

Supplementary Information

Catalytic co-pyrolysis of LDPE and PET with HZSM-5, H-Beta, and HY: Experiments and Kinetic Modelling

Sean Timothy Okonsky¹, J.V. Jayarama Krishna², Hilal Ezgi Toraman^{1-3*}

¹ Department of Chemical Engineering, Pennsylvania State University, University Park, Pennsylvania, USA, 16802

² Department of Energy and Mineral Engineering, Pennsylvania State University, University Park, Pennsylvania, USA, 16802

³ Institutes of Energy and the Environment, Pennsylvania State University, University Park, Pennsylvania, USA, 16802

*Corresponding Author: Email: hzt5148@psu.edu, Phone: 814-863-9261

Section S1. Py GC/MS Additive Area% Equations

To calculate the additive area% for catalytic co-pyrolysis experiments, Eqs. S1-S5 are used. For the preparation of Py-GC/MS samples, catalyst and polymer were added to a pre-mixture vial (PMV) in which the polymer and catalyst were well mixed together before being added to the quartz reaction tube. The actual weight of polymer which was pyrolyzed for a given experimental run i can be calculated using Eq. S1. *Mix weight pyrolyzed* (mg) is the weight of polymer/catalyst mixture added to the quartz reaction tube (~ 2.2 mg), *Polymer weight in PMV* (mg) represents the weight of polymer added to the pre-mixture vial, and *Total weight in PMV* (mg) is the weight of both catalyst and polymer which was added to the pre-mixture vial. The ratio of (*Polymer weight in PMV*/*Total weight in PMV*) for our experiments was always $\sim 1/11$ due to the catalyst:feedstock ratio being 10:1 for all experiments.

$$Actual\ polymer\ weight_i = Mix\ weight\ pyrolyzed_i \times \frac{Polymer\ weight\ in\ PMV}{Total\ weight\ in\ PMV} \quad (S1)$$

Once *Actual polymer weight* for a given experimental run i has been calculated, the normalized average area for compound or compound class X , represented as $Avg\ area\ (X)_{pol,cat}$, can be calculated using Eq. S2. $Area\ (X)_{pol,cat,i}$ is the GC/MS area observed for compound or compound class X for a given experimental run i . n corresponds to the number of experimental runs for a given polymer and catalyst. A normalization factor of 0.2mg was used as this was the target polymer weight for each experimental run. A similar equation (Eq. S3) is used for the average total area. $Total\ Area_{pol,cat,i}$ is the total chromatographic area integrated for a given experimental run i .

$$Avg\ Area\ (X)_{pol,cat} = \sum_{i=1}^n \frac{\frac{0.2mg}{Actual\ polymer\ weight_i} * Area\ (X)_{pol,cat,i}}{n} \quad (S2)$$

$$Avg\ Total\ Area_{pol,cat} = \sum_{i=1}^n \frac{\frac{0.2mg}{Actual\ polymer\ weight_i} * Total\ Area_{pol,cat,i}}{n} \quad (S3)$$

The LDPE:PET ratio denoted as $LP\ ratio_{cat}$ for a given catalyst is calculated using Eq. S4 and is used for the calculation of additive area%. Due to the LDPE:PET ratio being set as 1:1 wt./wt. in our study, $LP\ ratio_{cat}$ was always ~ 0.5 , however exact experimental values were used to ensure accuracy.

$$LP\ ratio_{cat} = \frac{LDPE\ weight\ in\ co-pyrolysis\ PMV_{cat}}{LDPE\ weight\ in\ co-pyrolysis\ PMV_{cat} + PET\ weight\ in\ co-pyrolysis\ PMV_{cat}} \quad (S4)$$

The additive area% for a compound or compound class “X” for a given catalyst is calculated using Eq. S5. The numerator of this equation corresponds to the area for X which would be expected to be observed based off results from single-stream pyrolysis experiments, and the denominator corresponds to the total area which would be expected to be observed based off results from single-stream experiments. Due to the total area for LDPE experiments being much larger than those observed from PET experiments, it is important to use the following equations for calculation of additive area%, rather than taking an average of the area% observed from LDPE and PET.

$$\text{Additive area\% (X)}_{cat} = \frac{LP \text{ ratio}_{cat} \times \text{Avg area (X)}_{LDPE,cat} + (1 - LP \text{ ratio}_{cat}) \times \text{Avg area (X)}_{PET,cat}}{LP \text{ ratio}_{cat} \times \text{Avg total area}_{LDPE,cat} + (1 - LP \text{ ratio}_{cat}) \times \text{Avg total area}_{PET,cat}} \times 100\% \quad (\text{S5})$$

Section S2. Flynn-Wall-Ozawa (FWO) method for deriving thermal pyrolysis kinetic parameters

For isoconversional approach to solving kinetics, thermograms are expressed in terms of conversion (α) where conversion is defined as:

$$\alpha_i = \frac{\text{mass}_{initial} - \text{mass}_i}{\text{mass}_{initial} - \text{mass}_{final}} \quad (\text{S6})$$

The reaction rate can be expressed as:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (\text{S7})$$

where A is the pre-exponential factor (min^{-1}), β is the heating rate (K/min), E is the activation energy (kJ/mol), R is the universal gas constant ($8.314\text{E}3 \text{ kJ/mol}$), and $f(\alpha)$ is the reaction model which depends on the reaction mechanism. The Flynn-Wall-Ozawa (FWO) method uses Doyle’s approximation to integrate the reaction rate equation,¹⁻³ simplifying it to be:

$$\ln\beta = \ln \frac{AE}{Rg(\alpha)} - 5.331 - 1.052 \frac{E}{RT} \quad (\text{S8})$$

For a constant conversion (α), the plot of $\ln\beta$ vs $\frac{1}{T}$, obtained from thermograms obtained at 5, 10, and 50K/min heating rates should be a straight line whose slope and intercept can be used to evaluate the activation energy and pre-exponential factor. The first-order reaction model $f(\alpha) = (1 - \alpha)$ which has a corresponding integral $g(\alpha) = -\ln(1 - \alpha)$ was used for our analysis.⁴ Activation energy and pre-exponential factor were determined for LDPE and PET pyrolysis for conversion values

ranging from 0.1, 0.2, ..., 0.9 and are shown in Table S1. The average activation energy and pre-exponential factor determined from FWO isoconversional method for LDPE and PET thermal pyrolysis were used as initial guesses for the n^{th} order reaction scheme.

Table S1

Pre-exponential factor (A), activation energy (E), and corresponding R^2 values calculated for LDPE and PET pyrolysis using FWO 1st order isoconversional approach

Conversion	LDPE			PET		
	A (s^{-1})	E (kJ/mol)	R^2	A (s^{-1})	E (kJ/mol)	R^2
0.1	7.72E+13	229.25	1.0000	4.52E+11	191.02	1.0000
0.2	6.90E+13	228.30	0.9994	3.02E+12	200.75	1.0000
0.3	8.99E+13	229.50	0.9991	4.72E+12	202.83	0.9997
0.4	7.10E+13	227.69	0.9985	5.37E+12	203.25	0.9997
0.5	9.52E+13	229.04	0.9986	9.39E+12	206.14	0.9999
0.6	7.67E+13	227.28	0.9984	1.34E+13	207.91	0.9999
0.7	1.03E+14	228.64	0.9985	1.17E+13	206.83	0.9999
0.8	7.43E+13	226.02	0.9976	1.35E+13	207.43	0.9999
0.9	7.93E+13	225.68	0.9975	1.63E+13	208.52	0.9994
Average	8.18E+13	227.93		8.65E+12	203.85	

Table S2 – Product distribution for pyrolysis of LDPE over various zeolites in a Pyroprobe micro-reactor

Chemical class	Chemical compound	LDPE/HZSM-5 area%	LDPE/H-Beta area%	LDPE/HY area%
C3 P/O	C3 hydrocarbons (Propane, Propylene)	15.50	12.68	8.92
C4 P/O	C4 hydrocarbons (Isobutane, Butane, 2-Butene)	25.42	40.31	33.18
C5 P/O	2-Methyl-1-butene	0.14	0.05	0.03
	Butane, 2-methyl	5.97	12.28	19.59
	Pentane	4.04	3.56	2.82
	2-Petene, (E)-	2.51	1.42	1.50
C6-C10 P/O	Butane, 2,2-dimethyl	-	0.12	0.05
	Pentane, 2-methyl	2.19	2.86	6.87
	Pentane, 3-methyl	0.86	1.21	3.60
	n-hexane	0.67	0.75	1.02
	1-Pentene, 3-methyl-	0.22	0.13	0.17
	Hexane, 2-methyl-	0.40	0.51	1.59
	Hexane, 3-methyl-	0.43	0.32	1.24
	Heptane	-	0.23	0.43
	1,3-Pentadiene, 2,3-dimethyl-	0.14	0.02	-
	1,4-Hexadiene, 4-methyl-	0.28	0.02	0.01
	Hexane, 2,4-dimethyl	-	0.09	0.23
	Heptane, 4-methyl-	0.03	-	0.04
	Heptane, 2-methyl-	0.18	0.10	0.50
	Heptane, 3-methyl-	0.09	0.06	0.43
	Octane	0.07	0.04	0.16
	2,4-Hexadiene, 2,5-dimethyl-	0.05	-	-
	Heptane, 2,5-dimethyl-	-	0.01	0.06
	Octane, 2-methyl-	-	0.02	0.19
	Octane, 3-methyl-	-	0.01	0.13
	Nonane	0.01	0.01	0.06
	Decane	-	0.01	0.03
Cycloalkanes and Cycloalkenes	Cyclopentene	0.20	-	-
	Cyclopentane methyl	1.15	0.39	0.63

Chemical class	Chemical compound	LDPE/HZSM-5 area%	LDPE/H-Beta area%	LDPE/HY area%
	Cyclopentane, 1,3-dimethyl-, cis-	0.21	0.16	0.29
	Cyclopentane, 1,2-dimethyl-, cis-	0.30	-	-
	Cyclohexane, methyl-	0.17	0.08	0.13
	Cyclopentane, ethyl-	0.26	-	-
	Cyclopentene, 4,4-dimethyl-	0.48	-	-
	Cyclopentane, 1-ethyl-3-methyl-, trans-	0.08	-	-
	Cyclopentane, 1-ethyl-3-methyl-, cis-	0.07	0.01	-
	Cyclopentene, 1-(1-methylethyl)-	0.09	-	-
	Cyclopentene, 1,2,3-trimethyl-	0.18	0.03	-
Monocyclic aromatic hydrocarbons (MAH)	Benzene	2.98	2.56	0.68
	Toluene	9.49	5.05	2.58
	Ethylbenzene	1.45	0.62	0.59
	p-Xylene	8.91	2.72	3.10
	m/o-Xylene	2.42	0.86	0.96
	Styrene	0.09	0.01	-
	Benzene, (1-methylethyl)-	0.05	0.01	-
	Benzene, propyl	0.14	0.06	0.03
	Benzene, 1-ethyl-3-methyl	2.55	0.61	0.55
	Mesitylene	0.23	0.22	0.56
	Benzene, 1-ethyl-4-methyl-	0.31	0.11	0.14
	Benzene, 1,2,4-trimethyl-	1.57	0.60	1.28
	Benzene, 1,2,3-trimethyl-	0.25	0.12	0.22
	Benzene, 1,3-diethyl	0.13	-	-
	Benzene, 1-methyl-4-propyl-	0.20	0.08	0.04
	Benzene, 2-ethyl-1,4-dimethyl-	0.26	0.12	0.14
	Benzene, 1-methyl-3-(1-methylethyl)-	0.13	0.08	0.12
	o-Cymene	0.35	0.09	0.09
	Benzene, 4-ethyl-1,2-dimethyl-	0.07	0.01	0.03
	Benzene, 1,2,4,5-tetramethyl-	0.03	0.03	0.09
	Benzene, 1,2,3,4-tetramethyl-	0.04	0.04	0.14
	2,4-Dimethylstyrene	0.26	0.03	0.00
	Benzene, 2-ethenyl-1,3,5-trimethyl-	0.21	0.03	-
Other Bicyclic hydrocarbons	Indane	0.16	0.04	0.01
	Indene	0.09	0.02	-

Chemical class	Chemical compound	LDPE/HZSM-5 area%	LDPE/H-Beta area%	LDPE/HY area%
	1H-Indene, 2,3-dihydro-5-methyl-	0.03	-	-
	Naphthalene, 1,2-dihydro-	0.16	-	-
	1,4-Dihydronaphthalene	0.13	-	-
	Naphthalene, 1,2,3,4-tetrahydro	0.08	-	-
	Naphthalene, 1,2,3,4-tetrahydro-6-methyl-	0.09	0.01	-
Polycyclic aromatic hydrocarbons (PAH)	Naphthalene	0.50	1.48	0.56
	Naphthalene, 2-methyl-	0.95	1.32	0.61
	Naphthalene, 1-methyl-	0.32	0.62	0.28
	Naphthalene, 2-ethyl-	0.13	0.09	0.02
	Naphthalene, 1,7-dimethyl-	0.42	0.30	0.24
	Naphthalene, 1,6-dimethyl-	0.26	0.33	0.25
	Naphthalene, 2,6-dimethyl-	0.16	0.15	0.08
	Naphthalene, 1,8-dimethyl-	0.05	0.12	0.09
	Naphthalene, 2-(1-methylethyl)-	0.11	0.04	0.02
	Naphthalene, 2,3,6-trimethyl-	0.02	0.04	0.05
	Naphthalene, 1,4,6-trimethyl-	0.02	0.04	0.05
	Naphthalene, 1,6,7-trimethyl-	0.01	0.03	0.04
	Fluorene	-	0.06	-
	Phenanthrene	-	0.65	0.14
	Anthracene, 2-methyl-	-	0.19	0.04
	Phenanthrene, 1-methyl-	-	0.20	0.05
	Phenanthrene, 2-methyl-	-	0.23	0.04
	Phenanthrene, 4-methyl-	-	0.08	0.01
	Anthracene, 1,4-dimethyl	-	0.05	0.02
	9,10-Dimethylanthracene	-	0.07	0.02
	Fluoranthene	-	0.11	0.01
	Pyrene	-	0.71	0.32
	Pyrene, 1-Methyl	-	0.13	0.06
	Pyrene, 4-Methyl	-	0.12	0.08
	Pyrene, 2-Methyl	-	0.14	0.06
	Total	98.03	98.73	98.37

Table S3 – Product distribution for pyrolysis of PET over various zeolites in a Pyroprobe micro-reactor

Chemical class	Chemical compound	PET/HZSM-5 area%	PET/H-Beta area%	PET/HY area%
	CO ₂	15.42	21.05	21.51
Oxygenated compounds	Acetaldehyde	0.52	3.02	7.52
	Pentanal	0.00	0.00	0.10
	Acetone	0.04	0.02	0.02
	Acetic acid	0.00	0.04	0.02
	Benzaldehyde	0.03	0.09	0.32
	Acetophenone	0.05	0.05	0.06
	Benzoic Acid	0.09	0.15	0.06
	Decanal	-	0.19	-
	Acetaldehyde, hydroxy-	0.03	0.11	-
	Benzene	43.46	55.70	54.38
Alkylated benzenes	Toluene	4.16	4.67	6.37
	Ethylbenzene	1.18	0.26	0.26
	p-Xylene	0.78	0.44	0.45
	m/o-Xylene	0.17	0.18	0.15
	Styrene	1.39	0.13	0.10
	Benzene, 1-ethyl-3-methyl	0.32	-	-
	Mesitylene	0.02	0.05	0.04
	α -Methylstyrene	0.07	-	-
	Benzene, 1,2,4-trimethyl-	0.29	0.16	0.14
	Benzene, 1,2,3-trimethyl-	-	0.04	0.02
	Benzene, 1-ethenyl-2-methyl	0.09	-	-
	Benzene, 2-ethyl-1,4-dimethyl-	-	0.06	0.01
Indanes and Indenes	Indane	0.44	0.03	
	Indene	3.25	0.17	0.06
	1H-Indene, 1-methyl-	0.14	-	-
	1H-Indene, 2,3-dihydro-4-methyl-	0.03	-	-
	1H-Indene, 3-methyl	0.15	-	-
	2-Ethyl-1-H-indene	0.06	-	-
Others	Naphthalene, 1,2-dihydro-	0.72	-	-
	1,4-Dihydronaphthalene	1.10	-	-
Polycyclic Aromatic Hydrocarbons (PAHs)	Naphthalene	9.93	4.31	0.65
	Naphthalene, 2-methyl-	6.06	0.56	0.08
	Naphthalene, 1-methyl-	0.97	0.24	0.03
	Naphthalene, 2-ethyl-	0.96	0.06	0.01
	Naphthalene, 1,7-dimethyl-	0.46	0.10	-

Chemical class	Chemical compound	PET/HZSM-5 area%	PET/H-Beta area%	PET/HY area%
	Naphthalene, 1,6-dimethyl-	0.36	0.07	0.01
	Naphthalene, 2-ethenyl	0.21	-	-
	Naphthalene, 1,8-dimethyl-	0.06	-	-
	Naphthalene, 2-(1-methylethyl)-	0.10	-	-
	Biphenyl	1.60	1.19	2.68
	Fluorene	0.63	0.77	1.51
	Diphenylmethane	0.03	-	-
	1H-Phenylene	0.21	-	-
	Stilbene	0.21	-	-
	1,1'-Biphenyl, 4-methyl-	0.06	0.05	0.08
	1,1'-Biphenyl, 3-methyl-	0.11	0.00	0.03
	9H-Fluorene, 2-methyl-	-	0.04	0.07
	Phenanthrene	0.09	1.65	0.48
	Anthracene	0.69	0.06	0.04
	Anthracene, 2-methyl-	-	0.06	-
	Phenanthrene, 1-methyl-	-	0.05	-
	Anthracene, 1-methyl-	0.16	-	-
	Phenanthrene, 2-methyl-	0.08	0.17	0.01
	Naphthalene, 1-phenyl	0.13	0.00	-
	1H-Indene, 2-phenyl-	0.37	-	-
	Naphthalene, 2-phenyl-	0.86	0.07	0.01
	Fluoranthene	-	0.43	0.08
	Pyrene	-	0.36	0.06
	7H-Benzanthrene	0.07	0.03	-
	7H-Benzo[c]fluorene	0.25	0.01	-
	Total	98.65	96.80	97.42

Table S4 – Product distribution for pyrolysis of LDPE and PET over various zeolites in a Pyroprobe micro-reactor

Chemical class	Chemical compound	LDPE+PET/H ZSM5 area%	LDPE+PET/H-Beta area%	LDPE+PET/H Y area%
Light gases	C3 hydrocarbons (propane, propylene)	9.27	11.97	8.67
	CO ₂	3.23	1.58	2.46

Chemical class	Chemical compound	LDPE+PET/H ZSM5 area%	LDPE+PET/H- Beta area%	LDPE+PET/H Y area%
C4 P/O + Acetaldehyde	C4 hydrocarbons (isobutane, butane, 2-Butene)	10.40	31.57	21.55
C5-C10 P/O	2-Methyl-1-butene	0.06	0.04	0.05
	Butane, 2-methyl	1.92	8.15	10.38
	Pentane	1.46	2.31	1.78
	2-Petene, (E)-	1.07	0.65	0.97
	Butane, 2,2-dimethyl	-	0.09	-
	Pentane, 2-methyl	0.64	1.53	3.34
	Pentane, 3-methyl	0.18	0.64	1.77
	n-hexane	0.20	0.41	0.58
	1-Pentene, 3-methyl-	0.05	0.02	0.08
	Hexane, 2-methyl-	0.11	0.27	0.93
	Hexane, 3-methyl-	0.11	0.17	0.60
	Heptane	-	-	0.22
	1,4-Hexadiene, 4-methyl-	0.10	-	-
	1-Heptene, 4-methyl-	-	-	0.06
	Hexane, 2,4-dimethyl	-	0.03	0.09
	Heptane, 2-methyl-	-	0.04	0.27
	Heptane, 3-methyl-	0.01	0.03	0.20
	Octane	0.03	0.01	0.09
	Octane, 2-methyl-	-	-	0.10
	Octane, 3-methyl-	-	-	0.06
	Nonane	-	-	0.03
	Decane	-	-	0.03
Cycloalkanes/ Cycloalkenes	Cyclopentene	0.08	0.01	-
	Cyclopentane methyl	0.35	0.19	0.29
	Cyclopentane, 1,3-dimethyl- , cis-	0.05	-	-
	Cyclopentane, 1,2-dimethyl- , cis-	0.05	0.04	-
	Cyclohexane, methyl-	0.04	0.07	0.04
	Cyclopentane, ethyl-	0.04	-	-
	Cyclopentene, 4,4-dimethyl-	0.18	-	-
	Cyclopentene, 1,2,3- trimethyl-	0.05	-	-
	Benzene	12.11	7.24	9.98
Alkylated benzenes	Toluene	9.08	7.93	11.60
	Ethylbenzene	1.78	0.89	1.96
	p-Xylene	6.72	3.32	4.85
	m/o-Xylene	1.77	1.03	1.50
	Styrene	0.33	0.03	0.03
	Benzene, (1-methylethyl)-	0.04	0.02	-

Chemical class	Chemical compound	LDPE+PET/H ZSM5 area%	LDPE+PET/H- Beta area%	LDPE+PET/H Y area%
	Benzene, propyl	0.10	0.06	0.10
	Benzene, 1-ethyl-3-methyl	1.32	0.67	1.02
	Mesitylene	0.13	0.24	0.56
	α -Methylstyrene	-	-	-
	Benzene, 1-ethyl-4-methyl-	0.16	0.11	0.16
	Benzene, 1,2,4-trimethyl-	1.30	0.65	1.42
	Benzene, 1,2,3-trimethyl-	0.14	0.13	0.25
	Benzene, 1,3-diethyl	0.04	-	0.03
	Benzene, 1,4-diethyl	-	0.05	-
	Benzene, 2-ethyl-1,4-dimethyl-	-	0.11	0.16
	Benzene, 1-methyl-2-propyl-	-	-	-
	Benzene, 1-methyl-3-(1-methylethyl)-	-	0.08	0.13
	o-Cymene	-	0.10	0.15
	Benzene, 1,2,4,5-tetramethyl-	-	0.01	0.10
	Benzene, 1,2,3,4-tetramethyl-	-	0.04	0.14
	2,4-Dimethylstyrene	0.24	0.03	0.02
	Benzene, 1-ethyl-2,4-dimethyl-	-	-	0.08
	Benzene, 2-ethenyl-1,3,5-trimethyl-	0.04	-	-
Indanes and Indenes	Indane	0.82	0.07	0.07
	Indene	1.07	0.04	0.04
	1H-Indene, 2,3-dihydro-5-methyl-	0.28	-	-
	1H-Indene, 2,3-dihydro-4-methyl-	0.34	-	-
	1H-Indene, 2,3-dihydro-1,2-dimethyl	0.05	0.01	-
	1H-Indene, 1,3-dimethyl-	0.05	-	-
	2-Ethyl-1-H-indene	0.10	-	-
Polycyclic aromatic hydrocarbons (PAHs)	Naphthalene	7.40	4.06	2.32
	Naphthalene, 2-methyl-	9.61	3.01	2.05
	Naphthalene, 1-methyl-	2.68	1.44	0.98
	Naphthalene, 2-ethyl-	1.59	0.20	0.10
	Naphthalene, 1,7-dimethyl-	1.30	0.58	0.49
	Naphthalene, 1,6-dimethyl-	0.74	0.67	0.62
	Naphthalene, 2,6-dimethyl-	0.46	0.29	0.23
	Naphthalene, 1,8-dimethyl-	0.20	0.25	0.23
	Naphthalene, 2,3-dimethyl-	0.03	0.10	0.09

Chemical class	Chemical compound	LDPE+PET/H ZSM5 area%	LDPE+PET/H- Beta area%	LDPE+PET/H Y area%
	Naphthalene, 2-(1-methylethyl)-	0.67	0.07	0.03
	Naphthalene, 2,3,6-trimethyl-	0.03	0.06	0.07
	Naphthalene, 1,4,6-trimethyl-	0.02	0.06	0.07
	Naphthalene, 1,4,5-trimethyl-	0.01	0.05	0.06
	Naphthalene, 1,6,7-trimethyl-	0.02	0.05	0.06
	Biphenyl	0.85	0.07	0.19
	Fluorene	0.28	0.18	0.23
	Diphenylmethane	0.14	-	-
	1H-Phenylene	0.11	-	-
	1,1'-Biphenyl, 4-methyl-	0.27	0.03	0.09
	1,1'-Biphenyl, 3-methyl-	0.45	0.01	0.04
	1,1'-Biphenyl, 2-ethyl-	0.03	-	-
	9H-Fluorene, 2-methyl-	0.10	0.06	0.08
	9H-Fluorene, 9-methyl-	0.01	0.04	0.05
	9H-Fluorene, 4-methyl-	0.06	-	-
	Phenanthrene	0.09	1.45	0.42
	Anthracene	0.49	0.03	0.01
	Anthracene, 2-methyl-	-	0.34	0.12
	Phenanthrene, 1-methyl-	0.02	0.39	0.13
	Anthracene, 1-methyl-	0.33	0.01	-
	Phenanthrene, 2-methyl-	0.09	0.38	0.12
	Phenanthrene, 4-methyl-	0.10	0.17	0.06
	Phenanthrene, 3,6-dimethyl-	-	0.07	0.03
	Anthracene, 1,4-dimethyl	0.03	0.09	0.05
	9,10-Dimethylanthracene	-	0.11	0.04
	3,4-Dimethylphenanthrene	-	0.06	0.02
	Naphthalene, 2-phenyl-	0.20	0.01	-
	Fluoranthene	-	0.21	0.07
	Pyrene	-	1.06	0.56
	Pyrene, 1-Methyl	-	0.19	0.08
	Pyrene, 4-Methyl	-	0.17	0.10
	Pyrene, 2-Methyl	-	0.18	0.07
	7H-Benzo[c]fluorene	0.08	-	-
	Benzo[k]fluoranthene	-	0.04	-
	Total	96.20	99.16	98.92

Table S5. Fitted results of NH₃-TPD experiments for zeolite catalysts. Peak temperatures and areas corresponding to weak, medium, and strong acid sites are displayed.

Samples	T _M (°C)				peak area (a.u.)			
	Weak	Medium	Strong	Total area (a.u.)	Weak	Medium	Strong	Fitted parameter, R ²
HZSM-5	120.5	200	383	12.109	2.696	4.588	4.825	0.99
H-Beta	124.3	200	350	8.139	3.211	1.743	3.185	0.98
HY	130.9	200	350	6.064	2.029	1.747	2.288	0.99

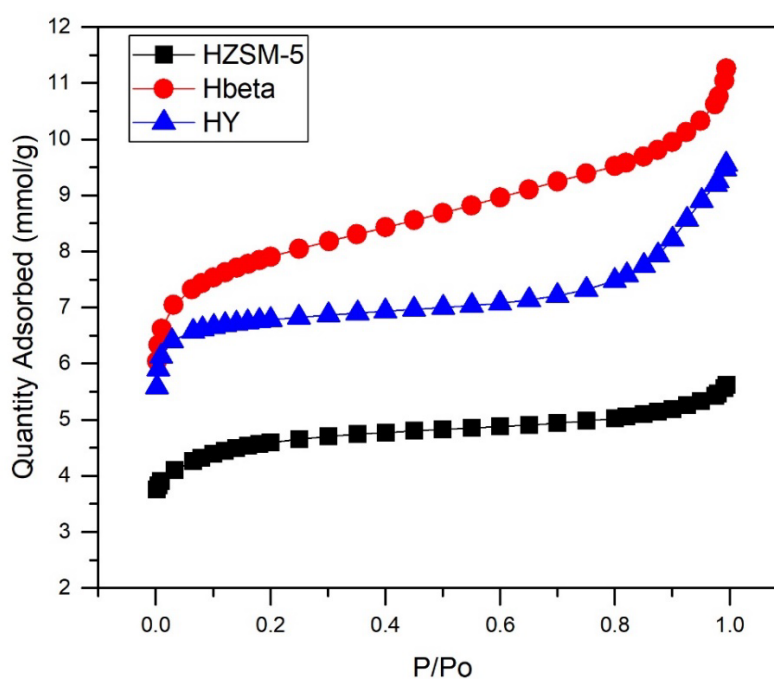


Figure S1. Single isotherm from N₂ physisorption of zeolites used in this study

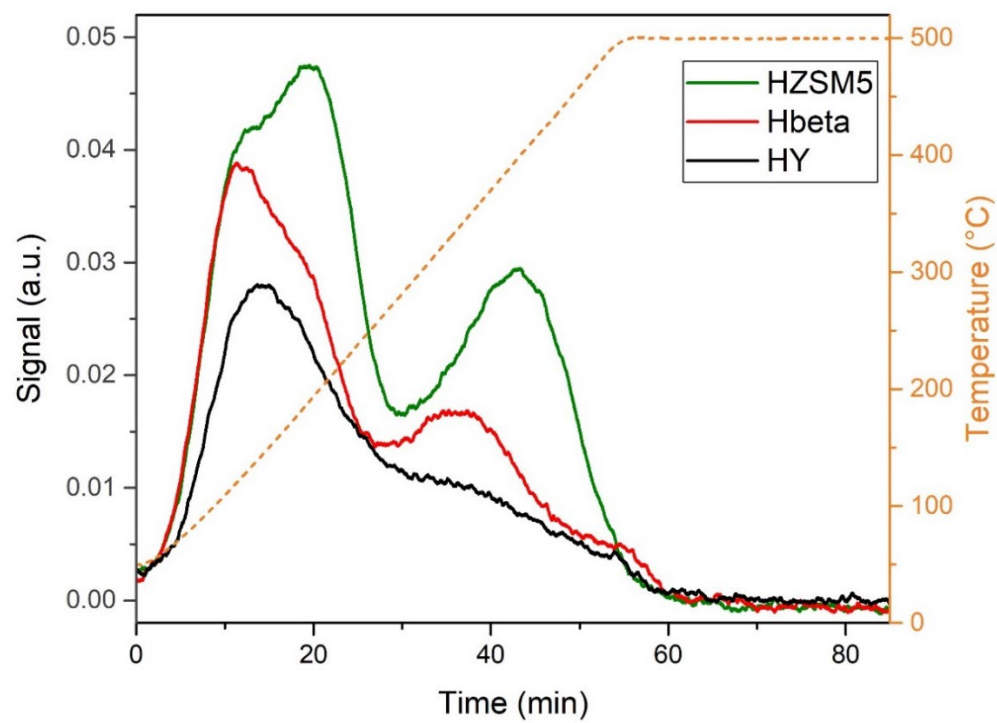


Figure S2. NH₃-TPD of zeolites

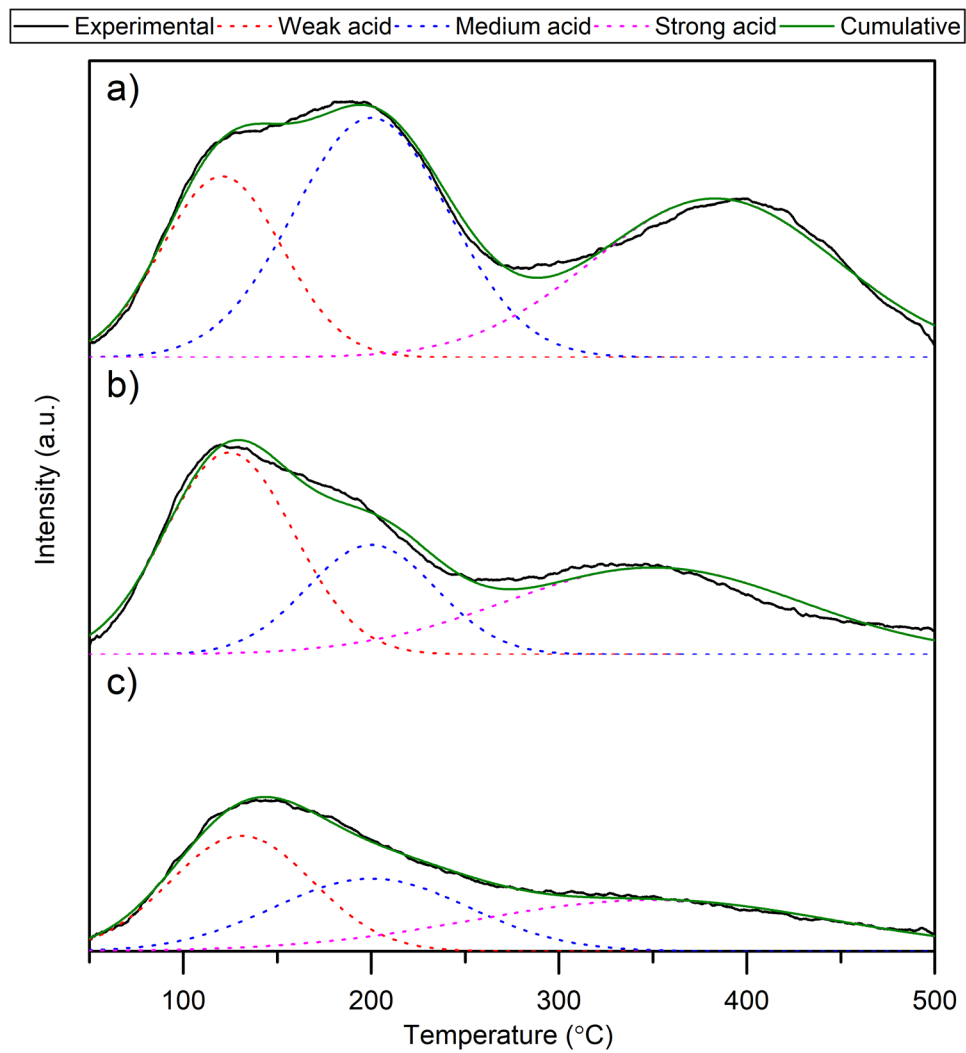


Figure S3. Fitted peaks for weak, medium, and strong acid sites determined from NH₃-TPD of HZSM-5 (a), H-Beta (b), and HY (c)

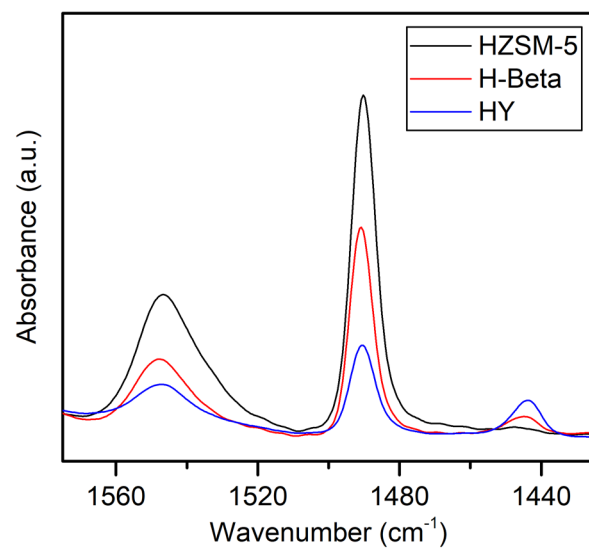


Figure S4. FTIR of pyridine adsorbed zeolites

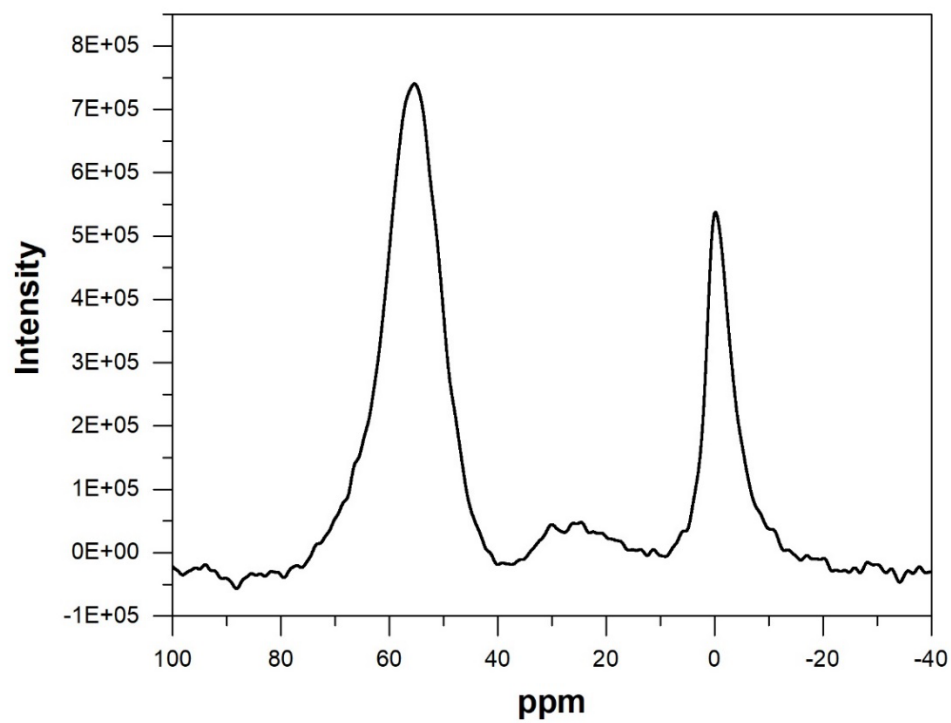


Figure S5. Al^{27} NMR of HZSM-5 (CBV 2314)

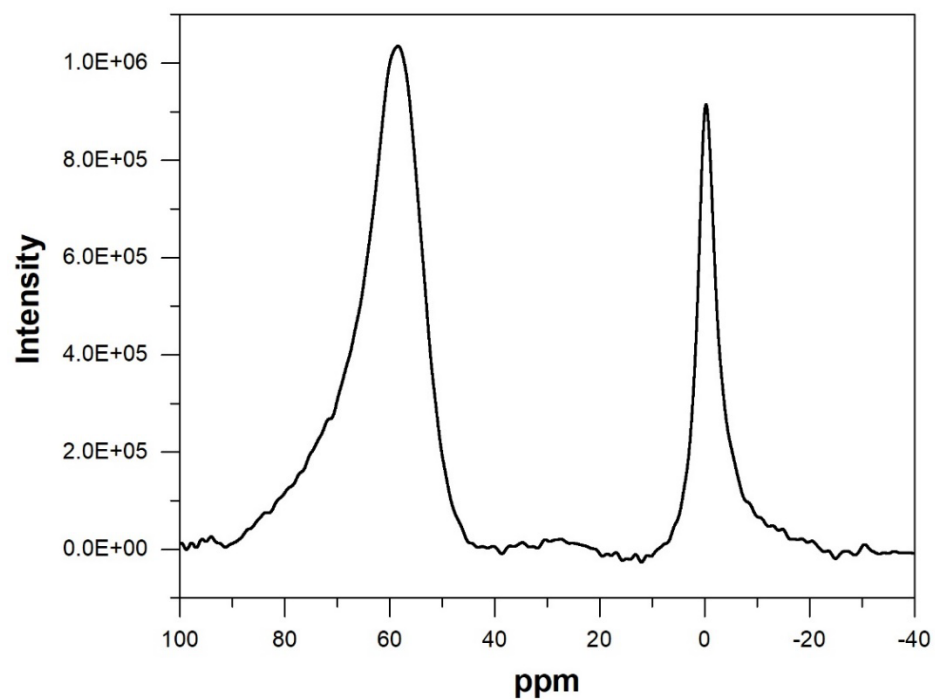


Figure S6. ^{27}Al NMR of H-Beta (CP814C)*

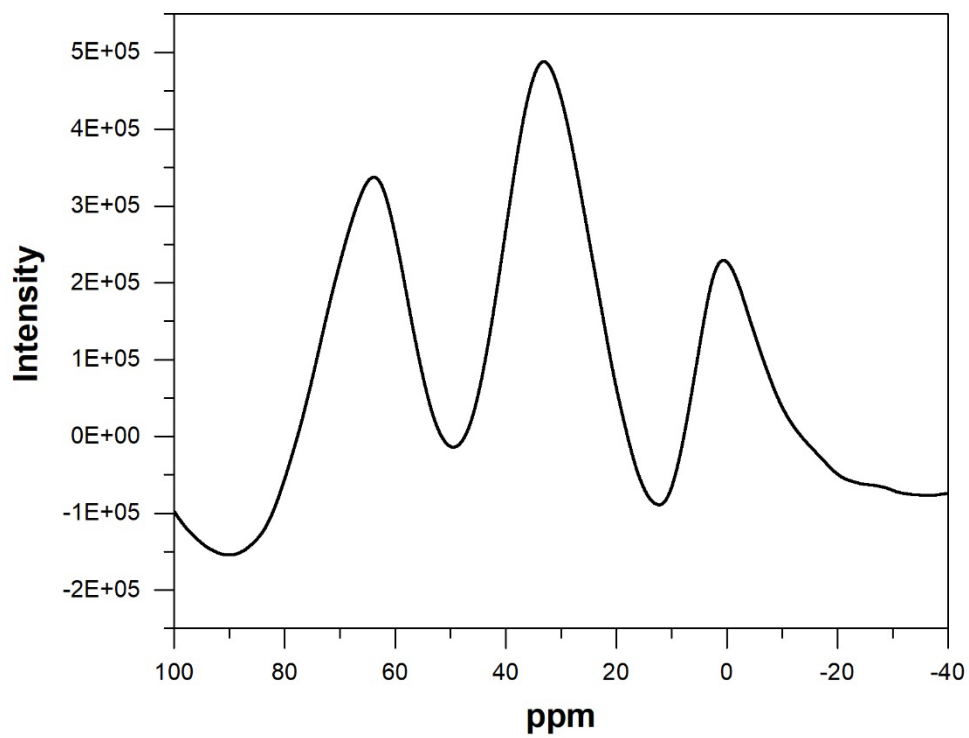


Figure S7. ^{27}Al NMR of HY (CBV600)

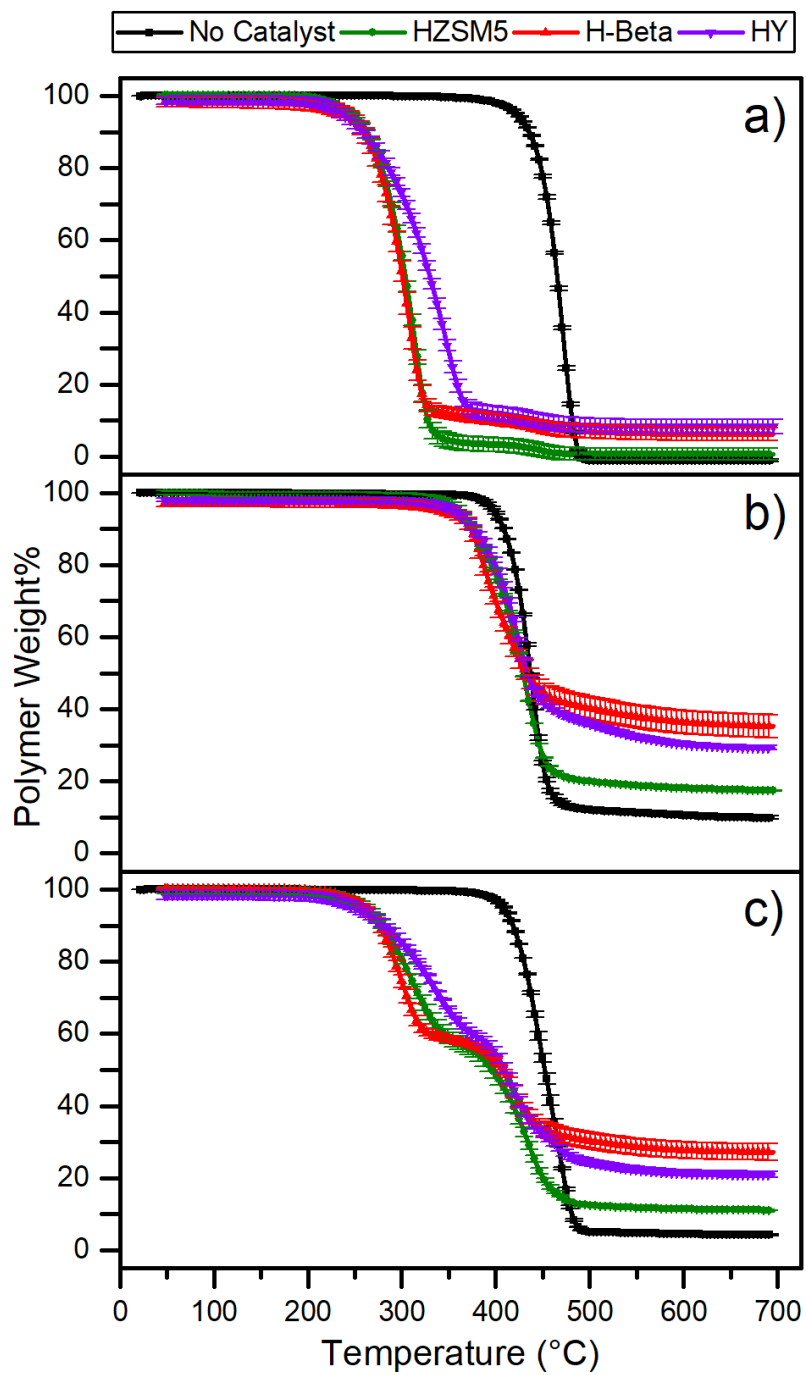


Figure S8. Polymer weight% curves with shown standard deviation for LDPE (a), PET (b), and LDPE+PET (c)

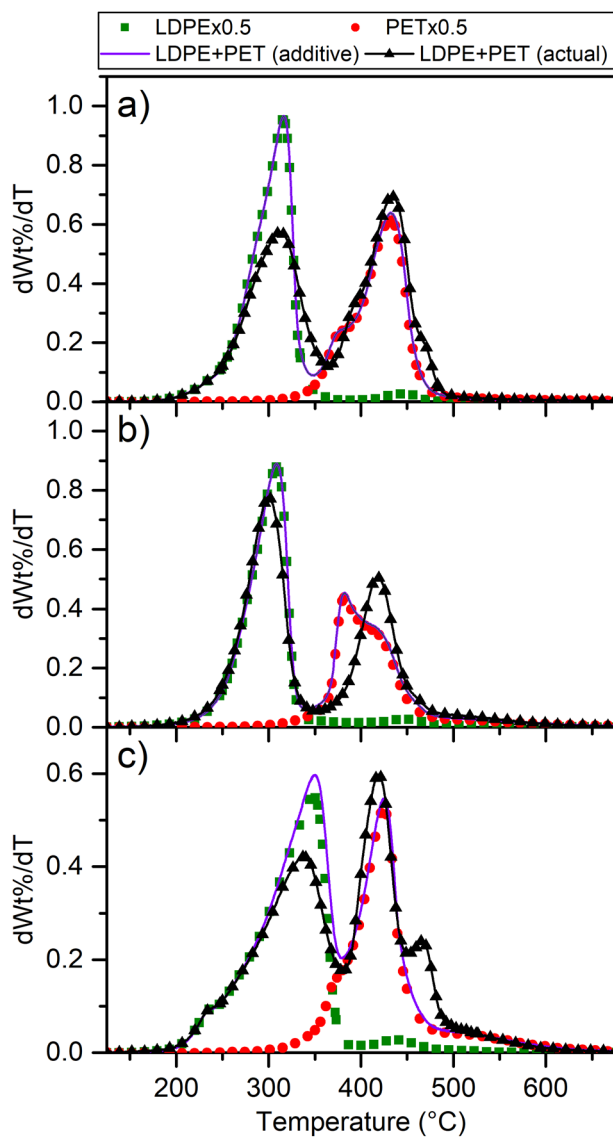


Figure S9. Comparison of additive and actual DTG curves for the catalytic co-pyrolysis of LDPE and PET with a) HZSM-5, b) H-Beta, and c) HY at 10°C/min heating rate, 1:1 LDPE:PET ratio, and 1:1 catalyst:feedstock ratio. Single-stream catalytic DTG curves for LDPE and PET multiplied by a factor of 0.5 are shown.

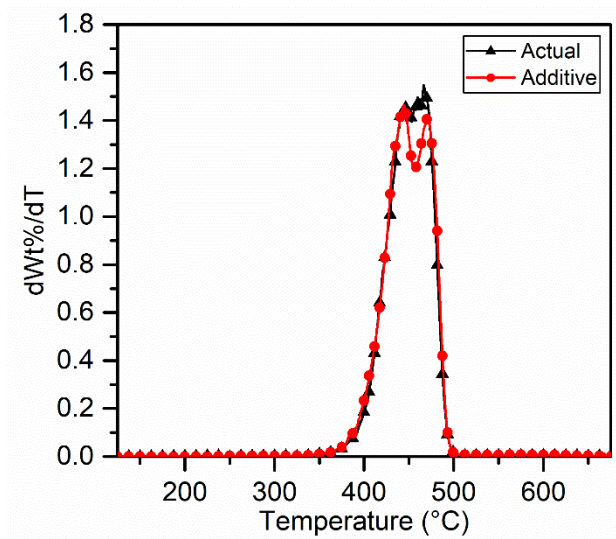


Figure S10. Actual and additive DTG curves for non-catalytic co-pyrolysis of LDPE and PET

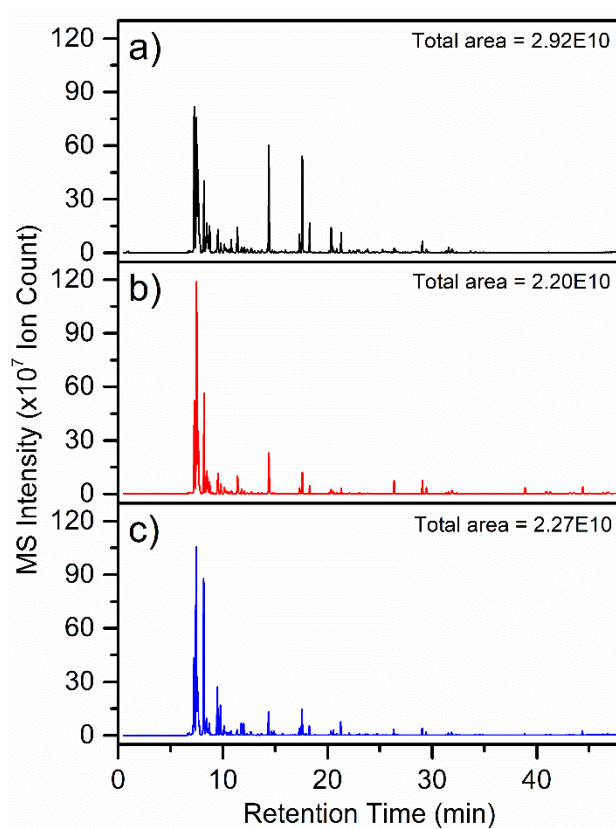


Figure S11. TIC plot for LDPE/HZSM-5 (a), LDPE/H-Beta (b), and LDPE/HY (c)

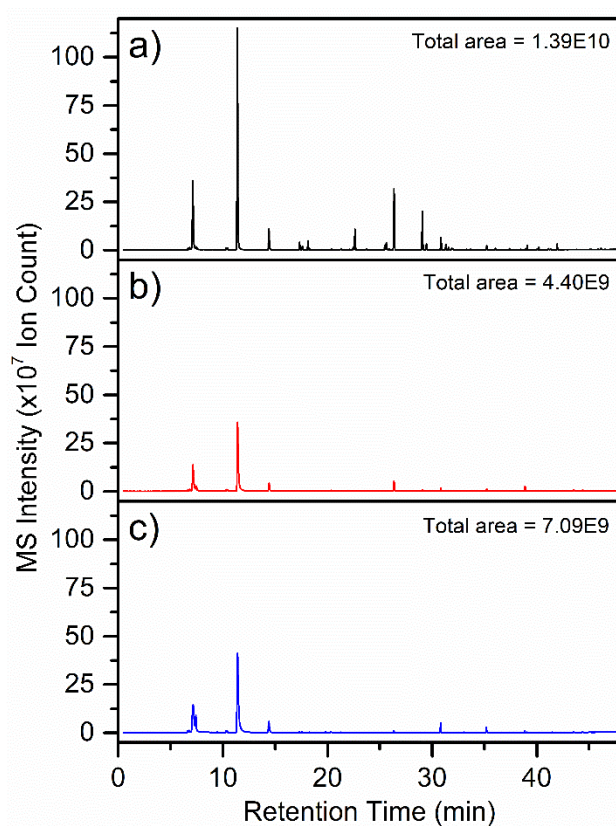


Figure S12. TIC plot for PET/HZSM-5 (a), PET/H-Beta (b), and PET/HY (c)

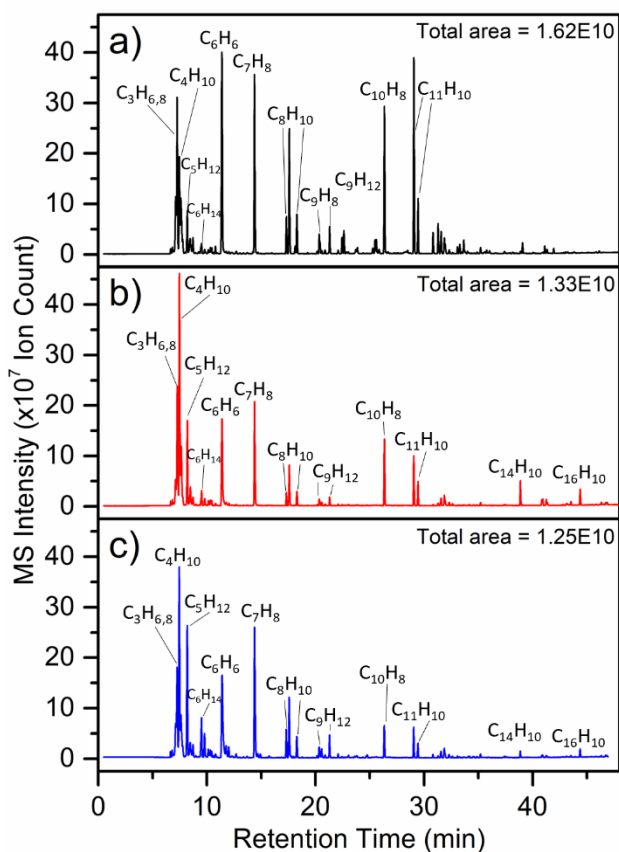


Figure S13. GC/MS total ion chromatograms of pyrolysates from co-pyrolysis of LDPE and PET with a) HZSM-5, b) H-Beta, and c) HY catalyst. ($C_3H_{6,8}$: Propylene and Propane, C_4H_{10} : Isobutane and Butane, C_5H_{12} : Butane, 2-methyl, C_6H_{14} : Pentane, 2-methyl, C_6H_6 : Benzene, C_7H_8 : Toluene, C_8H_{10} : Ethylbenzene, *p*-Xylene, and *m/o*-Xylene, C_9H_{12} : Benzene, 1-ethyl-3-methyl- and Benzene, 1,2,4-trimethyl-, $C_{10}H_8$: Naphthalene, $C_{11}H_{10}$: Naphthalene, 2-methyl, $C_{14}H_{10}$: Phenanthrene, $C_{16}H_{10}$: Pyrene)

References

1. Takeo, O. A New Method of Analyzing Thermogravimetric Data. *Bull. Chem. Soc. Jpn.* **38**, 1881–1886 (1965).
2. Flynn, J. H. & Wall, L. A. A quick, direct method for the determination of activation energy from thermogravimetric data. *J. Polym. Sci. Part B Polym. Lett.* **4**, 323–328 (1966).
3. Doyle, C. D. Kinetic Analysis of Thermogravimetric Data. *J. Appl. Polym. Sci.* **5**, 285–292 (1961).
4. Aboulkas, A., El harfi, K. & El Bouadili, A. Thermal degradation behaviors of polyethylene and polypropylene. Part I: Pyrolysis kinetics and mechanisms. *Energy Convers. Manag.* **51**, 1363–1369 (2010).