gas flow was 60 mL min^{-1} under an air atmosphere for pretreated sugarcane bagasse (SC1 and SC2) and under a nitrogen atmosphere for residual sugarcane bagasse. Approximately 10 mg of sample were used in this analysis.

Transmission Fourier transform infrared spectroscopy (FT-IR) was performed in a Thermo Scientific Nicolet 6700 FT-IR Infrared Spectrometer model Magna-IR 760 at a resolution of 4 cm^{-1}, number of scans = 16, DTGS detector KBr and region 4000-400 cm^{-1}, using KBr pellets. It was chosen to show all spectra only in the range of 2000-400 cm^{-1}.

The measurements of X-ray diffraction were performed in a Rigaku Ultima IV diffractometer with copper K_α x-ray (1.54 Å) and geometry θ - θ with radius of 185 mm. The values of the diffractograms were recorded increasing Bragg angles (2θ) from an angle of 5° to 80° with a pitch of 0.02° and a velocity of 10 °/s. Through the results obtained with the diffractogram, it was possible to estimate the crystallinity indexes of the fibers with the Equation (3) developed by Segal's empirical method[2].

$$CrI = \frac{(I_{002} - I_{am})}{I_{002}} \times 100 \quad (3)$$

CrI: Expresses the relative degree of crystallinity;

I_{002}: It is the maximum intensity of the (002) lattice diffraction (approximately 2θ between 22° and 23°);

I_{am}: It is the minimum intensity of diffraction with 2θ between 18° and 19°, representing amorphous part of lignocelluloses.

Scanning electron microscopy (SEM) was used to investigate the morphology of the pretreated sugarcane bagasse. It was used a JEOL JSM – 6510LV model in high vacuum and used with an acceleration voltage of 15 KV and a working distance of approximately 15 mm. Samples were metalized with carbon.

Physical-chemical characterization of the biocrude

The density was measured at room temperature (27.5 °C) and at temperatures of 40, 50, 65, 80 and 85 °C. Sample was weighed into a graduated vessel at each temperature. After weighing, the density was determined using the ratio of the measured mass (on an analytical balance with four decimals precision) and the filled volume of the vessel used.

The viscosity was determined by a rheometer (TA Instruments, model Discovery hybrid rheometer DHR-3) using steel Peltier plate of 40 mm diameter and a superior cone angle of 2.0°. Five measures were taken in peak hold of 40 to 80 °C, of 10 in 10 °C.

The specific calorific capacity was obtained using a calorimeter Pyris Diamond DSC (Perkin Elmer) coupled to a cooling accessory (Intracooler 2P) and a thermal analysis controller (TAC 7/DX). Specific heat measurement was performed at a temperature range of 15 to 75 °C with a heating rate of 10 °C min^{-1}. This analysis was performed in a nitrogen atmosphere under a flow of 20 mL min^{-1}.

The elemental analysis of CHN was performed by the elemental analyzer (Perkin Elmer 2400 series II) located in the Instrumentation Analytical Center of the University of São Paulo. The tests were performed in duplicate using 10 mg of sample in each of them. The samples were subjected to combustion in an atmosphere of pure oxygen, and the gases resulting from this combustion were quantified in a TCD (thermal conductivity detector) detector.

LC-MS analysis

The LC column used was Kinetex-C18 (150 mm× 3 mm, 2.6 μm particle size) maintained at 35 °C with the solvent flow rate of 350 μL min^{-1} and an injection volume of 5 μL.

- **Conditions of quantitative analysis**

Mass spectrometer used was a hybrid quadrupole-ion trap QTRAP 5500 (AB Sciex Instruments) with a turbo IonSpray ionization source operating in positive ion mode. Details of the experiment and analysis conditions are described elsewhere.[1]

- **Conditions of qualitative analysis**

Qualitative analysis was performed using an ultra-high-performance liquid chromatography system (Thermo Dionex UltiMate 3000) coupled to a high-resolution and accurate quadruple-Orbitrap hybrid mass spectrometer (Thermo QExactive Plus, Thermo Scientific) operating in both positive and negative electrospray ionization (ESI) modes.

The mobile phase was (A) 5 mM ammonium formate and (B) acetonitrile, where 0-2 min B 20%; 2-12 min B 80%; 12-14 min B 80%; 14.1-18 min B 20%. Simultaneous mass spectrometry full scan experiments in positive and negative ion modes were performed in the *m/z* range of 100-1000 at resolution of 70.000 (FWHM) combined with ddMS2 (data dependent analysis) experiments, where the three most intense ions of each scan were fragmented (MS^2) with normalized collision energy (NCE) ranging from 15-25. Source parameters were: spray voltage (IS) = +3.9 kV and -2.9 kV; source temperature = 350 °C; capillary temperature = 320 °C; S-lens = 60; sheath gas = 45; auxiliary gas = 15.

Due to their lack of protonation in positive ESI mode, most of the compounds were detected as ammonium adduct ions $[M+NH4]^+$. All identification was performed considering high accurate mass measurements (*m/z* error between the measured and theoretical values ≤5 ppm) and MS/MS experiment by collision-induced dissociation experiments.

Molecular networking analysis of biocrudes

Molecular Networking is one of the latest developments in tandem mass spectrometry data analysis used for compound structure elucidation and database matching. It relies on the comparisons of MS/MS fragmentation spectra across samples and the creation of a molecular network according to threshold values of spectra similarities. Precursor ions are labeled as nodes of the network and they are connected through edges according to spectra similarities, which shows the *m/z* differences between the nodes. One great advantage of using molecular networking for structure elucidation is the possibility to identify related structures due to similar MS/MS spectra. Thus providing insight of biomass transformation into biocrude for future works.

LC-MS/MS files obtained by data dependent MS/MS analysis were converted to mzXML format using MSConvert software and then imported into the GNPS platform to calculate the MN. MS/MS spectra were window filtered by choosing only the top 6 peaks in the +/- 50 Da window throughout the spectrum. The data was then clustered with MS-Cluster with a parent mass and fragment ion tolerance of 0.01 Da to create consensus spectra. Further, consensus spectra that contained less than 1 spectra were discarded. A network was then created where edges were filtered to have a cosine score above 0.7 and more than 3 matched peaks. Further edges between two nodes were kept in the network only if each of the nodes appeared in each other's respective top 10 most similar nodes.

Supplementary Section 2 - Figures

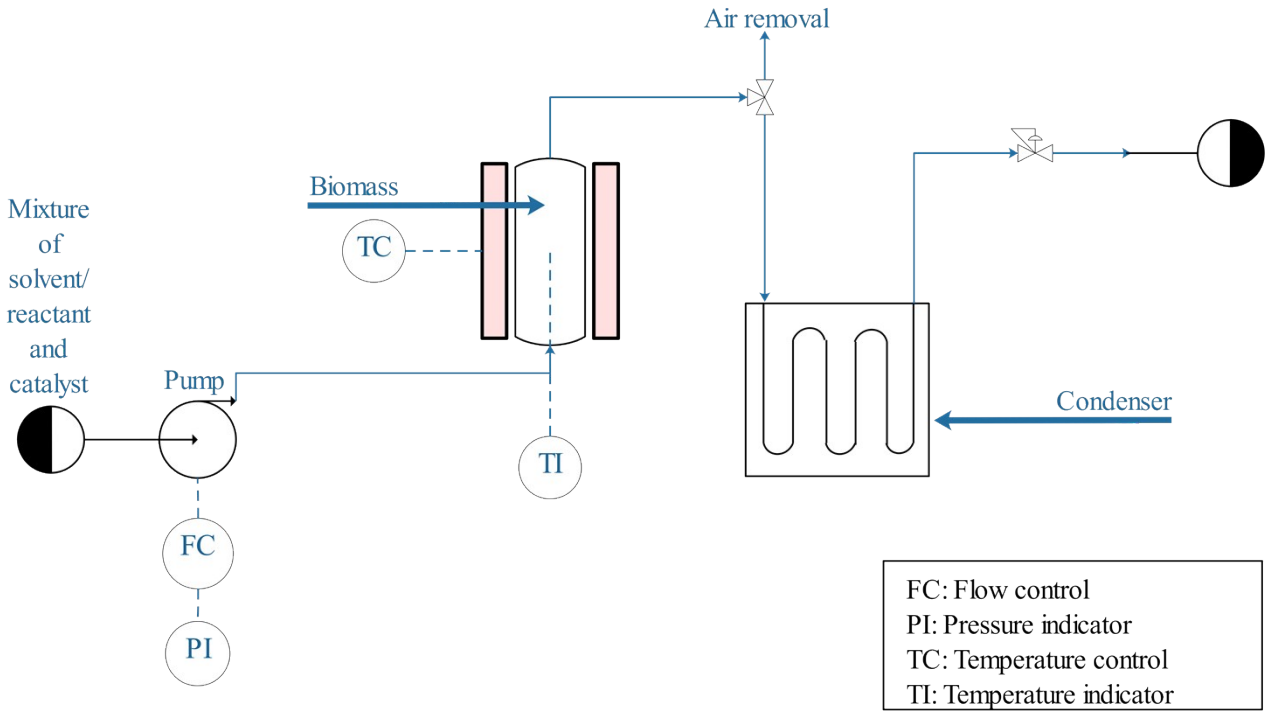

Figure S1. Semi-continuous system diagram for biocrude production.

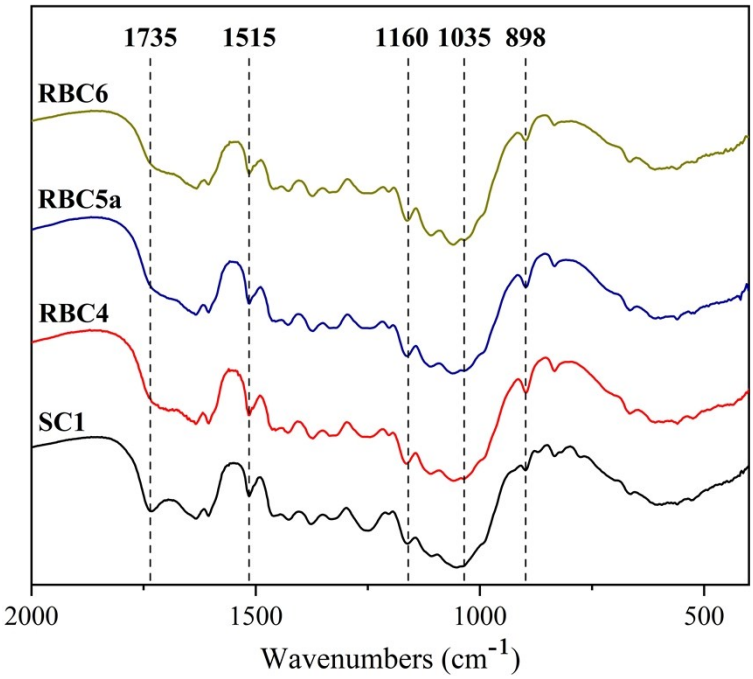

Figure S2. Infrared spectra of sugarcane bagasse SC1 and its residuals after submitted to different reaction conditions (RBC4, RBC5a and RBC6).

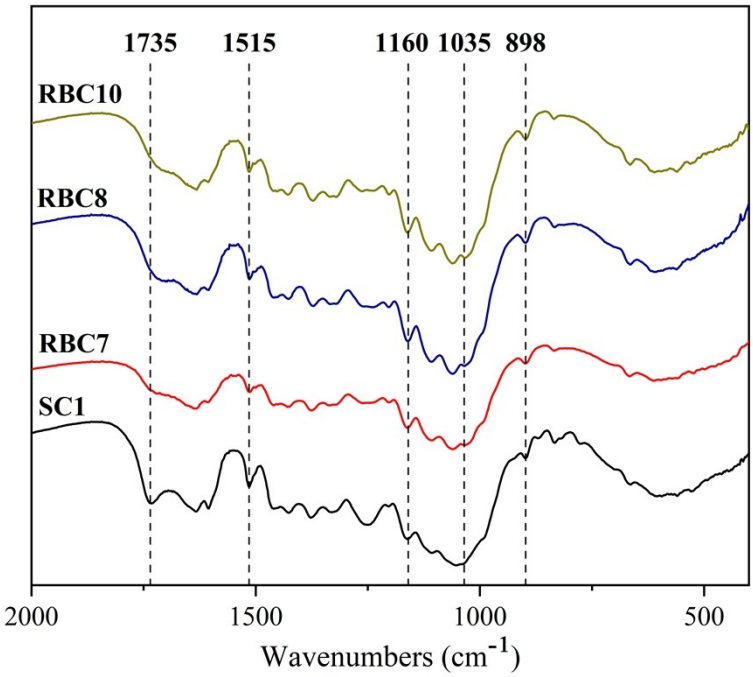

Figure S3. Infrared spectra of sugarcane bagasse SC1 and its residuals after submitted to different reaction conditions (RBC7, RBC8 and RBC10).

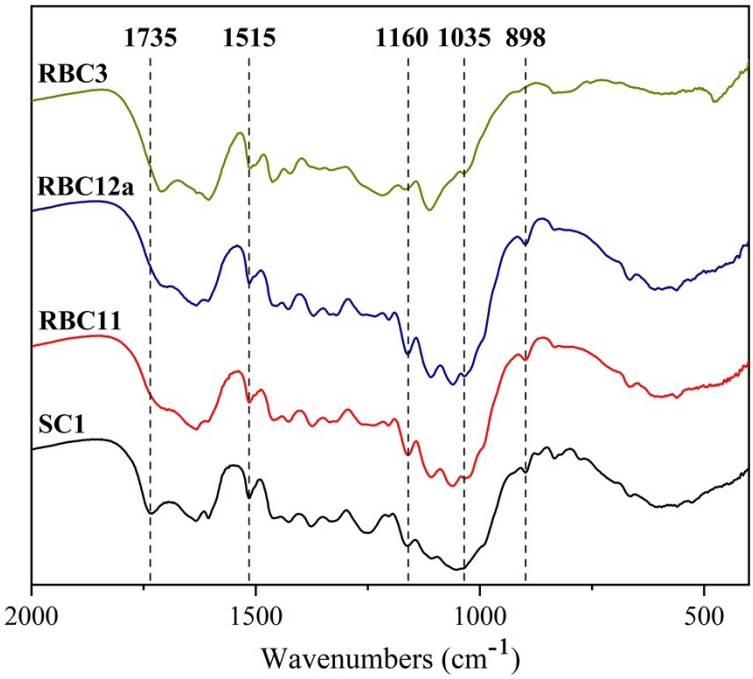

Figure S4. Infrared spectra of sugarcane bagasse SC1 and its residuals after submitted to different reaction conditions (RBC11, RBC12a and RBC3).

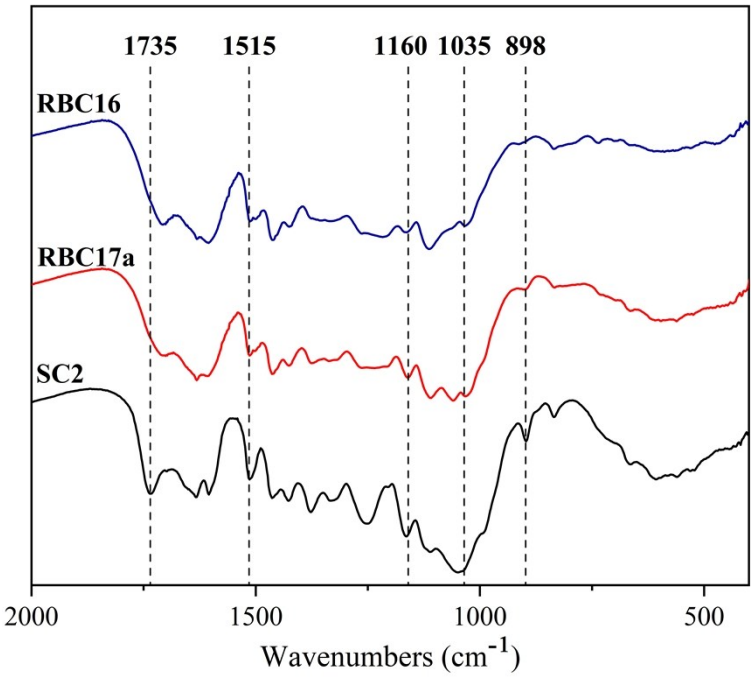

Figure S5. Infrared spectra of sugarcane bagasse SC2 and its residuals after submitted to different reaction conditions (RBC17a and RBC16).

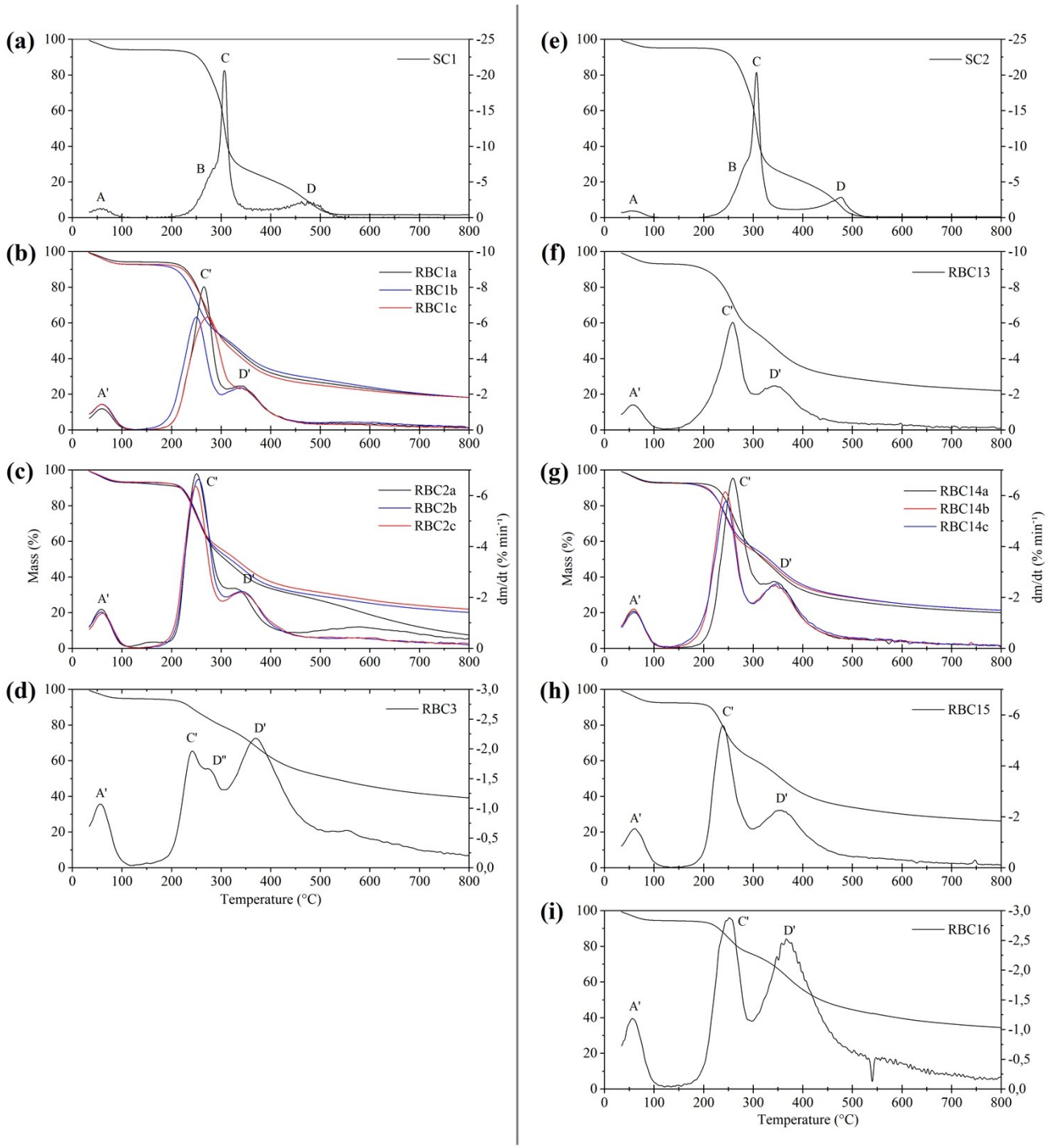

Figure S6. Thermogravimetry (TG) and differential thermogravimetry (DTG) analysis, under air atmosphere for SC1 and SC2, and under nitrogen atmosphere for residues, of reactions performed at 8.33 min residence time, 0.2% v/v acid concentration and reaction time of 1 h: (a) SC1; (b) residual sugarcane bagasse SC1 after reaction at 100 ºC; (c) residual SC1 after reaction at 120 ºC; (d) residual SC1 after reaction at 140 ºC; (e) SC2; (f) residual sugarcane bagasse SC2 after reaction at 100 ºC; (g) residual SC2 after reaction at 120 ºC; (h) residual SC2 after reaction at 140 ºC; (i) residual SC2 after reaction at 160 ºC. Profiles in triplicate are indicated in the figures. For experience made in triplicate the residue was named a, b, c, for example RBC1a, RBC1b and RBC1c are the residue of reactions BC1a, BC1b and BC1c, respectively.

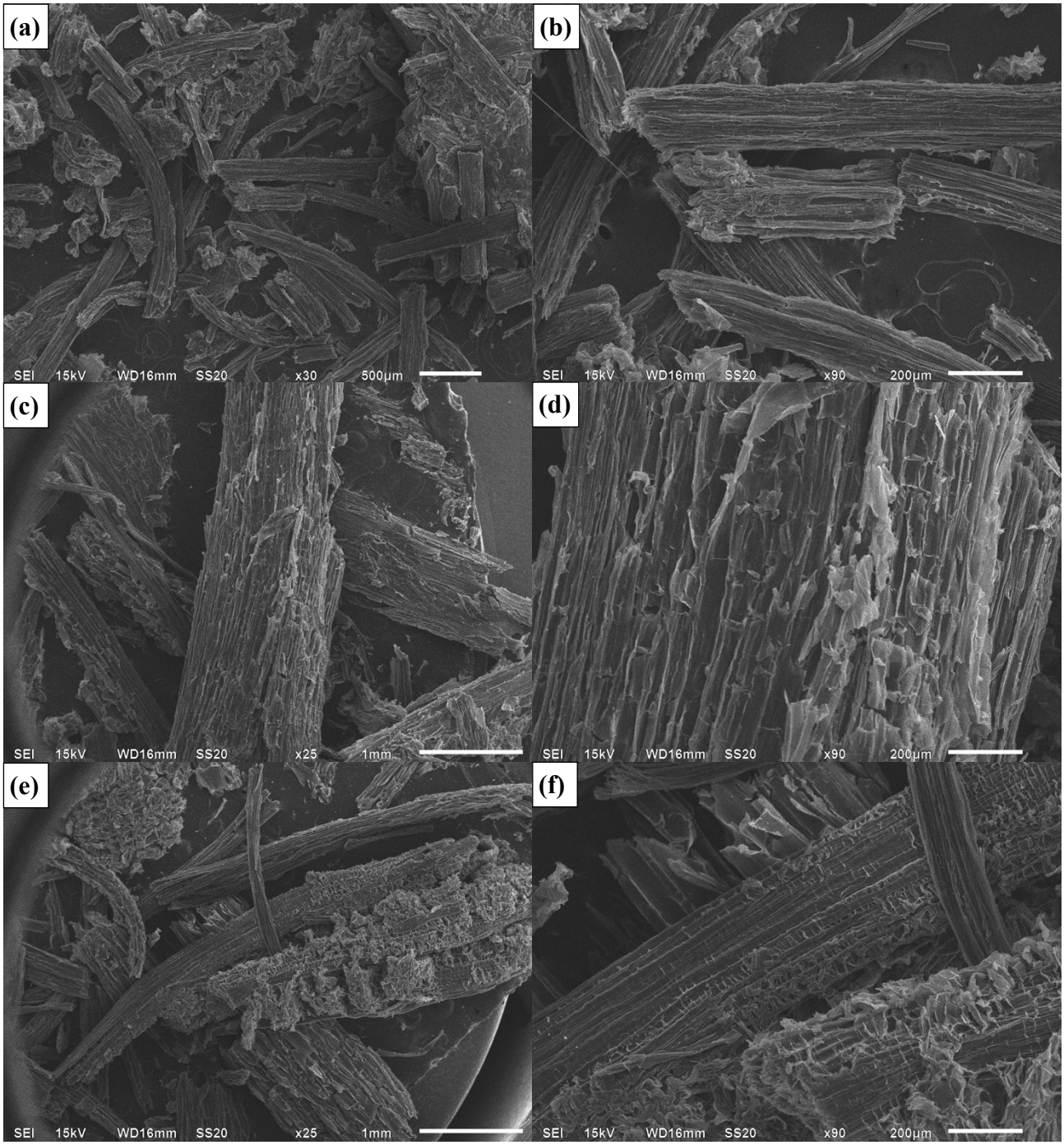

Figure S7. Scanning electron microscope (SEM) images of RBC3 (a-b), RBC15 (c-d) and RBC16 (e-f).

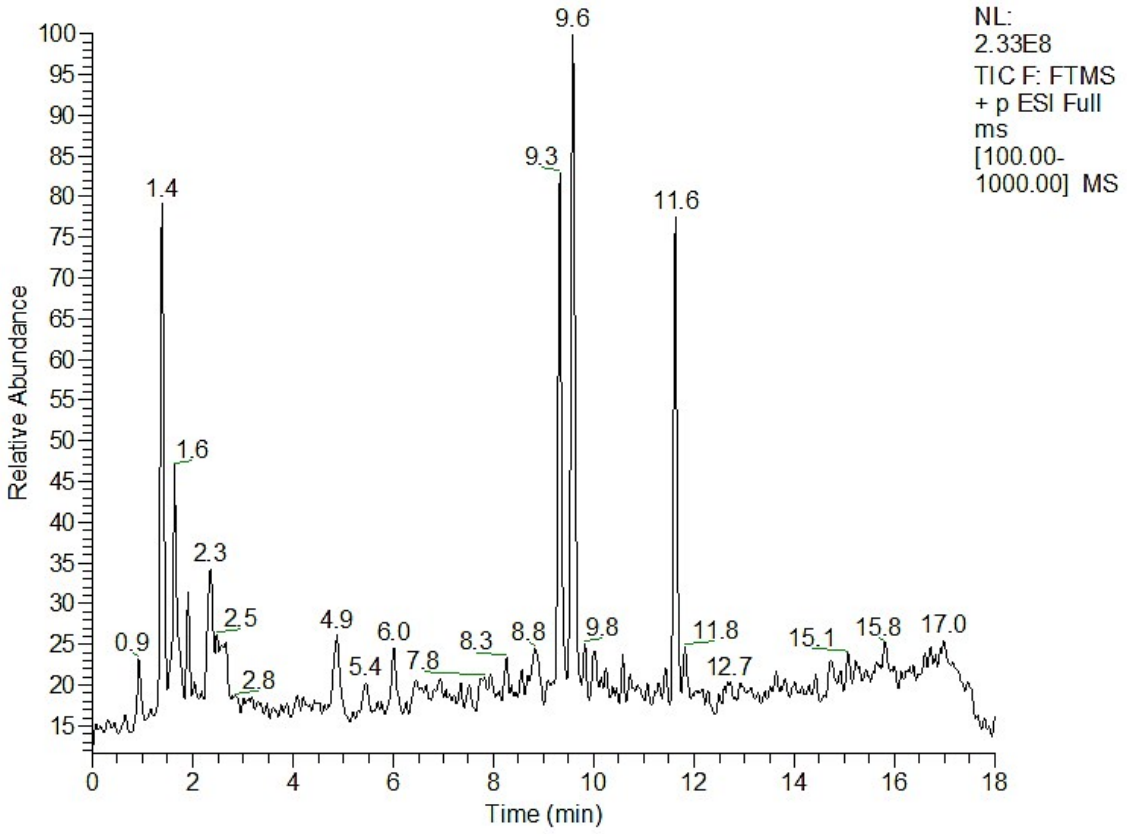

Figure S8. Representative LC-HRMS chromatogram in the positive electrospray ion mode (ESI +) of the biocrude BC10 (reaction conditions: temperature 100 °C; 8.33 min space time; 0.2% v/v acid concentration and time 1 h).

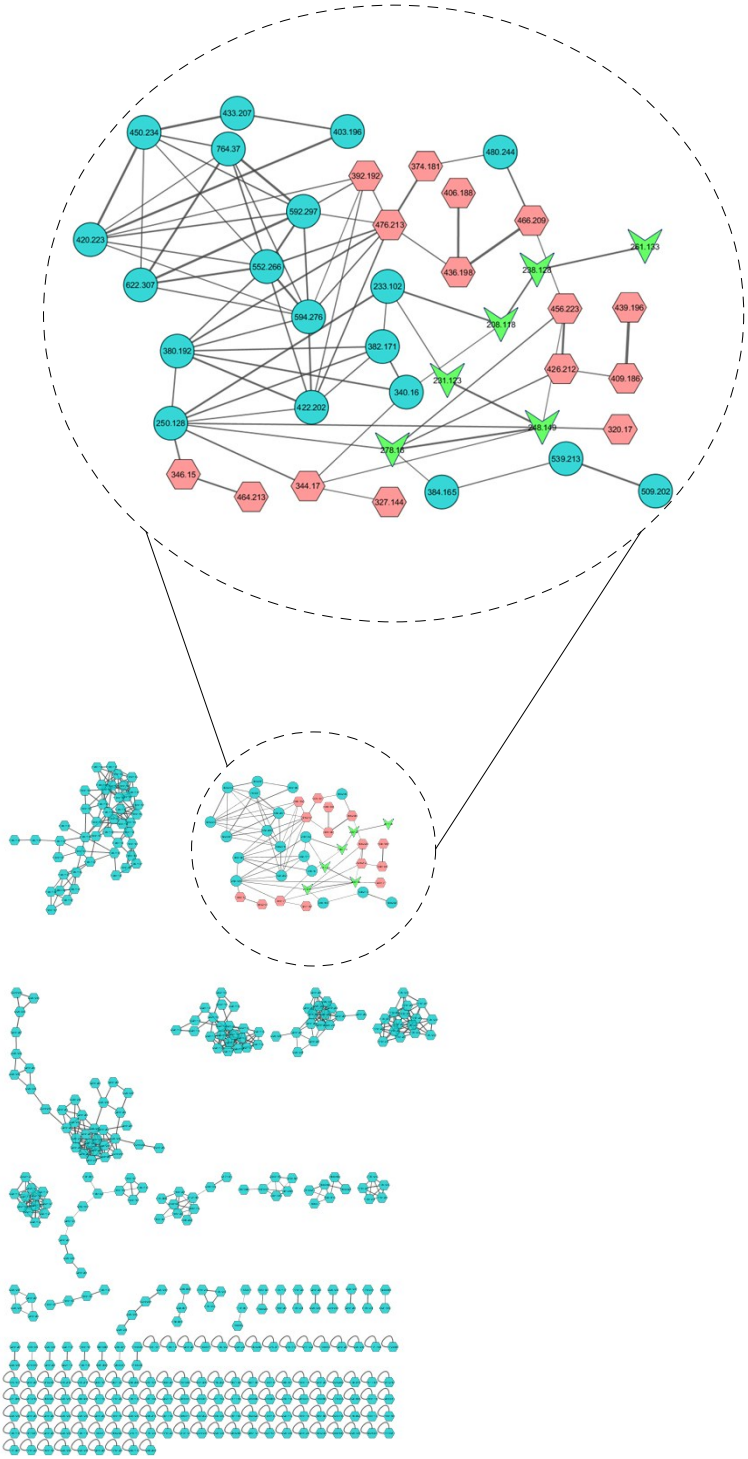

Figure S9. Total molecular network of biocrudes samples constructed using MS/MS fragmentation data from LC-HRMS analysis on positive electrospray ion mode. The region from carbohydrate acetonides is zoomed. Most of the network is composed by ions from the mobile phase or contaminants.

(a)

Sample	Content (%)			
	C	H	N	O*
BC1a	47.5	6.4	0.1	46.0
BC2a	51.5	6.9	0.1	41.5
BC3	55.3	6.9	0.1	37.7
BC10	54.4	6.9	0.1	38.6

* Oxygen content determined by subtraction.

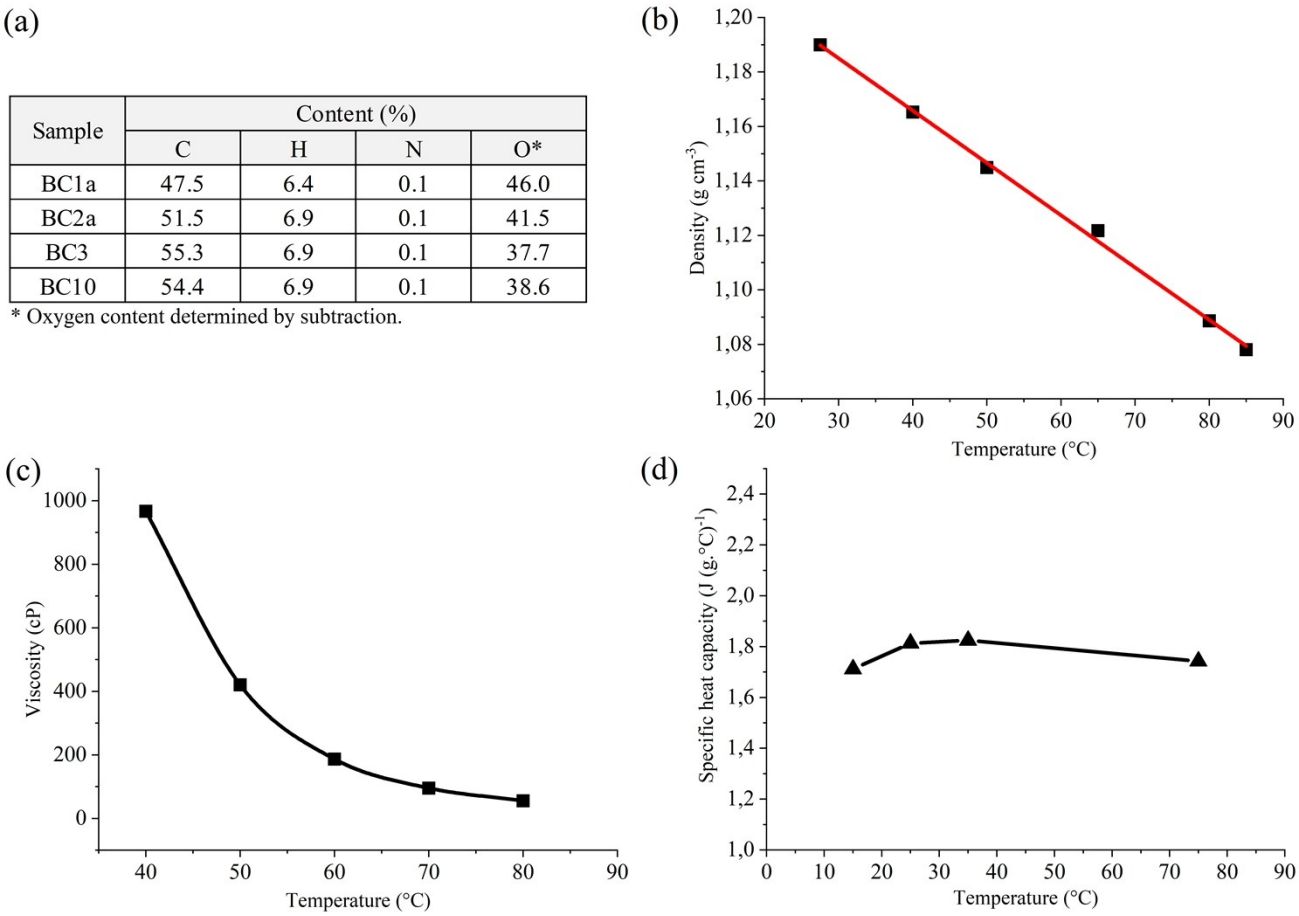

Figure S10. Biocrude properties: (a) Elemental composition (CHN) for biocrudes BC1a, BC2a, BC3 and BC10; (b) Density at 27,5-85 °C varied between 1.19-1.08 g cm^{-3} for BC10; (c) Viscosity at 40-80 °C varied between 966-55 cP for BC10; (d) Specific heat capacity at 15-75 °C varied between 1.712-1.743 J $(g.°C)^{-1}$ for BC10.

Supplementary Section 3 - Tables

Table S1. Thermogravimetric analysis of pretreated sugarcane bagasse SC1 and SC2.

Sample	Peak	Maximum peak temperature (°C)	Weight loss (%)	Residue (%)
SC1	**A**	56	5.9	1.8
	B	279	25.4	
	C	306	44.1	
	D	462	22.8	
SC2	**A**	53	5.0	0.5
	B	283	23.4	
	C	306	47.7	
	D	478	23.4	

Table S2. Reaction conditions for pretreated sugarcane bagasse SC1 and SC2 and related biocrudes and conversion.

Biomass	Sample*	Experimental conditions				
		T (°C)	**Sulfuric acid (% v/v)**	**Space time (min)**	**Time (h)**	**Conversion****
SC1	BC1 (a, b, c)	100	0.2	8.33	1	**39** (41/38/40)
	BC2 (a, b, c)	120	0.2	8.33	1	**59** (59/57/63)
	BC3	140	0.2	8.33	1	**90**
	BC4	100	0.2	5	1	**34**
	BC5 (a, b, c)	120	0.2	5	1	**45** (45/49/40)
	BC6	140	0.2	5	1	**61**
	BC7	100	0.2	8.33	2	**46**
	BC8	120	0.2	8.33	2	**63**
	BC9	100-140	0.2	8.33	1:30	**79**
	BC10***	120	0.2	29.28	1	**45**
	BC11	140	0.04	8.33	1	**66**
	BC12 (a, b, c)	140	0.12	8.33	1	**66** (58/68/73)
SC2	BC13	100	0.2	8.33	1	**35**
	BC14 (a, b, c)	120	0.2	8.33	1	**46** (48/44/47)

	BC15	140	0.2	8.33	1	**68**
	BC16	160	0.2	8.33	1	**79**
	BC17 (a, b, c)	160	0.04	8.33	1	**73** (74/71)

* Residue name of each experiment (sugarcane bagasse conversion data after conversion) was described as RBC in every discussion of this paper.
** When carried out in triplicate or duplicate, the average value is presented first, followed by conversion in each experiment. (a, b, c) after the samples indicates triplicate experiments.
*** Reaction carried out in large reactor (20 g of biomass: 20-fold higher compared to the other tests).

Table S3. Yield of biocrude (g), mass variation (wt.%) (defined as: (mass of biocrude - mass of converted biomass)/mass of biocrude), and quantification of 1,2-*O*-isopropylidene-α-D-xylofuranose and 1,2:3,5-di-*O*-isopropylidene-α-D-xylofuranose acetals (MX+DX), and 1,2-*O*-isopropylidene-α-D-glucofuranose and 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose acetals (MG+DG).

Sample	Biocrude (g)	Mass variation (wt.%)	MX+DX (%)	MG+DG (%)	Total (%)
BC1a	0.5148		31.29	7.96	39.25
BC1b	0.5767		25.17	12.77	37.94
BC1c	0.5742		22.20	15.49	37.69
BC1 (Average)	**0.5552**	**30**	**26.22**	**12.07**	**38.29**
BC2a	0.6422		18.84	16.21	35.05
BC2b	0.5684		15.79	13.23	29.02
BC2c	0.6649		13.74	15.79	29.52
BC2 (Average)	**0.6252**	**6**	**16.12**	**15.08**	**31.20**
BC3	**0.8900**	**-0.01**	**7.75**	**19.93**	**27.69**
BC4	**0.3561**	**5**	**28.48**	**6.99**	**35.46**
BC5a	0.5284		22.23	10.27	32.50
BC5b	0.7458		12.17	6.92	19.09
BC5c	0.5734		22.00	11.40	33.40
BC5 (Average)	**0.6159**	**27**	**18.80**	**9.53**	**28.33**
BC6	**0.7047**	**13**	**7.37**	**22.74**	**30.12**
BC7	**0.7299**	**37**	**21.93**	**16.77**	**38.70**
BC8	**0.9870**	**36**	**10.00**	**14.69**	**24.69**
BC9	**0.8134**	**3**	**14.55**	**16.43**	**30.98**
BC10	**9.2000**	**2**	**36.40**	**15.00**	**51.40**
BC11	**0.8006**	**18**	**10.04**	**17.07**	**27.11**
BC12a	0.7306		9.50	15.30	24.80
BC12b	0.8870		10.10	20.60	30.70
BC12c	0.8104		10.60	23.30	33.90
BC12 (Average)	**0.8093**	**13**	**10.07**	**19.73**	**29.80**
BC13	**0.4762**	**37**	**44.27**	**3.84**	**48.11**
BC14a	0.6794		36.67	3.12	39.78
BC14b	0.5576		36.55	2.04	38.59
BC14c	0.5789		40.26	1.93	42.19
BC14 (Average)	**0.6053**	**13**	**37.83**	**2.36**	**40.19**
BC15	**0.6969**	**37**	**15.46**	**22.39**	**37.85**

BC16	**1.0773**	**36**	**7.52**	**17.37**	**24.89**
BC17a	0.8557		11.45	20.77	32.22
BC17b	0.6546		17.83	13.68	31.51
BC17 (Average)	**0.7552**	**3**	**14.64**	**17.23**	**31.87**

Table S4. Yield (g) of 1,2-*O*-isopropylidene-α-D-xylofuranose (MX), 1,2:3,5-di-*O*-isopropylidene-α-D-xylofuranose (DX), 1,2-*O*-isopropylidene-α-D-glucofuranose (MG) and 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (DG) each 15 min for a total reaction time of 2 h using SC1 at 100 °C (BC7) and 120 °C (BC8), 8.33 min residence time and 0.2% v/v of acid concentration (sulfuric acid).

Sample	**Time (min)**	**Acetals yields (g)**				
		MX	**MG**	**DX**	**DG**	**Total**
BC7	**0**	0.0000	0.0000	0.0000	0.0000	0.0000
	15	0.0085	0.0007	0.0035	0.0059	0.0185
	30	0.0097	0.0005	0.0599	0.0384	0.1086
	45	0.0088	0.0028	0.0259	0.0157	0.0532
	60	0.0032	0.0007	0.0151	0.0128	0.0317
	75	0.0011	0.0004	0.0066	0.0084	0.0165
	90	0.0011	0.0006	0.0057	0.0105	0.0179
	105	0.0008	0.0004	0.0030	0.0068	0.0109
	120	0.0007	0.0005	0.0030	0.0097	0.0140
	135*	0.0006	0.0003	0.0027	0.0076	0.0112
	Total	**0.0345**	**0.0067**	**0.1255**	**0.1157**	**0.2825**
BC8	**0**	0.0001	0.0000	0.0002	0.0000	0.0003
	15	0.0046	0.0002	0.0068	0.0047	0.0164
	30	0.0131	0.0006	0.0495	0.0338	0.0970
	45	0.0000	0.0004	0.0073	0.0062	0.0139
	60	0.0018	0.0042	0.0013	0.0073	0.0146
	75	0.0000	0.0013	0.0045	0.0239	0.0297
	90	0.0010	0.0013	0.0037	0.0221	0.0281
	105	0.0000	0.0011	0.0027	0.0202	0.0241
	120	0.0000	0.0013	0.0020	0.0161	0.0194
	135*	0.0000	0.0000	0.0000	0.0002	0.0003
	Total	**0.0205**	**0.0103**	**0.0782**	**0.1346**	**0.2436**

* The point of 135 min refers to the residual biocrude inside the reactor after the reaction.

Table S5. Yield of 1,2-*O*-isopropylidene-α-D-xylofuranose and 1,2:3,5-di-*O*-isopropylidene-α-D-xylofuranose (MX + DX), and 1,2-*O*-isopropylidene-α-D-glucofuranose and 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (MG + DG) for a total reaction time of 1 h 30 min using SC1 at temperature ramps (100-140 °C) (BC9), 8.33 min residence time and 0.2% v/v of acid concentration (sulfuric acid).

Sample	**Temperature (°C)**	**Time (min)**	**Acetals yields (g)**		
			MX+DX	**MG+DG**	**Total**
BC9	**100**	**30**	0.0564	0.0278	0.0842
	120	**45**	0.0428	0.0296	0.0724

	120	**60**	0.0177	0.0321	0.0499
	140	**75**	0.0010	0.0441	0.0451
	140	**90**	0.0003	0.0001	0.0004
	-	**Total**	**0.1183**	**0.1337**	**0.2520**

Table S6. Compounds identified in the biocrudes by LC-HRMS/MS and molecular networking analysis.

ID	Compound name	Molecular Formula	Rt	m/z	Adduct	Error (ppm)	MS/MS fragments (HCD 12 for ESI+ and 25 for ESI-)
1	Xylose monoacetal	$C_8H1_4O_5$	2.0	208.11780	$[M+NH_4]^+$	0.7	173.081; 150.076; 132.065; 115.039; 73.029
2	Xylose diacetal (1)	$C_{11}H_{18}O_5$	7.9	248.14908	$[M+NH_4]^+$	0.7	231.122; 173.081; 155.070; 115.039
3	Pentose monoacetal acetate (2)	$C_{10}H_{16}O_6$	3.9	250.12827	$[M+NH_4]^+$	1.0	233.102; 175.060; 157.049; 115.039; 97.029
4	Dipentose monoacetal	$C_{13}H_{22}O_9$	1.8	340.15982	$[M+NH_4]^+$	1.1	232.133; 265.091; 229.070; 173.081; 133.049; 115.039
5	Dipentose monoacetal acetate	$C_{15}H_{24}O_{10}$	2.3	382.17032	$[M+NH_4]^+$	1.2	324.128; 307.102; 175.060; 115.039; 97.029
6	Dipentose diacetal	$C_{16}H_{26}O_9$	4.3	380.19119	$[M+NH_4]^+$	0.8	363.164; 305.1223; 287.112; 247.081; 173.081; 115.039
7	Dipentose diacetal acetate	$C_{18}H_{28}O_{10}$	8.6	422.20169	$[M+NH_4]^+$	0.9	405.175; 387.164; 347.133; 329.1222; 215.091; 97.029
8	Dipentose triacetal (3)	$C_{19}H_{30}O_9$	11.6	420.22232	$[M+NH_4]^+$	1.2	403.196; 345.154; 287.112; 201.075; 97.029
9	Tripentose triacetal	$C_{24}H_{38}O_{13}$	9.2	552.26532	$[M+NH_4]^+$	0.5	477.196; 419.155; 361.112; 345.154; 231.123; 173.081; 115.039
10	Tripentose triacetal acetate	$C_{26}H_{40}O_{14}$	11.2	594.27643	$[M+NH_4]^+$	1.3	519.208; 461.166; 433.155; 383.135; 215.091; 145.050
11	Tripentose tretracetal	$C_{27}H_{42}O_{13}$	13.3	592.29645	$[M+NH_4]^+$	0.1	575.270; 517.228; 459.186; 373.149; 315.107; 201.076; 115.039
12	Tetrapentose pentacetal	$C_{35}H_{54}O_{17}$	14.5	764.37000	$[M+NH_4]^+$	0.4	689.302; 631.260; 545.223; 487.181; 373.149; 201.076; 155.070
13	Pentose-glucuronic acid monoacetal	$C_{14}H_{22}O_{11}$	1.6	384.14957	$[M+NH_4]^+$	1.2	349.112; 271.080; 175.060; 157.049; 115.039
14	Pentose-ferulic acid monoacetal (4)	$C_{18}H_{22}O_8$	9.5	384.16483	$[M+NH_4]^+$	1.2	309.096; 177.054; 67.945
15	Dipentose-ferulic acid diacetal (5)	$C_{26}H_{35}O_{12}$	11.2	539.21210	$[M+H]^+$	0.4	481.170; 423.128; 309.096; 177.054
16	Dipentose-p-coumaric acid diacetal (6)	$C_{25}H_{32}O_{11}$	11.0	509.20230	$[M+H]^+$	1.1	451.160; 393.118; 279.086; 147.044; 115.039; 97.029
17	Glucose monoacetal	$C_9H_{16}O_6$	1.9	238.12817	$[M+NH_4]^+$	1.4	221.102; 203.091; 163.060; 145.050; 127.039; 97.029; 85.029
18	Glucose diacetal (7)	$C_{12}H_{20}O_6$	6.0	278.15945	$[M+NH_4]^+$	1.3	203.091; 185.081; 145.049;

							97.029; 59.050
19	Dihexose triacetal	$C_{21}H_{34}O_{11}$	9.2	480.24353	$[M+NH_4]^+$	0.8	463.216; 405.175; 387.164; 347.133; 261.133; 203.091; 127.039
20	Pentose-hexose triacetal (8)	$C_{20}H_{32}O_{10}$	10.0	450.23322	$[M+NH_4]^+$	0.3	433.206; 375.164; 357.154; 299.112; 231.122; 203.091
21	Dipentose-hexose tetracetal	$C_{28}H_{44}O_{14}$	11.3	622.30731	$[M+NH_4]^+$	0.6	547.239; 489.197; 433.207; 345.118; 231.087; 145.050; 97.029
22	Pentose-p-coumaric acid monoacetal	$C_{17}H_{18}O_7$	9.3	335.11395	$[M-H]^-$	1.0	277.072; 163.040; 145.029
23	Feruloylquinic acid	$C_{17}H_{18}O_9$	7.3	367.10364	$[M-H]^-$	0.5	307.082; 265.072; 235.061; 193.050; 175.040; 149.060
24	p-Coumaroylquinic acid	$C_{16}H_{18}O_8$	6.7	337.09329	$[M-H]^-$	1.2	277.072; 235.061; 163.039; 145.029; 119.049
25	p-Coumaric acid	$C_9H_8O_3$	4.4	163.03923	$[M-H]^-$	4.1	119.049; 97.730; 61.987
Rt = Retention time; (1) $[M+H]^+$ = 231.123; (2) $[M+H]^+$ = 233.102; (3) $[M+H]^+$ = 403.196; (4) $[M-H]^-$ = 365.124; (5) $[M-H]^-$ = 537.198; (6) $[M-H]^-$ = 507.188; (7) $[M+H]^+$ = 261.133; (8) $[M+H]^+$ = 433.207							

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