Electronic Supplementary Material (ESI) for Green Chemistry.

PILOT-SCALE HYDROTHERMAL PRETREATMENT AND OPTIMIZED SACCHARIFICATION ENABLES BISABOLENE PRODUCTION FROM MULTIPLE FEEDSTOCKS

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Table S1. Aromatic compounds detected in the untreated and PSR pretreated biomass using Py-GC/MS.

Num	Compound	Chemical formula	Retention time	Molecular weight	S_L*
1	guaiacol/mequinol/2-methoxyphenol	$C_7H_8O_2$	4.05	124	G
2	4-vinyl phenol (shows 2,3-dihydro benzofuran)-coumaran	C_8H_8O	7.65	120	H
3	p-ethylguaiacol (4-ethyl-2methoxy phenol)	$CH_{12}O_3$	9.42,10.19	152	G
4	4-vinylguaiacol (2-methoxy-4 vinyl phenol)	$C_9H_{10}O_2$	11.08, 11.7	150	G
5	2,6-dimethoxy phenol/syringol	$C_8H_{10}O_3$	12.8	154	S
6	Phenol, 2 methoxy-5-(2propenyl) 3-allyl-6-methoxyphenol	$C_{10}H_{12}02$	12.95	164	G
7	isovanillin/p-arisaldehyde	$C_8H_8O_3$	13.70, 14.15	152	G
8	Phenol 2, methoxy-5 (1 propenyl)	$C_{10}H_1I_{22}$	14.23	164	G
9	4-methoxy-3-methoxymethyl phenol	$C_9H_{12}O_3$	15.03	168	G
10	2-methoxy-5-(1-propenyl)-phenol (E)	$C_{10}H_{12}O_2$	15.17	164	G
11	vanillic acid	$C_8H_8O_4$	15.06	168	G
12	4-propenyl guaiacol (2-methoxy-4-propenyl phenol) isoeugenol	$C_{10}H_{12}O_2$	15.19	164	G
13	2-methoxy-4-methyl phenol (creosol)	$C_8H_{10}O_2$	6.27	137	G
14	4 hydroxy-3-methoxyphenylpropane, 2, methoxy-4 propyl phenol	$C_{10}H_{14}O_4$	13.23, 15.31	166	G
15	Phenol, 4-(3-hydroxy-1propenyl-2methoxy)	$C_{10}H_{12}O_3$	16.58, 17.33	180	G
16	3-tert-butyl-4-hydroxyarisole	$C_{11}H_{16}O_2$	17.12	180	G
17	phenol, 2,6 dimethoxy-4-(2-propenyl) (4-allyl-2,6-dimethoxy phenol)	$C_{11}H_{14}O_3$	19.03	194	S
18	phenol, 2,6 dimethoxy-4-(2-propenyl) (4-allyl-2,6-dimethoxy phenol)	$C_{11}H_{14}O_3$	17.31, 17.64, 18.01, 18.72, 19.03	194	S
19	phenol, 2,6 dimethoxy-4-(2-propenyl) (4-allyl-2,6-dimethoxy phenol)	$C_{11}H_{14}O_3$	17.64	194	S
20	phenol, 2,6 dimethoxy-4-(2-propenyl) (4-allyl-2,6-dimethoxy phenol)	$C_{11}H_{14}O_3$	18.33	194	S
21	4-hydroxy-3,5-dimethoxy benzaldehyde (galladehyde)	$C_9H_{10}O_4$	18.52	182	S
22	acetosyringone (4-hydroxy-3,5-dimethoxy acetophenone)	$C_{10}H_{12}O_4$	19.46	196	S

*S_L = Lignin subunits, *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S).

Table S2. Variables and responses of the experimental design matrix of the reduced response surface model for the saccharification of PSR pretreated biomass.

Factor 1	Factor 2	Factor 3	Glucose conversion (%)			
A: Temperature	B: pH	C: Enzyme loading (mg /g glucan)	Agave bagasse	Corn stover	Sugarcane bagasse	Wheat straw
45.0	5.25	27.5	50.1	72.2	49.6	49.6
48.0	5.7	40.9	66.9	60.9	50.8	50.8
48.0	4.8	14.1	44.2	73.1	36.8	36.75
48.0	5.7	14.1	51.4	71.8	40.0	40.0
48.0	4.8	40.9	60.9	63.5	49.5	49.5
52.5	5.25	4.96	40.2	59.9	27.7	27.7
52.5	5.25	27.5	74.4	53.3	51.2	51.2
52.5	4.50	27.5	54.0	72.2	49.1	49.1
52.5	5.25	27.5	69.5	73.8	50.5	50.5
52.5	5.25	27.5	70.3	75.0	49.4	49.4
52.5	5.25	27.5	66.9	74.7	47.7	47.9
52.5	5.25	50.0	76.1	72.2	83.7	83.7
52.5	5.25	27.5	66.9	69.7	45.5	45.5
52.5	5.25	27.5	62.6	69.0	49.2	49.2
52.5	6.0	27.5	56.9	60.6	48.9	48.9
57.0	4.8	14.1	31.8	46.3	29.5	29.5
57.0	5.7	14.1	33.6	57.8	26.8	26.8
57.0	4.8	40.9	55.2	46.7	38.3	38.3
57.0	5.7	40.9	54.4	57.1	42.2	42.2
60.0	5.25	27.5	44.3	52.5	33.7	33.7

Table S3. Pearson's correlation coefficient (r) between % xylan and % lignin content from S/G ratio, crystallinity index (CrI), "ash free" energy density (EDa) and molecular weight (MW) from untreated and pretreated biomass.

	S/G ratio	**CrI**	**EDa**	**MW**
Xylan (%)	-0.641	-0.197	-0.676	-0.878**
Lignin (%)	0.440	0.405	0.811*	0.899**

* and ** indicate significant differences at $P < 0.05$ and 0.01, respectively.

Table S4. Pearson's correlation coefficient (r) between % glucose conversion and % xylan, crystallinity index (CrI), S/G ratio, "ash free" energy density (EDa) and molecular weight (MW) from untreated and pretreated biomass.

	% Xylan	**CrI**	**S/G ratio**	**EDa**	**MW**
% Glucose conversion	-0.726*	0.459	0.226	0.674	0.936**

* and ** indicate significant differences at $P < 0.05$ and 0.01, respectively.

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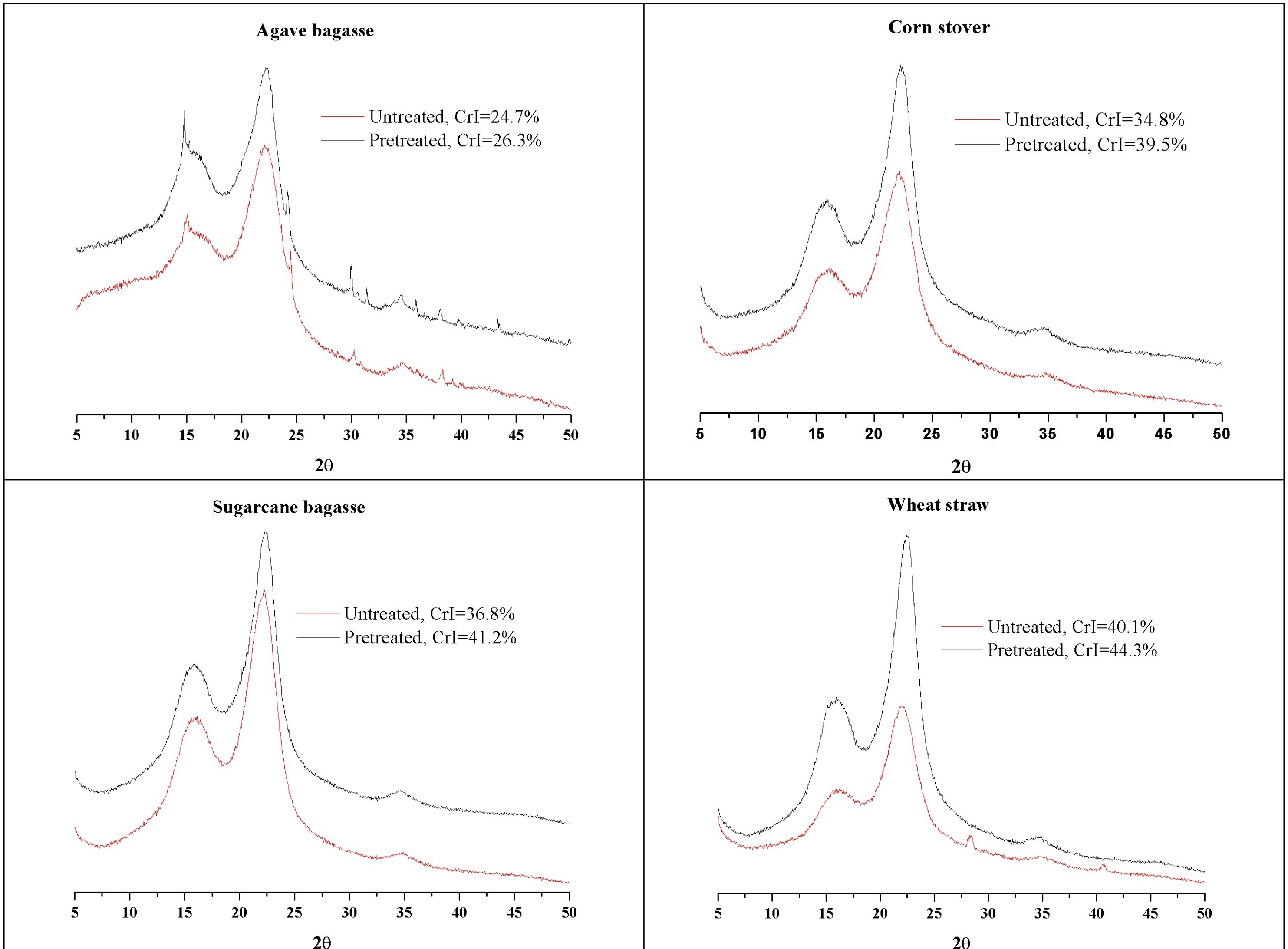

Figure S1. X-ray diffraction patterns of untreated and PSR pretreated biomass.

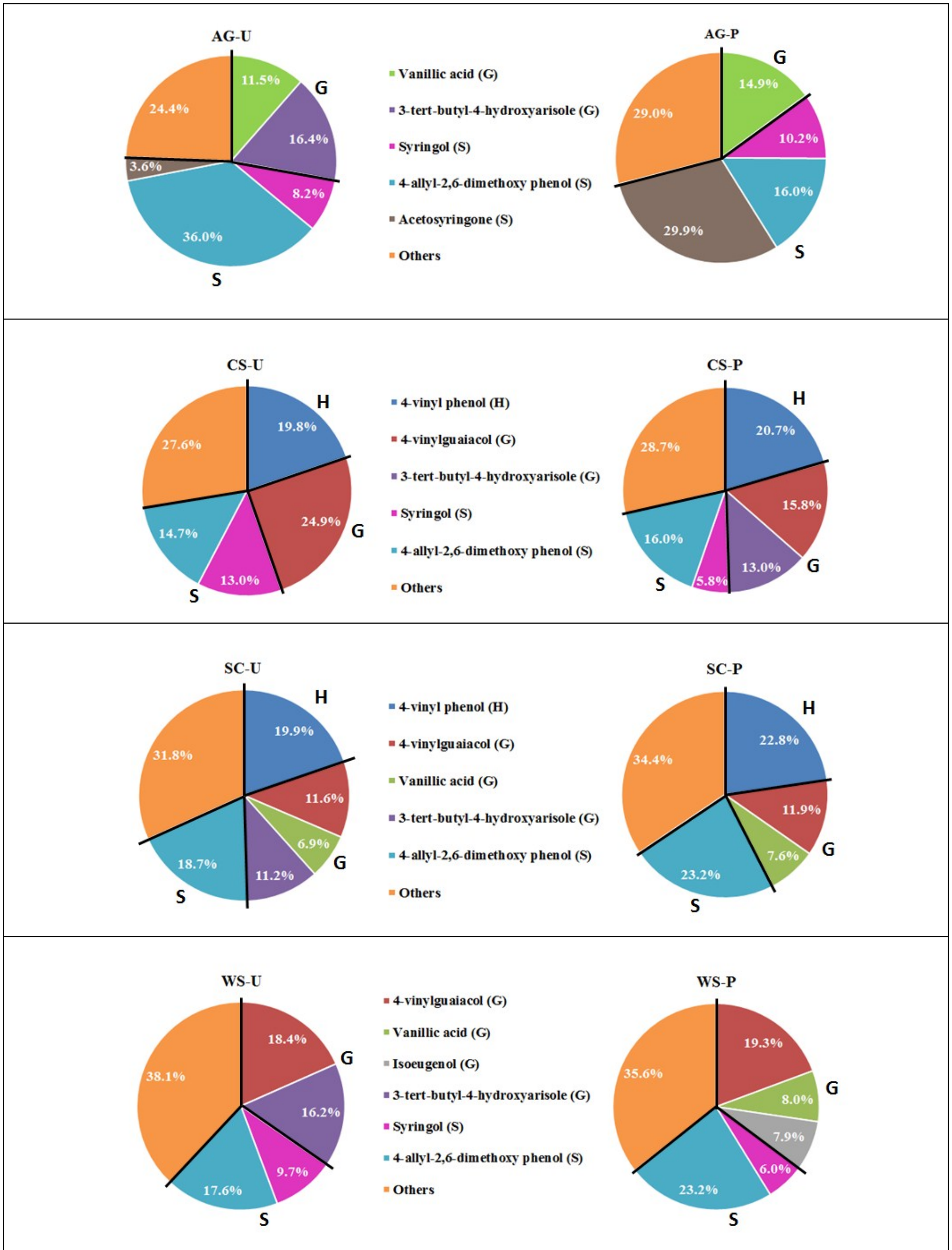

Figure S2. Relative abundance (%) of the main aromatic components detected by Py-GC/MS of untreated (U) and pretreated (P) agave bagasse(AG), corn stover (CS), sugarcane bagasse (SC), and wheat straw (WS). *Letters in parentheses correspond to lignin subunits as *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S).

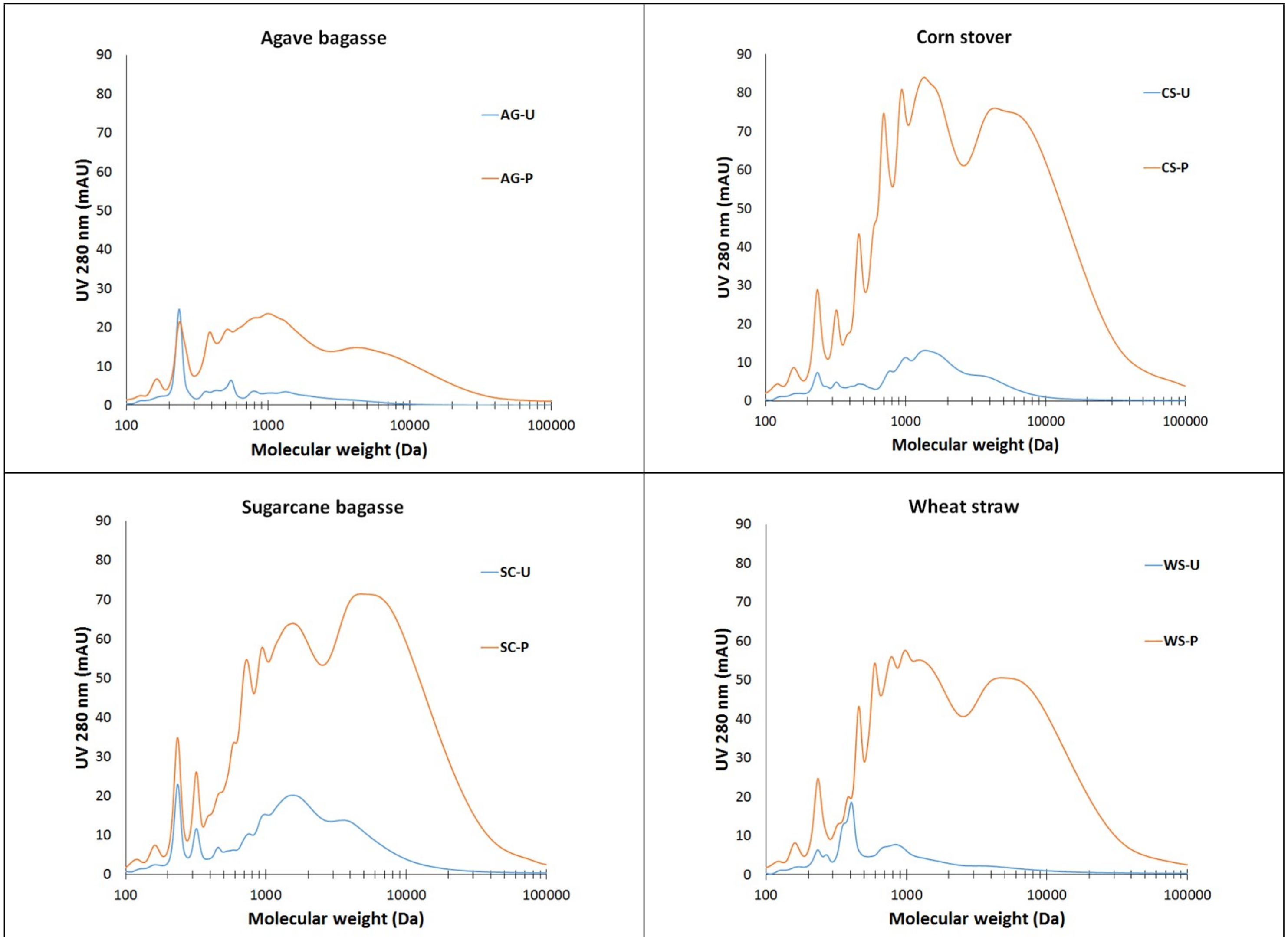

Figure S3. Molecular weight distribution obtained by gel permeation chromatography (GPC) of untreated (U) and pretreated biomass (P).

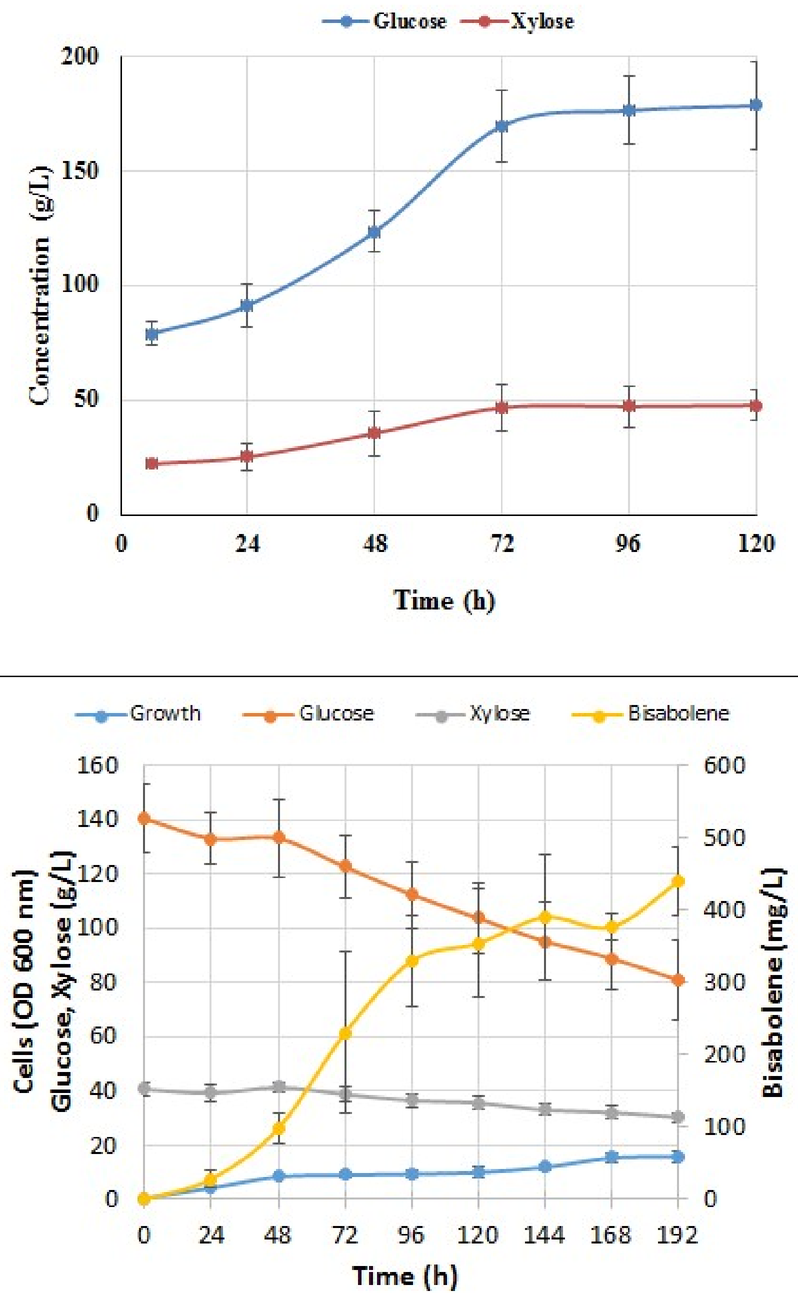

Figure S4. Release of glucose and xylose during 120-hour saccharification by applying a pulse-feeding strategy from 20 to 35% solids (top), sugar consumption and bisabolene production by fermentation with *Rhodosporidium toruloides* using the pulse-feeding hydrolysate from pretreated WS (bottom).