

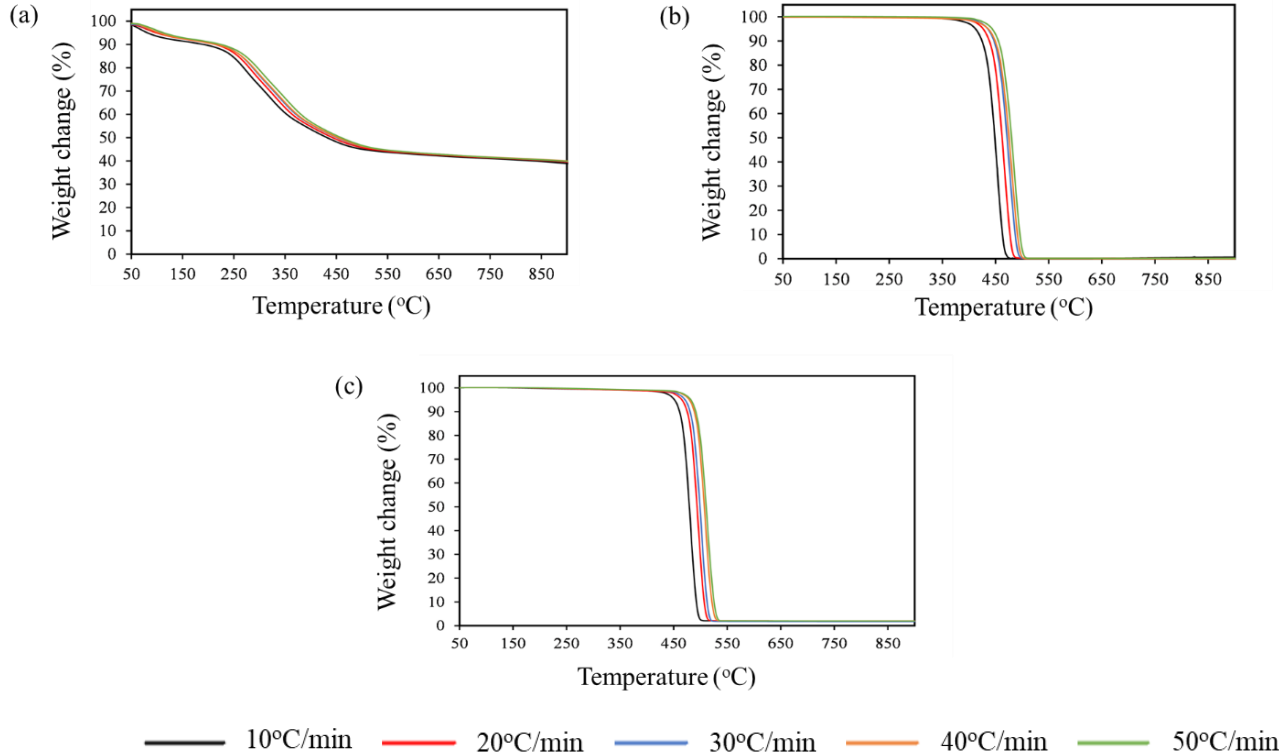
Synergistic Interactions between Sewage Sludge and Plastics during Co-pyrolysis

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Introduction

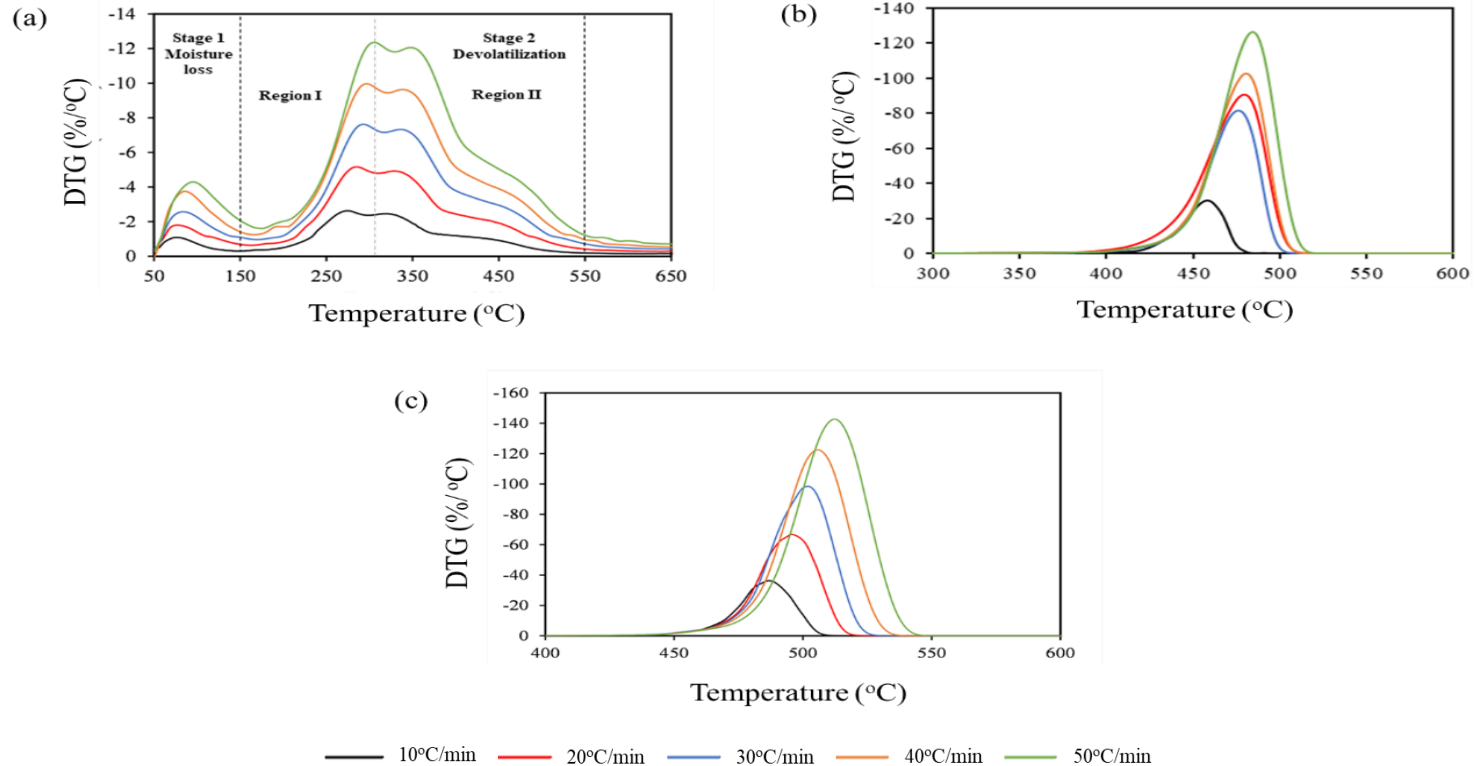
- **Sewage sludge (SS)** is a heterogeneous mixture of organic and inorganic constituents, produced as a by-product of wastewater treatment processes.
- While pyrolysis of SS would reduce waste going to landfill and greenhouse gas emission, effective energy recovery from SS is hindered by its low bio-oil composition.
- During **co-pyrolysis**, 2 or more materials are mixed and pyrolyzed together, which interacts to affect overall product composition and distribution.
- Polyolefins, such as **polypropylene (PP)** and **high-density polyethylene (HDPE)**, have high H content in its polymeric structure.
- Hence, co-pyrolysis of PP and HDPE with SS is studied to elucidate synergistic effects on activation energy and product distribution.

Thermogravimetric curves



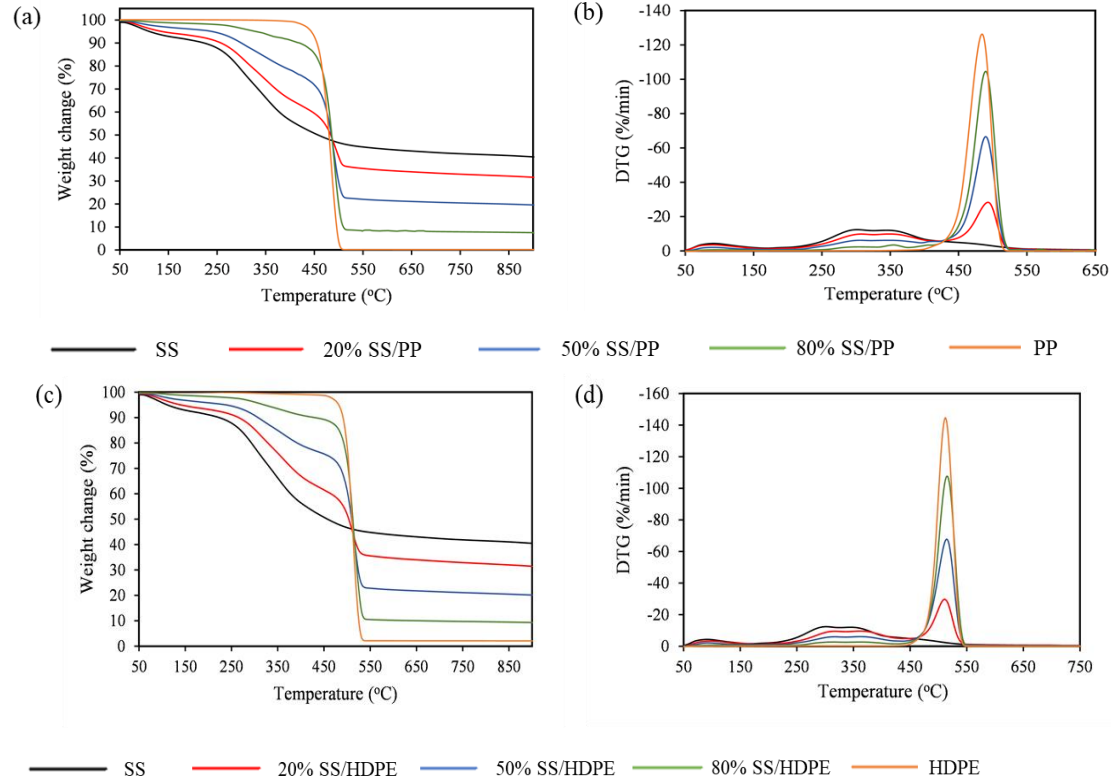
Thermogravimetric curves of (a) SS, (b) PP and (c) HDPE between 50 – 900°C at heating rates 10, 20, 30, 40, 50°C/min under constant N_2 flow (100 mL/min)

Differential thermogravimetric (DTG) curves



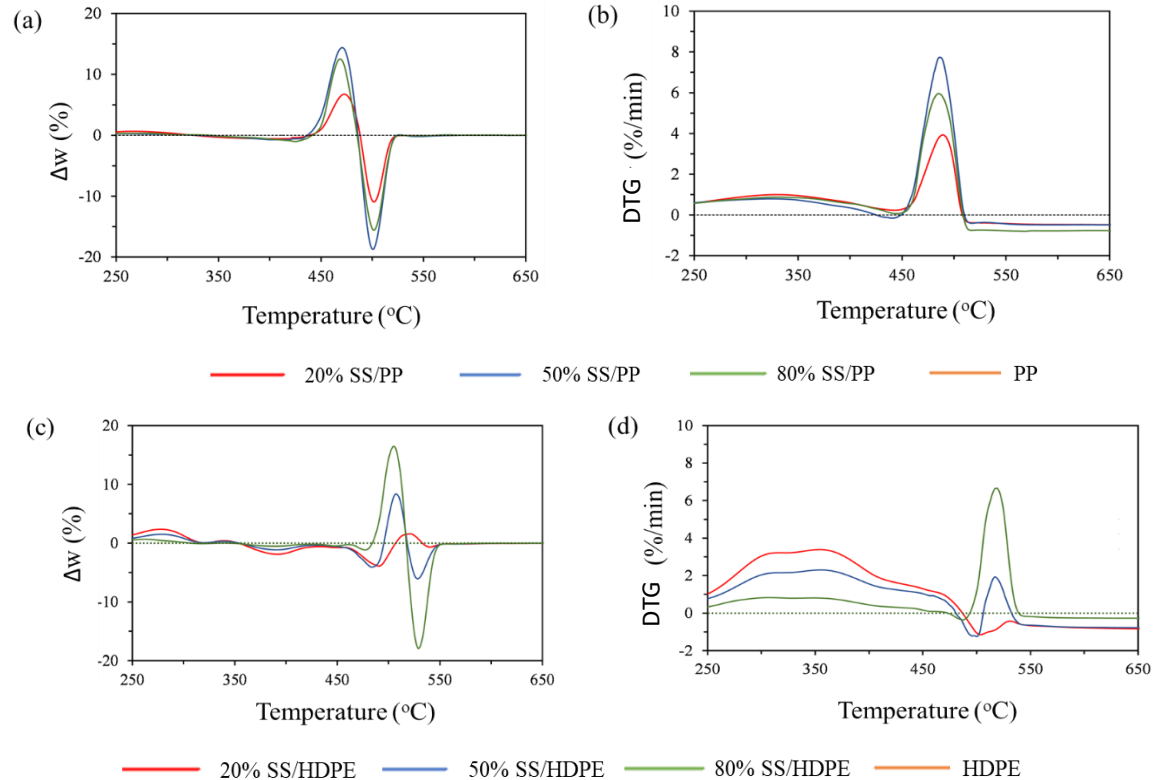
Differential thermogravimetric (DTG) curves of (a) SS, (b) PP and (c) HDPE between 40 – 900°C at heating rates 10, 20, 30, 40, 50°C/min under constant N₂ flow (100 mL/min)

Co-pyrolysis TGA and DTG curves



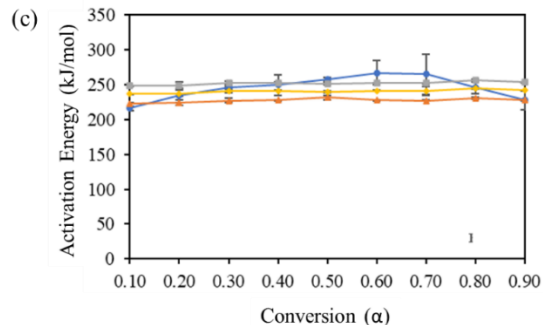
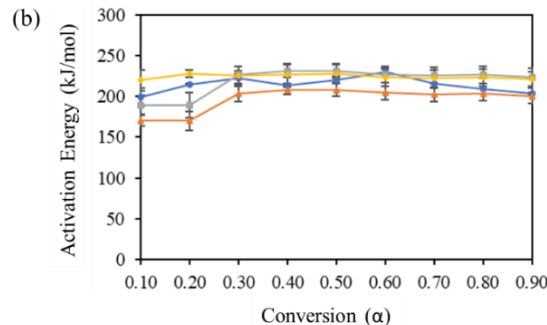
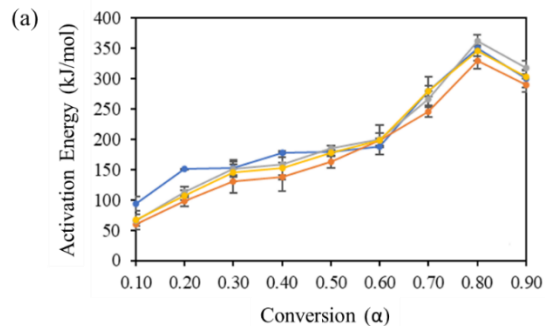
Co-pyrolysis TGA and DTG curves of 20%, 50%, and 80% SS/PP and SS/HDPE

Synergistic analysis of overall volatile conversion and rate of devolatilization



Synergistic analysis of overall volatile conversion and rate of devolatilization during SS/PP (a, b) and SS/HDPE co-pyrolysis

Activation energies of SS, PP, and HDPE



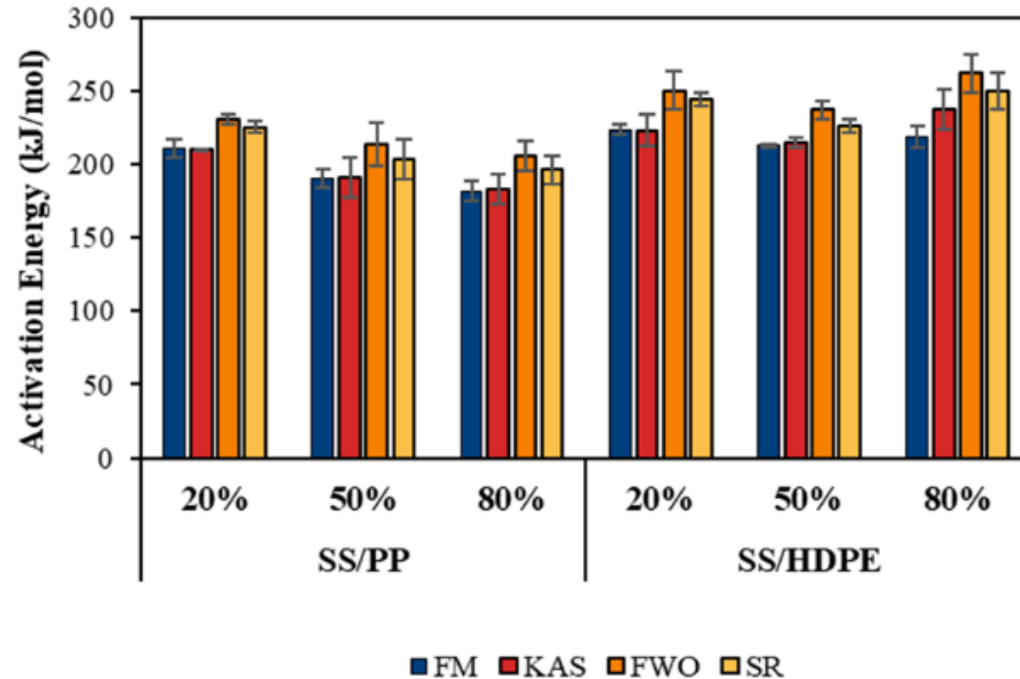
—●— FM
 —▲— KAS
 —■— OFW
 —◆— SR

Average activation energies for PP and HDPE

	FM	KAS	FWO	SR
PP (kJ/mol)	201.35	192.46	217.18	204.79
HDPE (kJ/mol)	246.66	227.72	252.26	240.74

Activation energies (kJ/mol) of SS, PP, and HDPE pyrolysis as determined by iso-conversional model-free methods: Friedman (FM), Flynn-Wall-Ozawa (FWO), Kissinger-Akarhira-Sunose (KAS), and Starink (SR).

Average activation energy of co-pyrolysis determined with model-free methods



Average activation energy (kJ/mol) of co-pyrolysis determined with iso-conversional model-free methods: Friedman (FM), Flynn-Wall-Ozawa (FWO), Kissinger-Akahira-Sunose (KAS), and Starink (SR).

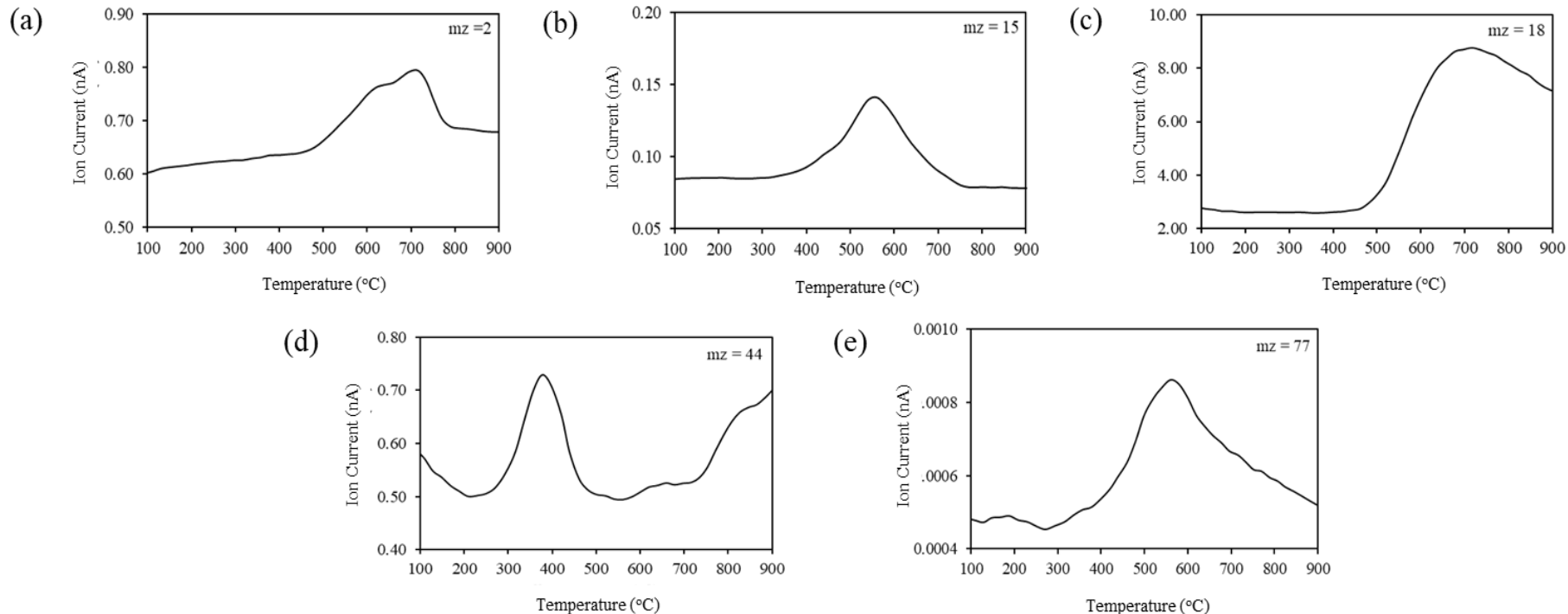
Activation energies of co-pyrolysis determined with model-free methods

	Friedman (FM)	Kissinger- Akahira-Sunose (KAS)	Flynn-Wall- Ozawa (FWO)	Starink (SR)
	E_A (kJ/mol)	E_A (kJ/mol)	E_A (kJ/mol)	E_A (kJ/mol)
SS/PP				
20%	$211.39 \pm 6.14^{\ddagger*}$	$210.87 \pm 0.05^{\ddagger}$	$230.89 \pm 3.26^{\ddagger}$	$225.62 \pm 4.34^{\ddagger}$
50%	$190.71 \pm 6.51^{\ddagger*}$	$191.16 \pm 13.89^{\ddagger}$	$213.36 \pm 14.62^{\ddagger}$	$203.62 \pm 13.95^{\ddagger}$
80%	$181.95 \pm 6.59^{\ddagger*}$	$182.99 \pm 10.56^{\ddagger*}$	$205.76 \pm 10.50^{\ddagger}$	$196.36 \pm 10.01^{\ddagger*}$
SS/HDPE				
20%	223.65 ± 3.25	$223.24 \pm 11.07^{\ddagger}$	$250.46 \pm 13.15^{\ddagger}$	$244.50 \pm 4.65^{\ddagger}$
50%	$213.05 \pm 1.00^{\ddagger*}$	$214.90 \pm 3.89^{\ddagger}$	$237.25 \pm 6.15^{\ddagger}$	$226.33 \pm 4.72^{\ddagger}$
80%	$218.91 \pm 7.85^{\ddagger*}$	237.69 ± 13.71	262.09 ± 12.76	250.08 ± 12.14

** Lower than individual feedstock*

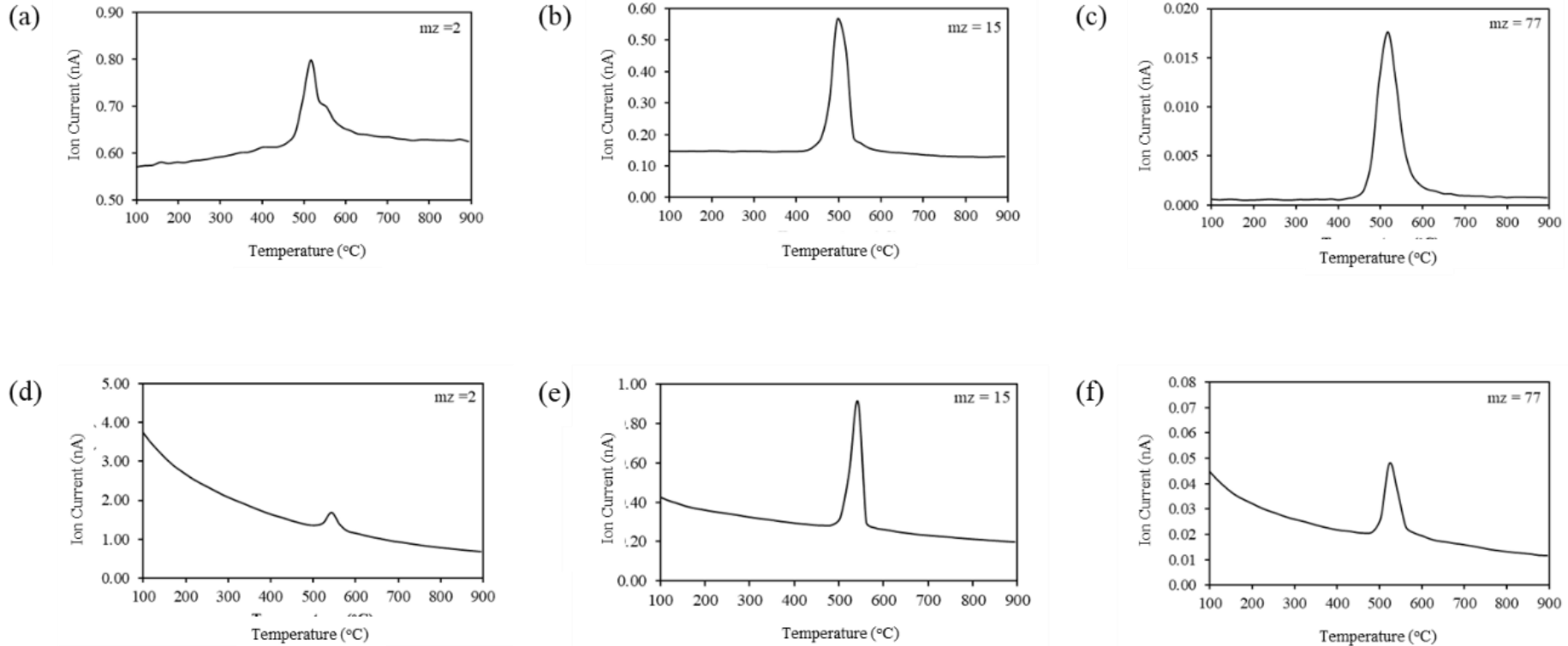
\ddagger Lower than weighted average

Evolved gas analysis during pyrolysis of sewage sludge (SS)



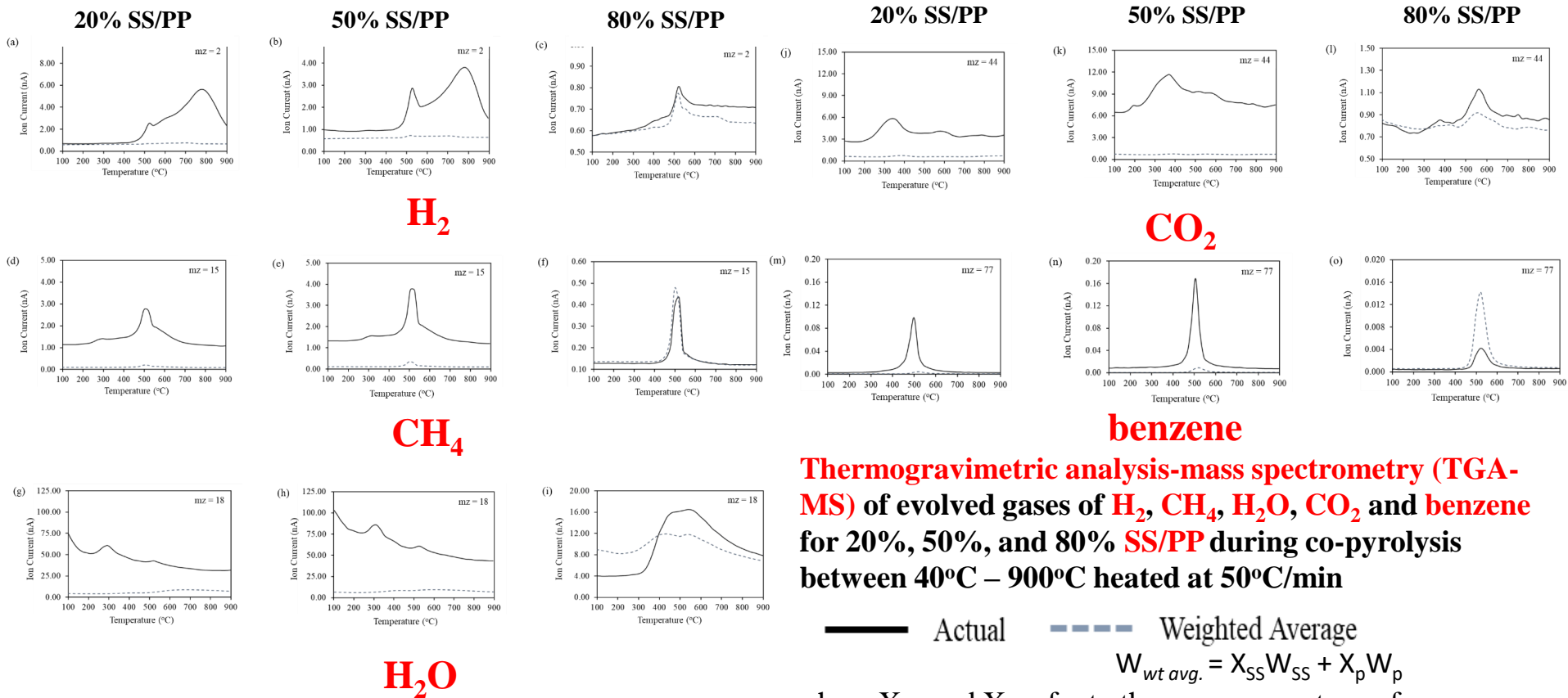
Evolution of (a) hydrogen (H_2 , $m/z = 2$), (b) methane (CH_4 , $m/z = 15$), (c) water (H_2O , $m/z = 18$), (d) carbon dioxide (CO_2 , $m/z = 44$) and (e) benzene (C_6H_6 , $m/z = 77$) during SS pyrolysis monitored with **thermogravimetric analysis-mass spectrometry (TGA-MS)**.

Evolved gas analysis during pyrolysis of PP and HDPE



Evolution of hydrogen (H_2 , $m/z = 2$), methane (CH_4 , $m/z = 15$) and benzene (C_6H_6 , $m/z = 77$) during (a-c) PP and (d-f) HDPE pyrolysis monitored with **thermogravimetric analysis-mass spectrometry (TGA-MS)**..

Evolved gas analysis during co-pyrolysis of SS and PP



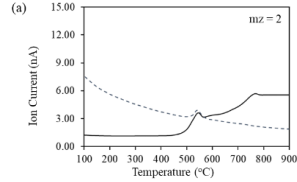
Thermogravimetric analysis-mass spectrometry (TGA-MS) of evolved gases of H_2 , CH_4 , H_2O , CO_2 and benzene for 20%, 50%, and 80% SS/PP during co-pyrolysis between 40°C – 900°C heated at 50°C/min

$$W_{wt\ avg.} = X_{SS}W_{SS} + X_PW_P$$

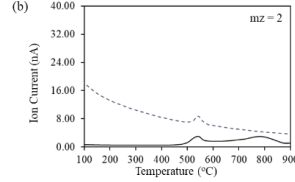
where X_{SS} and X_P refer to the mass percentage of sewage sludge and plastic in the mixed sample respectively

Evolved gas analysis during co-pyrolysis of SS and HDPE

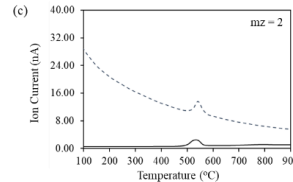
20% SS/HDPE



50% SS/ HDPE

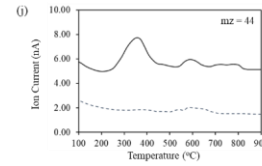


80% SS/ HDPE

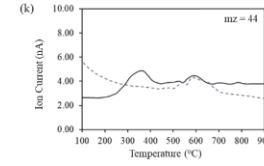


H₂

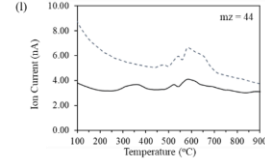
20% SS/ HDPE



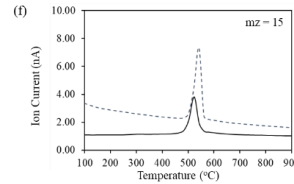
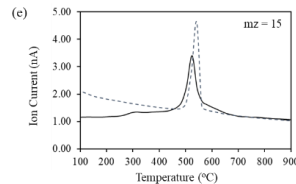
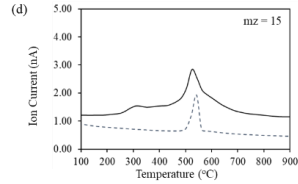
50% SS/ HDPE



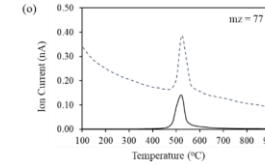
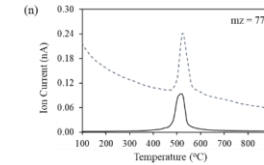
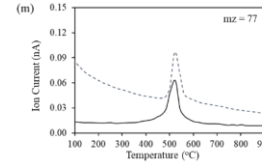
80% SS/ HDPE



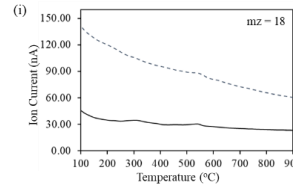
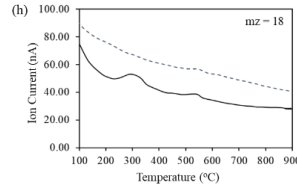
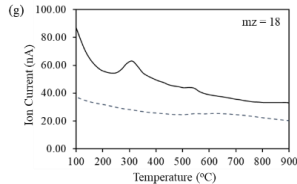
CO₂



CH₄



benzene



H₂O

Thermogravimetric analysis-mass spectrometry (TGA-MS) of evolved gases of 20%, 50%, and 80% SS/HDPE during co-pyrolysis between 40°C – 900°C heated at 50°C/min

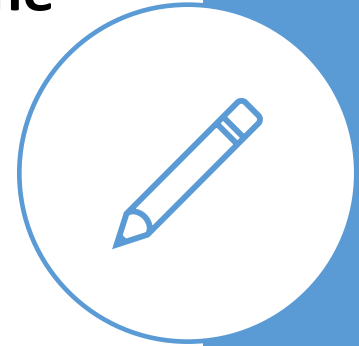
— Actual - - - - - Weighted Average

$$W_{wt\ avg.} = X_{SS}W_{SS} + X_pW_p$$

where X_{SS} and X_p refer to the mass percentage of sewage sludge and plastic in the mixed sample respectively

Summary

- Co-pyrolysis of sewage sludge (SS) with polypropylene (PP) and high density polyethylene (HDPE) were studied
- Synergistic reductions in activation energy were observed during co-pyrolysis
- Co-pyrolysis increased volatile conversion for SS/PP, and only some volatile components for SS/HDPE.
- Different interactions occurred during co-pyrolysis of sewage sludge with different plastics





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THANK YOU!