Supplementary Materials for

Influence of Functional Additives, Fillers, and Pigments on Thermal and Catalytic Pyrolysis of Polyethylene for Waste Plastics Upcycling

Harish Radhakrishnan [a], Abdulrahman ABA Mohammed [a], Isabel Coffman [a], Xianglan Bai [a, b*]

[a] Department of Mechanical Engineering, Iowa State University, Ames, IA 50011, USA

[b] Department of Chemical & Biological Engineering, Iowa State University, Ames, IA 50011, USA

* Corresponding author, bxl9801@iastate.edu

This PDF file includes:

Supplementary Text

- Additional materials

Tables S1 to S7

Supplementary Text

Additional materials

The purity and supplier information for all chemicals are listed below.

- Virgin high-density polyethylene (HDPE) in unstabilized form (DOW Chemicals)
- Kaolin, ≤1% Soluble impurities in acid (Sigma Aldrich #18672)
- Calcium Carbonate, ≥99.0% purity (Fisher Scientific #C64-500)
- Talc, ≥99.0% purity (Fisher Scientific #S25799)
- Barium Sulfate, ≥99.0% purity (Fisher Scientific #S25191A)
- Zinc stearate, purity 14.0% (ZnO) (Fisher Scientific #AA3323818)
- Aluminum trihydrate (ATH), purity 65% Al_2O_3, 34.8% H_2O, 0.15% Na_2O (Fisher Scientific #50-901-09532)
- Titanium dioxide (TiO_2) (as part of LLDPE masterbatches) from a US-based compounder
- Carbon black (as part of LLDPE masterbatches) from a US-based compounder
- Tris(2,4-di-tert-butylphenyl) phosphite (Irgafos 168), purity ≥97.0% (AmBeed #A127499-100g)
- Pentaerythrityl tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate) (Irganox 1010), purity ≥98.0% (AmBeed #A125422-100g)
- Poly(4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol-alt-1,4-butanedioic acid), purity ≥95.0% (Ambeed #A176835-5g) (Tinuvin 622 LD), purity ≥95.0% (AmBeed #A176835-5g)
- HZSM-5 zeolite catalyst, SiO_2/Al_2O_3 ratio of 23:1 (Zeolyst International #CBV 2314)
- Saturated alkanes (C_7-C_{40}), certified reference material, 1000 μg/mL each component in hexane (Sigma-Aldrich #49452-U)

- Polar ISO Column Test Mix for Polyarc, Restek reference standard, 250 µg/mL ea. in 1,2-Dichloroethane, 1 mL/ampul (Restek #35103)
- Custom mixed gas standard (He, CO, CO_2, CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, C_2H_4, C_3H_6, C_4H_8), 99.99% purity, Praxair, USA.
- Acetanilide OAS, pure chemical standard, 5g (EA consumables SKU# B2114)
- Nitric acid (TraceMetal™ Grade), 67 to 70% (HNO3, w/w) purity, 2.5L (Fisher Scientific #A509P212)

Supplementary Tables

Table S1. Inorganic elemental composition by ICP-OES for virgin HDPE.

Analytes	Concentration (ppm)
Sb	-
Ba	-
Ca	22
Cd	-
Cr	-
Cu	-
Pb	-
Mn	-
Ni	-
Fe	7
Zn	-
Co	-
Ti*	29
V	-
Mo	-
Al*	132
Mg	-
K	-
Na	-
Total	197

*The high relative concentrations for Ti and Al are characteristics of a pure Ziegler-Natta HDPE.

Table S2. Mass yields from pyrolysis of individual additives alone.

Additives	Mass yields (only gases, hydrocarbon liquids, and solid recovery)			
	C_1-C_4	**C_5-C_{20}**	**C_{20}+**	**Solid Recovery**
Kaolin	-	-	-	89.7
Talc	-	-	-	97.9
Calcium carbonate	-	-	-	98.7
Barium sulfate	-	-	-	99.4
Zinc stearate	9.7	18.0	-	13.3
Aluminum trihydrate	-	-	-	65.7
Titanium dioxide*	-	-	-	99.9
Carbon black*	-	-	-	99.5
Hindered phosphite AO	10.3	8.3	-	0.6
Hindered phenol AO	17.3	-	-	9.3
Hindered amine LS	11.3	19.9	-	-
AOs & LS mix	32.9	25.3	-	3.0

*per pigment basis and does not include LLDPE-masterbatch derived mass or pyrolysates

Table S3. Pyrolysis products from pyrolysis of zinc stearate.

RT (min)	Name	Formula
4.025	Propanenitrile	C3H5N
4.305	Cyclobutane, 1,1,2,3,3-pentamethyl-	C9H18
4.837	Cyclopentene	C5H8
5.1	2H-Pyran, 3,4-dihydro-	C5H8O
6.697	Cyclopentane, 1,2-dimethyl-, trans-	C7H14
6.983	Benzene	C6H6
9.174	Cyclopentane, 1,2,3-trimethyl	C8H16
9.701	Toluene	C7H8
12.121	1-Nonanol	C9H20O
15.079	Cyclopropane, 1-(2-methylbutyl)-1-(1-methylpropyl)-	C12H24
17.883	Cyclodecane, methyl-	C11H22
20.504	1-Dodecanol	C12H26O
22.896	Tridecane	C13H28
22.947	n-Tridecan-1-ol	C13H28O
25.236	1-Tetradecanol	C14H30O
27.33	Pentadecane	C15H32
27.393	n-Pentadecanol	C15H32O
27.582	Cyclopentadecane	C15H30
29.419	1-Hexadecanol	C16H34O
31.267	Heptadecane	C17H36
31.336	8-Heptadecene	C17H34
32.017	Benzene, decyl-	C16H26
35.175	Hexadecanal	C16H32O
35.673	Benzene, dodecyl-	C18H30
36.652	2-Heptadecanone	C17H34O
38.471	9-Cycloheptadecen-1-ol	C17H32O
39.799	2-Nonadecanone	C19H38O

Table S4. Pyrolysis products from pyrolysis of hindered phosphite additive (Irgafos 168).

RT (min)	Name	Formula
16.338	Benzene, tert-butyl-	C10H14
18.89	2-tert-Butyltoluene	C11H16
20.842	Benzene, 1-(1,1-dimethylethyl)-3-ethyl-	C12H18
22.913	Benzene, 1,3-bis(1,1-dimethylethyl)-	C14H22
23.777	Naphthalene, 1,2,3,4-tetrahydro-1,1,6-trimethyl-	C13H18
24.2	1H-Indene, 2,3-dihydro-1,1,2,3,3-pentamethyl-	C14H20
25.454	Naphthalene, 1,2,3,4-tetrahydro-1,1,6-trimethyl-	C13H18
25.94	1H-Inden-1-one, 2,3-dihydro-3,3,6-trimethyl-	C12H14O
26.072	Naphthalene, 1,2,3,4-tetrahydro-1-methyl-8-(1-methylethyl)-	C14H20
26.615	1H-Inden-1-one, 2,3-dihydro-3,3,5,6-tetramethyl-	C13H16O
27.233	Ethanone, 1-(2,4,5-triethylphenyl)-	C14H20O
27.594	Demethoxyencecalinol	C13H16O2
27.691	Phenol, p-tert-butyl-	C10H14O
28.137	1H-Inden-1-one, 2,3-dihydro-3,3,5,6-tetramethyl-	C13H16O
28.297	1H-Inden-1-one, 2,3-dihydro-3,3,5,6-tetramethyl-	C13H16O
28.349	2,3,3,4,7-Pentamethyl-2,3-dihydro-benzofuran	C13H18O
28.469	Phenol, 4-(1,1-dimethylethyl)-2-methyl-	C11H16O
29.425	Phenol, 2-(2-methyl-2-propenyl)-	C10H12O
29.499	2,3,3,4,7-Pentamethyl-2,3-dihydro-benzofuran	C13H18O
31.456	2,4-Di-tert-butylphenol	C14H22O
32.263	1-Indanone, 3,3,5,6,7-pentamethyl-	C14H18O
32.383	2,3,3,4,7-Pentamethyl-2,3-dihydro-benzofuran	C13H18O
32.429	2,3,3,4,7-Pentamethyl-2,3-dihydro-benzofuran	C13H18O
32.572	4-Butyl-indan-5-ol	C13H18O
42.282	Phenol, 2,4-bis(1,1-dimethylethyl)-, phosphite	C42H63O3P

Table S5. Pyrolysis products from pyrolysis of hindered phenol additive (Irganox 1010).

RT (min)	Name	Formula
21.806	Phenol	C6H6O
22.901	p-Cresol	C7H8O
24.996	Phenol, 4-ethyl-	C8H10O
26.02	Benzene, 1-ethyl-4-methoxy-	C9H12O
26.495	Phenol, 2-methyl-5-(1-methylethyl)-	C10H14O
26.993	Benzofuran, 2,3-dihydro-	C8H8O
27.988	1H-Inden-5-ol, 2,3-dihydro-	C9H10O
28.057	Phenol, 2-(1,1-dimethylethyl)-4-methyl-	C11H16O
28.337	Phenol, 2-methyl-6-(2-propenyl)-	C10H12O
29.47	Phenol, 2-(1,1-dimethylethyl)-4-ethyl-	C12H18O
29.516	Butylated Hydroxytoluene	C15H24O
29.636	Benzamide, 4-methoxy-N-(2-phenylethyl)-N-methyl-	C17H19NO2
29.768	1-(benzo[d][1,3]dioxol-4-yl)butan-1-one	C11H12O3
30.117	7-Methylnaphthalen-2-ol, Ac derivative	C13H12O2
30.432	Phenol, 2,6-bis(1,1-dimethylethyl)-4-ethyl-	C16H26O
30.563	Phenol, 2,4,6-tris(1-methylethyl)-	C15H24O
31.479	Benzofuran, 2,3-dihydro-2,2,4,6-tetramethyl-	C12H16O
31.605	3,5-di-tert-Butyl-4-hydroxybenzaldehyde	C15H22O2
32.211	4-(4-Isopropylphenyl)-5-methyl-1,3-thiazol-2-ylamine	C13H16N2S
32.411	2-Allyl-1,4-dimethoxy-3-vinyloxymethylbenzene	C14H18O3
33.333	7-Ethoxy-3-ethyl-4-methyl-2H-chromen-2-one	C14H16O3
34.054	4-(4-Butylphenyl)-1,3-thiazol-2-amine	C13H16N2S
36.835	Phenol, 2,6-bis(1,1-dimethylethyl)-	C14H22O
37.081	4'-Propoxy-2-methylpropiophenone	C13H18O2
38.128	Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, methyl ester	C18H28O3

Table S6. Pyrolysis products from pyrolysis of hindered amine light stabilizer additive (Tinuvin 622 LD)**.**

RT (min)	Name	Formula
3.95	2-Propenal	C3H4O
4.482	Cyclopentene	C5H8
4.98	Cyclopentene, 1-methyl-	C6H10
5.558	Cyclopentene, 1-methyl-	C6H10
5.976	Cyclopentene, 1-methyl-	C6H10
6.096	Cyclopentene, 1-methyl-	C6H10
6.273	1,4-Cyclohexadiene	C6H8
6.445	1-Methyl-1H-1,2,4-triazole	C3H5N3
6.983	3,5-Dimethylcyclopentene	C7H12
7.984	2H-Pyran, 3,6-dihydro-4-methyl-2-(2-methyl-1-propenyl)-	C10H16O
10.822	1,3-Cyclopentadiene, 5,5-dimethyl-2-ethyl-	C9H14
11.017	1,3-Cyclopentadiene, 5,5-dimethyl-2-ethyl-	C9H14
12.012	Pyridine, 2-methyl-	C6H7N
12.751	p-Xylene	C8H10
13.037	2,4-Heptadiene, 2,6-dimethyl-	C9H16
13.231	Cyclopentene, 1,2,3,4,5-pentamethyl-	C10H18
13.374	1H-Pyrrole, 4-ethyl-2,3-dimethyl-	C8H13N
13.575	2-Methyl-4-pyridinamine 1-oxide	C6H8N2O
13.632	Pyridine, 2,3-dimethyl-	C7H9N
15.074	1H-Pyrrole, 3-methyl-	C5H7N
15.64	1H-Pyrrole, 2,3,5-trimethyl-	C7H11N
15.68	Pyridine, 3-ethyl-2,6-dimethyl-	C9H13N
16.127	1,3-Cyclopentadiene, 5,5-dimethyl-2-ethyl-	C9H14
16.916	Pyridine, 2,4,6-trimethyl-	C8H11N
17.425	2-Pyrimidineacetic acid, ethyl ester	C8H10N2O2
21.116	2-Isopropyl-6-methylaniline	C10H15N
23.983	Succinic anhydride	C4H4O3
28.091	8-Methoxy-[1,2,4]triazolo[4,3-a]pyridine-3-thiol	C7H7N3OS
30.907	7-((3S,5R,7aS)-5-Propylhexahydro-1H-pyrrolizin-3-yl)heptan-2-ol	C17H33NO

Table S7. Pyrolysis products from pyrolysis of hindered antioxidants and stabilizer mixture.

RT (min)	Name	Formula
3.956	2-Propenal	C3H4O
5.558	Cyclopentene, 1-methyl-	C6H10
5.976	Cyclopentene, 1-methyl-	C6H10
6.102	Cyclopentene, 1-methyl-	C6H10
10.817	1,3-Cyclopentadiene, 5,5-dimethyl-2-ethyl-	C9H14
12.745	p-Xylene	C8H10
13.626	Pyridine, 2,3-dimethyl-	C7H9N
23.783	Naphthalene, 1,2,3,4-tetrahydro-1,1,6-trimethyl-	C13H18
24	Succinic anhydride	C4H4O3
24.2	1H-Indene, 2,3-dihydro-1,1,2,3,3-pentamethyl-	C14H20
26.02	Benzene, 1-ethyl-4-methoxy-	C9H12O
26.501	Phenol, 2-methyl-5-(1-methylethyl)-	C10H14O
27.988	1H-Inden-5-ol, 2,3-dihydro-	C9H10O
28.063	Phenol, 2-(1,1-dimethylethyl)-4-methyl-	C11H16O
28.343	1-Hexene, 2-(O-anisyl)-4-methyl-	C14H20O
28.463	Phenol, 4-(1,1-dimethylethyl)-2-methyl-	C11H16O
29.47	Phenol, 2-(1,1-dimethylethyl)-4-ethyl-	C12H18O
29.51	Butylated Hydroxytoluene	C15H24O
29.636	Benzamide, 4-methoxy-N-(2-phenylethyl)-N-methyl-	C17H19NO2
29.768	1-(benzo[d][1,3]dioxol-4-yl)butan-1-one	C11H12O3
30.432	Phenol, 2,6-bis(1,1-dimethylethyl)-4-ethyl-	C16H26O
30.947	2,4-Di-tert-butylphenol	C14H22O
31.467	Phenol, 2,5-bis(1,1-dimethylethyl)-	C14H22O
31.605	3,5-di-tert-Butyl-4-hydroxybenzaldehyde	C15H22O2
32.211	4-(4-Isopropylphenyl)-5-methyl-1,3-thiazol-2-ylamine	C13H16N2S
32.406	2-Allyl-1,4-dimethoxy-3-vinyloxymethylbenzene	C14H18O3
33.333	7-Ethoxy-3-ethyl-4-methyl-2H-chromen-2-one	C14H16O3
34.054	4-(4-Butylphenyl)-1,3-thiazol-2-amine	C13H16N2S
38.128	Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, methyl ester	C18H28O3
39.095	2-(2-Trimethylsilyloxy-5-methylphenyl)benzotriazole	C16H19N3OSi
42.576	Phenol, 2,4-bis(1,1-dimethylethyl)-, phosphite (3:1)	C42H63O3P