Electronic Supplementary Information

Towards closed-loop recycling of multilayer and coloured PET plastic waste by alkaline hydrolysis

Sibel Ügdüler[1], Kevin M. Van Geem[2], Ruben Denolf[1], Martijn Roosen[1], Nicolas Mys[1,3], Kim Ragaert[3], Steven De Meester[1,]*

[1]Laboratory for Circular Process Engineering, Department of Green Chemistry and Technology, Ghent University, Graaf Karel De Goedelaan 5, 8500 Kortrijk, Belgium

[2]Laboratory for Chemical Technology, Department of Materials, Textiles and Chemical Engineering, Faculty of Engineering & Architecture, Ghent University, Technologiepark 121 , B-9052 Zwijnaarde, Belgium

[3]Center for Polymer and Material Technologies (CPMT), Department of Materials, Textiles and Chemical Engineering, Faculty of Engineering and Architecture, Ghent University, Technologiepark 130, B-9052 Zwijnaarde, Belgium

**Corresponding author.*

E-mail address: Steven.DeMeester@UGent.be

A. Appendix

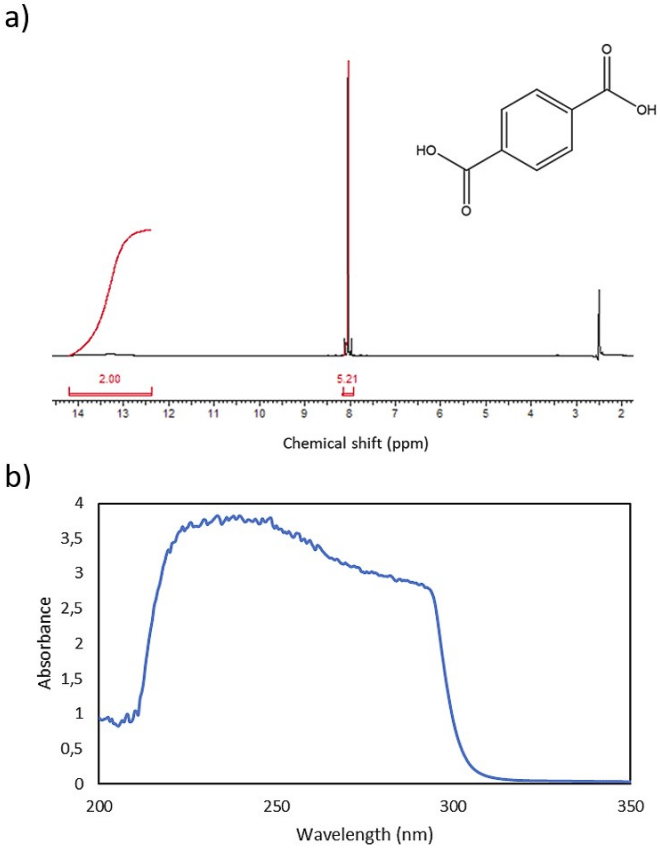


Figure A-1. (a) ^{1}H-NMR spectrum of TPA with d-DMSO (b) UV-VIS spectrum of TPA.

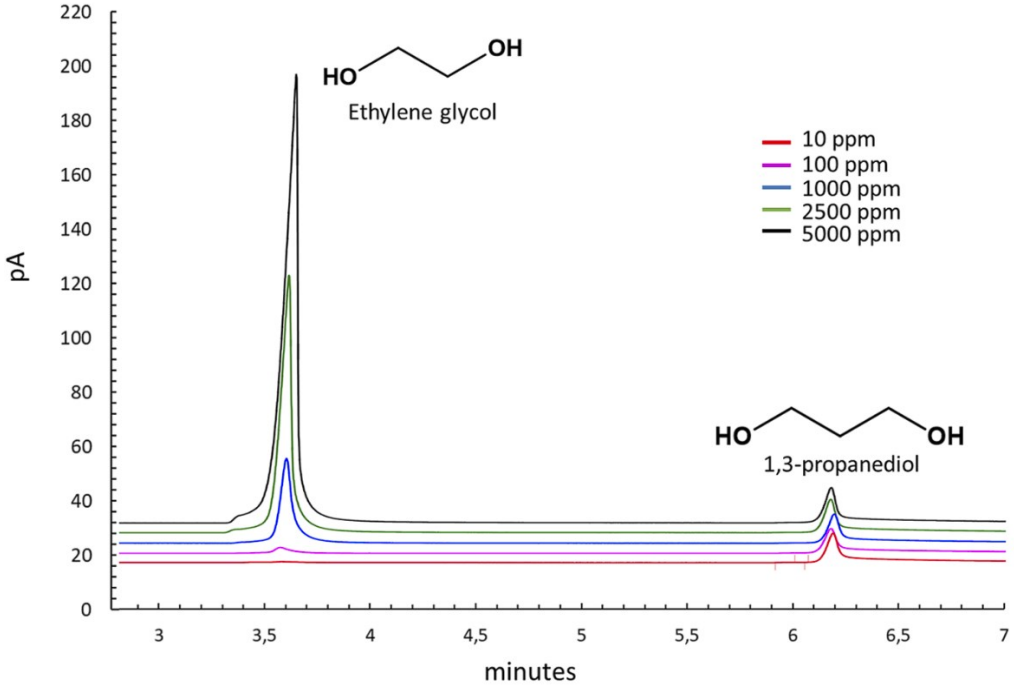


Figure A-2. GC-FID chromatogram of ethylene glycol and internal standard (1,3-propanediol) at different concentrations.

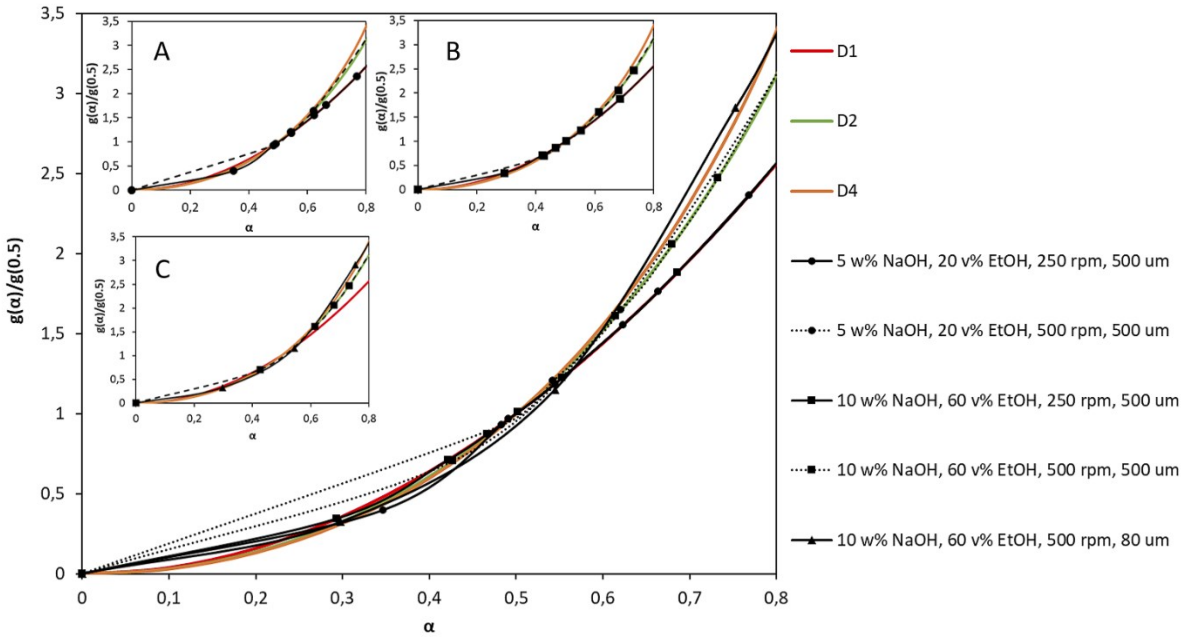


Figure A-3. Superimposition of experimental kinetic data on the best-fit diffusion kinetic models as shown in Figure 3-2, (A) at two different stirring rates (250 rpm and 500 rpm) in the presence of 5 w% NaOH and 20 v% EtOH; (B) at two different stirring rates (250 rpm and 500 rpm) in the presence of 10 w% NaOH and 60 v% EtOH; (C) at two different particle sizes (80 um and 500 um) in the presence of 10 w% NaOH and 60 v% EtOH.

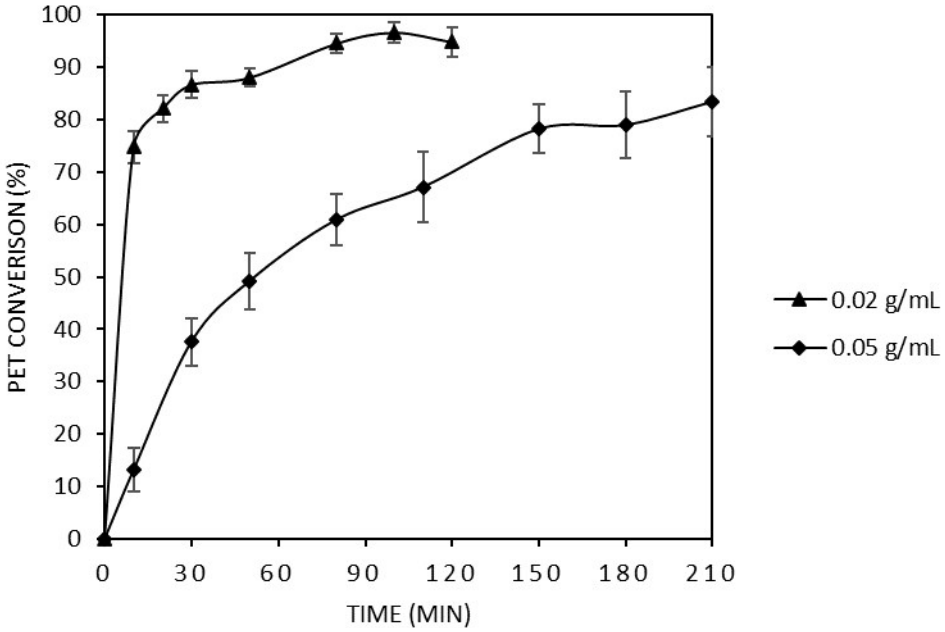


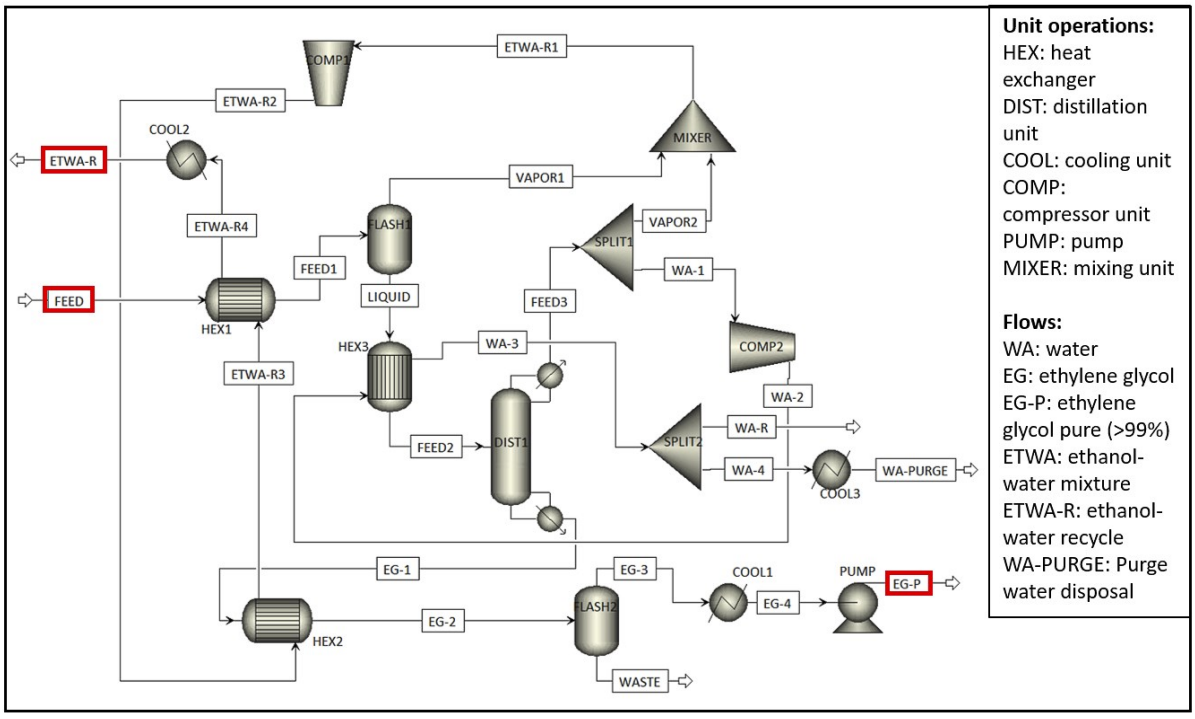
Figure A-4. PET conversion (%) versus time graph of pure PET grade with particle size lower than 500 µm, at 0.02 g/mL and 0.05 g/mL PET concentrations under optimal degradation conditions (60:40 v% EtOH:H_2O, 5 w% NaOH, at 80 °C and at 500 rpm stirring rate via an agitator).

Table A-1. Rate constants obtained from best-fit kinetic model for each PET sample with different particle size

Type of PET sample	Particle size (cm)	Rate constant (cm^{-1})	Best-fit model
Multilayer tray	0.05	0.0004	D2 (R^2=0.95)
	0.1	0.0033	D4 (R^2=0.96)
	0.16	0.0026	D4 (R^2=0.93)
	0.25	0.0016	D4 (R^2=0.90)
	0.315	0.0008	D2 (R^2=0.85)
	1	0.0003	D2 (R^2=0.91)
	4	0.00015	D2 (R^2=0.92)
Multilayer film	0.05	0.0009	D2 (R^2=0.97)
	0.1	0.0039	D4 (R^2=0.95)
	0.16	0.0031	D4 (R^2=0.94)
	0.25	0.0018	D4 (R^2=0.93)
	0.315	0.0013	D2 (R^2=0.96)
	1	0.0003	D2 (R^2=0.87)
	4	0.0002	D2 (R^2=0.85)
Bottle	0.05	0.0047	D4 (R^2=0.93)
	0.1	0.0038	D4 (R^2=0.96)
	0.16	0.0028	D4 (R^2=0.95)
	0.25	0.0024	D4 (R^2=0.91)
	0.315	0.0011	D2 (R^2=0.87)
	1	0.00017	D2 (R^2=0.88)
	4	0.0001	D2 (R^2=0.94)
Monolayer tray	0.05	0.006	D4 (R^2=0.92)
	0.1	0.0046	D4 (R^2=0.94)
	0.16	0.0033	D4 (R^2=0.92)
	0.25	0.0024	D4 (R^2=0.95)
	0.315	0.0022	D4 (R^2=0.89)
	1	0.0018	D2 (R^2=0.92)
	4	0.0017	D2 (R^2=0.95)
Monolayer film	0.05	0.009	D4 (R^2=0.85)
	0.1	0.0056	D4 (R^2=0.89)
	0.16	0.0048	D4 (R^2=0.91)
	0.25	0.0042	D4 (R^2=0.92)
	0.315	0.0033	D4 (R^2=0.91)
	1	0.0029	D2 (R^2=0.92)
	4	0.0017	D2 (R^2=0.94)
Pure PET	0.05	0.01	D4 (R^2=0.98)
	0.1	0.006	D4 (R^2=0.95)
	0.16	0.004	D4 (R^2=0.92)
	0.25	0.0003	D2 (R^2=0.91)
	0.315	0.0003	D2 (R^2=0.91)

Table A-2. Values used in Aspen Plus simulations of PET alkaline hydrolysis with and without excess water addition.

	S/L ratio (g/ml)	PET (kg/hr)	NaOH w%	NaOH added (kg/hr)	H_2SO_4 needed (L)	TPA formed (kg/hr)	EG formed (kg/hr)	excess water (L)	Na_2SO_4 formed (kg/hr)	water formed with acidification (L)
Hydrolysis without excess water addition	0,02	1000	5,00	2916,2	1952,1	843,5	321,0	0,0	5176,3	562,5
	0,03	1500	5,00	3124,3	2091,4	1265,3	481,5	0,0	5545,7	562,5
	0,04	2000	5,00	3332,5	2230,7	1687,1	642,1	0,0	5915,1	562,5
	0,05	2500	5,00	3540,6	2370,1	2108,9	802,6	0,0	6284,5	562,5
Hydrolysis with excess water addition	0,02	1000	5,00	2916,2	1952,1	843,5	321,4	4947,2	5176,3	562,5
	0,03	1500	5,00	3124,3	2091,4	1265,3	481,5	8849,4	5545,7	562,5
	0,04	2000	5,00	3332,5	2230,7	1687,1	641,7	12751,6	5915,1	562,5
	0,05	2500	5,00	3540,6	2370,1	2108,9	803,2	16653,8	6284,5	562,5



Scheme A-1. Aspen Plus process flow diagram of the recovery section for the ethylene glycol and water:ethanol separation plant (hydrolysis scenario 2: excess addition of water).

Table A-3. Parameters used in Aspen Plus simulation for each S/L ratio based on a scenario without excess water addition.

S/L ratio (g/mL)	Parameters		FEED	FEED1	FEED2	FEED3	FEED4	VAPOR1	VAPOR2	LIQUID	EG-1	EG-2	EG-3	EG-4	EG-P	WA-1	WA-2	WA-PURGE	ETWA-R1	ETWA-R2	ETWA-R3	ETWA-R4	ETWA-R5	ETWA-R
0.02	Temp (°C)		80,0	86,1	48,0	44,2	44,1	37,1	44,1	37,1	132,2	132,7	132,7	25,0	25,1	44,1	25,0	25,0	39,4	243,6	240,1	85,1	81,9	80,0
	Pressure (bar)		1,0	1,0	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	1,0	0,1	0,1	1,0	0,1	1,0	1,0	1,0	1,0	1,0
	EG mass flow	kg/hr	322,8	322,8	321,1	9,8E-02	9,8E-02	1,7	6,8E-03	321,1	321,0	321,0	321,0	321,0	321,0	9,2E-02	9,2E-02	9,2E-02	1,7	1,7	1,7	1,7	1,7	1,7
	EtOH mass flow		23316,2	23316,2	1994,0	1994,0	1994,0	21322,2	1981,3	1994,0	4,8E-06	4,8E-06	4,8E-06	4,8E-06	4,8E-06	12,8	12,8	12,8	23303,4	23303,4	23303,4	23303,4	23303,4	23303,4
	Water mass flow		20152,8	20152,8	8484,7	8484,6	8484,6	11668,1	7909,7	8484,7	7,0E-02	7,0E-02	7,0E-02	7,0E-02	7,0E-02	574,9	574,9	574,9	19577,8	19577,8	19577,8	19577,8	19577,8	19577,8
	Total mass flow		43791,8	43791,8	10799,8	10478,8	10478,8	32992,0	9890,9	10799,8	321,0	321,0	321,0	321,0	321,0	587,8	587,8	587,8	42882,9	42882,9	42882,9	42882,9	42882,9	42882,9
0.03	Temp (°C)		80,0	86,2	50,2	44,2	44,1	37,2	44,1	37,2	132,3	132,7	132,7	25,0	25,1	44,1	25,0	25,1	39,4	243,7	238,5	85,0	81,8	80,0
	Pressure (bar)		1,0	1,0	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	1,0	0,1	0,1	1,0	0,1	1,0	1,0	1,0	1,0	1,0
	EG mass flow	kg/hr	484,1	484,1	481,5	1,2E-01	1,2E-01	2,6	8,5E-03	481,5	481,4	481,4	481,4	481,4	481,4	1,2E-01	1,2E-01	1,2E-01	2,6	2,6	2,6	2,6	2,6	2,6
	EtOH mass flow		23316,2	23316,2	1997,3	1997,3	1997,3	21318,9	1984,4	1997,3	7,0E-06	7,0E-06	7,0E-06	7,0E-06	7,0E-06	12,9	12,9	12,9	19576,8	19576,8	19576,8	19576,8	19576,8	19576,8
	Water mass flow		20152,8	20152,8	8460,8	8460,7	8460,7	11692,0	7884,8	8460,8	1,0E-01	1,0E-01	1,0E-01	1,0E-01	1,0E-01	575,9	575,9	575,9	23303,3	23303,3	23303,3	23303,3	23303,3	23303,3
	Total mass flow		43953,1	43953,1	10939,6	10458,2	10458,2	33013,5	9869,3	10939,6	481,5	481,5	481,5	481,5	481,5	588,9	588,9	588,9	42882,8	42882,8	42882,8	42882,8	42882,8	42882,8

Table A-3 continued

S/L ratio (g/mL)	Parameters		FEED	FEED1	FEED2	FEED3	FEED4	VAPOR1	VAPOR2	LIQUID	EG-1	EG-2	EG-3	EG-4	EG-P	WA-1	WA-2	WA-PURGE	ETWA-R1	ETWA-R2	ETWA-R3	ETWA-R4	ETWA-R5	ETWA-R
0.04	Temp (°C)		80,0	86,3	52,3	44,2	44,1	37,2	44,1	37,2	132,2	132,7	132,7	25,0	25,1	44,1	25,0	25,1	39,4	243,8	236,8	85,0	81,8	80,0
	Pressure (bar)		1,0	1,0	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	1,0	0,1	0,1	1,0	0,1	1,0	1,0	1,0	1,0	1,0
	EG mass flow	kg/hr	645,5	645,5	642,0	1,3E-01	1,3E-01	3,5	8,7E-03	642,0	641,9	641,9	641,9	641,9	641,9	1,2E-01	1,2E-01	1,2E-01	3,5	3,5	3,5	3,5	3,5	3,5
	EtOH mass flow		23316,2	23316,2	2028,6	2028,6	2028,6	21287,6	2015,5	2028,6	1,1E-05	1,1E-05	1,1E-05	1,1E-05	1,1E-05	13,0	13,0	13,0	23303,2	23303,2	23303,2	23303,2	23303,2	23303,2
	Water mass flow		20152,8	20152,8	8503,2	8503,1	8503,1	11649,6	7926,1	8503,2	1,6E-01	1,6E-01	1,6E-01	1,6E-01	1,6E-01	576,9	576,9	576,9	19575,7	19575,7	19575,7	19575,7	19575,7	19575,7
	Total mass flow		44114,5	44114,5	11173,8	10531,8	10531,8	32940,7	9941,7	11173,8	642,1	642,1	642,1	642,1	642,1	590,1	590,1	590,1	42882,4	42882,4	42882,4	42882,4	42882,4	42882,4
0.05	Temp (°C)		80,0	86,3	54,6	44,2	44,1	37,3	44,1	37,3	132,1	132,7	132,7	25,0	25,1	44,1	25,0	25,1	39,5	243,8	235,2	85,0	81,8	80,0
	Pressure (bar)		1,0	1,0	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	1,0	0,1	0,1	1,0	0,1	1,0	1,0	1,0	1,0	1,0
	EG mass flow	kg/hr	806,9	806,9	802,6	1,5E-01	1,5E-01	4,3	1,0E-02	802,6	802,4	802,4	802,4	802,4	802,4	1,4E-01	1,4E-01	1,4E-01	4,3	4,3	4,3	4,3	4,3	4,3
	EtOH mass flow		23316,2	23316,2	2061,7	2061,7	2061,7	21254,5	2048,5	2061,7	1,5E-05	1,5E-05	1,5E-05	1,5E-05	1,5E-05	13,2	13,2	13,2	23303,0	23303,0	23303,0	23303,0	23303,0	23303,0
	Water mass flow		20152,8	20152,8	8550,0	8549,8	8549,8	11602,8	7971,9	8550,0	2,1E-01	2,1E-01	2,1E-01	2,1E-01	2,1E-01	577,9	577,9	577,9	19574,7	19574,7	19574,7	19574,7	19574,7	19574,7
	Total mass flow		44275,9	44275,9	11414,3	10611,6	10611,6	32861,6	10020,4	11414,3	802,6	802,6	802,6	802,6	802,6	591,2	591,2	591,2	42882,0	42882,0	42882,0	42882,0	42882,0	42882,0

Table A-4. Energy recoveries and consumptions in Aspen Plus simulation for each S/L ratio based on a scenario without excess water addition.

S/L ratio (g/mL)	Heat exchanged (kW)			Heat duty (kW)									Work (kW)		
	HEX1	HEX2	HEX3	FLASH1	FLASH2	FLASH3	DIST1 - REB	DIST1-COND	COOL1	COOL2	COOL3	COOL4	COMP1	PUMP1	PUMP2
0,02	11408,3	84,6	6039,3	0,0	-1,55E-02	-5,89E-03	1971,9	-1727,1	-385,8	-4307,5	-108,6	-12,9	4528,9	5,03E-02	2,43E-02
0,03	11420,5	126,9	6072,9	0,0	6,16E-06	-5,67E-03	1933,4	-1723,9	-386,5	-4221,2	-162,9	-12,9	4529,7	5,04E-02	3,64E-02
0.04	11380,2	169,2	6158,2	0,0	5,93E-05	1,31E-05	1910,7	-1735,9	-387,2	-4135,4	-217,2	-12,9	4530,4	5,05E-02	4,85E-02
0.05	11336,3	211,6	6248,6	0,0	5,99E-04	4,58E-05	1887,7	-1749,0	-387,9	-4048,1	-271,6	-12,9	4531,1	5,06E-02	6,06E-02

Table A-5. Parameters used in Aspen Plus simulation for each S/L ratio based on a scenario with excess water addition.

S/L ratio (g/mL)	Parameters		FEED	FEED1	FEED2	FEED3	LIQUID	EG-1	EG-2	EG-3	EG-4	EG-P	WA-1	WA-2	WA-3	WA-4	WA-R	WA-PURGE	VAPOR1	VAPOR2	ETWA-R1	ETWA-R2	ETWA-R3	ETWA-R4	ETWA-R
0.02	Temp (°C)		80,0	87,1	43,8	44,5	37,8	131,4	132,6	132,6	25,0	25,1	44,5	329,2	80,0	80,0	80,0	25,0	37,8	44,5	39,4	244,0	240,5	84,5	25,0
	Pressure (bar)		1,0	1,0	0,1	0,1	0,1	0,1	0,1	0,1	0,1	1,0	0,1	0,1	0,1	0,1	1,0	1,0	0,1	0,1	0,1	1,0	1,0	1,0	1,0
	EG mass flow	kg/hr	322,8	322,8	321,4	2,1E-01	321,4	321,2	321,2	321,2	321,2	321,2	9,5E-02	9,5E-02	9,5E-02	8,1E-03	1,4E-03	8,1E-03	1,4	1,1E-01	1,6	1,6	1,6	1,6	1,6
	EtOH mass flow		23316,2	23316,2	2303,7	2303,7	2303,7	1,8E-05	1,8E-05	1,8E-05	1,8E-05	1,8E-05	1061,8	1061,8	1061,8	90,9	970,9	90,9	21012,5	1241,9	23314,6	23314,6	23314,6	23314,6	23314,6
	Water mass flow		25100,0	25100,0	11953,6	11953,4	11953,6	2,1E-01	2,1E-01	2,1E-01	2,1E-01	2,1E-01	5509,5	5509,5	5509,5	471,6	5037,9	471,6	13146,4	6443,9	19590,3	19590,3	19590,3	19590,3	19590,3
	Total mass flow		48739,0	48739,0	14578,6	14257,2	14578,6	321,4	321,4	321,4	321,4	321,4	6571,4	6571,4	6571,4	562,5	6008,8	562,5	34160,4	7685,8	42906,5	42906,5	42906,5	42906,5	42906,5
0.03	Temp (°C)		80,0	88,9	46,2	44,8	39,0	131,7	132,7	132,7	25,0	25,1	44,8	337,2	80,0	80,0	80,0	25,0	39,0	44,8	39,5	244,5	239,3	83,1	80,0
	Pressure (bar)		1,0	1,0	0,1	0,1	0,1	0,1	0,1	0,1	0,1	1,0	0,1	0,1	0,1	0,1	1,0	1,0	0,1	0,1	0,1	1,0	1,0	1,0	1,0
	EG mass flow	kg/hr	484,2	484,2	481,5	2,3E-01	481,5	481,2	481,2	481,2	481,2	481,2	1,7E-01	1,7E-01	1,7E-01	8,8E-03	2,6E-03	8,8E-03	2,7	5,6E-02	2,8	2,8	2,8	2,8	2,8
	EtOH mass flow		23316,2	23316,2	1844,9	1844,9	1844,9	1,1E-05	1,1E-05	1,1E-05	1,1E-05	1,1E-05	1384,5	1384,5	1384,5	72,1	28,5	72,1	21471,3	460,4	23316,2	23316,2	23316,2	23316,2	23316,2
	Water mass flow		29002,2	29002,2	12545,7	12545,4	12545,7	2,3E-01	2,3E-01	2,3E-01	2,3E-01	2,3E-01	9414,5	9414,5	9414,5	490,4	495,4	490,4	16456,5	3130,9	19587,4	19587,4	19587,4	19587,4	19587,4
	Total mass flow		52802,6	52802,6	14872,0	14390,4	14872,0	481,5	481,5	481,5	481,5	481,5	10799,2	10799,2	10799,2	562,5	523,9	562,5	37930,6	3591,4	42906,5	42906,5	42906,5	42906,5	42906,5

Table A-5 continued

S/L ratio (g/mL)	Parameters		FEED	FEED1	FEED2	FEED3	LIQUID	EG-1	EG-2	EG-3	EG-4	EG-P	WA-1	WA-2	WA-3	WA-4	WA-R	WA-PURGE	VAPOR1	VAPOR2	ETWA-R1	ETWA-R2	ETWA-R3	ETWA-R4	ETWA-R
0.04	Temp (°C)		80,0	89,9	58,4	45,0	39,7	128,0	132,5	132,5	25,0	25,1	45,0	341,3	92,5	92,5	92,5	25,0	39,7	45,0	39,8	244,9	237,9	82,5	80,0
	Pressure (bar)		1,0	1,0	0,1	0,1	0,1	0,1	0,1	0,1	0,1	1,0	0,1	0,1	0,1	0,1	1,0	1,0	0,1	0,1	0,1	1,0	1,0	1,0	1,0
	EG mass flow	kg/hr	645,5	645,5	641,7	1,5	641,7	640,2	640,2	640,2	640,2	640,2	1,4	1,4	1,4	5,2E-02	1,3	5,2E-02	3,8	9,6E-02	3,9	3,9	3,9	3,9	3,9
	EtOH mass flow		23316,2	23316,2	17911,1	17911,1	17911,1	4,0E-05	4,0E-05	4,0E-05	4,0E-05	4,0E-05	1675,7	1675,7	1675,7	62,9	1612,9	62,9	21525,1	115,4	23319,6	23319,6	23319,6	23319,6	23319,6
	Water mass flow		32904,4	32904,4	14238,5	14237,1	14238,5	1,5	1,5	1,5	1,5	1,5	13319,9	13319,9	13319,9	499,6	12820,0	499,6	18665,9	917,2	19583,0	19583,0	19583,0	19583,0	19583,0
	Total mass flow		56866,1	56866,1	16671,4	16029,6	16671,4	641,7	641,7	641,7	641,7	641,7	14997,0	14997,0	14997,0	562,5	14434,2	562,5	40194,7	1032,7	42906,5	42906,5	42906,5	42906,5	42906,5
0.05	Temp (°C)		80,0	89,9	58,5	45,0	39,7	128,0	132,5	132,5	25,0	25,1	45,0	341,7	92,8	92,8	92,8	25,0	39,7	45,0	39,9	245,0	236,2	82,6	80,0
	Pressure (bar)		1,0	1,0	0,1	0,1	0,1	0,1	0,1	0,1	0,1	1,0	0,1	0,1	0,1	0,1	1,0	1,0	0,1	0,1	0,1	1,0	1,0	1,0	1,0
	EG mass flow	kg/hr	807,0	807,0	803,2	1,9	803,2	801,3	801,3	801,3	801,3	801,3	1,8	1,8	1,8	5,3E-02	1,7	5,3E-02	3,8	1,1E-01	3,9	3,9	3,9	3,9	3,9
	EtOH mass flow		23316,2	23316,2	2195,8	2195,8	2195,8	5,0E-05	5,0E-05	5,0E-05	5,0E-05	5,0E-05	2065,3	2065,3	2065,3	62,0	2003,3	62,0	21120,4	130,4	23320,1	23320,1	23320,1	23320,1	23320,1
	Water mass flow		36244,1	36244,1	17713,5	17711,6	17713,5	1,9	1,9	1,9	1,9	1,9	16659,7	16659,7	16659,7	500,4	16159,0	500,4	18530,6	1052,0	19582,5	19582,5	19582,5	19582,5	19582,5
	Total mass flow		60367,3	60367,3	20712,5	19909,3	20712,5	803,2	803,2	803,2	803,2	803,2	18726,8	18726,8	18726,8	562,5	18164,0	562,5	39654,8	1182,5	42906,5	42906,5	42906,5	42906,5	42906,5

Table A-6. Energy recoveries and consumptions in Aspen simulation for each S/L ratio based on a scenario with excess water addition.

S/L ratio (g/mL)	Heat exchanged (kW)			Heat duty (kW)							Work (kW)		
	HEX1	HEX2	HEX3	FLASH1	FLASH2	DIST1 - REB	DIST1 - COND	COOL1	COOL2	COOL3	COMP1	COMP2	PUMP
0.02	12112,7	85,0	4688,6	0,0	1,11E-04	4949,0	-941,9	-108,8	-9664,7	-34,8	4535,6	1008,0	2,43E-02
0.03	14308,7	127,1	7896,2	0,0	3,61E-05	2023,9	-952,5	-162,9	-7438,8	-35,1	4540,7	1704,0	3,64E-02
0.04	15646,5	171,6	10231,2	0,0	6,30E-04	924,9	-1065,0	-217,6	-6063,4	-67,8	4543,9	2399,7	4,85E-02
0.05	15296,7	214,8	12720,2	0,0	8,71E-04	1147,0	-1332,9	-272,4	-6372,2	-69,9	4544,8	3000,1	6,07E-02

Table A-7. Carbon footprint values of each step of PET alkaline hydrolysis process used in the LCA.

Process	Value	Unit
ethylene glycol production	1,90259	kg CO_2-eq/kg
purified terephthalic acid production	1,97340	kg CO_2-eq/kg
Incineration of PET with power recovery	1,60000	kg CO_2-eq/kg
ethanol production from sugar beet molasses	0,46255	kg CO_2-eq/kg
electricity, high voltage, production mix (BE)	0,26340	kg CO_2-eq/kWh
sodium hydroxide production (without water, in 50% solution state)	0,63290	kg CO_2-eq/kg
sulfuric acid production	0,10973	kg CO_2-eq/kg
treatment of waste electric and electronic equipment	0,05263	kg CO_2-eq/kg
treatment of municipal solid waste, incineration	1,60000	kg CO_2-eq/kg
treatment of wastewater	0,00033	kg CO_2-eq/kg
tap water production	0,00045	kg CO_2-eq/kg
microfiltration	2,00000	kWh/m^3
nanofiltration	7,00000	kWh/m^3

A.1. Effect of Na_2TP precipitation on the PET degradation rate

During PET hydrolysis, Na_2TP salt precipitates from the solvent due to limitations in solubility. This precipitation might affect the overall PET degradation rate by limiting the solvent diffusion. To test this hypothesis, different concentrations of PET resins (0.001 g/mL-0.1 g/mL) are hydrolysed under optimal degradation conditions. The theoretical amount of PET to observe the precipitation of Na_2TP during hydrolysis is calculated through elaborated solubility curve of Na_2TP. This graph is obtained via UV-VIS measurements of Na_2TP solubilized in 60:40 v% EtOH:H_2O solution in the temperature range of 20-80 °C (Figure A-5).

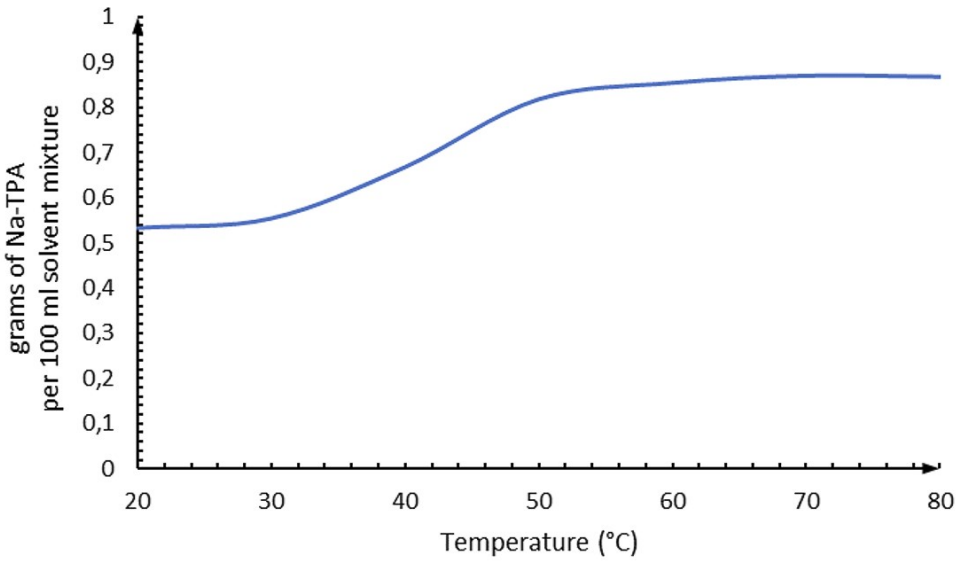


Figure A-5. Solubility of Na_2TP (g/100 mL solvent mixture) in the temperature range of 20-80 °C.

Based on the Na_2TP solubility curve, 0.001 g/mL, 0.01 g/mL and 0.1 g/mL of 80 µm PET resins are reacted with a solution consisting of 5 w% NaOH and 60:40 v% EtOH:H_2O solvent mixture at 80 °C under continuous stirring at 500 rpm with an agitator. During kinetic studies, Na_2TP precipitation was observed when 0.01 g/mL and 0.1 g/mL PET were used, while there was no precipitation with 0.001 g/mL PET resin. The degradation rate of each PET sample was followed through GC-FID measurements as discussed in section 2.2. According to the obtained data, around 92% conversion was obtained for each sample after 15 minutes of degradation. This shows that precipitation of Na_2TP does not have any significant effect on the PET degradation rate. It can be concluded that PET degradation rate depends only on the reactants. Since Na_2TP is a salt, it becomes inactive in nucleophilic substitution for the esterification (the reverse of depolymerization), which supports the hypothesis that PET

alkaline hydrolysis is an irreversible reaction and that the amount of PET waste to be hydrolyzed in a certain volume of medium is not limited by the precipitation step of the salt.

A.2. Characterization of the PET degradation medium and TPA via FTIR

In order to show the increase in concentration of disodium terephthalate (Na_2TP) during PET depolymerization at optimal degradation conditions and also to prove the conversion of ester bonds to carboxylic acid, an aliquot of liquid samples were collected from the reaction medium at every specific time interval and analyzed via FTIR spectroscopy using KBr pellets. After PET hydrolysis was completed, the reaction medium was acidified in order to convert Na_2TP to terephthalic acid (TPA) which was subsequently dried and mixed with KBr powder in the weight ratio of 1:100 to perform FTIR analysis. The spectra of the reaction medium at different time intervals and the obtained TPA are shown in Figure A-6.

In Figure A-6b, the peak at 940 cm^{-1} corresponds to O-H bending vibrations of the carboxyl (COOH) group in the TPA monomer. This peak does not appear in the spectra of the reaction medium, which clearly indicates that in the reaction medium, sodium is attached to TPA and thus ester groups exist instead of a carboxylic acid group.[74,75] Figure A-6a shows that these ester bonds do not belong to diethyl terephthalate which could be formed as a side product in case of insufficient NaOH in the medium because C-O-C bond stretch normally appearing as several strong bands between 1050-1250 cm^{-1} is not seen in the spectrum. In addition, primary alcohol C-O stretching appearing around 1000 cm^{-1} as a strong band is not seen as well, indicating the absence of diethyl terephthalate. In the study of Varghese et al. it is shown that when a carboxylate changes into a carboxylic acid group, the C=O and C-O peaks are replaced by two equivalent carbonyl bonds. Therefore, C=O vibrations occurring in carboxylic acid shifts to a lower wavenumber and the C-O vibrations shifts to a higher wavenumber.[76] This is also confirmed by the FT-IR spectra shown in Figure A-6. While the C-O stretching and C=O vibration of the TPA monomer is seen at 1423 cm^{-1} and at 1677 cm^{-1}, respectively, C-O stretching and C=O vibration in the reaction medium appears at 1387 cm^{-1} and at 1687 cm^{-1}, respectively. Furthermore, in Figure A-6a the intensity of the defined peaks increase by time, which shows the increase in the concentration of Na_2TP in the reaction medium. In both spectra, the absorption bands between 900-1050 cm^{-1} and also at around 2500 cm^{-1} are attributed to the C-C vibrations and C-H stretching of the aromatic structure.[77]

The broad band with several small subheads at around 3500 cm^{-1} is characteristic of the bonded OH group in the TPA.[78] In Figure A-6a, the very intense broad peak appearing at around 3400 cm^{-1} is attributed to the aqueous reaction medium containing water and ethanol. In this way, the conversion of ester group of Na_2TP to carboxylic acid group of TPA is clearly shown.

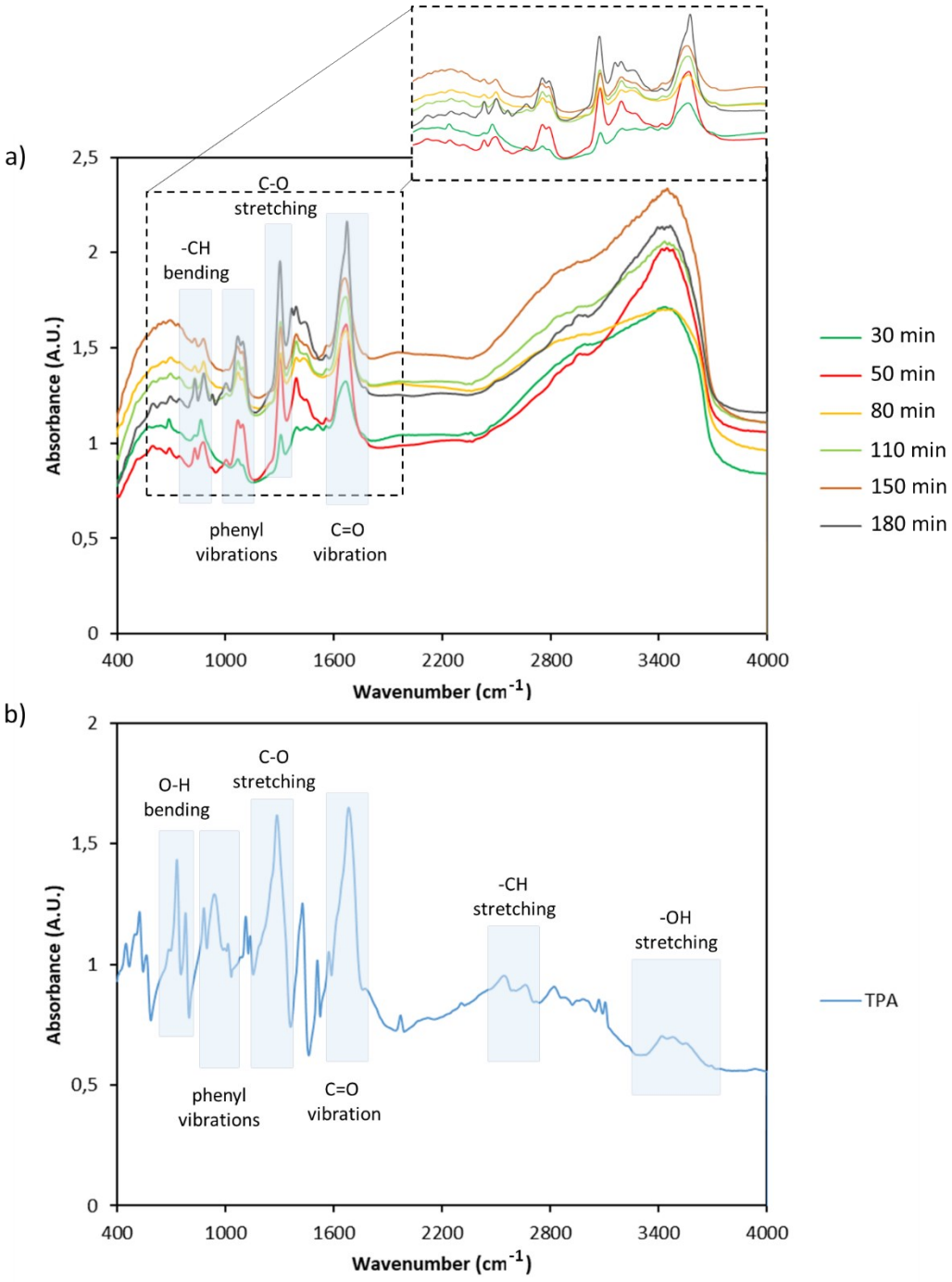


Figure A-6. FTIR spectra of (a) the PET degradation medium at different reaction times; (b) the TPA obtained after acidification of the medium.