

Viable recycling of polystyrene via hydrothermal liquefaction and pyrolysis.

Sogand Musivand ¹, Maria Paola Bracciale ^{1,*}, Martina Damizia ^{1,*}, Paolo De Filippis ¹ and Benedetta de Caprariis ¹

¹ Department of Chemical Engineering Materials and Environment, Sapienza University of Rome, Via Eudossiana 18, 00184, Rome, Italy; sogand.musivand@uniroma1.it (S.M.); paolo.defilippis@uniroma1.it (P.D.F.); benedetta.decaprariis@uniroma1.it (B.D.C.)

* Correspondence: mariapaola.bracciale@uniroma1.it (M.P.B.); martina.damizia@uniroma1.it (M.D.); Tel.: +390644585563

Supplementary Materials

2. Methods

2.2. Hydrothermal liquefaction

The scheme of the experimental setup is reported in Fig. S1 and is explained in detail in the authors' previous work [1]. The temperature (300-360 °C) was continuously measured with a K-type thermocouple inserted into the reactor; when the reactor reached the setting temperature, it was held at that temperature for the chosen reaction time (1-4 h). After the reaction finished occurring, the reactor was quenched in cold water to reach room temperature quickly, and then it was opened to take the products out for further analysis.

The reactor was vented off to measure the amount of the gas phase (by determining weight difference of the reactor before and after opening), and then the solid and liquid phase were separated by filtration. The oily phase, when present, is not miscible with water and thus was easily recovered, and part of the oily phase was adsorbed on the solid residue and recovered via an acetone extraction. The separated solid phase was then dried at 70 °C overnight for quantification, and the oily phase was separated from the acetone by using a rotating evaporator. To measure the amount of organics into the water phase, the water was removed at an ambient temperature, and we left the sample in a watch glass under the hood overnight.

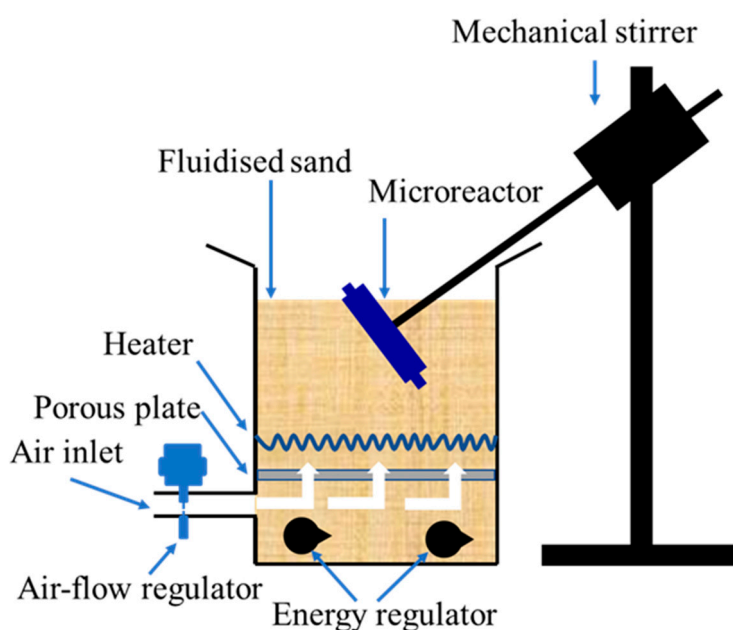


Figure S1. HTL setup.

2.3. Pyrolysis experiments

The pyrolysis process was conducted at temperatures of 400, 500 and 600 °C, and nitrogen was used as an inert carrier gas. The polymer sample (2 g) was loaded into the reactor by using a ceramic boat. The reactor was externally heated with a tubular electrical heater that was controlled with a K-type thermocouple, and the temperature of the reactor was controlled by a thermocouple located inside the reactor. The flow rate of nitrogen through the reactor was kept constant at 0.2 L/min. The reactor was heated from room temperature, and once the reactor reached the operative temperature, the reaction time of 30 min started. The vapors exiting from the reactor were condensed in a flask that was cooled with a cold water bath at 0 °C, and then they were collected. The yield of the liquid products is defined as the amount of liquid collected in the flask, and the yield of the residual char is the solid remaining inside the ceramic boat after the experiment.

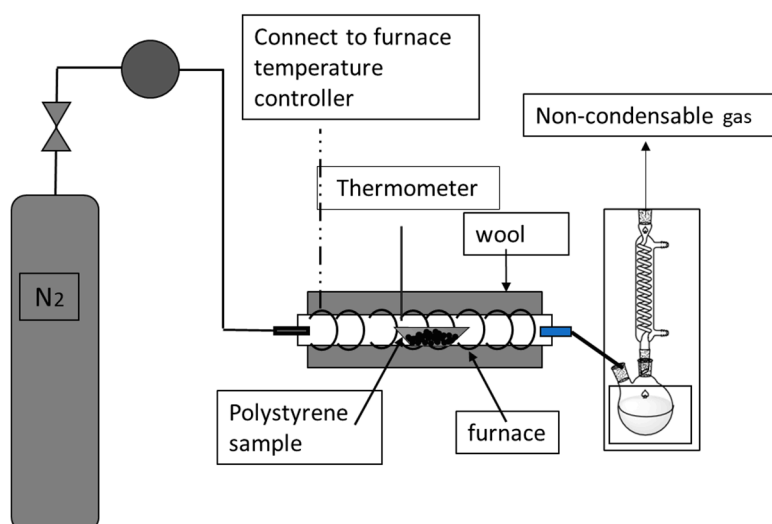


Figure S2. Pyrolysis setup.

2.4. Product characterization

The water phase organic compounds and oily phase compounds were diluted in ethyl acetate at a dilution ratio of 5 w/w. The chemical compounds were detected by using GC-MS and were identified by using the NIST mass spectral library. A GC analysis was performed by using a 6890 Mode Gas Chromatograph equipped with a mass spectroscopy detector (Agilent), helium as the carrier gas and a thin film (30 m \times 0.32 mm, 0.5 μ m film thickness) of an HP-DB wax column supplied from Agilent. The temperature ranged from 100 $^{\circ}$ C (held 2 min) to 250 $^{\circ}$ C at a heating rate of 10 $^{\circ}$ C/min (held 20 min). The injector temperature was 300 $^{\circ}$ C, and the injector split ratio was set to 30:1. The oily products were also analyzed by using an Elemental Analyzer (EA 3000, Eurovector) to measure the amount of C, H, N and O. The gas products of the pyrolysis were analyzed continuously by using a mass spectrometer (QGA-Hiden). To measure the amount of organics in the water phase, isobutanol was introduced as an internal standard to the mixture of the water phase, and then the mixture quantitatively analyzed by using GC-FID. A HP 5890 Series II Gas Chromatograph equipped with a flame ionization detector (Agilent) and HP-DB wax column (60 m \times 0.32 mm \times 0.25 μ m) was adopted. The theoretical response factors of the identified compounds were predicted by using the effective carbon number method [2].

Molecular and thermal characterizations of the solid products were performed by using Fourier-transform infrared spectroscopy (FT-IR) and a thermogravimetric analysis, respectively. Infrared spectra were acquired on a Bruker Vertex 70 spectrometer (Bruker Optic GmbH) equipped with a single-reflection Diamond ATR cell. The spectra were collected at a 3 cm^{-1} spectral resolution and had an average of 512 scans in the midinfrared range (400–4000 cm^{-1}).

The decomposition temperature of PS were investigated by using a thermogravimetric (TGA) analyzer (SDT Q600, TA Instruments). The samples in an open platinum crucible were heated from 30 up to 600 $^{\circ}$ C at a heating rate of 10 $^{\circ}$ C/min under a nitrogen flow rate of 100 mL/min.

3. Results and discussion

3.1. PS HTL

3.1.2. Characterization of the liquid products of PS HTL

In Fig. S3, the pictures of the obtained liquid products at 330 $^{\circ}$ C and 360 $^{\circ}$ C after 3 and 4 h of reaction time are reported.



Figure S3. Liquid products after 4 and 3 hours of reaction time at 330 °C and 360 °C.

Table S1. List of the compounds from the aqueous phase after PS HTL.

RT	Compounds	330 °C-3h	330 °C-4h	360 °C-3h	360 °C-4h
5.00	Benzene			0,3	
5.51	Toluene			4,4	8,7
6.00	Ethylbenzene		1,4	6,7	8,5
7.40	.alpha.-Methylstyrene		0,4	0,2	3,6
7.44	Benzaldehyde	1,9		9,5	11,5
8.77	Benzenemethanol, .alpha.-methyl-	9,7	5,8	12,8	6,8
8.93	Acetophenone	1,6	0,3	16,9	15,4
10.25	Benzoic Acid			4,6	2,5
10.47	Acetophenone, 4'-hydroxy-				2,3
14.19	Diphenylmethane		0,3	1,2	1,3
15.39	Bibenzyl		1,0	1,6	
16.99	Benzophenone			0,8	0,8
17.22	Benzene, 1,1'-(1,3-propanediyl)bis	19,6	19,8	12,8	22,6
17.49	Benzene, 1,1'-(1-butenylidene)bis-	13,0			1,9
18.01	(benzen,6heptynyl)	42,7	21,2		
18.59	Benzene, 1,1'-(3-methyl-1-prope...	3,4	7,7	6,7	6,9
18.86	Benzene, 1,1'-(1-butenylidene)bis-	9,7	16,8	1,0	

19.47	Benzene, 1,1'-(1,2-ethanediyl)bis-			4,9	4,9
19.51	Phenol, 2-(1-methylethyl)-	1,7			
19.66	Naphthalene, 1-phenyl-	1,5	11,8	1,9	0,7
22.08	Naphthalene, 2-(phenylmethyl)-	0,8	0,9	5,7	
24.32	1-Propene, 3-(2-cyclopentenyl)-...	0,4	12,1		
26.68	1,1':2',1''-Terphenyl, 4'-phenyl-			8,3	1,2

Table S2. List of the compounds from the oily phase at 360 °C after PS HTL.

RT	Compunds	3h	4h
4,707	Toluene	2,5	1,2
5,023	Ethylbenzene	3,1	1,1
5,245	Benzene, (1-methylethyl)-	1,6	0,4
5,818	Styrene	5,4	6,7
6,451	.alpha.-Methylstyrene	6,3	4,8
7,345	Benzene, 2-propenyl-	0,4	0,2
8,909	Benzaldehyde	0,5	1,3
10,385	Benzeneacetaldehyde		0,2
10,56	Acetophenone	0,9	1,4
12,321	Benzenemethanol, .alpha.-methyl	0,2	0,4
13,647	Naphthalene, 2-methyl	0,2	0,1
14,694	Diphenylmethane	1,0	0,6
15,404	Benzene, 1,1'-(1-methyl-1,2-ethyl)	3,4	0,5
15,588	Bibenzyl	1,6	0,9
15,827	(E)-Stilbene	0,5	0,4
16,187	1-Propene, 3-(2-cyclopentenyl)-2-methyl-1,1- diphenyl	0,6	0,3
16,73	Benzene, 1,1'-(1-methyl-1,3-propenyl)	3,5	
16,742	Benzene, 1,1'-(1-methyl-1,2-ethanediyl)bis-		2,0

16,866	Benzene, 1,1'-(1-methyl-1,3-propanediyl)bis-	15,9	12,0
17,4	Benzene, (1,3-dimethyl-3-butenyl)-	2,3	2,2
17,636	1,2-Diphenylpropane	1,2	0,7
17,73	Pentane, 1,4-diphenyl	0,4	0,1
17,91	Naphthalene, 1,2,3,4-tetrahydro-2-phenyl-	6,1	10,1
18,359	Benzene, 1-methyl-2-(2-phenylethyl)		0,8
18,34	Benzene, (1-methylethyl)		0,8
18,568	1-Propene, 3-(2-cyclopentenyl)-2-methyl-1,1-	2,3	1,4
18,662	2,5-Diphenyl-1,5-hexadiene		0,2
18,85	1,2-Diphenylpropane	8,3	5,9
18,944	Benzene, 1,1'-(3-methyl-1ethyl)	0,9	0,9
19,077	Benzene, 1,1'-(3-methyl-1-propene-1,3-diyl)bis-	4,8	
19,081	Benzene, 1,1'-(3-methyl-1-propenyl)	0,2	4,5
19,188	Benzophenone		0,3
19,415	Ethylene, 1,1-diphenyl-		3,1
19,504	1,1':2',1''-Terphenyl, 4'-phenyl-		6,1
19,607	Benzene, 1,1'-(1-butene-1,4-diyl)bis-, (Z)		2,8
19,608	Propane, 1-methyl-1-phenyl	2,2	
20,244	1-Pentene, 1,5-diphenyl-	0,4	
22,275	Benzene, 1,1'-(1,2-ethanediyl)bis[4-methyl-		1,3
23,062	Naphthalene, 2-phenyl-	2,5	1,5
24,297	1-Propene, 3-(2-cyclopentenyl)-2-methyl-1,1- diphenyl	2,1	0,2
27,316	Naphthalene, 2-(phenylmethyl)-	3,1	1,6
27,56	1,2-Propanediol, 3-benzy	0,4	1,0
28,051	1-Propene, 3-(2-cyclopentenyl)-2-methyl-1,1- diphenyl	5,7	1,9
29,569	Ethanol, 2-(2-ethoxyethoxy)-		0,2
30,228	p-Terphenyl		1,7

30,381	'-Terphenyl, 5'-methyl	0,2	0,4
32,37	Benzeneacetic acid, phenylmethyl ester	9,0	11,5
39,984	1-Propene, 3-(2-cyclopentenyl)-2-methyl-1,1- diphenyl		4,0

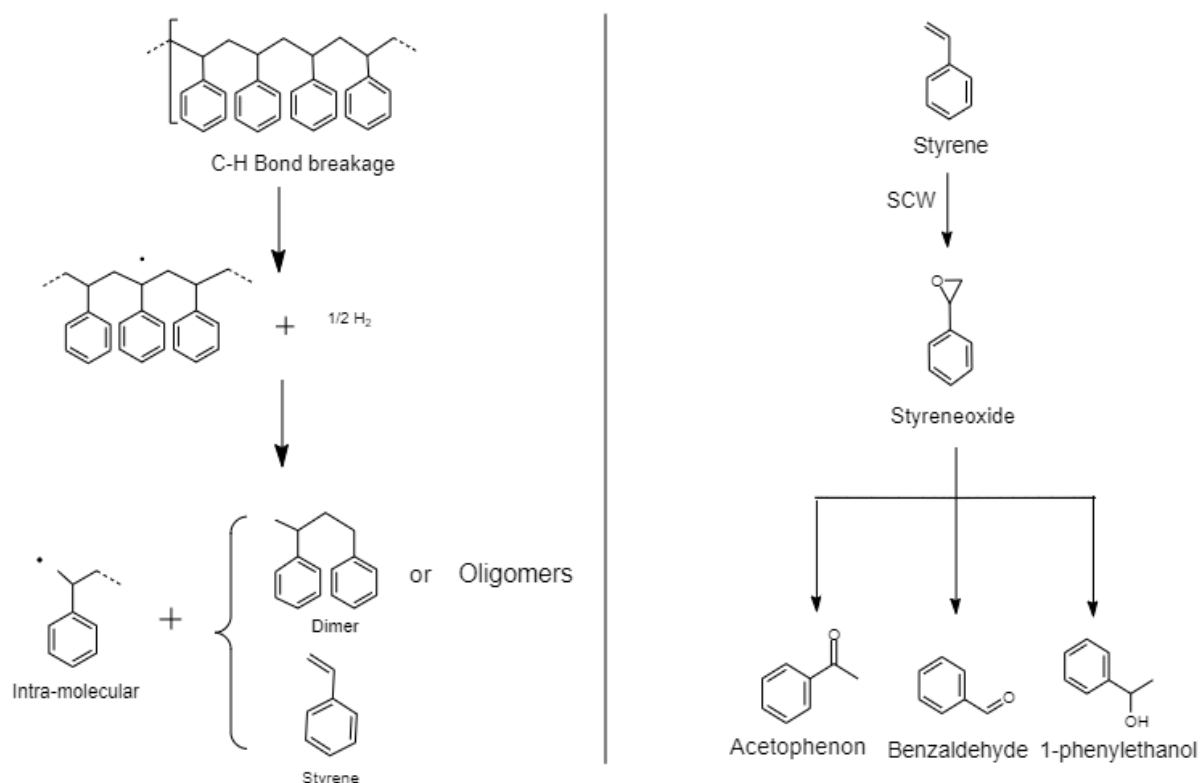


Figure S4. Hydrothermal degradation mechanism of PS in subcritical water.

The degradation of polystyrene followed a typical free-radical chain mechanism, where initiation, propagation and termination were the relevant reactions that occurred. In the first stage, the polystyrene chain broke down into a monomer via zip depolymerization. Subsequent addition reactions and the hydrothermal cracking of the C-C bond led to the formation of phenyl radicals, phenylmethyl radicals and alkyl radicals [3]. This does not explain the presence of oxygen, which was derived from the reaction of the produced radicals and the water in near-critical conditions. As reported in other works [4], in fact, oxygenated compounds could result from the nucleophilic participation of water in addition reactions. For example, acetophenone could result from the nucleophilic participation of water, which leads to a 1,2-addition product, 1-phenylethanol (Fig. S4). The deprotonation of the 1-phenylethanol to yield more stable acetophenone is promoted by the C=O double bond conjugation on the aromatic ring.

3.1.3. Characterization of the solid product of PS HTL

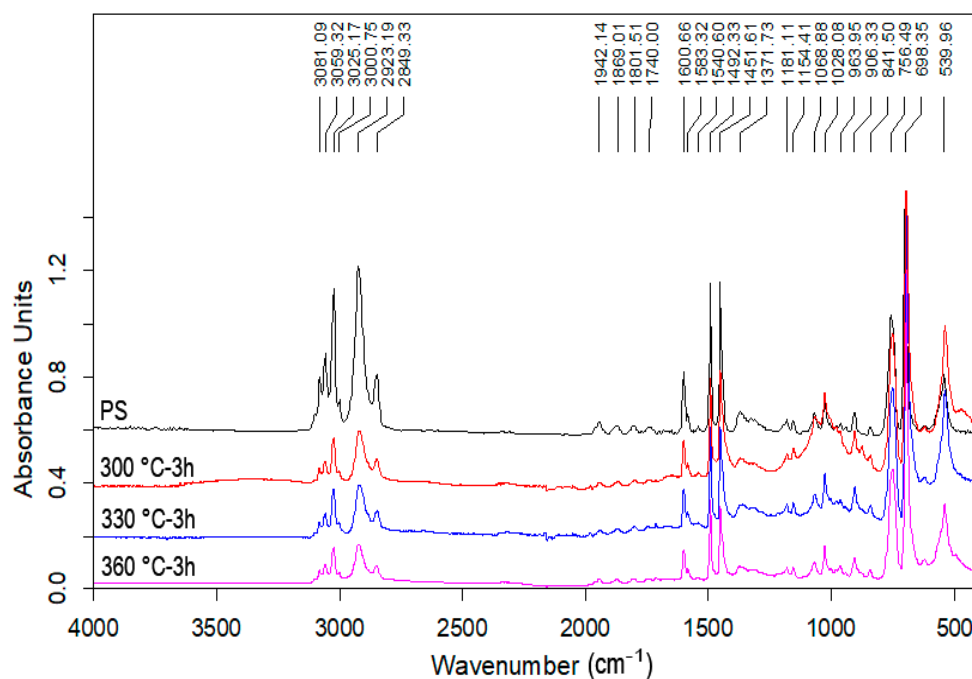


Figure S5. FT-IR spectrum of PS and PS solid residues obtained at 300, 330 and 360 °C after 3 h of reaction time.

Table S3. Bands corresponding to vibrational modes and functional groups of polystyrene.

Band assignments	Wavenumber (cm ⁻¹)
C-H stretching in aromatic ring (phenyl)	3081, 3059, 3025
stretching C-H bonds methylene (C-H ₂)	2923, 2849
aromatic ring stretching (phenyl)	1600
C=C stretching of benzene ring	1492; 1452
bending C-H bonds	1371
bending C-H	1028
rock methylene (C-H ₂)	756
monosubstitution (phenyl)	698

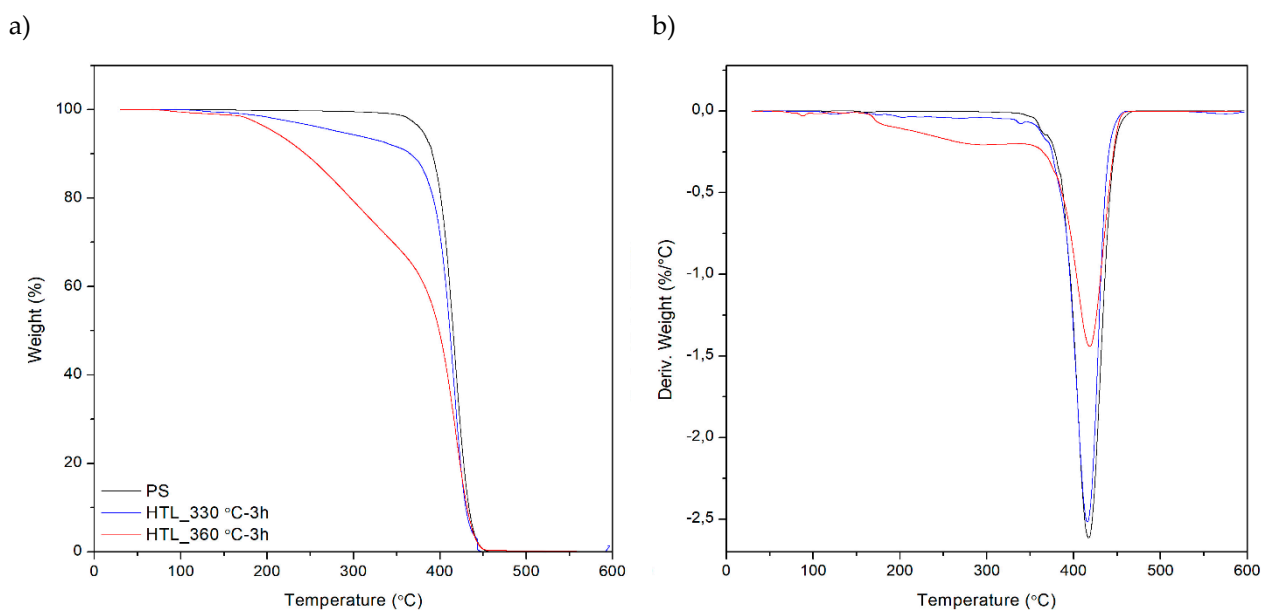


Figure S6. (a) TG and (b) DTG curve of polystyrene samples.

3.2.2. Chemical composition of PS pyrolysis oil

The pyrolysis of polystyrene is a typical radical chain mechanism [5] that proceeds through three principal steps: initiation, propagation and termination reactions (Fig. S7). In the initiation step, random chain breaking determines the C-C bond cleavage to form the benzyl radical and a primary radical. The propagation step occurs by sequencing intermolecular or intramolecular H-abstraction and β -scission reactions of the C-C bond (unzipping reactions) in the generated radicals, which leads to five-, six- or seven-membered ring intermediates (back biting reactions), a secondary benzylic radical and a polymer species with an unsaturated end. The β -scission process of the secondary benzylic radical leads to the formation of a styrene and another secondary radical with one less monomer unit, which can undergo further unzipping to give another monomer or a back-biting reaction followed by another β -scission reaction to give a dimer and another secondary radical. Termination consists of the disproportionation reaction of the primary radical, which results in toluene and a molecular chain with an unsaturated end that in turn decomposes into α -methylstyrene and a further secondary radical [6,7].

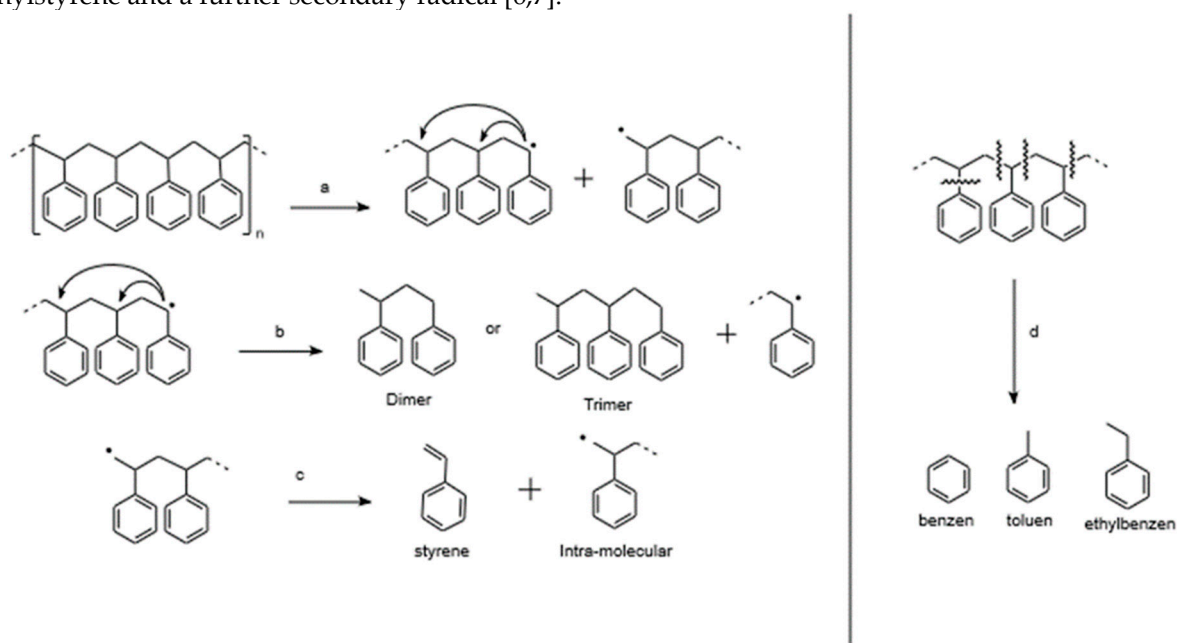


Figure S7. Schematic of the reactions occurring during the pyrolysis of polystyrene: (a) homolytic cleavage of the C-C bond; (b) β -cleavage of the C-C bond accompanied by the formation of styrene, trimer and dimer; (c) 1,7-hydrogen transfer; (d) plausible processes for the generation of volatile species such as benzene, toluene and ethylbenzene.

References

1. Tai, L.; Musivand, S.; de Caprariis, B.; Damizia, M.; Hamidi, R.; Ma, W.; De Filippis, P. Co-Treatment of Plastics with Subcritical Water for Valuable Chemical and Clean Solid Fuel Production. *J. Clean. Prod.* **2022**, *337*, doi:10.1016/J.JCLEPRO.2022.130529.
2. Feitosa, L.F.; Berhault, G.; Laurenti, D.; Teixeira Da Silva, V. Effect of the Nature of the Carbon Support on the Guaiacol Hydrodeoxygenation Performance of Nickel Phosphide: Comparison between Carbon Nanotubes and a Mesoporous Carbon Support. *Ind. Eng. Chem. Res.* **2019**, *58*, 16164–16181, doi:10.1021/ACS.IECR.9B00491.
3. Zhao, X.; Xia, Y.; Zhan, L.; Xie, B.; Gao, B.; Wang, J. Hydrothermal Treatment of E-Waste Plastics for Tertiary Recycling: Product Slate and Decomposition Mechanisms. *ACS Sustain. Chem. Eng.* **2019**, *7*, 1464–1473, doi:10.1021/acssuschemeng.8b05147.
4. Onwudili, J.A.; Williams, P.T. Degradation of Brominated Flame-Retarded Plastics (Br-ABS and Br-HIPS) in Supercritical Water. *J. Supercrit. Fluids* **2009**, *49*, 356–368, doi:10.1016/J.SUPFLU.2009.03.006.
5. Park, Y.; Hool, J.N.; Curtis, C.W.; Roberts, C.B. Depolymerization of Styrene-Butadiene Copolymer in near-Critical and Supercritical Water. *Ind. Eng. Chem. Res.* **2001**, *40*, 756–767, doi:10.1021/IE000502L.
6. Levine, S.E.; Broadbelt, L.J. Reaction Pathways to Dimer in Polystyrene Pyrolysis: A Mechanistic Modeling Study. *Polym. Degrad. Stab.* **2008**, *93*, 941–951, doi:10.1016/J.POLYMDEGRADSTAB.2008.01.029.
7. Faravelli, T.; Pincioli, M.; Pisano, F.; Bozzano, G.; Dente, M.; Ranzi, E. Thermal Degradation of Polystyrene. *J. Anal. Appl. Pyrolysis* **2001**, *60*, 103–121, doi:10.1016/S0165-2370(00)00159-5.