Electronic Supporting Information

Highly efficient and selective CO_2-adjuncted dehydration of xylose to furfural in aqueous media with THF

Ana Rita C. Morais[1,2] and Rafal Bogel-Lukasik[1*]

[1] Unidade de Bioenergia, Laboratório Nacional de Energia e Geologia, I.P., Estrada do Paço do Lumiar 22, 1649-038 Lisboa, Portugal. *e-mail: rafal.lukasik@lneg.pt; fax: +351217163636; phone: +351210924600 ext. 4224

[2] LAQV/REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

Experimental and material section

Material and chemicals

The CO_2 used in experiments was purchased from Air Liquid, AlphaGaz™ gamma, Paris, France with ≥ 99.99 % purity (w/w). For all reactions and chemical analyses the following reagents were used: distilled water (18.2 MΩ/cm) was produced by the PURELAB Classic Elga system and ethanol with 96 % purity (v/v) for gas phase capturing was acquired from Carlo Erba Group – Arese, Italy. The aqueous solution of xylose was originated from D-xylose (Sigma Aldrich) with 99.99 % of purity. Reagent THF (Merck, D-6100 Darmstadt) with purity of 99.5 % was used in all THF-assisted dehydration experiments.

Dehydration experiments

The acid-catalysed dehydrations were carried out in aqueous media in presence of THF as extracting solvent. The reaction system contained a mixture of aqueous solution of D-xylose and THF consisted of 15:0, 12:3, 10:5, 7.5:7.5, 5:10, 3:12 and 2:1 (v/v). The reactions were performed in a stainless steel 160 mL reactor (series 4655, Parr Instruments Company, Moline, Illinois, USA) coupled with Parr 4842 unit used to control and monitor reaction parameters (pressure, temperature and stirring). An external fabric mantle was used to heat the reactor, while an internal stainless steel loop was used to cool the system with cold water. The xylose dehydration experiments were carried out at established isothermal conditions (160 °C and 180 °C) and various holding times (from 10 min to 120 min). In all experiments where CO_2 was used as catalyst, the initial CO_2 pressure was 50 bar. All solutions were mixed at constant speed (70 rpm) using a magnetic drive. In an effort to decrease the CO_2 density variations due to changes of initial temperature, the reactor was pressurised with CO_2 with initial temperature of -9 °C and the reaction was started when the temperature of mixture was 22 °C. When the final holding time was reached, the reactor was immediately cooled down to quench the reaction. A slow depressurisation of reaction mixture was performed when temperature was lower than 25 °C. The depressurised gaseous phase passed through a vial filled into 5 g of ethanol placed in the ice bath and later analysed as described below.

Chemical analysis

The liquid and gaseous phases were analysed separately by running on High-Performance Liquid Chromatography (HPLC) using an Agilent 1100 series HPLC system, Santa Clara, CA, USA equipped with a Bio- Rad Aminex HPX-87H column (Hercules, CA, USA). The set conditions of the column were as follow: 50 °C and mobile phase was 5 mM of H_2SO_4 flowing at a rate of 0.6 mL/min. A refractive index (RI) detector was used to examine xylose content. The furfural analyses were performed using a UV/Vis detector at 280 nm. All samples were analysed in duplicated. All experimental errors related with measurements described above pertain solely to the calibration technique used to quantify the concentrations of products.

Phase equilibria prediction

The phase equilibria of systems constituted by THF, H_2O and CO_2 were predicted using ADF 2014 software of Scientific Computing & Modelling. For this purpose COSMO-SA 2013-ADF model was used. The predicted compositions of solid and liquid phases for all examined reactions are given in Tables S1-S4.

Table S1. The composition of liquid (x) and vapour (y) phase together with the composition of the feed (x_{feed}) for reactions listed in Table 1.

Entry	T_{final} °C	$t_{at\ final\ T}$ min	$p_{inicialCO2}$ bar	[xylose] g/L	$V_{aq.}:V_{THF}$ mL/mL	$x_{H2O\ feed}$	$x_{THF\ feed}$	$x_{CO2\ feed}$	x_{H2O}	x_{THF}	x_{CO2}	y_{H2O}	y_{THF}	y_{CO2}
1	180	60	-	18.8	15:0	1.00	0.00	0.00	1.00	0.00	0.00	1.00	0.00	0.00
2	180	60	-	12.5	10:5	0.90	0.10	0.00	0.95	0.05	0.00	0.05	0.94	0.01
3	160	30	50.7	18.8	25:0	0.37	0.00	0.63	0.98	0.00	0.02	0.00	0.00	1.00
4	160	60	51.7	18.8	25:0	0.37	0.00	0.63	0.98	0.00	0.02	0.00	0.00	1.00
5	180	30	51.5	18.8	25:0	0.37	0.00	0.63	0.98	0.00	0.02	0.00	0.00	1.00
6	180	60	51.2	18.8	25:0	0.38	0.00	0.62	0.97	0.00	0.03	0.00	0.00	1.00
7	180	60	48.2	12.5	10:5	0.56	0.06	0.38	0.87	0.08	0.05	0.00	0.03	0.97
8	180	60	50.8	12.5	20:10	0.69	0.08	0.24	0.83	0.09	0.08	0.00	0.02	0.98
9	180	60	49.4	12.5	40:20	0.81	0.09	0.10	0.85	0.10	0.05	0.00	0.04	0.96

Table S2. The composition of liquid (x) and vapour (y) phase together with the composition of the feed (x_{feed}) for reactions listed in Table 2.

Entry	T_{final} °C	$t_{at\ final\ T}$ min	$p_{inicialCO2}$ bar	[xylose] g/L	$V_{aq.}:V_{THF}$ mL/mL	$x_{H2O\ feed}$	$x_{THF\ feed}$	$x_{CO2\ feed}$	x_{H2O}	x_{THF}	x_{CO2}	y_{H2O}	y_{THF}	y_{CO2}
10	180	60	50.2	12.5	15:0	0.63	0.00	0.37	0.98	0.00	0.02	0.00	0.00	1.00
11	180	60	49.4	12.5	12:3	0.58	0.03	0.39	0.93	0.04	0.03	0.00	0.02	0.98
7	180	60	48.2	12.5	10:5	0.56	0.06	0.38	0.87	0.08	0.05	0.00	0.02	0.98
12	180	60	49.9	12.5	7.5:7.5	0.44	0.10	0.47	0.71	0.15	0.15	0.00	0.02	0.98
13	180	60	49.6	12.5	5:10	0.36	0.16	0.49	0.56	0.24	0.20	0.00	0.02	0.98
14	180	60	49.5	12.5	3:12	0.23	0.20	0.57	0.31	0.28	0.42	0.00	0.01	0.99

Table S3. The composition of liquid (x) and vapour (y) phase together with the composition of the feed (x_{feed}) for reactions depicted in Figure 1.

T_{final} °C	$t_{at\ final\ T}$ min	$p_{inicialCO2}$ bar	[xylose] g/L	$V_{aq.}:V_{THF}$ mL/mL	$x_{H2O\ feed}$	$x_{THF\ feed}$	$x_{CO2\ feed}$	x_{H2O}	x_{THF}	x_{CO2}	y_{H2O}	y_{THF}	y_{CO2}
180	60	49.6	9.4	10:5	0.53	0.06	0.41	0.85	0.09	0.06	0.00	0.02	0.98
180	60	49.6	9.4	7.5:7.5	0.45	0.10	0.45	0.73	0.15	0.12	0.00	0.02	0.98
180	60	48.9	9.4	5:10	0.33	0.15	0.52	0.49	0.21	0.30	0.00	0.01	0.98
180	60	50.1	6.3	12:3	0.57	0.03	0.40	0.92	0.04	0.04	0.00	0.02	0.97
180	60	50.1	6.3	10:5	0.51	0.06	0.44	0.84	0.09	0.07	0.00	0.02	0.98
180	60	50.3	6.3	7.5:7.5	0.42	0.09	0.49	0.70	0.15	0.15	0.00	0.02	0.98
180	60	50.6	6.3	5:10	0.33	0.15	0.52	0.50	0.22	0.28	0.00	0.01	0.99
180	60	49.1	6.3	3:12	0.22	0.20	0.58	0.31	0.28	0.41	0.00	0.01	0.98

Table S4. The composition of liquid (x) and vapour (y) phase together with the composition of the feed (x_{feed}) for reactions depicted in Figure 2.

T_{final} °C	$t_{at\ final\ T}$ min	$p_{inicialCO2}$ bar	[xylose] g/L	$V_{aq.}:V_{THF}$ mL/mL	$x_{H2O\ feed}$	$x_{THF\ feed}$	$x_{CO2\ feed}$	x_{H2O}	x_{THF}	x_{CO2}	y_{H2O}	y_{THF}	y_{CO2}
180	10	50.4	12.5	10:5	0.54	0.06	0.40	0.84	0.09	0.08	0.00	0.03	0.97
180	20	52.1	12.5	10:5	0.53	0.05	0.42	0.85	0.09	0.07	0.00	0.03	0.97
180	30	51.4	12.5	10:5	0.54	0.06	0.40	0.86	0.08	0.06	0.00	0.03	0.97
180	45	50.9	12.5	10:5	0.55	0.06	0.39	0.84	0.09	0.07	0.00	0.03	0.97
180	60	48.2	12.5	10:5	0.56	0.06	0.38	0.87	0.08	0.05	0.00	0.03	0.97
180	90	49.5	12.5	10:5	0.56	0.06	0.38	0.85	0.09	0.06	0.00	0.03	0.97
180	120	50.0	12.5	10:5	0.56	0.06	0.38	0.83	0.09	0.08	0.00	0.03	0.97
180	10	50.6	9.4	7.5:7.5	0.45	0.10	0.45	0.73	0.16	0.12	0.00	0.02	0.98
180	20	51.1	9.4	7.5:7.5	0.44	0.10	0.46	0.72	0.15	0.13	0.00	0.02	0.98
180	30	51.8	9.4	7.5:7.5	0.44	0.10	0.46	0.71	0.15	0.15	0.00	0.02	0.98
180	45	49.8	9.4	7.5:7.5	0.44	0.10	0.46	0.71	0.15	0.14	0.00	0.02	0.98
180	60	49.6	9.4	7.5:7.5	0.45	0.10	0.45	0.73	0.15	0.12	0.00	0.02	0.98
180	90	50.1	9.4	7.5:7.5	0.46	0.10	0.44	0.71	0.15	0.14	0.00	0.02	0.98
180	120	50.9	9.4	7.5:7.5	0.46	0.10	0.44	0.73	0.15	0.12	0.00	0.02	0.98
180	10	49.5	6.3	5:10	0.35	0.14	0.51	0.52	0.23	0.29	0.00	0.01	0.99
180	20	50.1	6.3	5:10	0.33	0.14	0.53	0.50	0.21	0.29	0.00	0.01	0.99
180	30	50.7	6.3	5:10	0.32	0.14	0.53	0.51	0.22	0.27	0.00	0.01	0.99
180	45	49.8	6.3	5:10	0.33	0.15	0.52	0.48	0.21	0.31	0.00	0.01	0.99
180	60	50.6	6.3	5:10	0.33	0.15	0.52	0.50	0.22	0.28	0.00	0.01	0.99

180	90	49.2	6.3	5:10	0.33	0.15	0.52	0.49	0.21	0.30	0.00	0.01	0.99
180	120	49.6	6.3	5:10	0.33	0.15	0.53	0.48	0.21	0.31	0.00	0.01	0.99

The example of the obtained phase envelopes is given in the Figure S1.

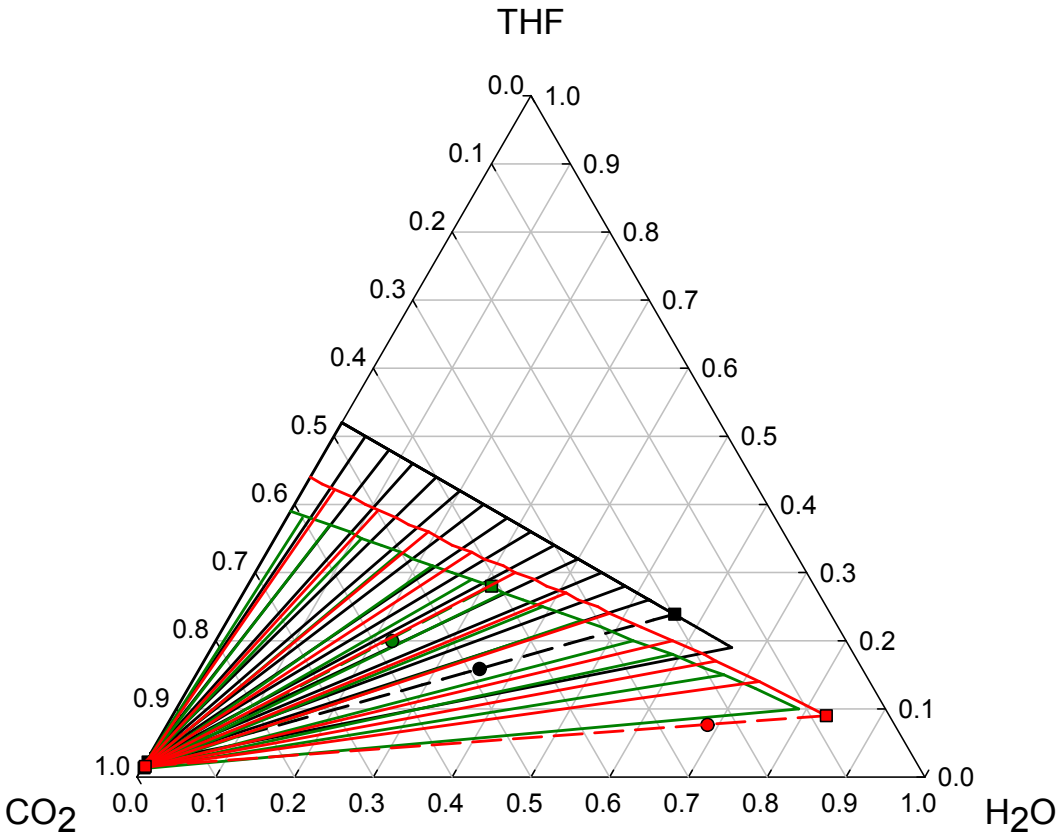

Figure S1. The phase envelopes of system containing CO_2 (50 bar), THF and H_2O for 180 °C and for final pressure of 99 bar (black – entry 13) or 117 bar (red – entry 8) or 127 bar (green – 6.3 g/L xylose concentration in feed, $V_{aq.}$:V_{THF} ratio of 3:12 mL/mL). The closed circle represents the overall composition of the reaction mixture and the dash line depicts tie-line connecting points (closed squares) describing either liquid or gas phase compositions.

Experimental error analysis

The randomly selected dehydration experiments were performed at least in duplicate to examine the reproducibility of the performed works. This approach was not employed in case of all experiments due to the impossibility to reproduce exactly the same experimental conditions, namely the amount of CO_2 (number of moles of CO_2) placed in the reactor. Even with the methodology presented above regarding the conditions at which CO_2 was introduced to the system, the number of CO_2 moles varies producing every time different conditions. The only method allowing to establish the

correctness of the produced data is the obtained tendency observed analysing the entire set of data.

Mathematic formulas

Xylose conversion and furfural selectivity were calculated using the following formulas:

$$Xylose\ conversion\ (X_{Xylose}) = \frac{[xylose]_{feed} \times V_{feed} - [xylose]_{final} \times V_{final}}{[Xxlose]_{feed} \times V_{feed}} \times 100\%$$ and

$$Furfural\ yield\ (Y_{furfural}) = \frac{[furfural] \times V_{final}}{[xylose]_{feed} \times V_{feed}} \times 100\%$$ and

$Selectivity\ to\ furfural\ (S_{furfural}) = \frac{Y_{furfural}}{X_{xylose}}$, where $[xylose]_{feed}$ means initial xylose concentration (mol/mL), $[xylose]_{final}$ represents xylose concentration after reaction (mol/mL), V_{feed} represents the volume of xylose solution (mL), V_{final} indicates the total volume of xylose solution and THF after reaction (mL).

The reaction (heating and holding time) profiles

The reaction profiles are given in Tables S5-S8.

Table S5. The heating and holding time profiles for reactions presented in Table 1.

Entry	1			2			3			4			5		
T_{final}/ºC	180			180			160			160			180		
$t_{at\ final\ T}$/min	60			60			30			60			30		
$p_{inicialCO2}$/bar	-			-			50.7			51.7			51.5		
[xylose]/ g/L	18.8			12.5			18.8			18.8			18.8		
$V_{aq.}$:V_{THF} /mL/mL	15:0			10:5			25:0			25:0			25:0		
	t (min)	T (ºC)	p (bar)	t (min)	T (ºC)	p (bar)	t (min)	T (ºC)	p (bar)	t (min)	T (ºC)	p (bar)	t (min)	T (ºC)	p (bar)
	0.00	21	0.1	0.00	22	0.3	0.00	20	50.7	0.00	20	51.7	0.00	21	51.5
	1.00	25	0.2	1.00	31	0.5	1.00	24	53.8	1.00	28	58.0	1.00	25	57.3
	2.00	38	0.3	2.00	43	0.6	2.00	24	58.8	2.00	37	63.8	2.00	30	64.5
	3.00	65	0.6	3.00	81	1.5	5.00	31	66.7	5.00	68	74.1	5.00	51	71.1
	4.00	76	0.8	4.00	94	2.5	7.00	47	72.1	7.00	100	82.5	7.00	68	79.4
	5.00	94	1.3	5.00	102	3.1	9.00	68	77.4	9.00	120	89.5	9.00	81	84.7
	6.00	100	1.5	6.00	108	3.7	11.00	89	84.2	11.00	136	95.3	11.00	91	88.9
	7.00	111	2.0	7.00	114	4.5	12.00	100	88.2	13.00	154	101.1	12.00	100	92.4
	8.00	115	2.3	8.00	121	5.3	13.00	107	91.2	13.93	160	104.1	15.00	128	103.6
	9.00	126	2.9	9.00	124	5.7	15.00	128	99.1	14.93	163	104.7	17.00	148	110.8
	10.00	131	3.3	10.00	131	6.4	17.00	145	106.2	15.93	157	103.6	32.00	166	118.5

	11.00	138	3.9	11.00	137	7.3	18.52	160	112.5	18.93	161	105.1	20.98	180	124.7
	12.00	145	4.7	12.00	141	7.8	20.52	160	111.9	23.93	159	104.1	21.98	178	123.5
	13.00	152	5.4	13.00	147	8.8	23.52	160	114.1	28.93	159	103.8	37.98	176	137.9
	14.00	159	6.6	14.00	153	9.4	28.52	162	111.3	33.93	162	101.7	25.98	178	123.4
	15.00	165	7.6	15.00	158	10.2	33.52	161	110.9	38.93	158	99.8	30.98	181	137.8
	16.00	173	9.0	16.00	165	11.1	38.52	159	109.3	43.93	162	98.6	38.98	179	118.0
	17.00	180	10.0	17.00	172	12.1	48.52	158	102.4	48.93	159	96.0	50.98	178	111.0
	17.32	180	10.5	18.00	178	13.1				53.93	161	94.8			
	22.32	180	10.3	18.37	180	13.4				58.93	159	82.7			
	27.32	180	10.6	23.37	180	13.4				63.93	159	91.6			
	37.32	179	10.5	28.37	180	14.8				68.93	158	90.2			
	47.32	179	10.5	38.37	179	14.7				73.93	157	88.7			
	57.32	179	10.6	48.37	179	14.7									
	67.32	179	10.6	58.37	180	14.7									
	77.32	180	10.6	68.37	179	14.7									
				78.37	179	14.7									

Table S5. *continuation.*

Entry	6			7			8			9		
T_{final}/ºC	180			180			180			180		
$t_{at\ final\ T}$/min	60			60			60			60		
$p_{inicialCO2}$/bar	51.2			48.2			50.8			49.4		
[xylose]/ g/L	18.8			12.5			12.5			12.5		
$V_{aq.}$:V_{THF} /mL/mL	25:0			10:5			20:10			40:20		
	t (min)	T (ºC)	p (bar)	t (min)	T (ºC)	p (bar)	t (min)	T (ºC)	p (bar)	t (min)	T (ºC)	p (bar)
	0.00	20	51.2	0.00	37	48.2	0.00	29	50.9	0.00	28	49.5
	1.00	25	60.4	1.00	36	54.1	1.00	33	53.5	1.00	36	51.9
	2.00	31	68.9	2.00	42	57.9	2.00	42	58.5	2.00	44	53.8
	5.00	59	78.3	3.00	52	59.9	3.00	49	62.1	3.00	59	56.4
	7.00	90	89.4	4.00	58	61.7	4.00	58	65.3	4.00	80	58.2
	8.45	100	97.4	5.00	68	64.5	5.00	69	68.5	5.00	96	60.5
	10.00	120	102.2	6.00	77	66.6	6.00	77	71.3	6.00	110	61.3
	12.00	137	109.2	7.00	90	68.9	7.00	82	74.2	7.00	123	63.8
	15.00	167	137.6	8.00	100	71.7	8.00	92	77.1	8.00	133	65.6
	17.00	178	128.9	9.00	115	73.4	9.00	100	79.0	9.00	149	69.0
	17.78	180	129.9	10.00	121	74.7	10.00	108	80.8	10.00	160	71.3
	18.78	180	129.6	11.00	131	76.1	11.00	118	84.1	11.00	166	73.2
	37.78	177	128.3	12.00	137	77.8	12.00	131	88.7	12.00	173	75.2
	27.78	179	126.3	13.00	143	79.3	13.00	133	91.7	13.00	179	79.2

	32.78	182	127.0	14.00	150	80.9	14.00	147	96.4	13.63	180	80.2
	37.78	178	121.6	15.00	160	84.2	15.00	152	99.3	18.63	179	84.4
	42.78	178	118.7	16.00	166	85.1	16.00	156	101.3	23.63	177	86.8
	78.78	182	117.1	17.00	172	88.6	17.00	161	104.8	33.63	181	90.9
	52.78	181	114.0	18.00	174	89.6	18.00	168	107.9	43.63	179	91.6
	57.78	177	109.6	32.00	180	91.4	32.00	172	110.9	53.63	180	93.4
	62.78	180	108.4	24.00	181	91.4	20.00	176	113.8	63.63	180	93.2
	67.78	179	104.3	29.00	178	92.1	21.00	180	117.0	73.63	180	93.6
	72.78	180	104.3	39.00	177	90.3	26.00	181	132.8			
	77.78	180	103.6	49.00	181	88.4	31.00	181	121.0			
				59.00	182	87.5	41.00	178	120.4			
				69.00	178	87.0	51.00	177	120.3			
				79.00	178	83.7	61.00	181	137.7			
							71.00	180	121.6			

Table S6. The heating and holding time profiles for reactions presented in Table 2.

Entry	10			11			7			12			13			14		
T_{final}/ºC	180			180			180			180			180			180		
$t_{at\ final\ T}$/min	60			60			60			60			60			60		
$p_{inicialCO2}$/bar	50.2			49.4			48.2			49.9			49.6			49.5		
[xylose]/ g/L	12.5			12.5			12.5			12.5			12.5			12.5		
$V_{aq.}$:V_{THF} /mL/mL	15:0			12:3			10:5			7.5:7.5			5:10			3:12		
	t	T	p	t	T	p	t	T	p	t	T	p	t	T	P	t	T	p
	(min)	(ºC)	(bar)	(min)	(ºC)	(bar)	(min)	(ºC)	(bar)	(min)	(ºC)	(bar)	(min)	(ºC)	(bar)	(min)	(ºC)	(bar)
	0.00	24	50.3	0.00	21	49.4	0.00	37	48.2	0.00	32	49.9	0.00	32	49.6	0.00	24	49.5
	1.00	36	52.6	1.00	28	51.2	1.00	36	54.1	1.00	33	53.4	1.00	37	51.8	1.00	31	50.3
	2.00	47	55.7	2.00	37	54.3	2.00	42	57.9	2.00	48	58.8	2.00	48	54.1	2.00	46	59.1
	3.00	62	60.6	3.00	57	58.7	3.00	52	59.9	3.00	67	64.8	3.00	70	60.7	3.00	59	65.4
	4.00	77	64.9	4.00	71	61.4	4.00	58	61.7	4.00	82	68.7	8.00	129	73.8	4.00	72	69.6
	5.00	97	67.6	5.00	81	63.6	5.00	68	64.5	5.00	92	71.6	9.00	137	75.9	5.00	83	74.0
	6.00	112	69.5	6.00	98	65.8	6.00	77	66.6	6.00	99	74.2	10.00	142	78.8	6.00	100	78.6
	7.00	128	71.9	7.00	100	66.3	7.00	90	68.9	7.00	113	78.2	11.00	147	80.8	7.00	108	81.9
	8.00	144	75.5	8.00	110	67.6	8.00	100	71.7	8.00	123	81.5	12.00	152	85.2	8.00	132	86.1
	9.00	155	77.8	9.00	137	69.8	9.00	115	73.4	9.00	128	84.6	13.00	157	88.0	9.00	127	90.8
	10.00	161	80.1	10.00	132	71.8	10.00	121	74.7	10.00	134	89.0	14.00	162	90.6	10.00	134	94.9
	11.00	171	82.5	11.00	144	74.6	11.00	131	76.1	11.00	144	94.9	15.00	169	93.2	11.00	140	98.7
	12.00	177	85.3	12.00	151	76.4	12.00	137	77.8	13.00	157	102.0	16.00	178	97.3	12.00	146	102.9
	12.43	180	86.1	13.00	157	78.1	13.00	143	79.3	14.00	163	105.0	27.27	180	98.6	13.00	149	108.9

	17.43	181	91.0	14.00	166	81.3	14.00	150	80.9	15.00	167	108.4	21.27	177	99.8	14.00	156	113.0
	37.43	179	93.9	15.00	172	82.9	15.00	160	84.2	16.00	173	111.4	26.27	181	102.8	15.00	163	117.7
	32.43	181	96.8	15.03	180	85.3	16.00	166	85.1	17.23	180	116.5	36.27	178	103.0	16.00	166	132.9
	42.43	180	98.1	20.03	178	89.3	17.00	172	88.6	37.23	179	118.9	46.27	178	103.2	17.00	174	125.1
	52.43	180	98.6	25.03	179	92.3	18.00	174	89.6	27.23	182	120.8	56.27	179	104.0	18.27	179	129.4
	62.43	180	99.1	35.03	178	93.9	32.00	180	91.4	37.23	177	119.0	66.27	179	104.3	23.27	179	129.9
	72.43	179	99.5	45.03	178	95.0	24.00	181	91.4	47.23	182	137.6	76.27	180	104.4	28.27	179	131.8
				55.03	180	97.1	29.00	178	92.1	57.23	182	137.4				38.27	179	133.0
				65.03	178	96.8	39.00	177	90.3	67.23	179	122.0				48.27	182	135.5
				75.03	180	98.1	49.00	181	88.4	77.23	180	121.6				58.27	181	135.2
							59.00	182	87.5							68.27	178	133.6
							69.00	178	87.0							78.27	180	134.6
							79.00	178	83.7									

Table S7. The heating and holding time profiles for reactions presented in Figure 1.

T_{final}/ºC	180			180			180		
$t_{at\ final\ T}$/min	60			60			60		
$p_{inicialCO2}$/bar	49.6			49.6			48.9		
[xylose]/ g/L	9.4			9.4			9.4		
$V_{aq.}$:V_{THF} /mL/mL	10:5			7.5:7.5			5:10		
	t (min)	T (ºC)	p (bar)	t (min)	T (ºC)	p (bar)	t (min)	T (ºC)	p (bar)
	0.00	18	47.5	0.00	29	49.6	0.00	37	48.9
	1.00	27	52.4	1.00	32	51.2	1.00	27	49.2
	2.00	38	58.0	2.00	41	55.6	4.00	71	69.3
	3.00	53	62.3	3.00	53	60.7	5.00	84	74.0
	4.00	69	65.9	4.00	65	64.0	6.00	111	80.5
	5.00	81	68.7	5.00	71	65.5	7.00	125	85.5
	6.00	99	72.2	6.00	82	67.9	8.00	130	88.9
	7.00	114	76.5	7.00	89	69.7	9.00	137	92.9
	8.00	123	80.3	8.00	97	71.6	10.00	141	95.9
	9.00	127	83.1	9.00	107	74.2	11.00	145	100.1
	10.00	139	86.1	10.00	112	75.6	12.00	146	105.2
	11.00	150	89.7	11.00	120	78.1	13.00	152	109.0
	12.00	159	93.4	12.00	135	82.6	14.00	169	118.0
	13.00	165	95.6	13.00	142	84.7	15.00	173	121.0
	14.00	173	99.0	14.00	148	87.2	16.00	177	124.6

	14.65	180	101.9	15.00	153	89.4	17.00	180	126.8
	32.65	180	107.2	16.00	160	91.8	17.62	173	121.0
	24.65	180	109.6	17.00	166	94.5	62.62	179	128.3
	34.65	181	112.7	18.00	171	96.8	27.62	182	131.7
	44.65	181	114.0	32.00	177	99.9	62.62	180	131.2
	54.65	181	114.2	32.85	180	102.0	47.62	177	130.5
	64.65	176	114.2	24.85	177	103.0	57.62	179	131.9
	74.65	180	114.1	29.85	181	105.7	67.62	179	133.1
				39.85	182	106.9	77.62	180	133.6
				49.85	181	107.5			
				59.85	180	106.7			
				69.85	180	107.7			
				79.85	180	107.5			

Table S7. *continuation.*

T_{final}/ºC	180			180			180			180			180		
$t_{at\ final\ T}$/min	60			60			60			60			60		
$p_{inicialCO2}$/bar	50.1			50.1			50.3			50.6			49.1		
[xylose]/ g/L	6.3			6.3			6.3			6.3			6.3		
$V_{aq.}$:V_{THF} /mL/mL	12:3			10:5			7.5:7.5			5:10			3:12		
	t (min)	T (ºC)	p (bar)	t (min)	T (ºC)	p (bar)	t (min)	T (ºC)	p (bar)	t (min)	T (ºC)	p (bar)	t (min)	T (ºC)	p (bar)
	0.00	20	50.1	0.00	32	50.1	0.00	32	50.3	0.00	27	50.6	0.00	24	49.1
	1.00	37	51.5	1.00	27	52.7	1.00	31	52.7	1.00	36	56.3	1.00	37	56.1
	2.00	34	56.0	2.00	37	57.7	2.00	39	57.1	2.00	43	61.7	2.00	46	58.9
	3.00	50	61.0	3.00	51	62.6	3.00	52	62.1	3.00	54	67.5	3.00	58	64.8
	4.00	64	64.3	4.00	61	65.5	4.00	69	66.5	4.00	64	71.4	4.00	76	70.5
	5.00	87	69.3	5.00	82	69.8	5.00	84	70.3	5.00	76	75.0	5.00	91	75.6
	6.00	100	71.7	6.00	91	72.0	6.00	96	73.6	6.00	89	79.3	6.00	100	77.3
	7.00	110	73.9	7.00	109	76.1	7.00	107	76.3	7.00	98	82.4	7.00	114	81.8
	8.00	132	76.0	8.00	132	79.4	8.00	132	80.2	8.00	108	85.9	8.00	125	85.9
	9.00	129	78.5	9.00	137	81.3	9.00	125	83.6	9.00	118	89.7	9.00	135	91.4
	10.00	133	79.9	10.00	136	85.0	10.00	130	86.1	10.00	127	93.8	10.00	141	95.7
	11.00	144	82.3	11.00	140	88.4	11.00	136	90.3	11.00	138	99.1	11.00	148	101.2
	12.00	156	85.9	12.00	148	91.1	12.00	148	96.7	12.00	147	104.7	12.00	152	104.1
	13.00	161	87.9	13.00	155	93.7	13.00	154	99.7	13.00	159	109.9	13.00	153	108.9
	14.00	170	92.0	14.00	161	97.2	14.00	158	102.5	14.00	163	112.9	14.00	160	113.3

	15.23	180	95.8	15.00	168	99.9	15.00	166	106.2	15.00	169	115.8	16.00	174	137.9
	20.23	180	97.6	16.00	174	103.4	16.00	171	109.2	16.00	173	132.2	16.98	180	127.1
	25.23	181	99.6	16.85	180	106.7	17.00	176	112.5	17.00	180	123.8	21.98	180	128.1
	35.23	182	102.6	21.85	180	106.7	17.57	180	114.8	37.00	179	126.6	26.98	177	129.1
	45.23	182	105.0	26.85	178	110.3	37.57	182	115.9	27.00	179	126.5	36.98	181	133.1
	55.23	178	106.4	36.85	180	111.7	27.57	180	116.5	37.00	179	127.3	46.98	180	132.9
	65.23	180	107.3	46.85	180	112.3	37.57	179	117.9	47.00	175	125.5	56.98	178	131.1
	75.23	180	107.6	56.85	179	113.4	47.57	177	118.5	57.00	177	125.0	66.98	180	132.6
				66.85	178	114.6	57.57	177	132.9	67.00	179	126.2	76.98	180	133.0
				76.85	180	114.9	67.57	179	120.8	77.00	180	127.6			
				81.85	181	115.5	77.57	181	122.0						

Table S8. The heating and holding time profiles for reactions presented in Figure 2.

T_{final}/ºC	180			180			180			180			180			180		
$t_{at\ final\ T}$/min	10			20			30			45			90			120		
$p_{inicialCO2}$/bar	50.4			52.1			51.4			50.9			49.5			50.0		
[xylose]/ g/L	12.5			12.5			12.5			12.5			12.5			12.5		
$V_{aq.}$:V_{THF} /mL/mL	10:5			10:5			10:5			10:5			10:5			10:5		
	t (min)	T (ºC)	p (bar)	t (min)	T (ºC)	p (bar)	t (min)	T (ºC)	p (bar)	t (min)	T (ºC)	p (bar)	t (min)	T (ºC)	p (bar)	t (min)	T (ºC)	p (bar)
	0.00	23	50.4	0.00	32	52.1	0.00	33	51	0.00	21	50.9	0.00	24	49.5	0.00	21	50.0
	1.00	25	52.6	1.00	34	54.1	1.00	37	53	1.00	25	52.8	1.00	27	51.3	1.00	27	54.0
	2.00	35	58.3	2.00	43	57.6	2.00	47	56	2.00	36	58.0	2.00	37	56.6	2.00	39	60.6
	3.00	44	62.6	3.00	53	60.6	3.00	56	60	3.00	49	61.7	3.00	49	61.0	3.00	52	65.1
	4.00	54	66.0	4.00	63	63.6	4.00	67	62	4.00	64	65.0	4.00	57	63.6	4.00	64	68.5
	5.00	64	68.7	5.00	75	66.3	5.00	79	65	5.00	73	67.4	5.00	69	65.9	5.00	81	72.2
	6.00	75	71.7	6.00	91	69.5	6.00	95	68	6.00	89	71.0	6.00	86	69.7	6.00	94	75.4
	7.00	89	75.5	7.00	106	73.0	7.00	111	71	8.00	113	78.8	7.00	95	72.7	7.00	100	77.2
	8.00	104	79.3	8.00	116	75.0	8.00	119	72	9.00	124	82.5	8.00	112	76.0	8.00	108	83.2
	9.00	113	81.6	9.00	123	76.8	9.00	128	74	10.00	137	85.6	9.00	118	77.5	9.00	117	87.1
	10.00	121	84.4	10.00	131	78.6	10.00	135	76	11.00	142	88.1	10.00	128	80.1	10.00	123	89.9
	11.00	128	87.0	11.00	138	80.6	11.00	142	78	12.00	146	91.4	11.00	137	82.8	11.00	132	92.2
	12.00	134	89.3	12.00	144	83.0	12.00	149	80	13.00	158	94.1	12.00	143	85.0	12.00	136	95.2
	13.00	141	91.9	13.00	155	86.2	13.00	157	83	14.00	166	97.2	13.00	149	87.3	13.00	141	97.6
	14.00	147	94.9	14.00	158	87.5	14.00	161	85	15.00	172	101.0	14.00	154	88.9	14.00	150	101.8

	15.00	154	98.1	15.00	164	90.4	15.00	168	87	16.00	176	105.2	15.00	162	92.7	15.00	157	105.4
	16.00	162	101.8	16.00	173	93.3	16.00	176	90	16.41	181	106.1	16.00	171	96.7	16.00	166	109.8
	17.00	169	105.2	17.00	180	95.6	16.57	180	92	21.41	181	109.6	17.00	179	100.5	17.00	174	114.4
	18.45	180	111.5	22.00	179	98.2	21.57	178	91	26.41	180	113.8	17.02	180	101.2	17.07	180	117.9
	23.45	177	112.5	27.00	178	98.8	26.57	177	93	36.41	180	115.0	22.02	180	101.2	22.07	180	120.4
	28.45	180	114.2	37.00	180	101.6	36.57	180	94	46.41	180	117.1	27.02	179	102.6	27.07	178	121.9
							46.57	180	94	56.41	180	117.6	37.02	182	105.6	37.07	179	122.7
										61.41	180	118.0	47.02	179	105.5	47.07	179	123.7
													57.02	180	106.0	57.07	180	122.8
													67.02	181	106.2	67.07	180	123.6
													77.02	181	107.0	77.07	180	125.6
													87.02	180	107.9	87.07	178	123.7
													97.02	180	108.4	97.07	177	123.7
													107.02	179	109.0	107.07	180	120.4
																117.07	180	121.2
																127.07	180	122.0
																137.07	181	122.6

Table S8. *continuation.*

T_{final}/ºC	180			180			180			180			180			180		
$t_{at\ final\ T}$/min	10			20			30			45			90			120		
$p_{inicialCO2}$/bar	50.6			51.1			51.8			49.8			50.1			50.9		
[xylose]/ g/L	9.4			9.4			9.4			9.4			9.4			9.4		
$V_{aq.}$:V_{THF} /mL/mL	7.5:7.5			7.5:7.5			7.5:7.5			7.5:7.5			7.5:7.5			7.5:7.5		
	t (min)	T (ºC)	P (bar)	t (min)	T (ºC)	p (bar)	t (min)	T (ºC)	p (bar)	t (min)	T (ºC)	p (bar)	t (min)	T (ºC)	p (bar)	t (min)	T (ºC)	p (bar)
	0.00	34	50.6	0.00	33	51.1	0.00	29	51.8	0.00	21	49.9	0.00	34	50.1	0.00	21	50.9
	1.00	39	54.4	1.00	36	54.4	1.00	34	56.8	1.00	28	49.3	1.00	39	52.8	1.00	25	52.8
	2.00	51	59.6	2.00	44	58.7	2.00	42	60.3	2.00	41	55.8	2.00	54	58.4	2.00	36	58.0
	3.00	59	62.4	3.00	54	62.3	3.00	51	64.8	3.00	53	60.1	3.00	67	62.4	3.00	49	61.7
	4.00	73	66.1	4.00	64	64.9	4.00	66	70.2	4.00	73	63.5	4.00	83	66.1	4.00	64	65.0
	5.00	84	68.7	5.00	75	67.6	5.00	72	72.4	5.00	87	66.5	5.00	99	68.8	5.00	73	67.4
	6.00	96	71.5	6.00	87	70.6	6.00	84	75.8	6.00	100	70.1	6.00	111	71.5	6.00	89	71.0
	7.00	107	73.9	7.00	100	73.7	7.00	94	78.4	7.00	112	73.1	7.00	122	74.9	8.00	113	78.8
	8.00	117	76.9	8.00	110	76.4	8.00	105	81.2	8.00	120	75.9	8.00	128	77.8	9.00	124	82.5
	9.00	127	79.6	9.00	118	78.7	9.00	115	84.8	9.00	126	78.2	9.00	130	80.9	10.00	137	85.6
	10.00	142	83.9	10.00	133	83.1	10.00	127	88.7	10.00	133	82.5	10.00	144	85.0	11.00	142	88.1
	11.00	152	87.2	11.00	145	87.5	11.00	142	93.9	11.00	134	86.1	11.00	152	88.0	12.00	146	91.4
	12.00	157	89.4	12.00	150	89.4	12.00	147	97.0	12.00	148	91.2	12.00	158	90.8	13.00	158	94.1
	13.00	162	91.4	13.00	154	91.7	13.00	152	99.7	13.00	152	93.3	13.00	164	92.5	14.00	166	97.2
	14.00	168	94.3	14.00	160	94.1	14.00	158	102.9	14.00	158	96.1	14.00	169	96.0	15.00	172	101.0

	15.00	173	97.1	15.00	164	97.0	15.00	165	106.4	15.00	165	99.0	15.00	176	98.9	16.00	176	105.2
	16.00	180	100.4	16.00	172	101.3	16.00	170	109.8	17.00	175	105.4	16.00	180	101.6	16.41	181	106.1
	21.00	180	100.4	17.00	176	102.3	17.00	177	113.7	18.00	180	108.9	15.92	180	91.8	21.41	181	109.6
	26.00	180	101.4	17.09	180	104.7	17.52	180	115.9	23.00	180	108.9	20.92	180	101.6	26.41	180	113.8
				22.09	180	105.6	22.52	180	116.6	28.00	177	110.8	25.92	177	102.6	36.41	180	115.0
				32.09	178	106.4	27.52	180	117.3	38.00	179	113.9	35.92	178	104.2	46.41	180	117.1
				52.09	181	108.1	37.52	180	118.5	48.00	180	114.5	45.92	179	106.0	56.41	180	117.6
							47.52	181	119.8	58.00	182	116.4	55.92	178	105.5	61.41	180	118.0
										63.00	180	116.4	65.92	180	105.8			
													75.92	180	106.0			
													85.92	180	106.4			
													95.92	181	107.1			
													105.92	181	107.5			

Table S8. *continuation.*

T_{final}/ºC	180			180			180			180			180			180		
$t_{at\ final\ T}$/min	10			20			30			45			90			120		
$p_{inicialCO2}$/bar	49.5			50.0			50.7			49.8			49.2			49.6		
[xylose]/ g/L	6.3			6.3			6.3			6.3			6.3			6.3		
$V_{aq.}$:V_{THF} /mL/mL	5:10			5:10			5:10			5:10			5:10			5:10		
	t (min)	T (ºC)	p (bar)	t (min)	T (ºC)	p (bar)	t (min)	T (ºC)	p (bar)	t (min)	T (ºC)	p (bar)	t (min)	T (ºC)	p (bar)	t (min)	T (ºC)	p (bar)
	0.00	37	49.5	0.00	22	50.0	0.00	23	50.7	0.00	20	49.8	0.00	22	49.2	0.00	23	49.6
	1.00	39	53.2	1.00	30	53.8	1.00	27	52.0	2.00	40	58.6	1.00	28	51.0	1.00	29	51.6
	2.00	51	58.7	2.00	42	59.7	2.00	35	57.3	3.00	56	65.8	2.00	42	59.1	2.00	48	62.9
	3.00	67	64.2	4.00	65	68.7	3.00	44	62.7	4.00	69	70.1	3.00	56	65.1	4.00	56	65.8
	4.00	85	68.6	5.00	78	73.4	4.00	54	66.9	5.00	79	73.9	4.00	72	71.5	5.00	70	71.0
	5.00	97	71.5	6.00	91	77.2	5.00	66	71.2	6.00	94	77.9	5.00	84	74.5	6.00	84	75.1
	6.00	100	72.2	7.00	100	89.1	6.00	76	75.1	8.00	118	85.7	6.00	95	78.4	7.00	99	79.7
	7.00	122	77.5	8.00	112	84.2	7.00	88	78.9	9.00	127	90.3	7.00	105	81.1	8.00	100	80.2
	8.00	132	80.6	9.00	121	88.5	8.00	98	82.1	10.00	131	93.9	8.00	117	84.9	9.00	119	87.9
	9.00	140	84.1	10.00	126	92.4	9.00	23	50.7	11.00	136	98.5	9.00	128	91.1	10.00	127	92.0
	10.00	138	87.8	11.00	131	96.9	10.00	108	86.0	12.00	138	103.4	10.00	132	93.7	11.00	127	96.6
	11.00	145	91.5	12.00	133	101.5	11.00	117	89.8	13.00	146	107.9	11.00	133	95.9	13.00	140	106.7
	12.00	152	94.9	13.00	141	106.3	12.00	124	93.3	14.00	154	113.0	12.00	138	101.7	14.00	147	111.2
	13.00	158	98.3	14.00	146	109.5	13.00	134	97.4	16.00	171	123.6	13.00	144	105.4	15.00	160	118.5
	14.00	172	104.9	15.00	162	118.4	14.00	141	100.7	17.00	176	126.2	14.00	164	117.2	16.00	164	121.3

	15.00	175	106.8	16.00	166	121.0	15.00	149	105.1	17.97	180	130.7	15.00	170	120.1	17.00	170	125.3
	16.00	180	110.8	17.00	170	124.5	16.00	161	111.6	22.97	180	133.5	16.00	176	124.9	18.00	176	130.0
	21.00	180	111.2	18.00	176	128.3	17.00	164	114.0	27.97	180	135.6	17.00	180	128.5	19.32	180	133.0
	26.00	180	113.6	22.07	180	132.5	18.00	172	119.6	37.97	180	135.5	18.00	164	117.2	24.32	180	133.0
				23.92	181	134.7	19.00	178	123.3	47.97	180	135.4	23.00	180	128.5	29.32	180	134.8
				28.92	180	136.3	19.73	180	125.0	57.97	180	135.2	28.00	180	130.7	39.32	179	135.8
				38.92	181	138.6	24.73	181	127.1	62.97	179	135.2	38.00	178	131.2	49.32	179	138.5
							29.73	180	127.0				48.00	177	131.8	59.32	177	136.0
							39.73	178	128.2				58.00	178	132.5	69.32	178	136.7
							49.73	181	130.0				68.00	178	133.7	79.32	180	138.0
													78.00	178	133.0	89.32	181	138.1
													88.00	179	133.9	99.32	182	139.3
													98.00	180	134.7	109.32	181	138.9
													108.00	182	135.5	119.32	181	138.3
																129.32	180	138.1
																139.32	180	137.8