Unraveling the Pyrolytic Behavior and Kinetics of Single Polymers and Plastic-Rich Municipal Solid Waste Using Thermal Analysis

NATIONAL ENERGY TECHNOLOGY LABORATORY

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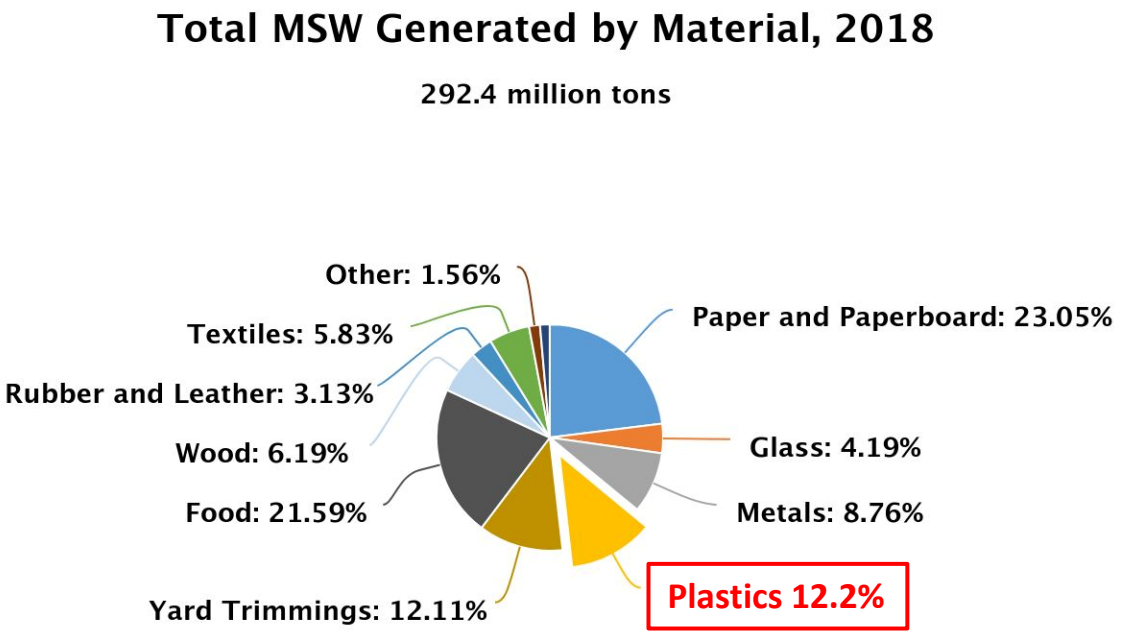
Municipal Solid Waste Management



MSW (Recycling & Composting) as a Percentage of Generation

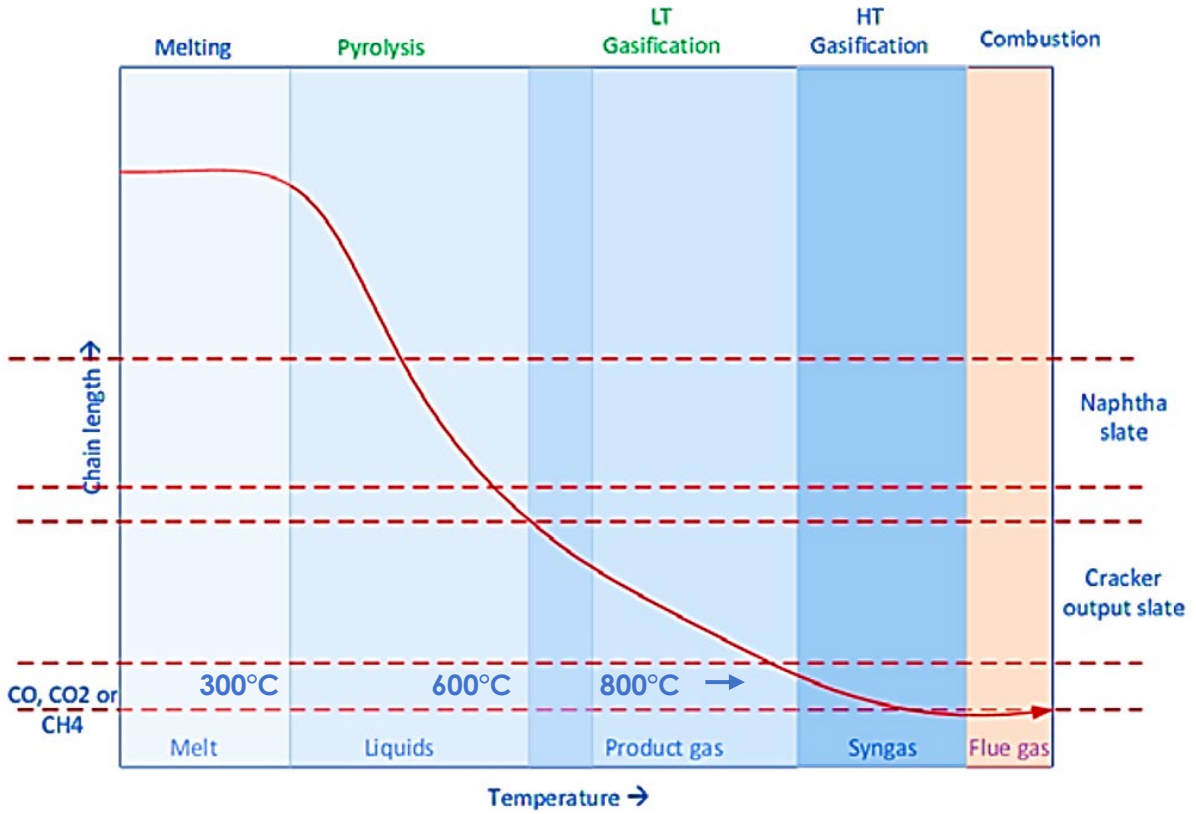
MSW	1960	1980	2000	2010	2018
Paper and Paperboard	17%	21%	43%	63%	68%
Glass	2%	5%	23%	27%	25%
Plastics		<1%	6%	8%	9%
Yard Trimmings			52%	58%	63%

- In the U.S., municipal solid waste (MSW) generation surged from 88.1 million tons in 1960 to 292.4 million tons in 2018.
- Plastic recycling improved but remained low, from 1% in 1980 to 9% in 2018, necessitating targeted initiatives to mitigate plastic pollution.
- Advanced and sustainable recycling strategies are urgently needed for effective MSW management.

U.S. Environmental Protection Agency. (2020). National Overview: Facts and Figures about Materials, Waste, and Recycling.

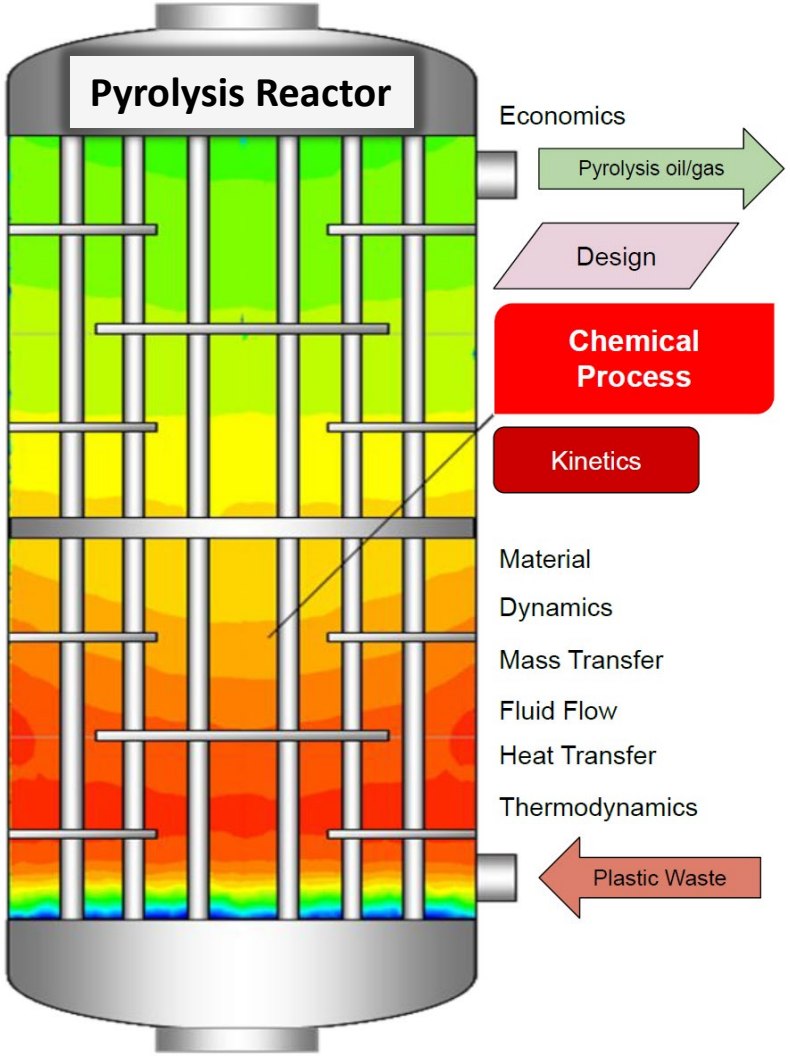
Thermochemical Recycling

- The thermochemical recycling process uses heat to break the bonds in feedstocks, resulting in shorter molecular chains.
- Liquefaction, pyrolysis, and gasification play a crucial role in commercially recycling plastic waste due to their current feasibility and scalability.
- These methods offer better alternatives to traditional handling (landfill, incineration) of diverse types of plastic waste.



Vreugdenhil, B. (2021). Gasification applications in industrial and agricultural infrastructures. IEA Bioenergy: Task 33.

Technical Challenges



- Complex Chemistry Involving Multiple Parallel Reactions
- Optimal Reactor Design and Reliable Kinetic Models
- Complete Understanding of the Chemical Reaction Process of Mixed Plastic Waste

Project Goals

Investigation of pyrolysis behavior of:

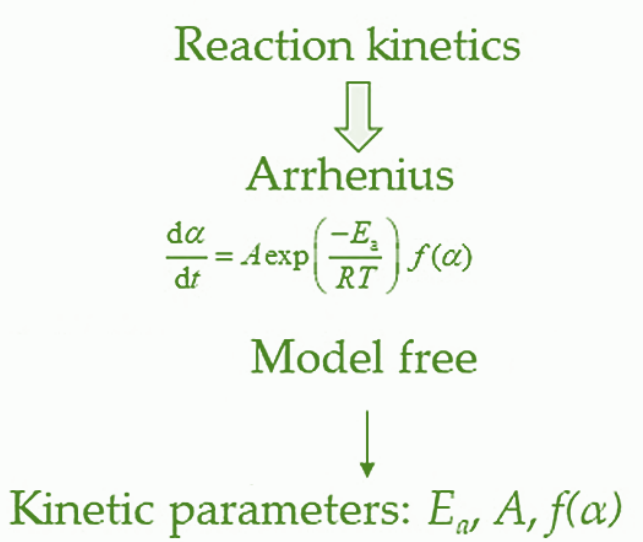
- Single polymers
- MSW plastic-rich

Kinetic analysis of plastic decomposition

- Kinetic triplets (activation energy Ea, pre-exponential factor A, reaction mechanism)

Determination of thermodynamic parameters

- Enthalpy change (ΔH)
- Gibbs free energy change (ΔG)
- Entropy change (ΔS)



Properties of Feedstocks

Four samples were used in the study:

- MSW plastic-rich
- Waste Polyethylene (PE)
- Waste Polypropylene (PP)
- Waste Polyethylene Terephthalate (PET)

Source

- MSW plastic-rich: Oak Ridge National Laboratory (ORNL)
- Single polymer waste: Idaho National Laboratory (INL)

MSW plastic-rich represents the average composition of plastic in municipal solid waste

Cryogenic grinding Mill

Polyethylene (PE)

Before **After**

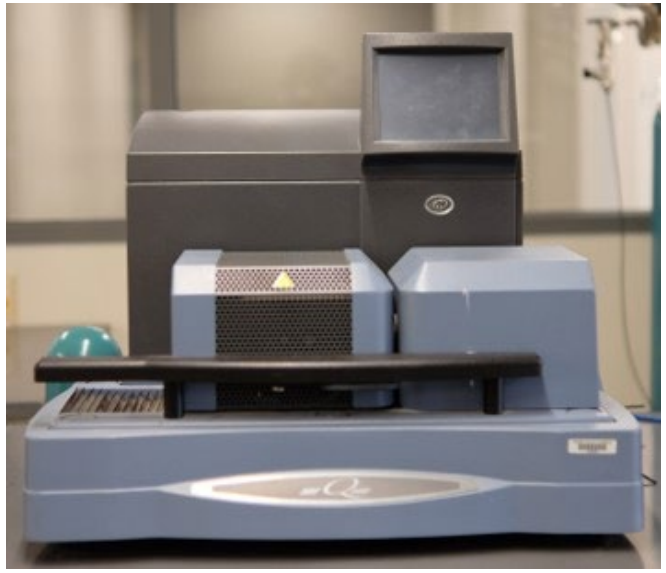
Particle Size (µm)
105-250

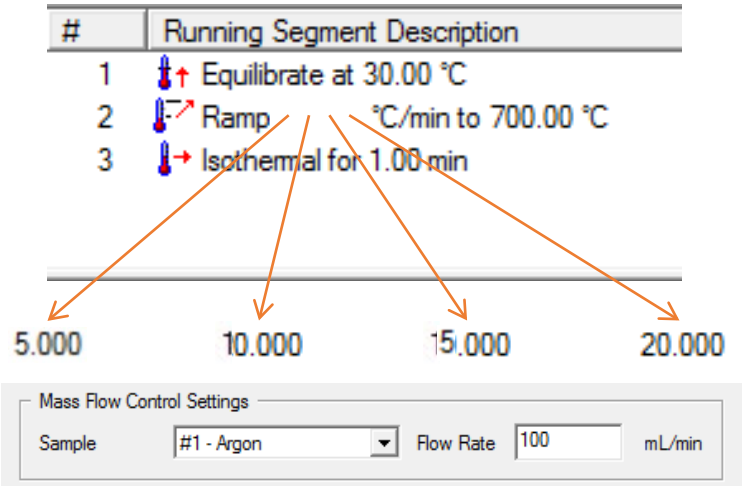
Sample	Ultimate and Proximate Analysis								
	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen (Diff.)**	% Moisture	% Volatile	% Ash	% Fixed C
MSW Plastic-Rich	73.02	9.99	BDL	BDL	12.71	0.88	94.75	3.40	0.97
INL-PET	61.91	4.56	BDL	BDL	32.84	0.01	88.54	9.37	2.09
INL-PE	86.13	13.87	BDL	BDL	0.00	0.01	99.99	0.00	0.00
INL-PP	86.05	13.95	BDL	BDL	0.00	0.02	99.98	0.00	0.00

*Duplicate measurements, BDL = Below Detection Limit.
**O = 100 - (C+H+N+S+M+A), M and A are moisture and ash contents determined from proximate analysis.

MSW Plastic-Rich	Bottles (%)	Food cont. (%)	Durable (%)	Other (%)	Total (%)
PET	43	15	0	11	23
HDPE	32	6	13	30	21
LDPE	4	0	29	0	6
PP	11	73	0	30	30
Other	11	3	0	0	5
Unknown	0	0	58	30	13

Experimental Setup

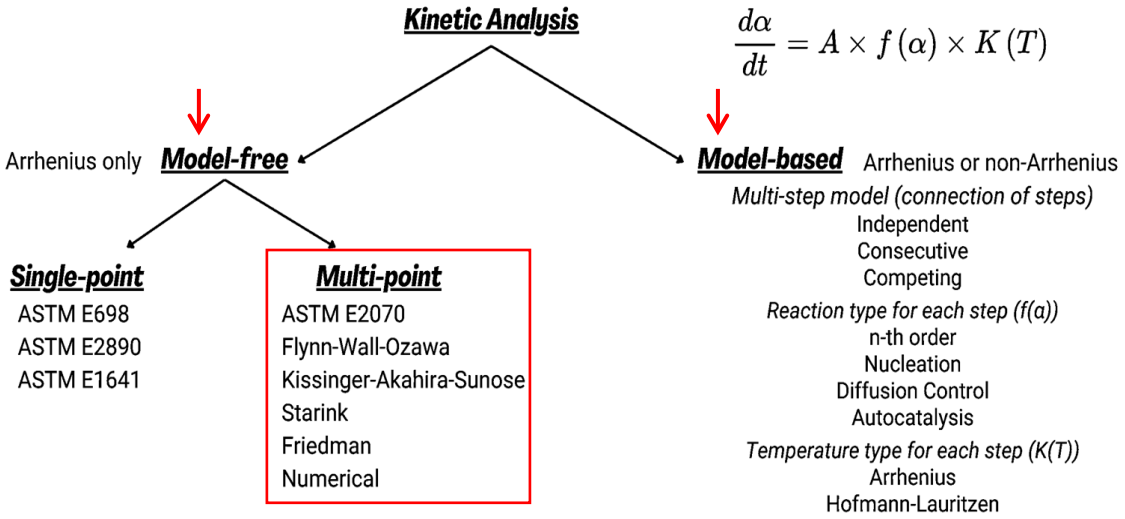




Experimental conditions:

- Sample cups: Al_2O_3, 90 µL
  - Thermally stable, inert, easy to clean
- Particle size: 100-250 µm
  - Optimal heat transfer
- Sample amount: 8-12 mg
  - Allow uniform heating
- Gas flow rate: UHP Ar, 100 mL/min
  - Ensure inert atmosphere
- Heating rate: 5, 10, 15, 20 °C/min
  - Within the range specified by ASTM1641-16
- Final temperature: 700 °C
  - Obtain max degree of conversion
- Number of runs: 2
  - Verify data reproducibility

Methodology: Kinetic Analysis



$$\frac{d\alpha}{dt} = A * f(\alpha) * k(T) \qquad \alpha = Degree\ of\ Conversion$$

$$\frac{d\alpha}{dt} = Ae^{\frac{-E_a}{RT}} f(\alpha)$$

Differential method

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \int_{T_0}^{T_{max}} \frac{A}{\beta} e^{\frac{-E_a}{RT}} dT$$

Integral method

Assumptions:

- Single kinetic equation describes the pyrolysis process
- Activation energy (Eα) and pre-exponential factor (A) depend on α
- Reaction rate at the same conversion is only a function of α
- Temperature and total effect (total mass loss) must be the same for all curves
- Changes of mechanism should be at the same conversion value

Multi-point Isoconversional Method	Expression	Plot	Slope Equal To
FWO (Integral)	$ln(\beta) = ln\left[\frac{AE_a}{Rg(\alpha)}\right] - 5.33 - 1.0516\frac{E_a}{RT}$	$ln(\beta)$ vs. $\frac{1}{T}$	$-1.0516\frac{E_a}{R}$
KAS (Integral)	$ln\left(\frac{\beta}{RT^2}\right) = ln\left[\frac{AE_a}{E_a g(\alpha)}\right] - \frac{E_a}{RT}$	$ln\left(\frac{\beta}{RT^2}\right)$ vs. $\frac{1}{T}$	$-\frac{E_a}{R}$
Starink (Integral)	$ln\left(\frac{\beta}{RT^{1.92}}\right) = C_s - 1.0008\frac{E_a}{RT}$	$ln\left(\frac{\beta}{RT^{1.92}}\right)$ vs. $\frac{1}{T}$	$-1.0008\frac{E_a}{R}$
Friedman (Differential)	$ln\left(\frac{d\alpha}{dt}\right) = ln[A(\alpha)f(\alpha)] - \frac{E_a}{RT}$	$ln\left(\frac{d\alpha}{dt}\right)$ vs. $\frac{1}{T}$	$-\frac{E_a}{R}$

Methodology: Reaction Model and Pre-Exponential Factor

Criado Master-Plot

$$G(\alpha) = \int_0^{\alpha} \frac{d(\alpha)}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^{T} \exp\left(-\frac{E}{RT}\right) dT \approx \frac{A}{\beta} \int_0^{T} \exp\left(-\frac{E}{RT}\right) dT = \frac{AE}{\beta R} P(u)$$

Model Free Kinetic Analysis

Differential or Integral Equation

Estimation of activation energy without assuming specific reaction models.

Theoretical Kinetic Models

Criado Master-Plot Method to visualize

Experimental Data Plots

Comparison of experimental data with theoretical models.

Kinetic Triplets

- Activation Energy (Eα), Pre-exponential Factor (A) & Reaction Model

Theoretical Kinetic Models for Solid-State Kinetics

Mechanism models	Differential form f(α)	Integral form g(α)
First order (F1)	$1-\alpha$	$-\ln(1-\alpha)$
Second order (F2)	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$
Third order (F3)	$(1-\alpha)^3$	$[(1-\alpha)^{-2}-1]/2$
One-dimensional (D1)	$1/2\alpha$	α^2
Two-dimensional (D2)	$[-\ln(1-\alpha)]^{-1}$	$[(1-\alpha)\ln(1-\alpha)]+\alpha$
Three-dimensional (D3)	$3(1-\alpha)^{2/3}/[2(1-(1-\alpha)^{1/3})]$	$[1-(1-\alpha)^{1/3}]^2$
Diffusion controlled(D4)	$3/2[(1-\alpha)^{-1/3}-1]$	$1-(2\alpha/3)-(1-\alpha)^{2/3}$
Two-dimensional (A2)	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
Three-dimensional (A3)	$3(1-\alpha)[-\ln(1-\alpha)]^{3/2}$	$[-\ln(1-\alpha)]^{1/3}$
Four-dimensional (A4)	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
One-dimensional (R1)	1	α
Two-dimensional (R2)	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
Three-dimensional (R3)	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
Power law (P2)	$2\alpha^{1/2}$	$\alpha^{1/2}$
Power law (P3)	$3\alpha^{2/3}$	$\alpha^{1/3}$
Power law (P4)	$4\alpha^{3/4}$	$\alpha^{1/4}$

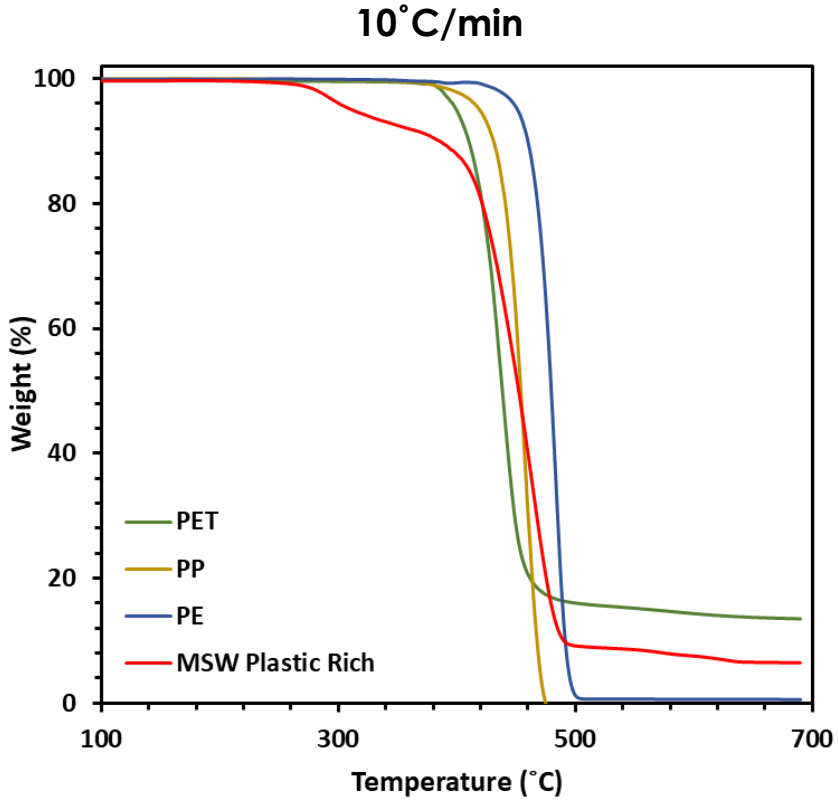
Results: TGA Profiles

Weight Loss Rate as a Function of Temperature

Thermogravimetric Analysis (TGA) Weight loss of a substance is monitored as a function of temperature (non-isothermal).

Key Findings

- TGA weight loss curves reveal different decomposition profiles for each component, as polymers degrade distinctively at varying temperatures.
- MSW plastic-rich sample starts decomposing at a lower temperature than single polymers (PP, PE, and PET) indicating weak initial thermal stability due to unknown components (biomass/food waste).
- MSW plastic-rich weight loss is more gradual compared to the sharp weight loss seen in PP, PE, and PET. This gradual weight loss indicates a broader range of decomposition temperatures, due to the mixture of different plastic polymers in composition of the sample.
- MSW plastic-rich sample's incomparable degradation process can possibly be due to interdependent interactions among its mixed polymers.



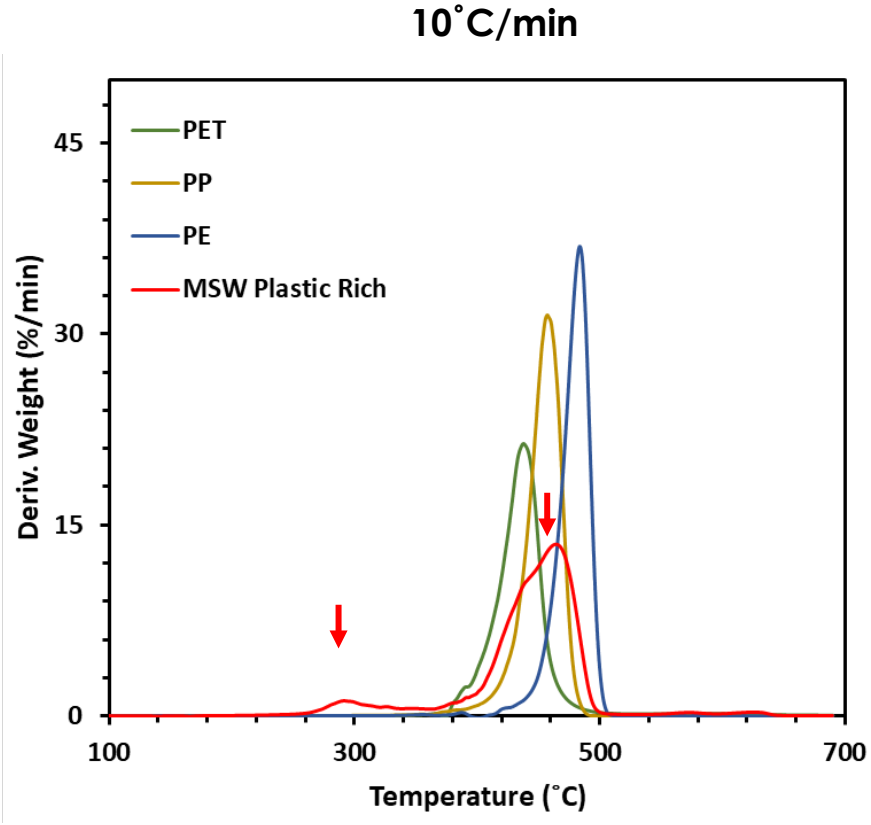
Results: Derivative Thermogravimetric Graphs

Derivative of the Weight Loss as Function of Temperature

Derivative Thermogravimetric Curves (DTG): Derivative of the weight loss curve peaks on a DTG indicates the point (temperature) of greatest weight loss rate.

Key Findings

- The MSW plastic-rich sample shows two distinct DTG peaks: the first at a lower temperature due to unknown components, and the second ranges in the decomposition temperatures of single polymers (PET, PP, and PE).
- Maximum decomposition rate (peak height) of the MSW plastic-rich sample is lower, suggesting its decomposition occurs over a wider temperature range, resulting in a more gradual weight loss.
- MSW plastic-rich sample shows a broader range of decomposition temperatures than single polymers (PET, PP, PE), indicating a more complex degradation process due to its mixed composition.



Results: DSC Profiles

Heat Flow Curves as Function of Temperature

Differential Scanning Calorimetry (DSC): Measures the temperature and heat flow associated with transitions in materials.

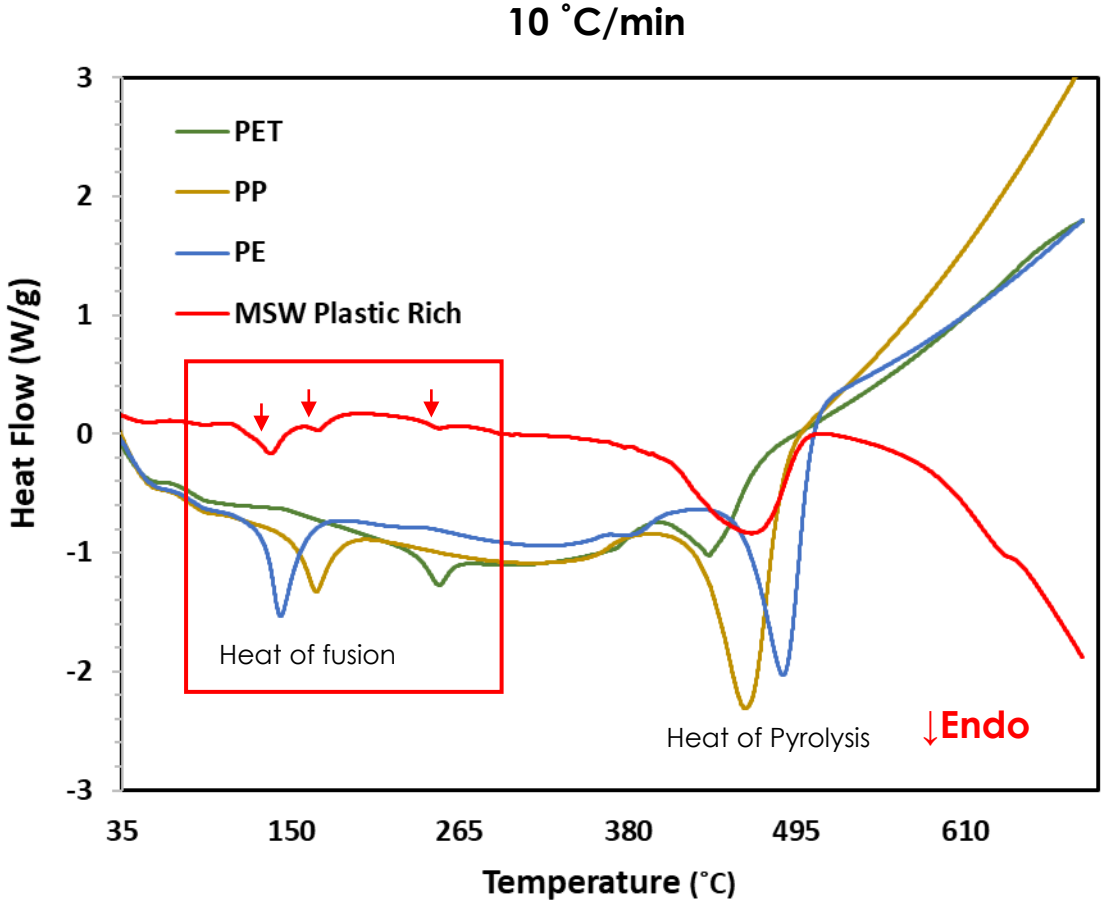
Key Findings

- Heat of Fusion: First peaks corresponds to the solid-to-liquid phase transition (melting)
- High crystallinity

  PE>PP>MSW plastic-rich>PET

- Heat of Pyrolysis: Second peak indicates sample decomposition to volatiles
- Higher thermal stability

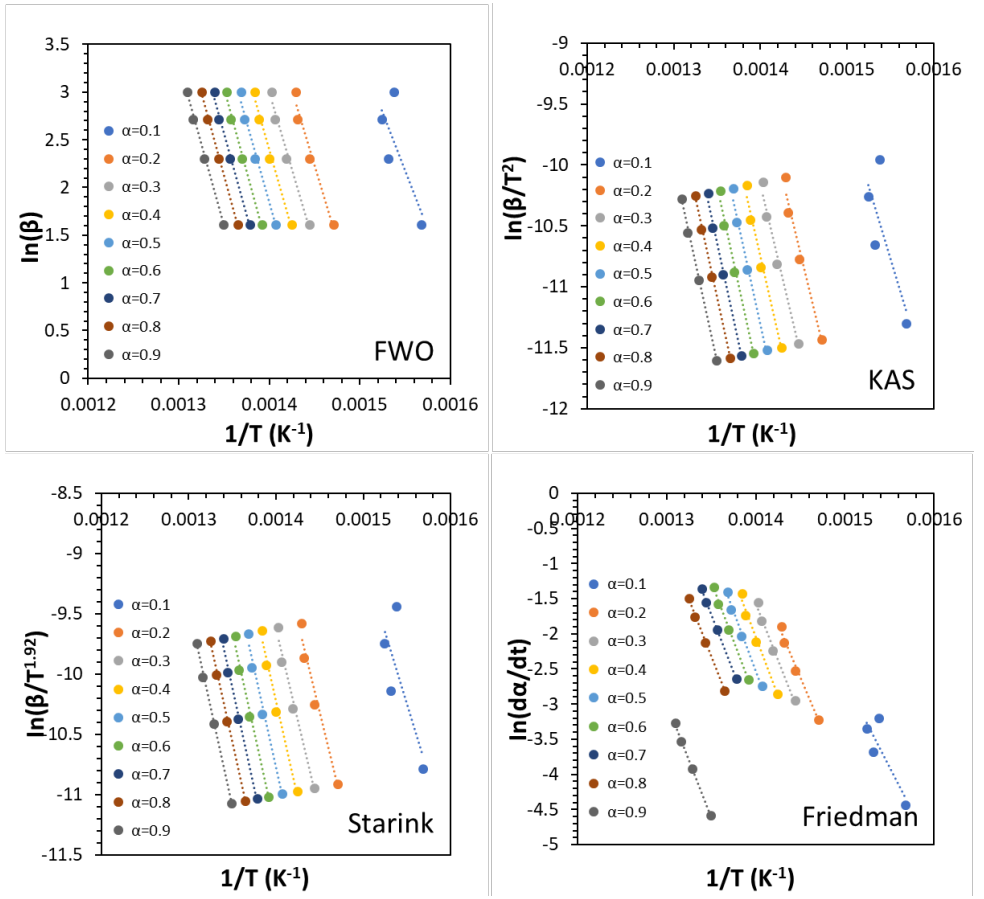
  PE>PP>MSW plastic-rich>PET



MSW Plastic-Rich Sample Calculations for Eα

Regression Plots from Experimental Data

R^2				
Regression Plots	FWO	KAS	Starink	Friedman
	$ln(\beta)$ vs. $\frac{1}{T}$	$ln\left(\frac{\beta}{RT^2}\right)$ vs. $\frac{1}{T}$	$ln\left(\frac{\beta}{RT^{1.92}}\right)$ vs. $\frac{1}{T}$	$ln\left(\frac{d\alpha}{dt}\right)$ vs. $\frac{1}{T}$
0.1α	0.63	0.60	0.60	0.75
0.2α	0.97	0.96	0.96	0.98
0.3α	0.98	0.98	0.98	0.98
0.4α	0.98	0.98	0.98	0.98
0.5α	0.98	0.98	0.98	0.99
0.6α	0.99	0.99	0.99	0.99
0.7α	0.99	0.99	0.99	1.00
0.8α	1.00	1.00	1.00	1.00
0.9α	1.00	1.00	1.00	1.00



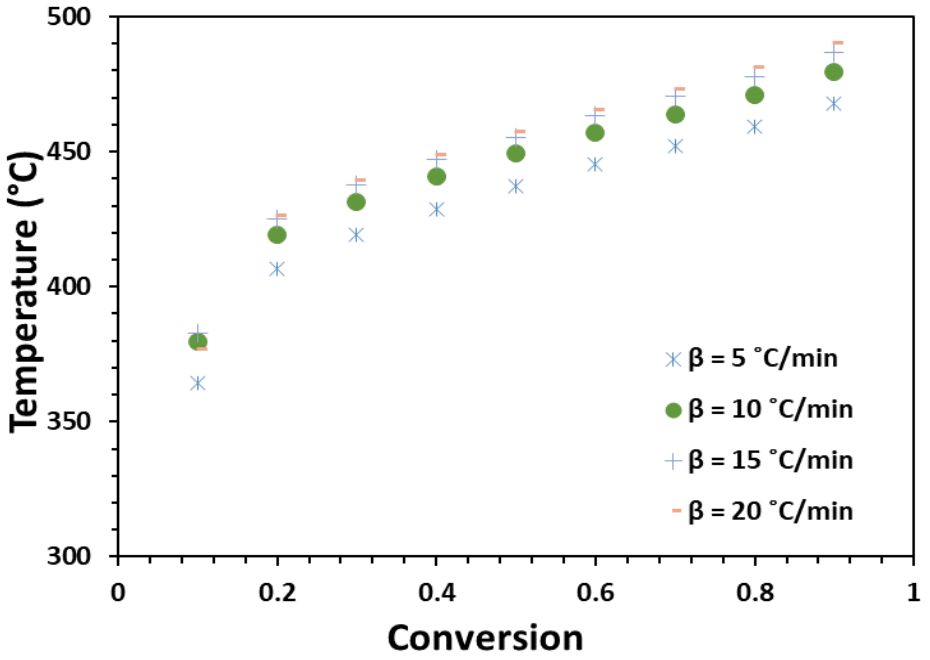
Regression lines are created from TGA data to model thermal decomposition rate.

Key Findings

- The R^2 values for all model-free methods regression lines (near 1) validate our model's accuracy. Low R^2 at 0.1 indicates slight reaction variations in the initial stages of MSW plastic-rich sample.

MSW Plastic-Rich Sample Calculations for Eα

10˚C/min	FWO Eα (kJ/mol)	KAS Eα (kJ/mol)	Starink Eα (kJ/mol)	Friedman Eα (kJ/mol)
Slope Equal To	$-1.0516\frac{E_a}{R}$	$-\frac{E_a}{R}$	$-1.0008\frac{E_a}{R}$	$-\frac{E_a}{R}$
0.1α	196	195	196	207
0.2α	246	247	248	253
0.3α	251	252	252	268
0.4α	260	262	262	281
0.5α	270	272	272	278
0.6α	273	275	275	274
0.7α	273	275	275	270
0.8α	271	273	273	270
0.9α	270	271	271	270
Avg	**257**	**258**	**258**	**263**



Apparent Activation Energy (Eα) Using different isoconversional methods.

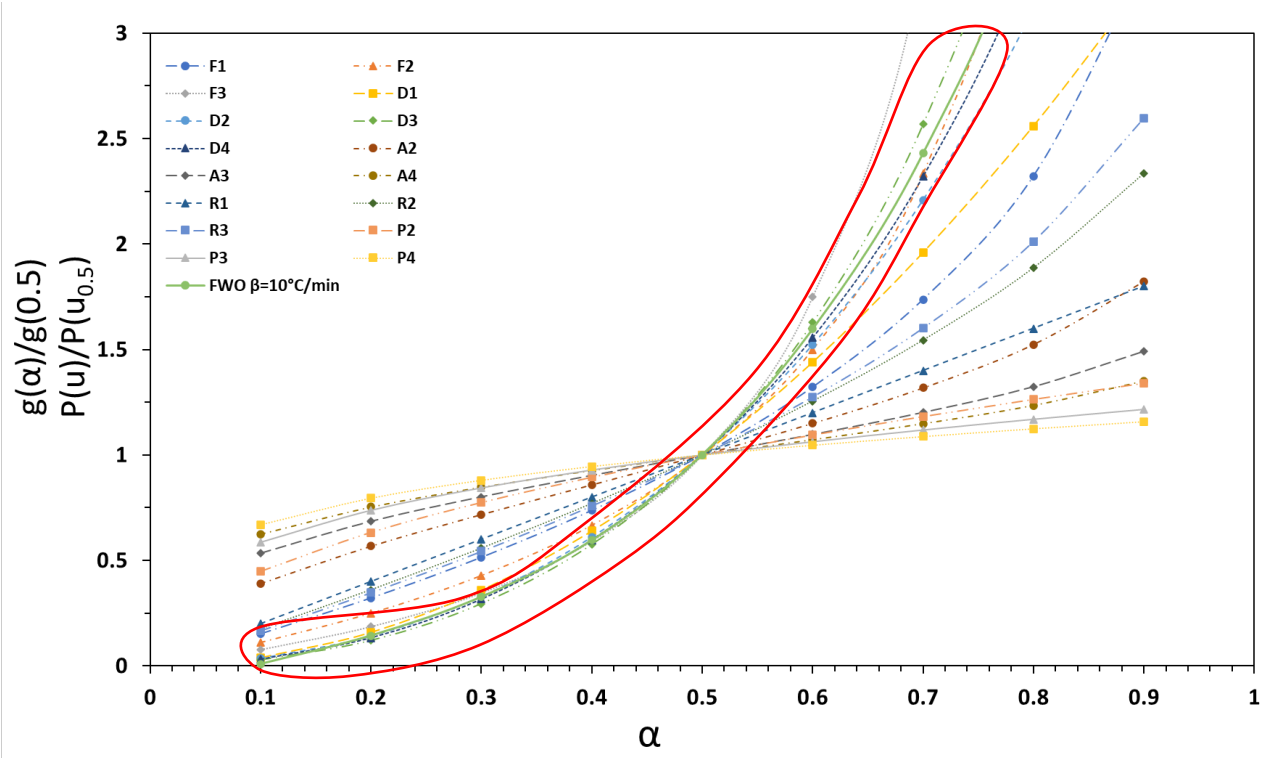
- TGA-derived Eα values are low initially, stabilize at α ≥ 0.3, indicating a shift from unknown (biomass/food) decomposition to plastic degradation.

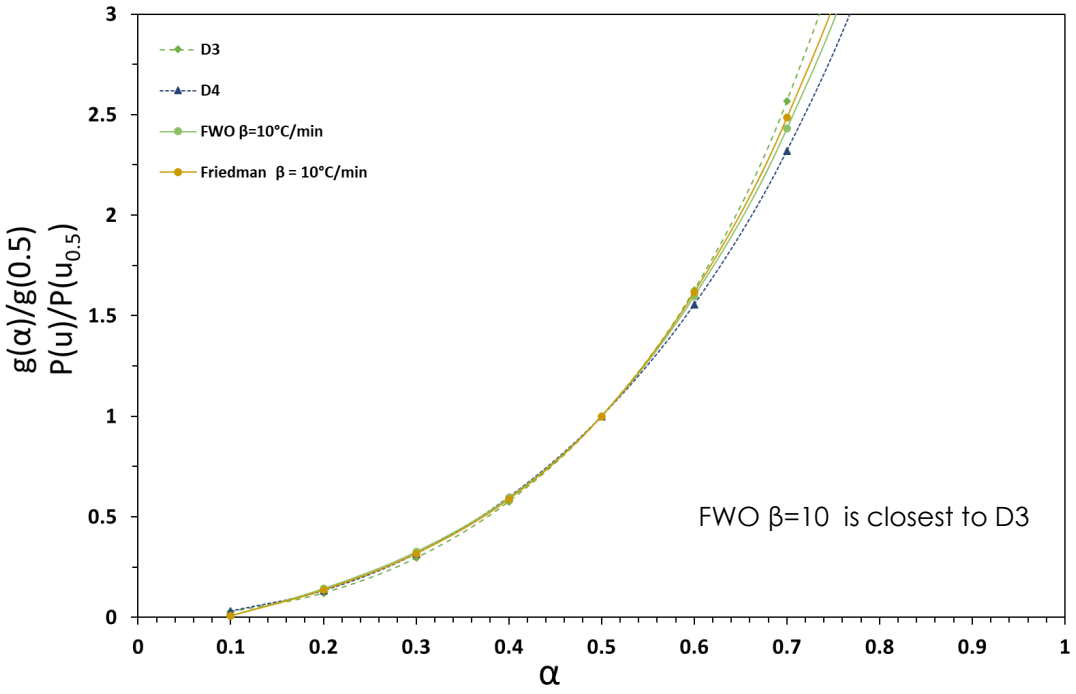
Decomposition Temperature at each α at different heating rates.

- As heating rates increase, decomposition temperatures rise, suggesting that the reduced heating time necessitates higher temperatures to achieve sample decomposition at each α.

MSW Plastic-Rich Sample Calculations for Pre-Exponential

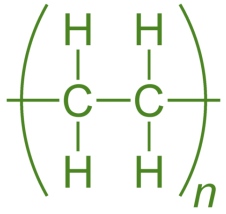
Master Plots Data Fitting From Model-Free Method

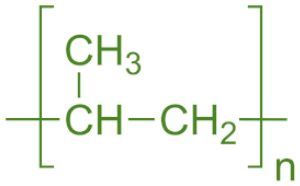


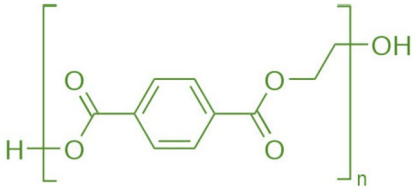


- Three-dimensional diffusion (D3) model was obtained from fitting experimental data (Average Absolute Distance Calculation) derived from Flynn-Wall-Ozawa (FWO) method at 10 °C/min in the master plot.

Kinetic Parameters for All Samples







Sample	Conversion range (α)	Kinetic Parameters			
		Method	Eα (kJ/mol)	A min^{-1}	Kinetic Model
PE	0.1-0.9	FWO	283.81	2.72E+19	A2
		KAS	285.99	3.89E+19	
		Starink	286.26	4.06E+19	
		Friedman	247.31	6.93E+16	
PP	0.1-0.9	FWO	229.46	1.17E+16	R1
		KAS	229.18	1.15E+16	
		Starink	229.48	1.21E+16	
		Friedman	197.19	7.18E+13	
PET	0.1-0.9	FWO	195.11	2.59E+13	R3
		KAS	193.45	1.94E+13	
		Starink	193.76	2.05E+13	
		Friedman	179.88	3.19E+12	
MSW Plastic-Rich	0.1-0.9	FWO	256.68	9.28E+16	D3
		KAS	265.87	1.17E+17	
		Starink	266.14	1.22E+17	
		Friedman	270.35	2.87E+17	

Thermodynamic Parameters for All Samples

Thermal Degradation Characteristics									
Sample	**Tm (°C)**	**Td_i (°C)**	**Td_max (°C)**	**Td_f (°C)**	**DTG_max (wt.%/min)**	**Heat of Fusion (J/g)**	**ΔH (kJ/mol)**	**ΔG (kJ/mol)**	**ΔS (kJ/mol-K)**
PE	142.79	452.54	485.03	501.30	43.77	87.40	277.51	219.15	0.08
PP	166.57	372.93	429.66	464.99	25.60	44.21	223.21	213.68	0.01
PET	250.56	392.45	439.53	470.05	26.27	18.96	189.2	216	-0.04
MSW Plastic-Rich	137.46	297.15	465.36	494.76	15.81	24.80	250.55	228.42	0.03

T_m- Melting temperature. T_{di}- Initial decomposition temperature. T_{dmax}- Maximum decomposition temperature. T_{df}- Final decomposition temperature. DTG_{max}- Maximum rate of weight loss.

Summary

- The TGA analysis of single polymers and MSW plastic-rich gave useful information about the reaction kinetics, and thermodynamic properties, which help better understand the plastic waste thermochemical recycling process.
- The model-free multipoint isoconversional analysis method is valid for calculating kinetic parameters for single polymers and MSW plastic-rich.
- TGA weight loss curves reveal different decomposition profiles for each component, as polymers degrade distinctively at varying temperatures.
- MSW plastic-rich sample's incomparable degradation process is likely due to interconnected interactions among its mixed components.
- Further research focused on understanding the impact of mixtures on reaction products compared to single polymers will give us more useful information to better understand reaction mechanisms and the overall decomposition process, to optimize conditions to get desired results.

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