Electronic Supplementary Materials

Thermal and catalytic pyrolysis of a synthetic mixture representative of packaging plastics residue

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Table S1. Detected aromatic compounds by GC–MS in light oils/wax of thermal and catalytic pyrolysis at 450 ℃, with relative area ≥ 0.1% and similarity ≥ 85%.

Retention Time (min)	Attribution	Formula	Thermal	HZSM5	HUSY
2.85	Benzene	C_6H_6		0.2	10.36
4.42	Toluene	C_7H_8	2.5	1.7	1.5
6.13	Ethylbenzene	C_8H_{10}	0.5	1.0	3.9
6.3	p-Xylene	C_8H_{10}		0.5	3.3
6.78	Styrene	C_8H_8	9.5	23.9	0.3
7.5	Benzene. (1-methylethyl)-	C_9H_{12}			0.9
8.23	Benzene. propyl-	C_9H_{12}		0.1	0.1
8.42	Benzene. 1-ethyl-2-methyl-	C_9H_{12}			0.4
8.5	Benzene. 1-ethyl-3-methyl-	C_9H_{12}		0.2	0.2
8.63	Benzene. 1-ethyl-4-methyl-	C_9H_{12}			0.3
8.96	α-Methylstyrene	C_9H_{10}	0.6	0.4	
9.28	Benzene. 1.2.3-trimethyl	C_9H_{12}			0.6
10.17	(Z)-1-Phenylpropene	C_9H_{10}		0.2	
10.38	Indane	C_9H_{10}			0.3
10.64	Benzene. 1-propynyl-	C_9H_8		0.2	
10.98	Benzene. 1-ethyl-2.4-dimethyl-	$C_{10}H_{14}$			0.1
11.49	Benzene. 2-ethyl-1.4-dimethyl-	$C_{10}H_{14}$			0.1
11.78	Benzene. 1-ethenyl-4-ethyl-	$C_{10}H_{12}$			0.3
12.63	Benzene. 4-ethyl-1.2-dimethyl-	$C_{10}H_{14}$			0.2
12.73	Benzene. 1-methyl-3-(1-methylethyl)-	$C_{10}H_{14}$			0.2
17.16	3.4-Dimethylcumene	$C_{11}H_{16}$			0.1
17.7	Naphthalene. 2-methyl-	$C_{11}H_{10}$			0.1
18.26	Benzene. heptyl-	$C_{13}H_{20}$	0.1		

19.56	Benzene. (3-methyl-1-methylenepentyl)-	$C_{13}H_{18}$	0.1		
20.92	Naphthalene. 1.2-dimethyl-	$C_{12}H_{12}$			0.1
26.52	Benzene. 1.1'-(1.3-propanediyl)bis-	$C_{16}H_{18}$	0.1		
27.98	Naphthalene. 1.2.3.4-tetrahydro-2-phenyl-	$C_{16}H_{16}$	0.3	0.3	

Table S2. Detected aliphatic compounds by GC–MS in light oils/wax of thermal and catalytic pyrolysis at 450 °C, with relative area ≥ 0.1% and similarity ≥ 85%.

Retention Time (min)	Attribution	Formula	Thermal	HZSM5	HUSY
2.04	Pentane. 2-methyl-	C_6H_{14}			0.3
2.14	Pentane. 3-methyl-	C_6H_{14}			0.2
2.17	1-Pentene. 2-methyl-	C_6H_{12}	0.3		
2.29	Cyclopentane. bromo-	C_5H_9Br		0.1	
2.41	2-Pentene. 3-methyl-. (E)-	C_6H_{12}		0.2	
2.49	Pentane. 2.4-dimethyl-	C_7H_{16}			0.2
2.76	2.4-Dimethyl 1.4-pentadiene	C_7H_{12}	0.1		
2.89	1-Pentene. 3-ethyl-	C_7H_{14}		0.1	
2.90	Hexane. 2-methyl-	C_7H_{16}			1.1
2.94	Pentane. 2.3-dimethyl-	C_7H_{16}			0.4
3.01	Hexane. 3-methyl-	C_7H_{16}			1.0
3.16	1-Hexene. 2-methyl-	C_7H_{14}		0.1	
3.21	1-Heptene	C_7H_{14}	0.1	0.1	
3.32	(Z)-3-Heptene	C_7H_{14}		0.2	
3.33	Heptane	C_7H_{16}	0.2		
3.37	1.3-Pentadiene. 2.4-dimethyl-	C_7H_{12}	0.1	0.2	
3.38	(Z)-4-Methyl-2-hexene	C_7H_{14}		0.9	0.3
3.43	2-Heptene. (E)-	C_7H_{14}		0.1	0.1
3.48	3-Methyl-3-hexene	C_7H_{14}		0.2	0.1
3.79	Hexane. 2.5-dimethyl-	C_8H_{18}			0.6
3.82	Hexane. 2.4-dimethyl-	C_8H_{18}			0.7
4.21	1-Ethylcyclopentene	C_7H_{12}		0.1	
4.23	2-Heptene. 4-methyl-. (E)-	C_8H_{16}	0.1	0.1	
4.28	Hexane. 2.3-dimethyl-	C_8H_{18}			0.4
4.38	Heptane. 2-methyl-	C_8H_{18}			1.1
4.40	Heptane. 4-methyl-	C_8H_{18}	0.6	0.4	
4.41	Pentane. 3-ethyl-	C_7H_{16}			0.6
4.45	Hexane. 3.4-dimethyl-	C_8H_{18}			0.1
4.48	Cyclohexene. 3-methyl-	C_7H_{12}		0.2	
4.51	Heptane. 3-methyl-	C_8H_{18}			1.3
4.83	1-Octene	C_8H_{16}	0.5		

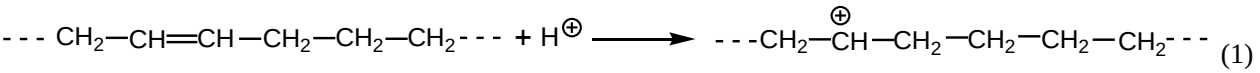
4.93	3-Hexene. 3.4-dimethyl-. (Z)-	C_8H_{16}		0.1	
4.99	Octane	C_8H_{18}	0.3	0.2	
5.00	4-Methyl-1.4-heptadiene	C_8H_{14}		0.3	
5.05	3-Heptene. 4-methyl-	C_8H_{16}			0.1
5.06	Methyl ethyl cyclopentene	C_8H_{14}		0.1	
5.08	3-Hexene. 2.5-dimethyl-	C_8H_{16}			0.1
5.10	Cyclohexane. 1.2-dimethyl- (cis/trans	C_8H_{16}			0.1
5.13	2-Hexene. 3.5-dimethyl-	C_8H_{16}		0.1	
5.15	Cyclohexene.3-(2-propenyl)-	C_9H_{14}		0.1	
5.21	Cyclopentane. 1.1.3.4-tetramethyl-. cis-	C_9H_{18}	0.2	0.1	
5.40	Heptane. 2.4-dimethyl-	C_9H_{20}			0.3
5.50	Heptane. 2.6-dimethyl-	C_9H_{20}	0.3		0.3
5.54	Cyclohexene. 1.4-dimethyl-	C_8H_{14}		1.6	
5.55	2-Hepten-4-one. 2-methyl-	$C_8H_{14}O$	0.1		
5.56	Cyclohexane. 1.3.5-trimethyl-	C_9H_{18}	0.4	0.3	
5.60	Heptane. 2.5-dimethyl-	C_9H_{20}			1.1
5.73	2.4-Dimethyl-1-heptene	C_9H_{18}	5.1	3.7	
6.00	Heptane. 2.3-dimethyl-	C_9H_{20}			0.2
6.05	1-Octene. 3-methyl-	C_9H_{18}			0.1
6.06	Cyclohexane. 1.3.5-trimethyl-. (1α.3α.5β)-	C_9H_{18}	0.8	0.6	
6.07	Heptane. 4-ethyl-	C_9H_{20}			0.1
6.18	Octane. 4-methyl-	C_9H_{20}			0.9
6.74	1-nonene	C_9H_{18}	0.8	0.2	
6.92	Nonane	C_9H_{20}	0.3		
7.20	3.4-Nonadiene	C_9H_{16}	0.2		
7.26	Heptane. 3.5-dimethyl-	C_9H_{20}			0.1
7.29	Pentane. 3-ethyl-2.4-dimethyl-	C_9H_{20}			0.1
7.47	Octane. 2.5-dimethyl-	$C_{10}H_{22}$			0.4
7.71	Octane. 2.6-dimethyl-	$C_{10}H_{22}$			0.4
7.83	Octane. 3.6-dimethyl-	$C_{10}H_{22}$			0.4
8.22	Heptane. 4-(1-methylethyl)-	$C_{10}H_{22}$			0.3
8.33	Nonane. 5-methyl-	$C_{10}H_{22}$			0.1
8.39	Nonane. 4-methyl-	$C_{10}H_{22}$			0.3
8.48	Nonane. 2-methyl-	$C_{10}H_{22}$			0.5
8.65	Nonane. 3-methyl-	$C_{10}H_{22}$			0.3
9.18	1-Decene	$C_{10}H_{20}$	1.5		
9.41	Decane	$C_{10}H_{22}$	0.3		
9.58	Nonane. 2.6-dimethyl-	$C_{11}H_{24}$	0.2	0.2	
9.69	Decane. 4-methyl-	$C_{11}H_{24}$	0.2	0.1	
9.89	Nonane. 2.5-dimethyl-	$C_{11}H_{24}$			0.2
10.12	Octane. 6-ethyl-2-methyl-	$C_{11}H_{24}$			0.1
10.93	Heptane. 4-ethyl-	C_9H_{20}			0.1
11.03	Decane. 4-methyl-	$C_{11}H_{24}$			0.1

11.15	Decane. 2-methyl-	$C_{11}H_{24}$			0.2
11.33	Decane. 3-methyl-	$C_{11}H_{24}$			0.1
11.46	1-Octene. 3.7-dimethyl-	$C_{10}H_{20}$		0.	
11.47	1-Octanol. 3.7-dimethyl-	$C_{10}H_{20}2O$	0.5	0.3	
11.59	1-Decene. 8-methyl-	$C_{11}H_{22}$	0.4	0.2	
11.92	1-Undecene	$C_{11}H_{22}$	0.3		
12.16	Undecane	$C_{11}H_{24}$	0.2		
13.96	Undecane. 2-methyl-	$C_{12}H_{26}$			0.1
14.74	1-Dodecene	$C_{12}H_{24}$	0.3		
14.97	Dodecane	$C_{12}H_{26}$	0.2		
17.51	1-Tridecene	$C_{13}H_{26}$	0.3		
17.70	4-Nonanol. 2.6.8-trimethyl-	$C_{12}H_{26}O$	0.6		
17.75	Undecane. 4.7-dimethyl-	$C_{13}H_{28}$	0.4		
17.93	3-Decene. 2.2-dimethyl-. (E)-	$C_{12}H_{24}$	0.1		
17.94	2-Isopropyl-5-methyl-1-heptanol	$C_{12}H_{24}$	0.2	0.1	
18.16	1-Octanol. 2-butyl-	$C_{12}H_{26}O$	0.5	0.2	
20.17	3-Tetradecene. (Z)-	$C_{14}H_{28}$	0.2		
20.34	Tetradecane	$C_{14}H_{30}$	0.1		
22.70	7-Hexadecene. (Z)-	$C_{16}H_{32}$	0.2		
22.89	Hexadecane	$C_{16}H_{34}$	0.1		
23.23	2-Hexyl-1-octanol	$C_{14}H_{30}O$	0.2		
25.11	7-Hexadecene. (Z)-	$C_{16}H_{34}$	0.1		
25.28	Hexadecane	$C_{16}H_{32}$	0.1		
27.39	9-Octadecene. (E)-	$C_{16}H_{36}$	0.1		
27.55	Octadecane	$C_{18}H_{38}$	0.1		
28.11	1-Decanol. 2-hexyl-	$C_{16}H_{34}O$	0.1		
28.75	3-Eicosene	$C_{20}H_{40}$	0.1		

APPENDIX - Mechanism of catalytic degradation in the presence of acid zeolites

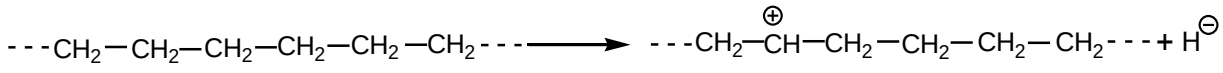
The first step of the catalytic cracking of organic polymers is the formation of a surface carbenium ion (R-CH^+), which is due to the presence of Brönsted and/or Lewis acid sites on the zeolitic catalyst [16,52,53]:

- Brønsted acid sites (Scheme 1) can donate a proton to an alkene that may be present as a defect site of the polymer chains or may have been previously formed by thermal cracking.



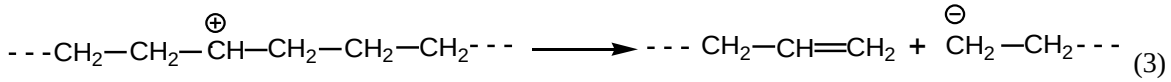
(1)

- Lewis acid sites (Scheme 2) can abstract a hydride from an alkane (the same can occur on strong Brønsted sites).



(2)

Then, the newly formed on-chain carbenium ion undergoes β-scission, as in Scheme 3, forming a smaller alkene and a smaller carbenium ion.

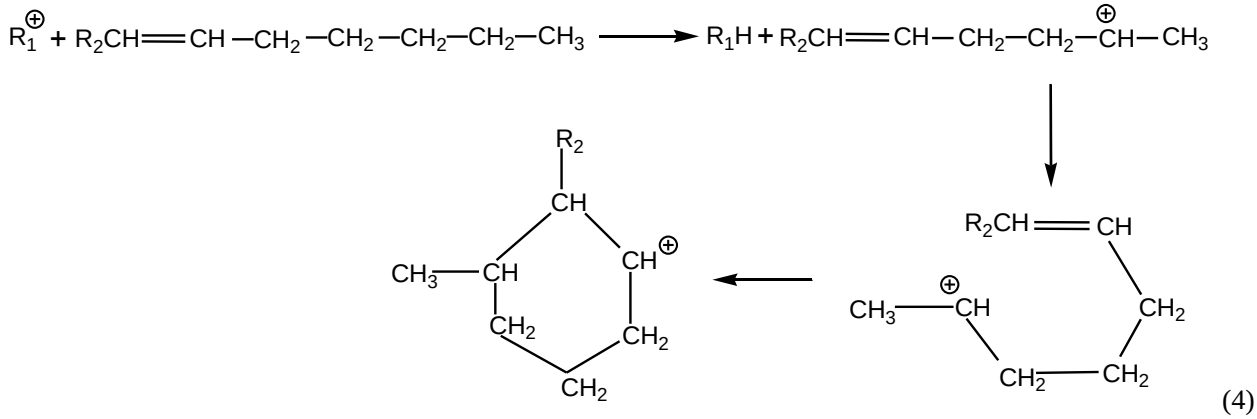


(3)

The propagation step is proceeded by hydride abstraction from a larger alkane molecule, which allows the smaller carbenium ion to desorb from the acid site as an alkane and leaves a new larger carbenium ion on the zeolite acid site to propagate the reaction. Alternatively, the carbenium ion can donate the proton back to the acid site and desorb as an alkene; termination corresponds to desorption of the absorbed carbenium ion to give an olefin and the return of the acid site to its initial state.

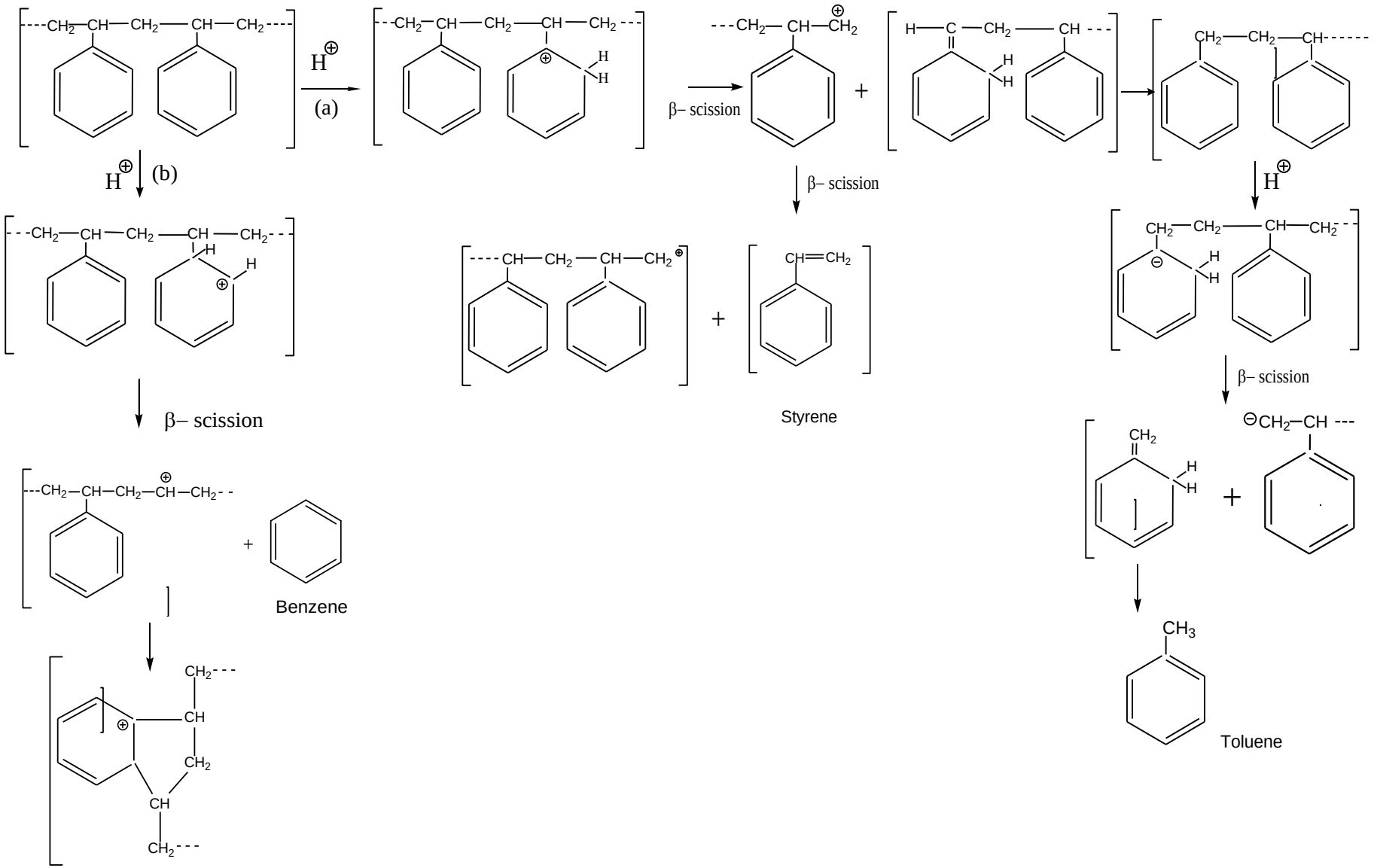
This way, the molecular weight of the main polymer chains may be reduced through successive attacks by acidic sites, other carbenium ions, or chain cleavage, yielding an oligomer fraction (approximately C30–C80). Further cleavage of the oligomer fraction (β-scission of chain-end carbenium ions) leads to gas formation on the one hand and a liquid fraction on the other.

In addition, the carbenium ion intermediates can undergo isomerization reactions, such as hydrogen or methyl-group shifts, which give rise to branched molecules. Moreover, cyclization reactions provide a route to the formation of aromatics, as shown in Scheme 4, where an olefinic carbenium ion may experience an intramolecular attack on the double bond.



(4)

When styrene-based polymers (e.g., PS) are involved, the same catalytic mechanism described above might account for the formation of aromatic compounds, such as benzene, toluene, and styrene, from plastic degradation. The initiation reaction is always the catalytic addition of hydrogen to the polymer aromatic ring, which gives rise to different carbenium ions (Scheme 5) [54].


H⊕
(a)
β– scission
H⊕ (b)
β– scission
β– scission
Styrene
H⊕
β– scission
Benzene
Toluene

(5)