Physical and Chemical Behavior of Post Consumer Plastic Compared to Virgin Plastic during Pyrolysis

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Background

- In 2018, 35 million tons of plastics waste was generated in the United States (12.2% of all MSW).[1, 2]
- Only 8.7% of this were recycled.[1, 2]
- Post-consumer resins (PCR) or plastics were functionalized for consumer applications and thus contain various additives and inorganic contents even after washing.
- PCRs are mostly landfilled, with 50% being PE.
- Chemical recycling, such as pyrolysis, can convert waste plastics into building block monomers.

Plastic Bales

Landfills

[1] https://www.epa.gov/facts-and-figures-about-materials-waste-and-recycling/national-overview-facts-and-figures-materials (accessed Apr 13, 2022).
[2] www.epa.gov/facts-and-figures-about-materials-waste-and-recycling/plastics-material-specific-data (accessed Apr 13, 2022).

Objective of the research

1. How chemical changes in plastics during pyrolysis is correlated to their physical changes?
2. How fast the plastic decomposes during fast pyrolysis?
3. How product composition changes during fast pyrolysis with different conversion times?
4. In the above questions, what are the differences between virgin and post-consumer plastics?

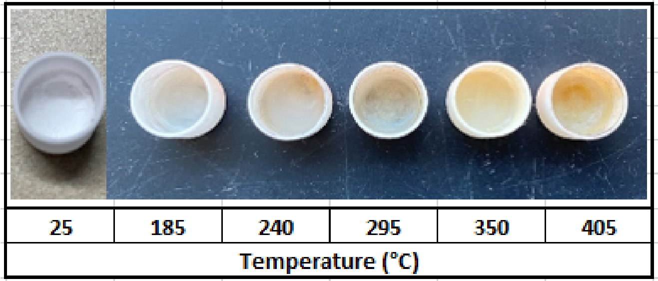
Feedstock: PCR PE & Virgin PE

PE	Total Inorganics content (%)	N %	C %	H %	S %	O%	Ash (%)	Mw (Da)	PDI
Virgin	0.03	0.00	85.58	13.23	0.00	0.00	0.00	57402	1.8
PCR	0.31	0.04	84.62	13.41	0.01	0.00	0.62	73963	2.15

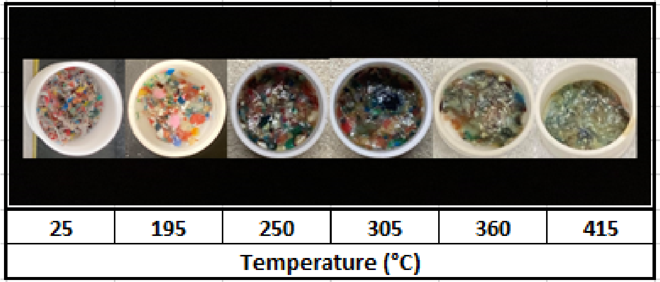
- Post-consumer resin (PCR) PE collected from material recovery facilities (MRFs) were washed and cryogenically milled. Virgin PE was acquired in powder form.
- PCR PE contained more impurities or inorganic contents such as Al, Sb, Cr, Fe, Cd, Ti, Ni, Ca and Mg from different additives.

What happens to rheology and molecular weight distribution during pyrolysis prior to plastic devolatilization?

- Virgin and PCR PE are pyrolyzed using TGA at 10°C/min.
- Temperature ramp melt rheology tests of the same plastics were conducted under inert environment using the same heating profile used in TGA (10°C/min).
- During TGA tests, plastic samples remaining in cups were collected at five different temperatures from 185 up to 415 °C, and quenched samples were analyzed for their molecular weight distribution.



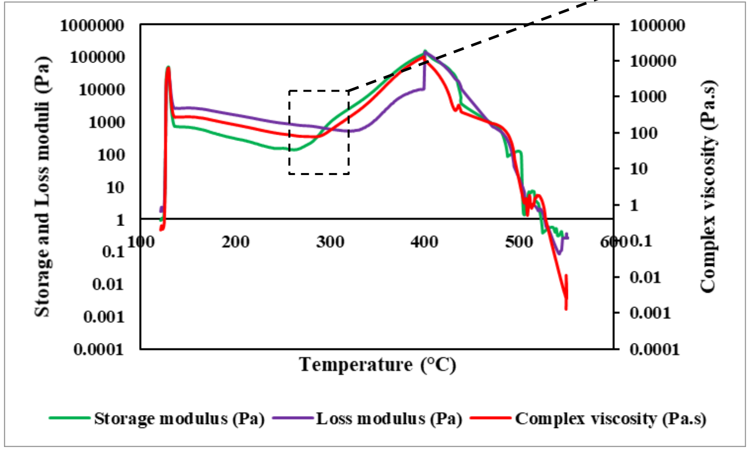
Virgin PE



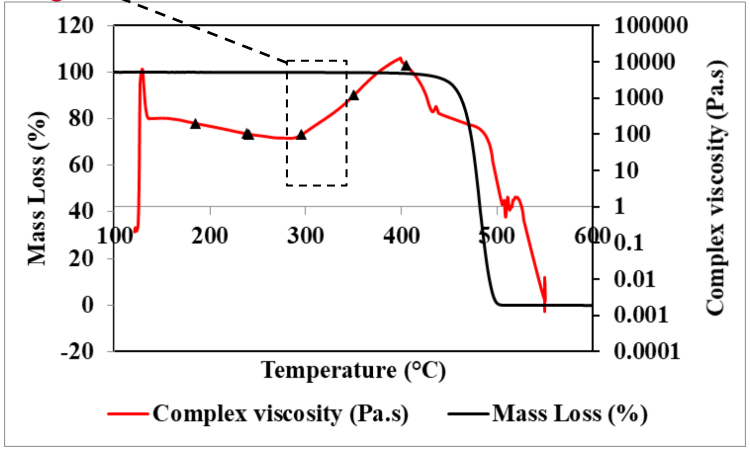
PCR PE

Virgin PE as the feedstock

Cross-linking



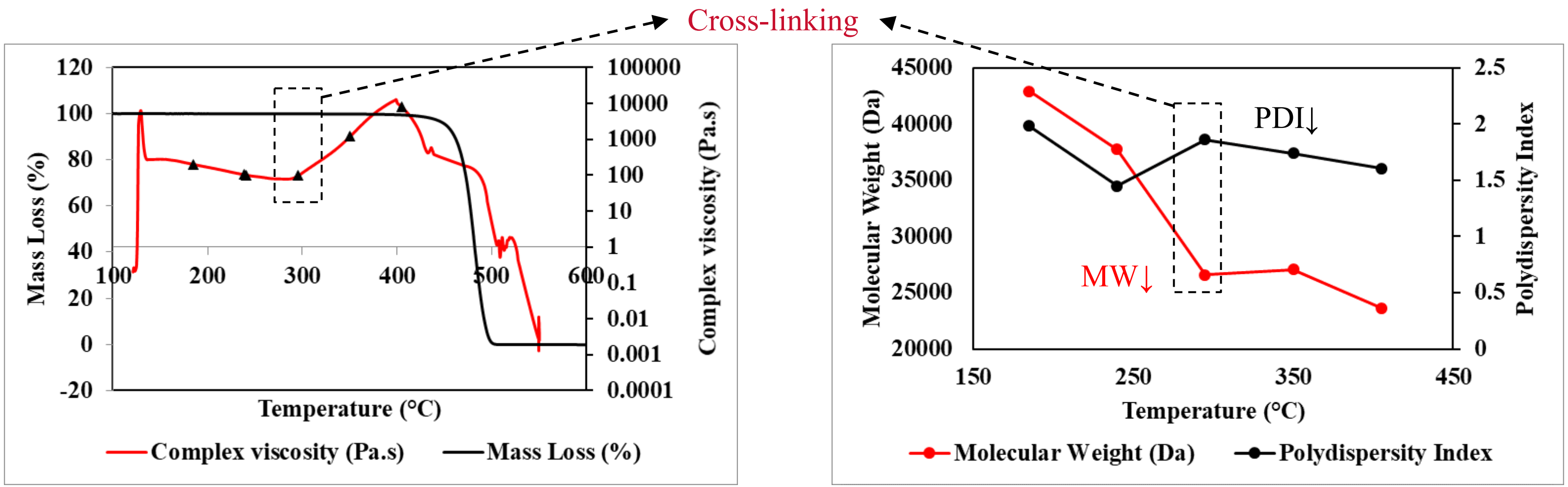
Rheology



TGA vs. viscosity

- From TGA profile, mass loss of PE does not occur until 400 °C.
- Polymer viscosity first decreased and then increased after 295 °C with increasing temperature, accompanied by thermoset behavior of the molten phase.
- Sudden decrease in viscosity was observed after devolatilization onset.

Virgin PE as the feedstock



TGA vs. viscosity

GPC

- Chain cleavage of polymer started in molten phase. The viscosity increase after 295° C was accompanied by increase in M_W and polydispersity of the polymer, possibility caused by cross-linking/re-polymerization.
- M_W and polydispersity in the molten phase decreased after devolatilization onset.

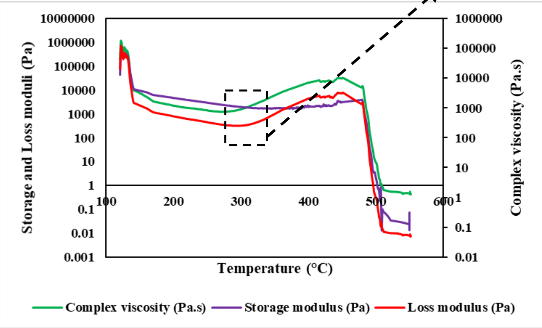
PCR PE as the feedstock

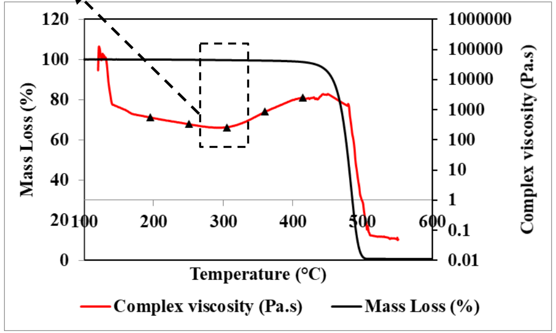
Rheology

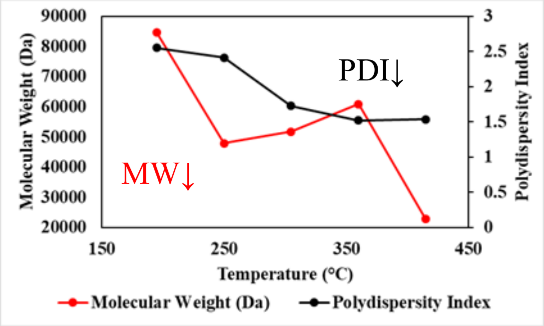
Cross-linking

TGA vs. viscosity

GPC



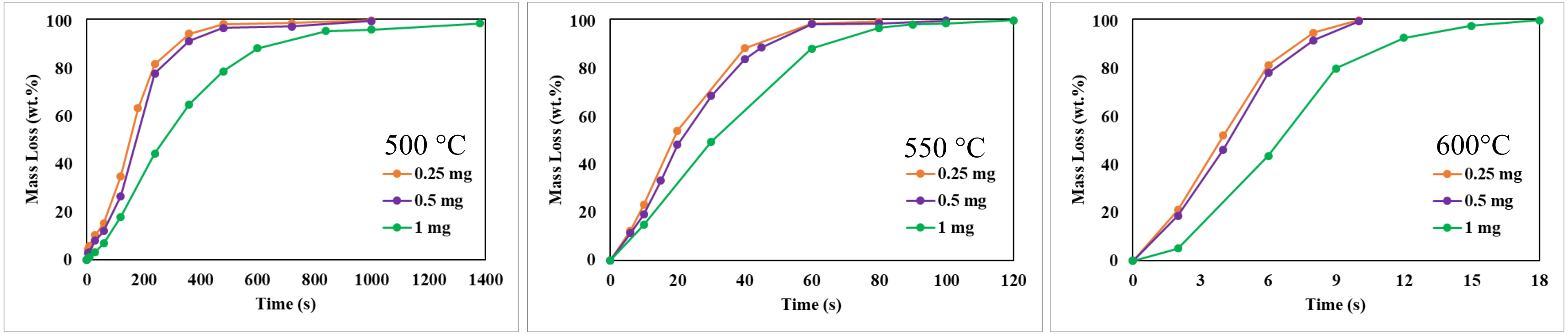




- Mass loss of PCR PE starts at a higher temperature of 410 °C.
- Polymer melting and cross-linking happened at higher temperatures for PCR PE.
- Overall viscosity was higher for PCR than virgin PE in their molten states.
- *More severe cross-linking led to higher molecular weight increase in PCR PE.*
- Higher viscosity of PCR in the mass loss phase may affect vapor escape.

Mass transfer limitations during fast pyrolysis of plastic polymers

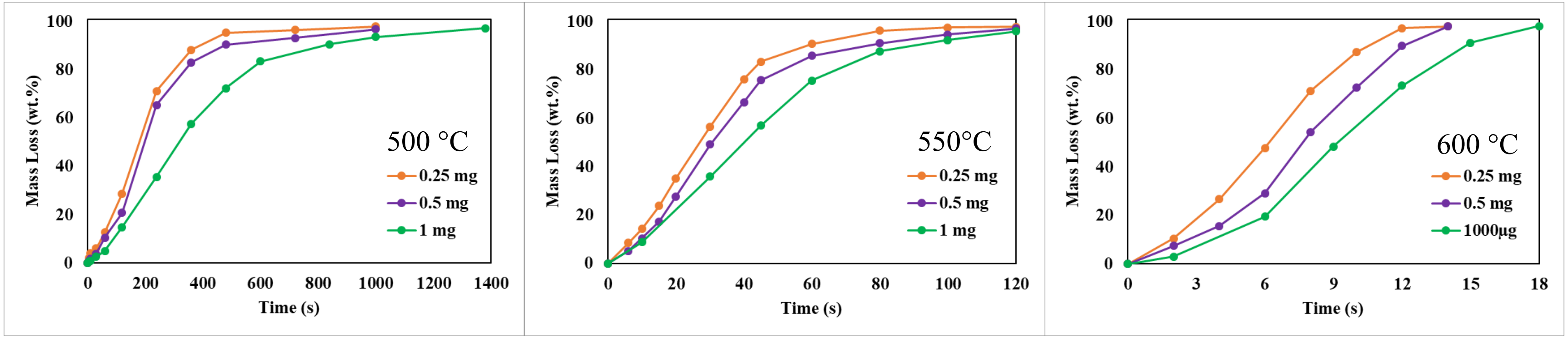
Virgin PE, sample size: 0.25, 0.5, and 1 mg



- During fast pyrolysis using micro-pyrolyzer, solid residues of polymers were collected at different pyrolysis times and the data is used to build isothermal mass loss profiles.
- It took more than 1000s for virgin PE to complete devolatilization at 500 °C.
- Higher pyrolysis temperatures significantly reduced conversion time.
- Significant mass transfer limitation was observed with the sample size over 0.5 mg.

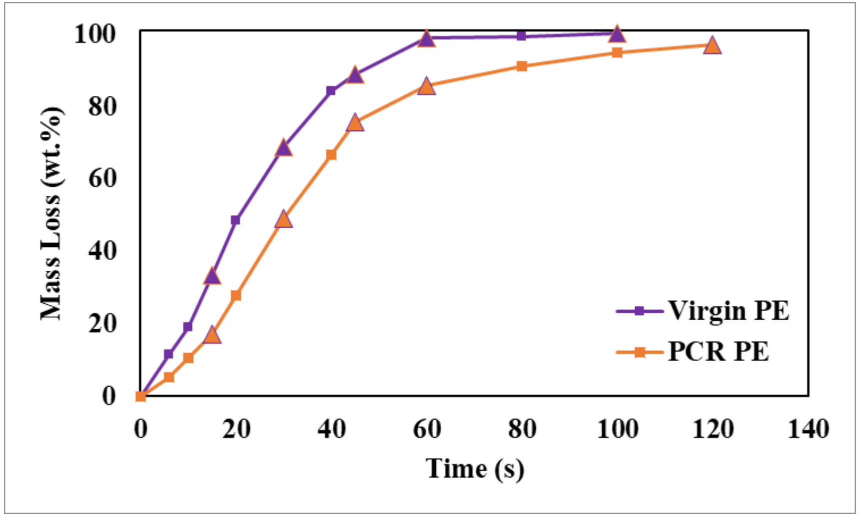
Mass transfer limitations during fast pyrolysis of plastic polymers

PCR PE, sample size: 0.25, 0.5, and 1 mg



- Mass transfer limitation was more pronounced for PCR PE than virgin PE. Even with 0.5 mg, mass transfer limitation was observed at 600 °C.
- Devolatilization rate of PCR PE slower for PCR PE for all conditions.

Mass loss profiles: virgin vs PCR plastics

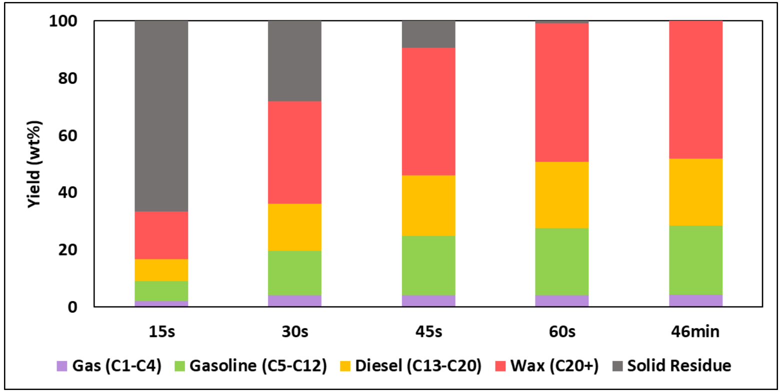


0.5mg, 550°C, Vapor residence time: < 1s

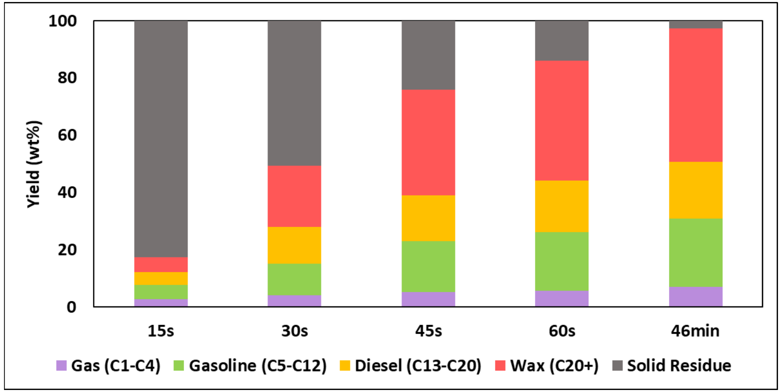
- During pyrolysis, volatile products evolved at different conversion times (15s, 30s, 45s, 60s and 46 min) were analyzed to obtain time-resolved product distributions corresponding to the mass loss at the given times.

Time-resolved product distribution during fast pyrolysis

0.5mg, 550°C, Vapor residence time: < 1s



Virgin PE

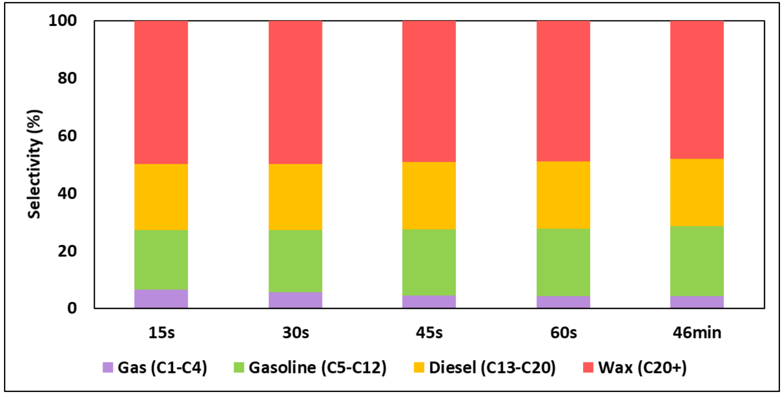


PCR PE

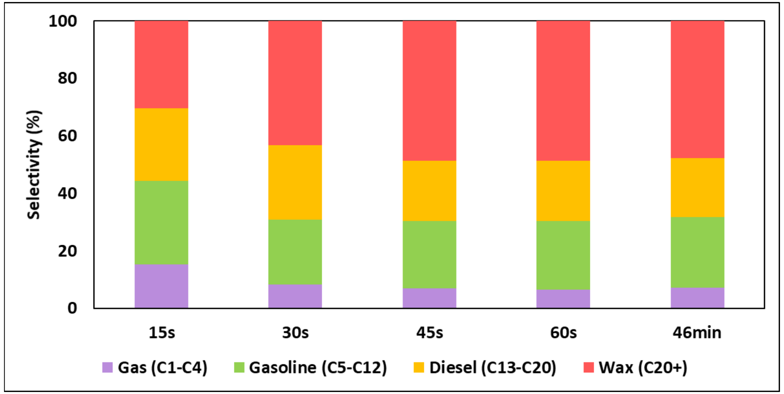
- At 550°C, virgin and PCR PEs had liquid yields of up to 95 and 90 C%, respectively.
- Virgin and PCR PEs produced gas yields of 3.9 C% and 6.3 C%, respectively.
- PCR PE left a larger solid residue which is in trend with the higher ash content of the feedstock.

Time-resolved product selectivity during fast pyrolysis

0.5mg, 550°C, vapor residence time: < 1s



Virgin PE



PCR PE

- For PCR PE, gas and gasoline range products are produced at higher selectivity at the initial stage (<30s), while the selectivity of different fractions become similar at higher conversions.
- For virgin PE, the selectivity of different liquid/gas fractions relatively unchanged over the entire course of the conversion.
- Selectivity of waxes comparable for both plastics, while PCR produced more gases.

Conclusions

1. Chain cleavage and crosslinking occurred in molten phase before polymers volatilizes, which increased viscosity and MW of the polymers.
2. PCR PE was more viscous and crosslinking/re-polymerization was severe than virgin PE.
3. Fast pyrolysis is not really fast for PE polymers unless temperature is above 600 °C.
4. Significant mass transfer limitation presents during fast pyrolysis and it was more pronounced for PCR PE.
5. Devolatilization rate was slower while more gaseous products and char are produced for PCR PE.

Acknowledgements

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U.S. DEPARTMENT OF ENERGY | Office of ENERGY EFFICIENCY & RENEWABLE ENERGY

CUWP

Chemical Upcycling of Waste Plastics

Questions?

Supplementary Information

ICP-OES

Plastic Feedstocks	PPM										Total	Total (%)
	Al	Sb	Cd	Cr	Fe	Pb	Ti	Ni	Ca	Mg		
HDPE-1A	184.6567	-*	-*	-*	5.5686	-*	-*	-*	53.9805	53.1052	297.3110	0.0297
HDPE-1B	34.5770	-*	-*	6.3603	5.5487	-*	-*	-*	21.6793	1.1241	69.2894	0.0069
HDPE-3	324.1239	-*	117.6090	92.0357	201.3341	273.6355	83.7647	101.9682	1829.3877	98.1875	3122.0463	0.3122
LDPE-1B	89.4598	-*	-*	2.7861	5.3186	-*	11.3319	-*	28.9631	0.4936	138.3531	0.0138
LDPE-3	204.2661	-*	-*	2.2342	3.6376	-*	9.3149	-*	99.7470	6.0490	325.2488	0.0325
PP-1A	170.0945	-*	-*	-*	13.9265	-*	-*	-*	57.7215	15.4735	257.2160	0.0257
PP-1B	132.9088	-*	-*	2.5331	2.8009	-*	-*	-*	80.7686	10.7867	229.7980	0.0230
PP-3	125.5742	-*	-*	13.0976	29.8119	-*	93.2329	49.5014	786.0638	144.9198	1242.2016	0.1242
PS-1A	98.0449	-*	-*	-*	-*	-*	-*	-*	41.7843	0.5996	140.4288	0.0140
PS-1B	178.8678	-*	-*	-*	3.1936	-*	2.0109	-*	96.5924	1.5030	282.1676	0.0282
PS-3	386.9670	-*	-*	-*	43.0718	-*	170.9136	-*	219.5886	24.7472	845.2882	0.0845
PET-1A	115.4653	######	-*	-*	-*	-*	-*	-*	39.7902	1.6996	337.9951	0.0338
PET-1B	137.6877	-*	-*	10.0371	3.9187	-*	7.6543	44.2057	44.4472	1.9559	249.9067	0.0250
PET-3	143.8635	######	-*	2.2143	7.6815	-*	1.6241	-*	46.0099	1.9342	437.8689	0.0438
PVC-1A	78.0132	-*	-*	-*	-*	-*	-*	-*	34.1745	1.1662	113.3539	0.0113

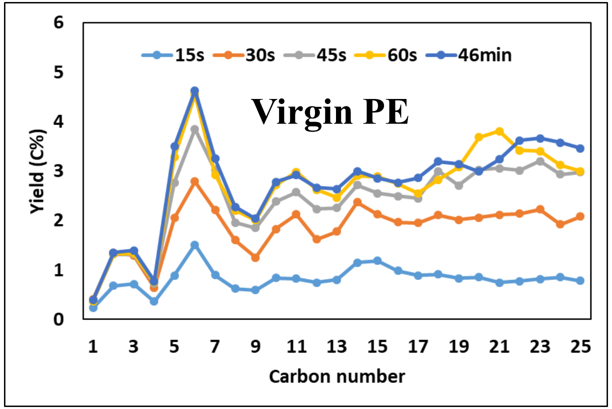
-* (value below LOD); red (value between LOD and LOQ)

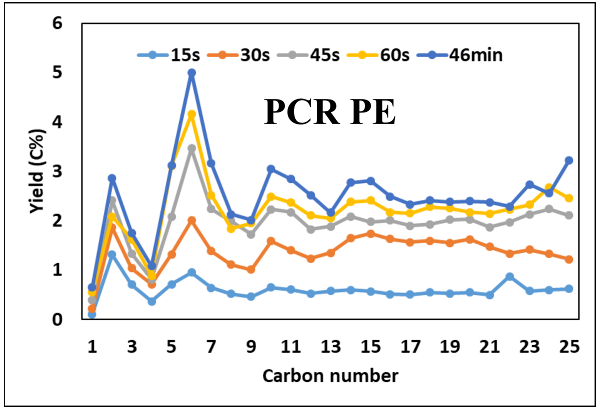
Elemental Analysis

										SD (%)		
Plastics	MF	C % (Theoretical)	H % (Theoretical)	O % (Theoretical)	N %	C %	H %	S %	O% or impurities	C	H	O
HDPE-1A	$(C_2H_4)_n$	85.63	14.37	0.00	0.00	85.58	13.23	0.00	1.19	0.05	0.47	0.42
HDPE-1B	$(C_2H_4)_n$	85.63	14.37	0.00	0.01	85.66	13.54	0.01	0.79	0.18	0.07	0.24
HDPE-3	$(C_2H_4)_n$	85.63	14.37	0.00	0.04	84.62	13.41	0.01	1.92	0.21	0.04	0.24
LLDPE-C4	$(C_2H_4)_n$	85.63	14.37	0.00	0.01	85.40	13.55	0.00	1.04	0.02	0.01	0.04
LLDPE-C8	$(C_2H_4)_n$	85.63	14.37	0.00	0.03	85.50	13.35	0.01	1.10	0.11	0.27	0.22
LDPE-1B	$(C_2H_4)_n$	85.63	14.37	0.00	0.02	85.48	13.34	0.00	1.15	0.02	0.34	0.33
LDPE-3	$(C_2H_4)_n$	85.63	14.37	0.00	0.02	84.82	13.43	0.00	1.73	0.11	0.04	0.12
PP-1A	$(C_3H_6)_n$	85.63	14.37	0.00	0.00	86.02	13.72	0.00	0.25	2.58	0.41	2.98
PP-1B	$(C_3H_6)_n$	85.63	14.37	0.00	0.00	85.92	13.61	0.00	0.47	0.45	0.06	0.52
PP-3	$(C_3H_6)_n$	85.63	14.37	0.00	0.01	84.71	13.17	0.00	2.11	0.63	0.29	0.71
PS-1A	$(C_8H_8)_n$	92.26	7.74	0.00	0.01	92.16	7.36	0.00	0.48	0.09	0.04	0.11
PS-1B	$(C_8H_8)_n$	92.26	7.74	0.00	0.01	92.04	7.14	0.01	0.81	0.16	0.01	0.17
PS-3	$(C_8H_8)_n$	92.26	7.74	0.00	0.04	90.39	7.02	0.00	2.55	0.09	0.28	0.23
PETE-1A	$(C_{10}H_8O_4)_n$	62.50	4.20	33.30	0.00	62.38	3.79	0.01	33.82	0.12	0.01	0.13
PETE-1B	$(C_{10}H_8O_4)_n$	62.50	4.20	33.30	0.01	62.41	3.73	0.00	33.85	0.27	0.02	0.29
PETE-3	$(C_{10}H_8O_4)_n$	62.50	4.20	33.30	0.04	62.29	3.58	0.00	34.08	0.33	0.14	0.23

Time-resolved changes in individual hydrocarbon yield

0.5mg, 550°C, vapor residence time: < 1s



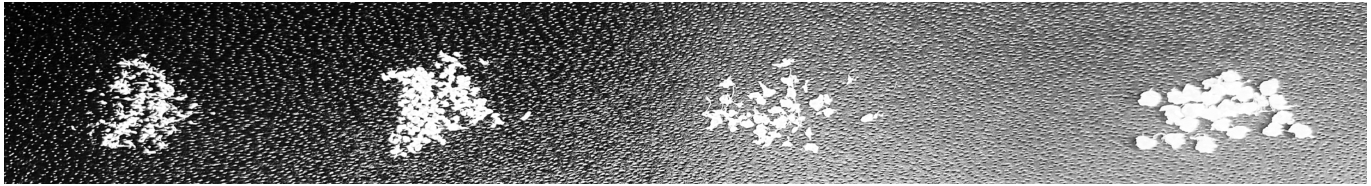


- Product yields across C_1-C_{25} hydrocarbons are mostly proportional for different pyrolysis times.

Effect of particle size on plastic pyrolysis

HDPE (level 1)

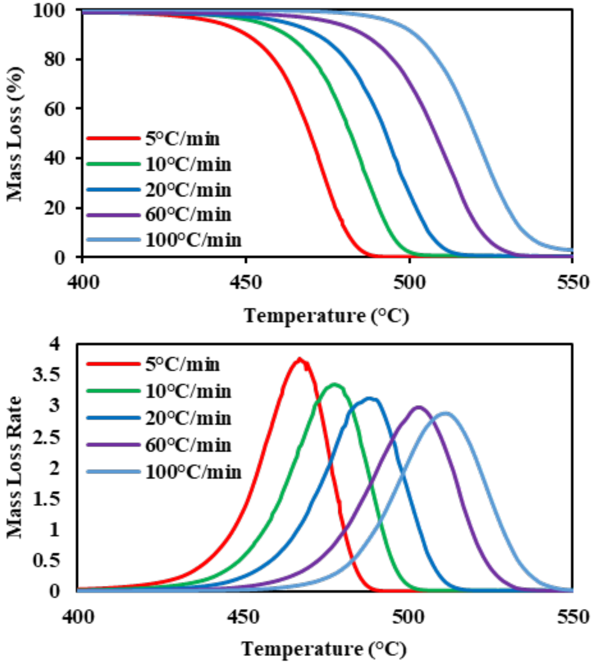
- TGA experiments
    - minor inter-particle heat transfer limitation.
- Fast pyrolyzer experiments
    - lower particle sizes produced higher liquid yields.



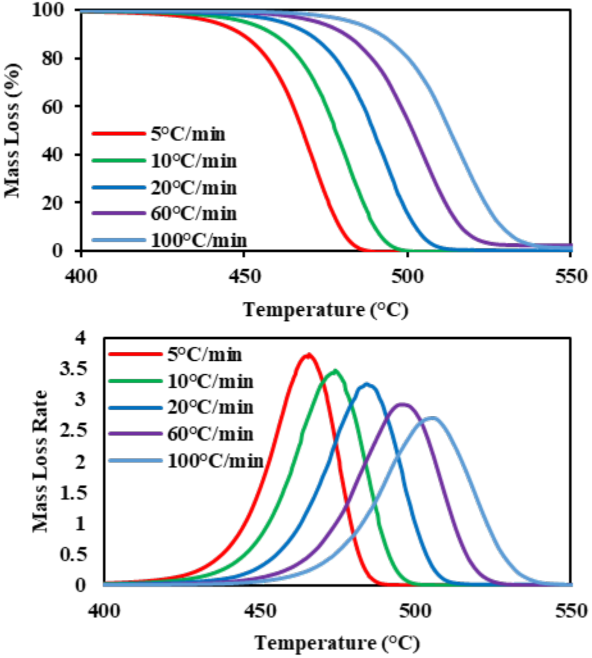
125-250μm 425-500μm 850-1000μm 1400-1700μm

Gray-scale picture of different particle sizes of same HDPE

TGA results of different HDPEs (heating rates: 5-100°C/min)



Level 1A



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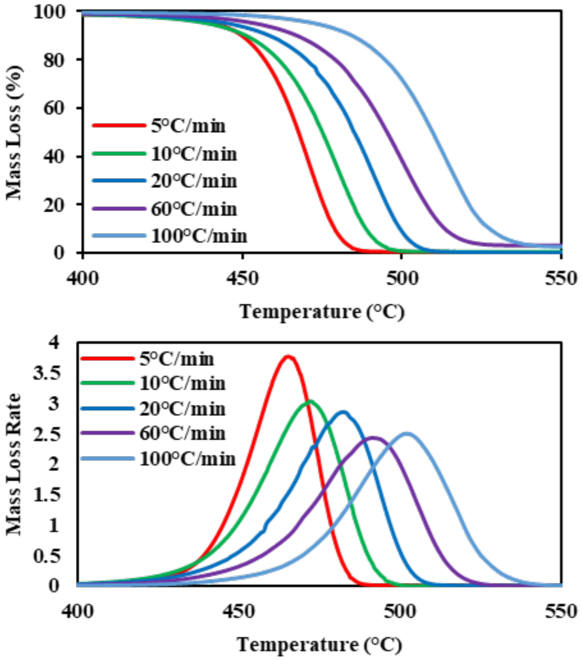
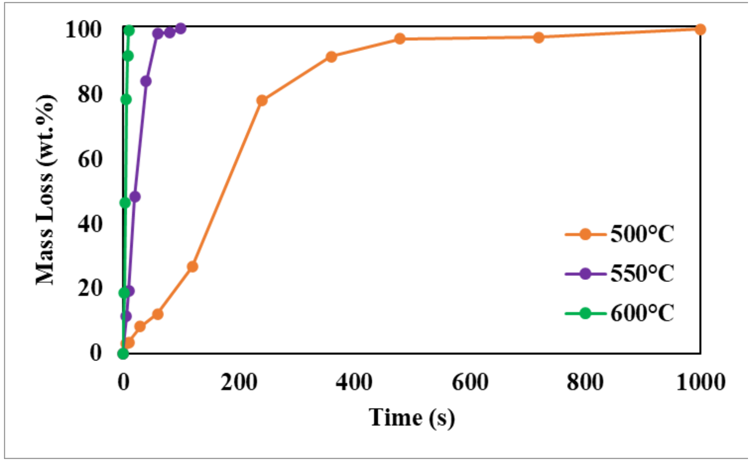


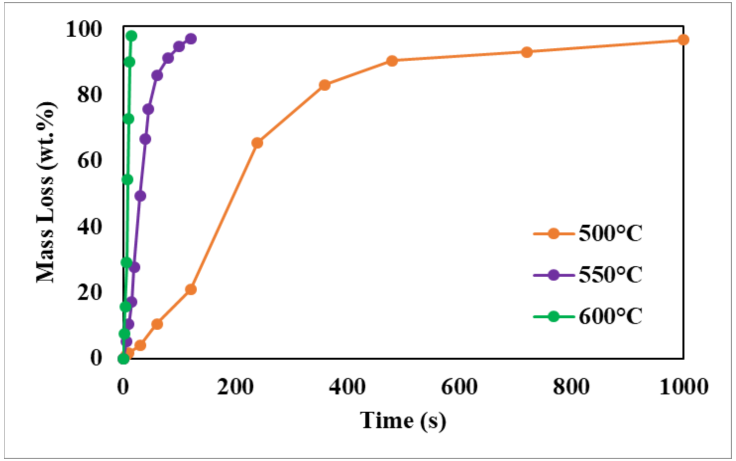
Level 3

How fast plastic decomposes during fast pyrolysis?

Virgin vs. PCR PE, sample size: 0.5 mg



Virgin PE



PCR PE

- Decomposition rate increases rapidly for PE at temperatures above 500°C.
- Plastics stay in molten phase much longer than Biomass taking minutes instead of seconds to pyrolyze.

Activation energies during slow pyrolysis vs. fast pyrolysis

Activation energy (kJ/mol)	Slow pyrolysis (non-isothermal TGA)			Fast pyrolysis (isothermal μ-pyrolyzer)
	Friedman	KAS	FWO	Arrhenius
HDPE (virgin)	261.7	265.1	264.1	258.8
HDPE (PCR)	269.7	275.3	272.6	243.8

- Activation energies of plastics decreased for fast pyrolysis compared to slow pyrolysis in TGA. Better conditions for fast pyrolysis kinetics?
- Mass loss profiles are collected at high heating rates of the fast pyrolyzer (150°C/s).