Waste-based value-added feedstocks from tire pyrolysis oil distillation: defossilization of the petrochemical industry

Supplementary Information

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Tables

Table S1. Experimental campaign and detailed GC characterization of the light fraction

Run	Temp. Reboiler (ºC)	RR	LTT (wt%)						
			Benzene	Toluene	Ethyl-benzene	p+m-Xylene	Styrene + o-Xylene	BTEX	Limonene
1	190	---	19.51	47.65	3.18	8.33	1.47	80.14	0.01
2	210	---	14.35	40.19	6.31	18.16	4.22	83.20	0.05
3	230	---	11.98	34.15	6.49	20.29	5.68	78.60	0.12
4	250	---	9.71	28.52	5.95	18.57	5.47	68.20	0.26
5	270	---	8.95	26.23	5.47	17.37	5.21	63.20	0.23
6	190	1.5	---	---	---	---	---	---	---
7	210	1.5	14.25	41.33	6.75	19	4.19	85.50	0.02
8	230	1.5	11.73	33.53	6.71	20.66	5.49	78.10	0.03
9	250	1.5	10.18	29.11	5.91	18.52	5.13	68.90	0.09
10	270	1.5	10.59	29.95	5.85	18.77	5.23	70.40	0.08

Table S2. Experimental campaign and detailed GC characterization of the heavy fraction

Run	Temp. Reboiler (ºC)	RR	HTT (wt%)						
			Benzene	Toluene	Ethyl-benzene	p+m-Xylene	Styrene + o-Xylene	BTEX	Limonene
1	190	---	0.64	1.89	3.22	9.42	3.09	18.26	0.19
2	210	---	0.63	1.53	0.99	5.48	2.74	11.37	0.51
3	230	---	0.44	1.27	1.34	1.55	0.93	5.53	0.44
4	250	---	0.27	1.28	0.52	1.78	0.64	4.49	0.12
5	270	---	0.04	0.20	0.10	0.39	0.16	0.89	0.08

6	190	1.5	---	---	---	---	---	---	---
7	210	1.5	0.21	1.52	1.24	2.74	1.88	7.59	0.19
8	230	1.5	0.44	2.11	0.82	2.48	1.05	6.90	0.19
9	250	1.5	0.54	2.49	0.83	1.87	0.94	6.67	0.19
10	270	1.5	0.38	1.13	0.27	0.93	0.29	3.0	0.08

Tale S3. BTEX concentrations reported in the literature from the pyrolysis of ELTs

Type of waste tire	Pyrolysis conditions	Catalyst	Pyrolysis yields	BTEX in the TPO	Ref
Truck tires	Reactor: Fixed-bed. Sample: 300g. Temperature: 800 ºC. Heating rate: 15-25 ºC/min	No catalyst	TPO: 44.7 wt%; TPG: 16.8 wt%; RRCB: 38.52 wt%	Aromatics: 65.4 wt%	RS1
Passenger car tires	Reactor: Py-GC/MS. Sample: ~10 g. Temperature: 400-500 ºC	No catalyst	Yields predicted by mathematical models	Optimum pyrolytic condition for yield of BTX (26.5 g per 100 g tire rubber)	RS2
From a recycling plant	Reactor: Self-designed optical precision heat control device. Sample: 0.40 g. Temperature: 425 - 575 °C. Heating rates: 60 - 6000 °C/min	No catalytic	TPO yields in the range of 55-57 wt%	Up to 41.5 area% with high heating rates	RS3
Passenger cars	Reactor: Fixed bed. Temperature: 500 °C. Heating rate: 10 °C/min. Gas residence time: 30 s approx.)	ZSM-5 (si/Al 40). Y-Zeolite (CBV-400). Y-Zeolite (CBV-780. Catalyst/feed ratio: 0-1.5	TPO yields in the range of 32-33 wt%. Catalyst presence reduces TPO yield. Increasing catalyst/tire feed ratio decreases TPO yield further and increases gas and coke formation.	Toluene reached a maximum value in the oil of 24 wt.%, benzene 5 wt.%, m/p-xylenes 20 wt.% and o-xylene 7 wt.%. (Total= 56wt%)	RS4
Origin not provided	Reactor: Fixed-bed. Sample: 1g. Temperature: 400-600 ºC	Fe_2O_3, CuO, CaO. Addition ratios: 5, 10, and 15 % of metal oxide	TPO: 48-50 wt% ; TPG: 9-12 wt%; RRCB: 39-40 wt%	Fe_2O_3 promotes cyclization and dehydrogenation to produce monoaromatics (57.4% relative area)	RS5
Sidewall rubber of automotive vehicle scrap tires	Reactor: Continuous stirred batch. Sample: 150g of scrap tires. Temperature: 430-500 °C. Heating rate: 15 °C/min	ZSM-5, USY, β, SAPO-11, and ZSM-22. The catalytic pyrolysis was performed using 1.0 wt% (on a scrap tire weight basis)	HZSM-5: TPO: 55.65 wt%; TPG: 6.49 wt%; RRCB: 37.86 wt%. USY: TPO: 53.49 wt%; TPG: 9.97 wt%; RRCB: 36.54 wt%. β zeolite: TPO: 54 wt%; TPG: 8.24 wt%; RRCB: 37.76 wt%	HZSM-5: MAHs: 45.8 wt% (PAHs: 4.3 wt%). USY: MAHs: 45.4 wt% (PAHs: 3.4 wt%). β zeolite: MAHs: 46.7 wt% (PAHs: 3.3 wt%)	RS6
Origin not	Reactor: Fixed bed. Sample: 30 g.	Zeolites: KL,	TPO: 42-43 wt%; TPG:	MAHs = 44-45 wt%	RS7

Type of waste tire	Pyrolysis conditions	Catalyst	Pyrolysis yields	BTEX in the TPO	Ref
provided	Temperature: 500 ºC. Heating rate: 10 ºC/min	HMOR, HBeta, HZSM-5, and HY	11-13 wt%; RRCB: 41-43 wt%		
Small domestic cars	Initial Evaluation: Reactor: Pyroprobe coupled with GC/MS. Sample: 0.60 mg. Temperature: 500-800 °C. Residence time: 5-30 s. Atmospheres: He, CH_4, H_2, N_2, O_2 Catalytic Pyrolysis: Reactor: fixed-bed. Sample: 3g. Temperature: 750 °C. Heating rate: 500 °C/s. Carrier Gas: CH4. Residence time: 30 s	Different zeolite catalysts. The catalysts were loaded in a quartz tube by mixing with the raw materials at 10 wt. %.	The yields of pyrolysis products are not shown.	Non-catalytic: 40.91 % MAHs were obtained at 500 °C/s and 750 °C in helium atmosphere. Catalytic: The Hβ catalyst is conducive to the formation of MAHs (up to 53.09 area %). The MCM-41Q catalyst is beneficial to the formation of BTEX (22.35 area %), as the content of MAHs was 46.09 area%	RS8
Origin not provided.	Reactor: Py-GC/MS. Sample: 1 mg. Temperature: 400-450 ºC. Heating rate: 2000 °C/s	Noble metals (Pd, Pt, Au) supported on titanate nanotubes (NT-Ti). The catalysts to feedstocks mass ratio was held at 1:4	The yields of pyrolysis products are not shown	The BTX production was enhanced by the presence of catalysts with a selectivity order as follows Pd > Pt ≈ Au > support > non-catalys. Values up to 50 area % of Monoaromatics	RS9
Origin not provided	Reactor: Two-staged pyrolysis–catalysis (fixed bed reactor). Sample: 10g. Temperature: 500 °C	Y-type (USY) zeolite. Catalyst/tire ratios of 0.25, 0.5, 0.75 and 1.0	Non-catalytic: TPO: 45.9 wt%; TPG: 16.5 wt%; RRCB: 37.59 wt%. TPO yield decreased as increasing the catalyst/tire ratio. Values lower than 30 wt%	Values up to 63 wt% of BTEX (catalyst/tire ratio of 0.5)	RS10
Origin not provided	Reactor: CDS 5200 Pyroprobe coupled to GC/MS. Sample: 10g. Temperature: 350, 400, and 450 °C	(Pd, Ni or Co)/SiO_2. Metal catalysts based on Ni, Co, and Pd	The yields of pyrolysis products are not shown	BTX: Pd (30.1 %) > Ni (22.2 %) > Co (10.2 %) > non-catalyzed (8.8 %)	RS11

Type of waste tire	Pyrolysis conditions	Catalyst	Pyrolysis yields	BTEX in the TPO	Ref
		supported on SiO_2). Catalyst-to-tire ratio of 8:1			
Truck tire	Reactor: Quartz Tube. Sample: 2 g. Temperature: 500 ºC	Metal-modified USY (Fe, Co, Ni, Cu, Zn). 2 g of waste tire and 0.4 g catalyst	TPO yield decreased from 42 to 34 wt%, approximately.	The highest relative content of monoaromatics reached 63.70 relative area % over 1%Cu/USY (42.92 mg/g)	RS12
Origin not provided	Reactor: Tandem micro pyrolyzer (Rx-3050 TR) coupled with GC/MS. Sample: 1 mg. Temperature: 400-600 ºC. Investigations: Zinc content and catalytic temperature.	RRCB and Zinc loaded RRCB was used as catalyst. Catalyst-to-tire ratio (5:1, 10:1, 15:1, 20:1, 25:1, and 30:1)	The yields of pyrolysis products are not shown	BTEX yield which was 2.4 times higher than that from uncatalyzed case. The optimal TPO products were obtained at 600 °C with catalyst-to-tire ratio of 20. The relative content of BTEX reached 54.70%	RS13

Table S4. Elemental and calorific analyses of the resulting heavy fraction

Run	Temp. Reboiler (ºC)	RR	Elemental composition, as received (wt%)				HCV (MJ/kg)
			C	H	N	S	
1	190	No	89.0	8.6	1.3	1.1	40.1
2	210	No	89.0	8.6	1.1	1.0	39.5
3	230	No	89.2	8.2	0.6	0.8	39.2
4	250	No	89.7	8.1	1.0	1.0	39.3
5	270	No	89.0	8.0	1.3	1.1	40.1
6	190	1.5	---	---	---	---	
7	210	1.5	89.1	8.2	1.5	1.0	39.3
8	230	1.5	89.4	8.1	0.8	0.9	41.1
9	250	1.5	89.1	8.0	1.4	1.0	41.4
10	270	1.5	89.2	8.0	1.2	0.8	39.8

Table S5. GC/MS results of the resulting heavy fraction

Run	Temp. Reboiler (ºC)	RR	BTEX		Substituted Benzenes		Indanes, indenes		Heterocyclic compounds		PAH		Others		Total
			RA (%)	RSD (%)	RA (%)	RSD (%)	RA (%)	RSD (%)	RA (%)	RSD (%)	RA (%)	RSD (%)	RA (%)	RSD (%)	
1	190	No	40.2	2.0	36.0	1.0	1.5	4.5	1.7	3.2	19.2	1.4	1.3	3.5	100.0
2	210	No	32.4	2.5	40.3	1.2	1.7	1.7	1.9	1.5	22.2	1.2	1.6	1.2	100.0
3	230	No	29.6	1.4	46.8	0.1	2.0	2.3	1.7	2.8	18.1	1.4	1.7	0.4	100.0
4	250	No	9.1	1.4	27.6	0.1	3.9	2.0	4.7	0.8	52.9	0.3	1.7	0.7	100.0
5	270	No	3.0	3.0	21.0	2.9	2.8	3.2	5.2	6.1	65.6	1.5	2.3	2.2	100.0
6	190	1.5	---	---	---	---	---	---	---	---	---	---	---	---	---
7	210	1.5	19.7	0.3	39.7	0.3	2.3	0.7	2.7	9.8	33.8	0.5	1.8	1.9	100.0
8	230	1.5	17.2	0.5	42.5	0.0	2.4	0.3	2.9	1.2	33.0	0.3	2.0	0.4	100.0
9	250	1.5	16.3	0.5	38.8	0.8	2.9	1.1	3.1	2.3	37.0	0.8	2.0	1.3	100.0
10	270	1.5	9.7	1.4	26.0	0.5	2.4	2.5	4.0	0.0	55.6	0.4	2.2	0.2	100.0

Figures

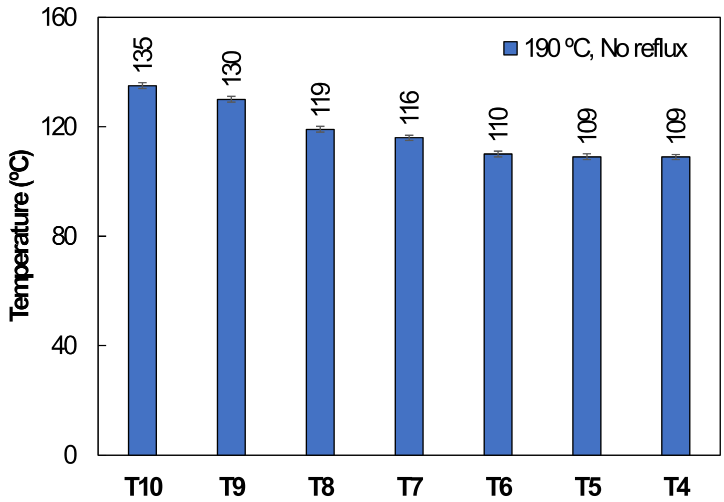

Fig. S1. Steady-state temperature profile of the column (run # 1)

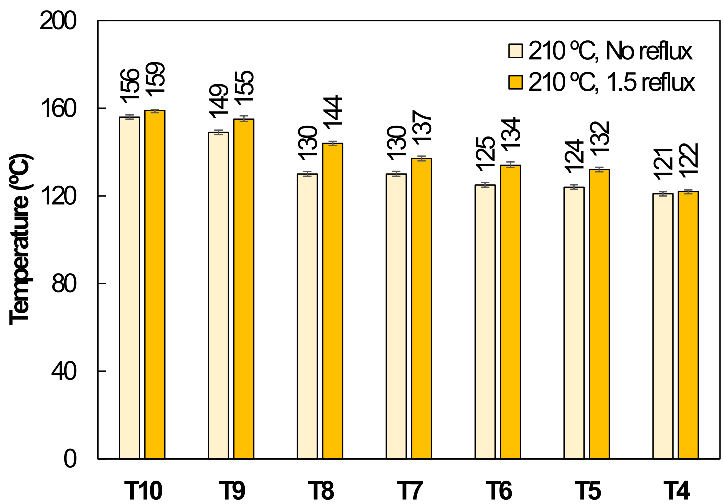

Fig. S2. Steady-state temperature profile of the column (runs 2 and 7)

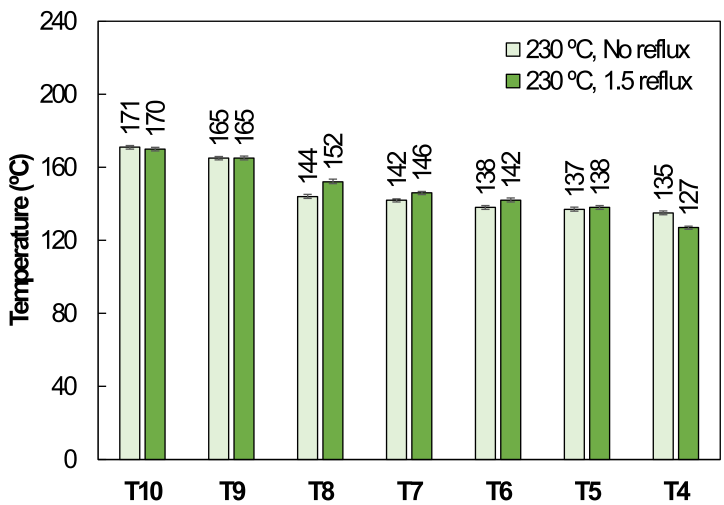

Fig. S3. Steady-state temperature profile of the column (runs 3 and 8)

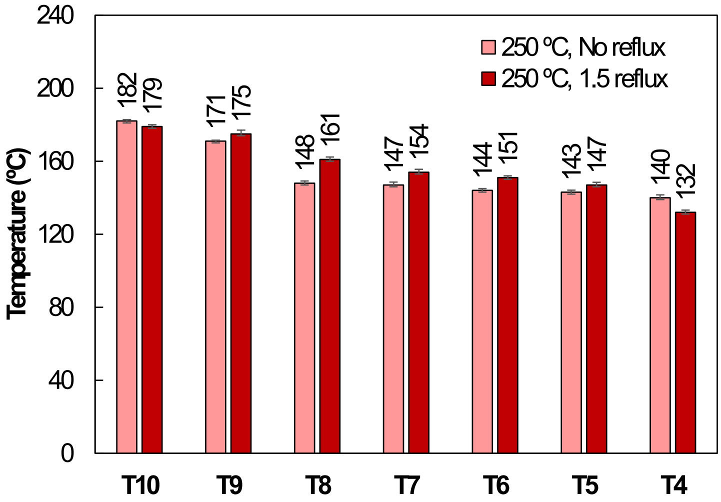

Fig. S4. Steady-state temperature profile of the column (runs 4 and 9)

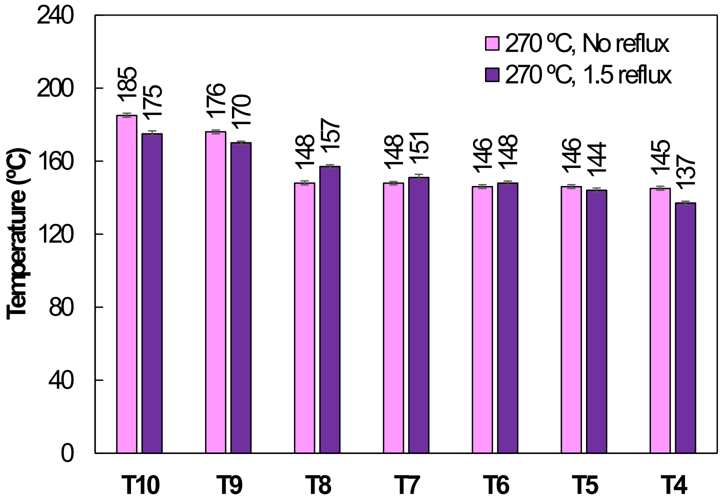

Fig. S5. Steady-state temperature profile of the column (runs 5 and 10)

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