

Chemical recycling of flame-retarded plastics:

Reducing the bromine content in the pyrolysis oil using calcium-based sorbents

Razan Alshargawi, Britta Bergfeldt, Daniela Merz,
Frank Richter, Grazyna Straczewski, Niklas Netsch,
Salar Tavakkol, Dieter Stapf

Karlsruhe Institute of Technology (KIT)

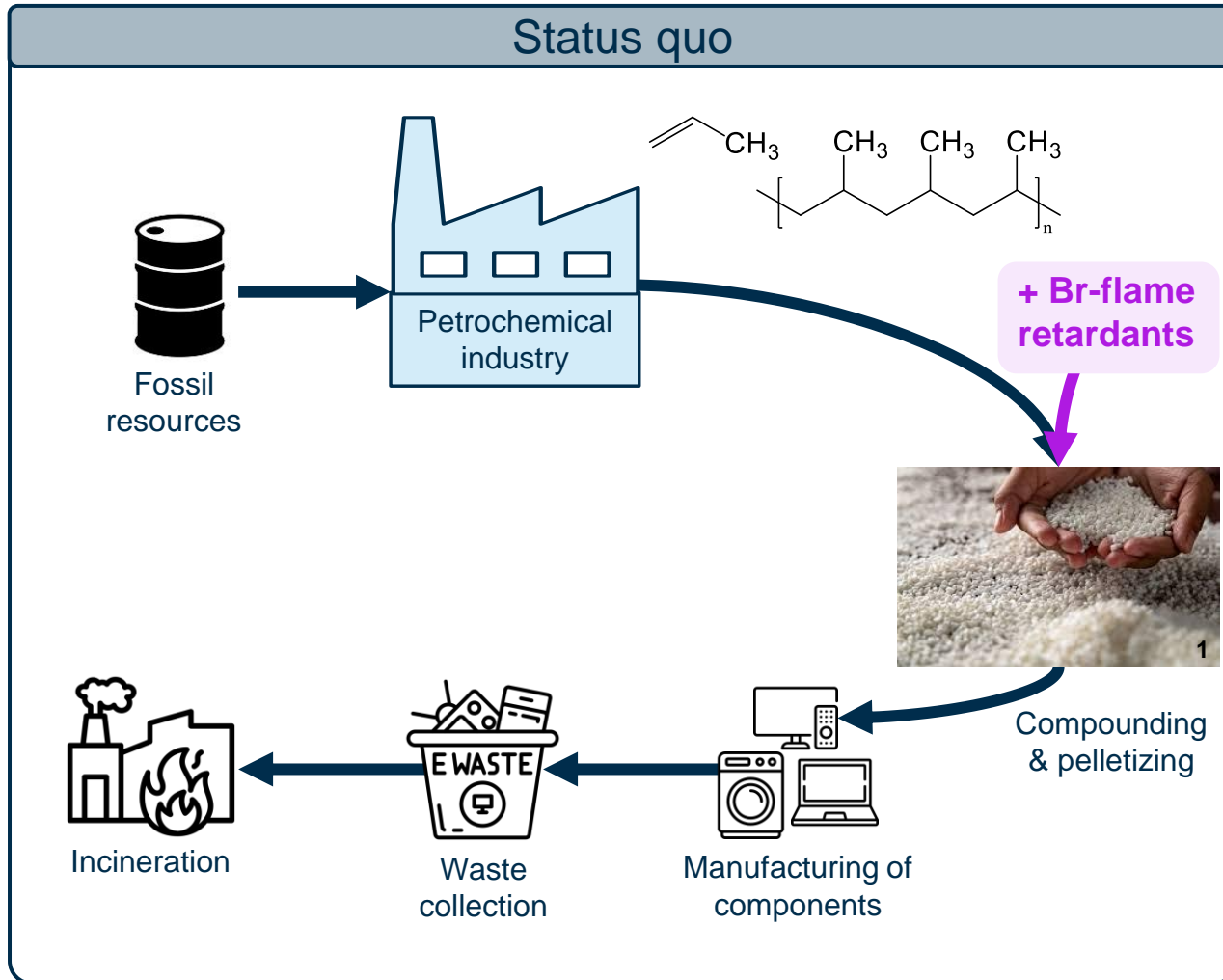
05. June 2025



EUROPEAN MEETING ON FIRE
RETARDANT POLYMERIC MATERIALS
03.-06.June Madrid, Spain.

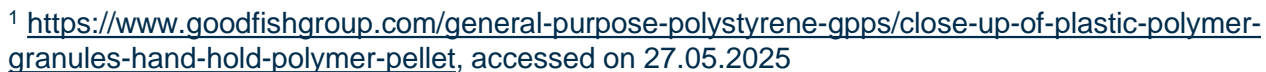


Background

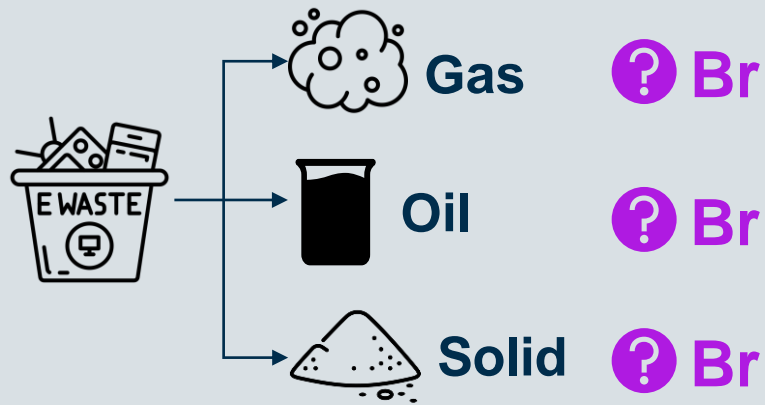


¹ <https://www.goodfishgroup.com/general-purpose-polystyrene-gpps/close-up-of-plastic-polymer-granules-hand-hold-polymer-pellet>, accessed on 27.05.2025

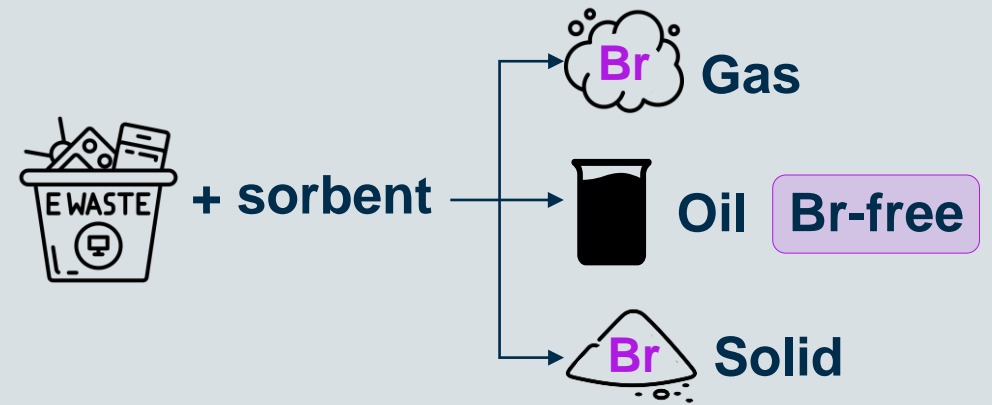
Circular economy



Objectives

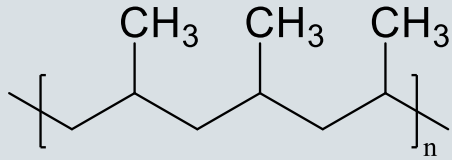


Investigate the **bromine distribution** across pyrolysis **products**

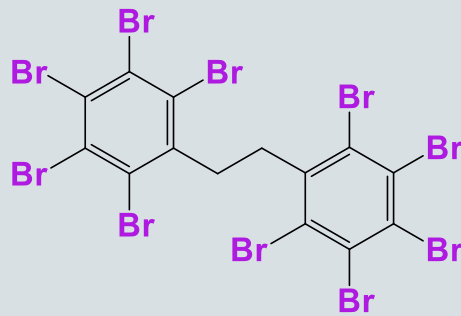


Evaluate the potential of **sorbents** to **reduce bromine** content in the **oil**

Model samples



PolyPropylene (PP)



**DecaBromoDiPhenyl
Ethane (DBDPE)**

Composition in mass-%

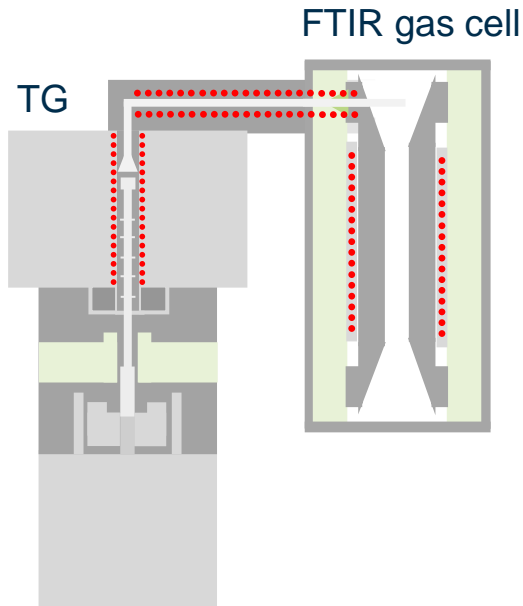
	PP	DBDPE	Br
PP	100	–	–
DBDPE	–	100	81.3 *
PP-DBDPE blend	79	21	17.4 **

* Calculated for $C_{14}H_4Br_{10}$

** Quantified via combustion ion chromatography (C-IC)

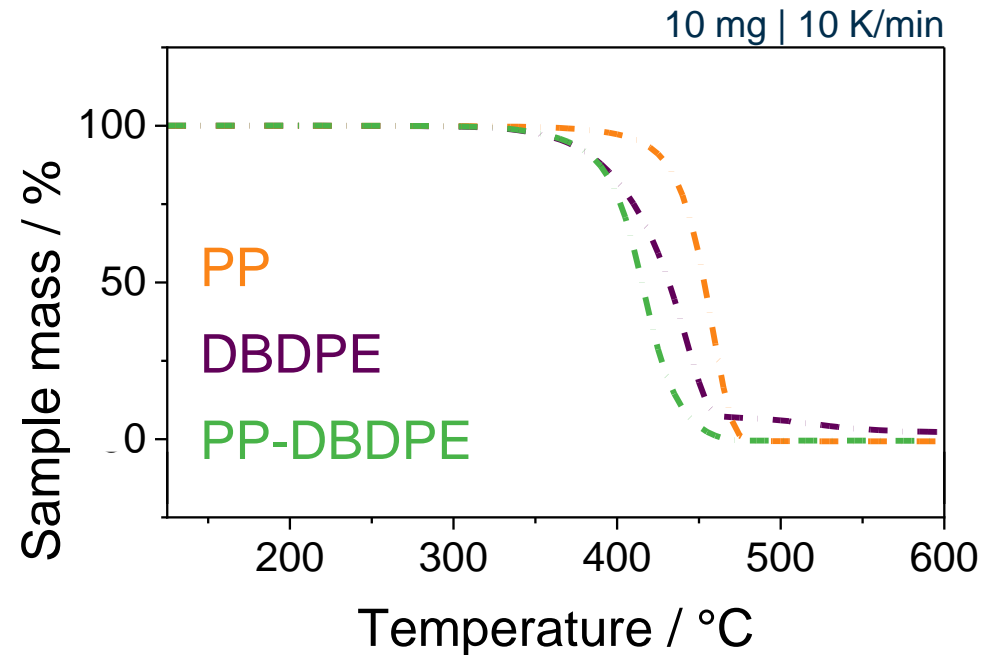
Decomposition behavior

Is bromine released as HBr?



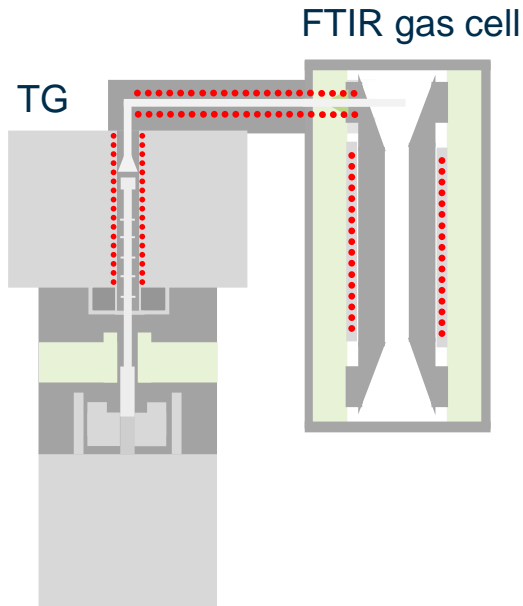
TG-FTIR

Sample mass: 10 mg
Heating rate: 10 K/min
N₂ atmosphere



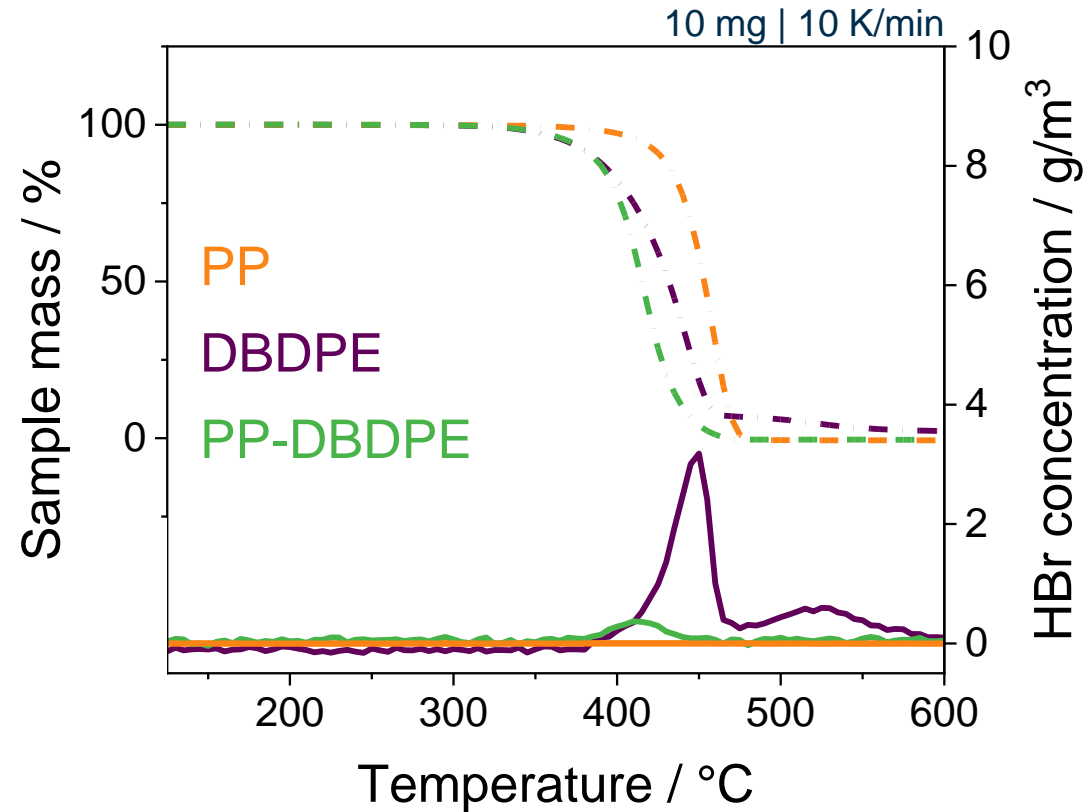
Decomposition behavior

Is bromine released as HBr?



TG-FTIR

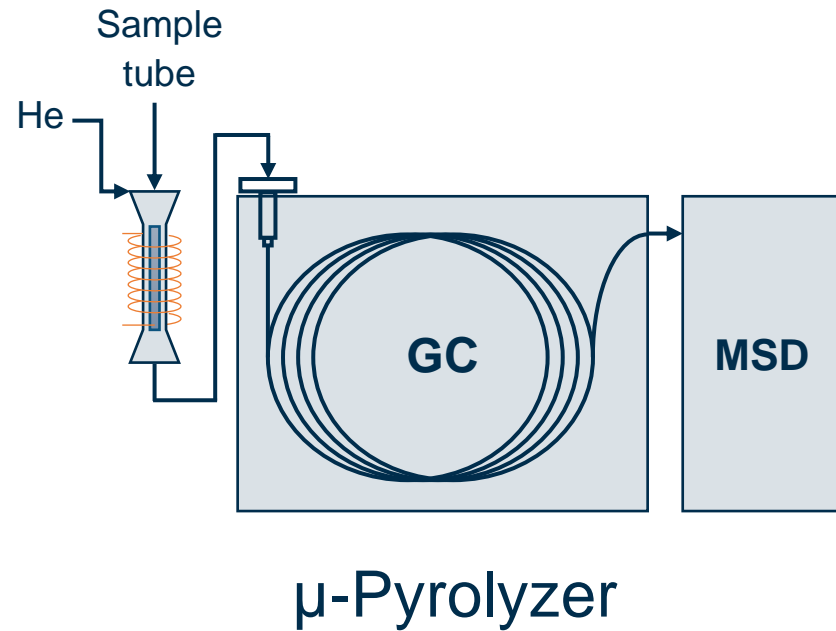
Sample mass: 10 mg
Heating rate: 10 K/min
N₂ atmosphere



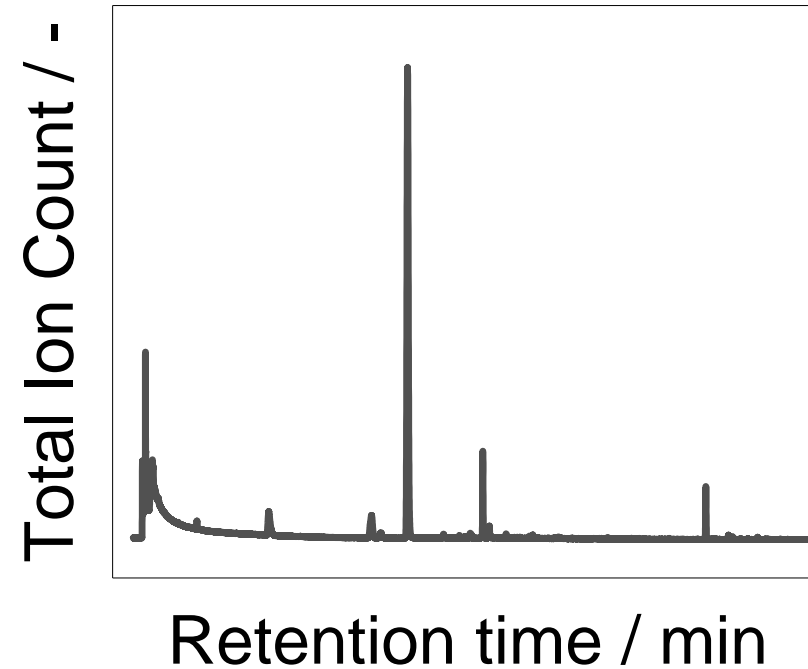
- DBDPE: ≤ 9 mass-% of Br is released as HBr
- PP-DBDPE: ≤ 5 mass-% of Br is released as HBr

Decomposition behavior

In which chemical form is bromine released?

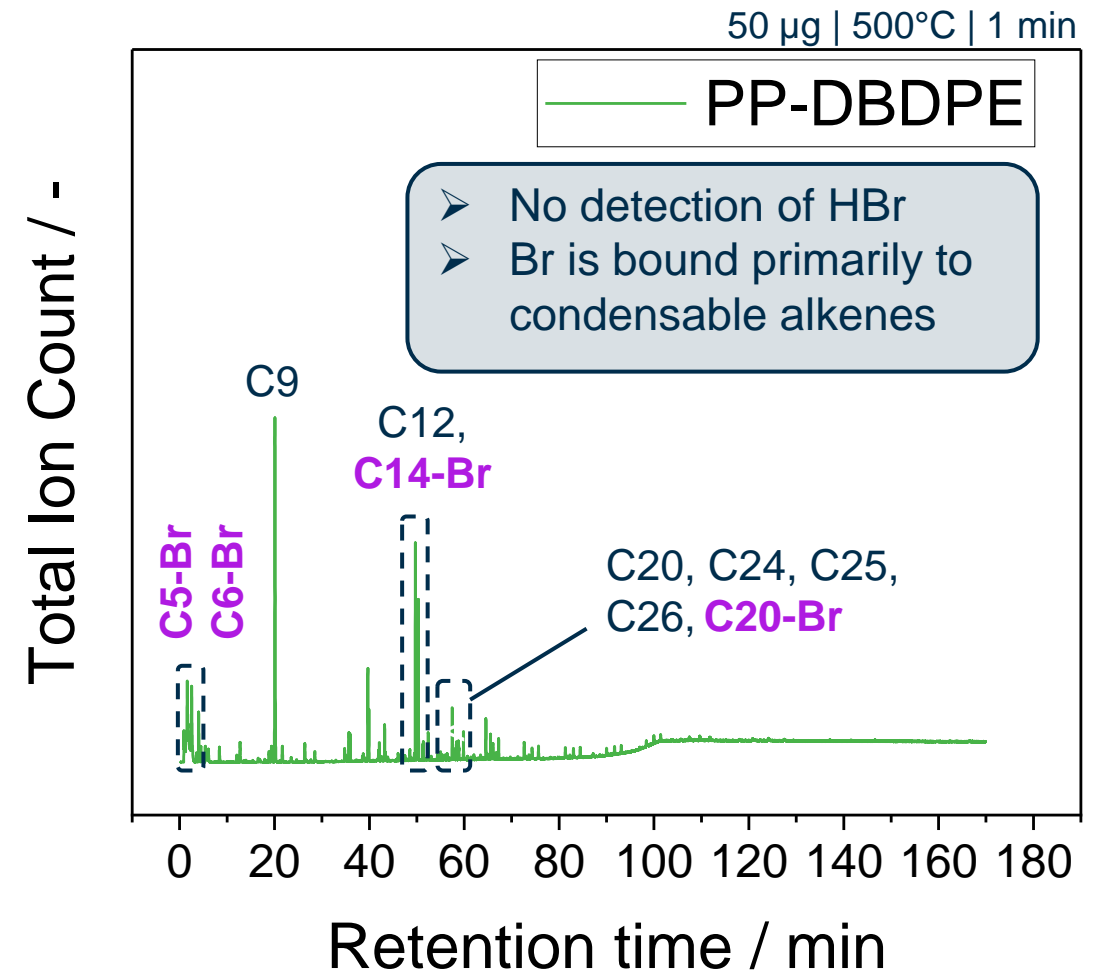
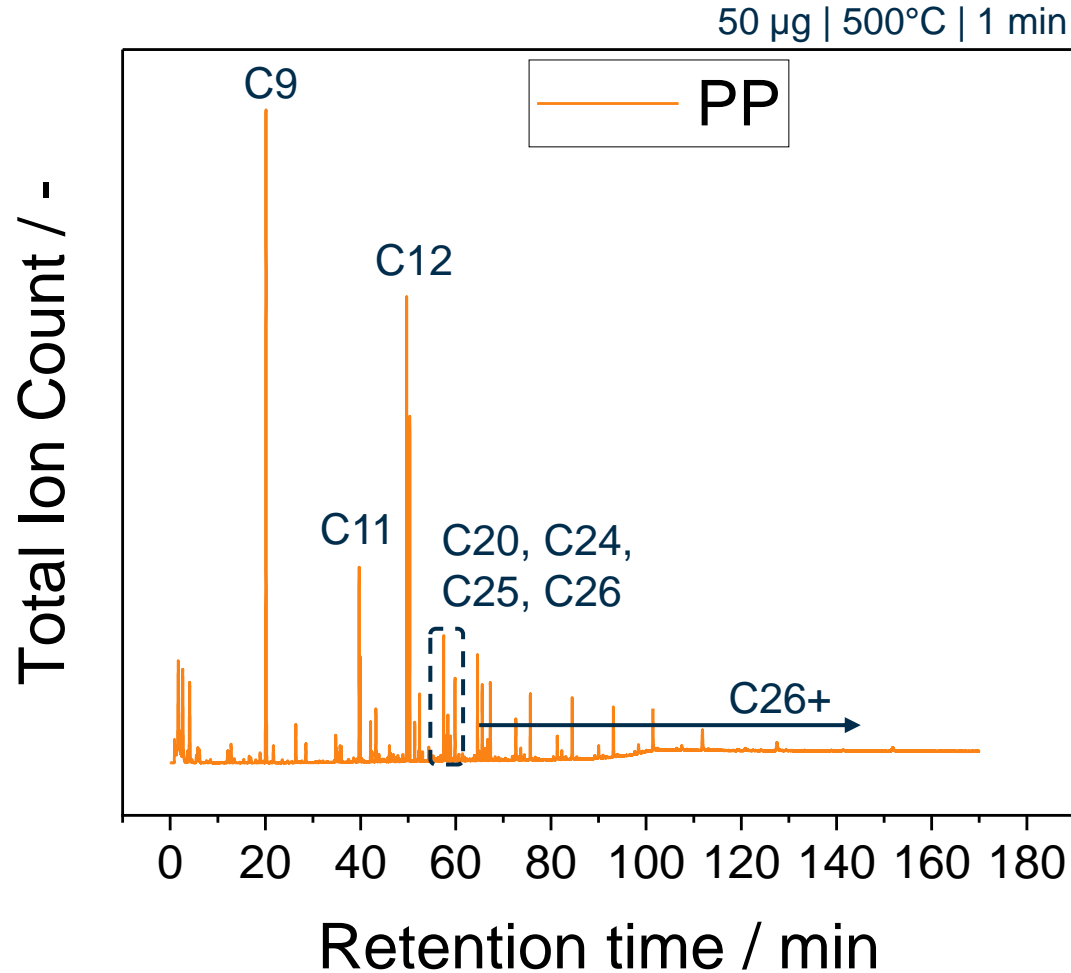


Sample mass: 50 μ g
 $T_{\text{reactor, set point}}$: 500°C
Duration: 1 min
He atmosphere

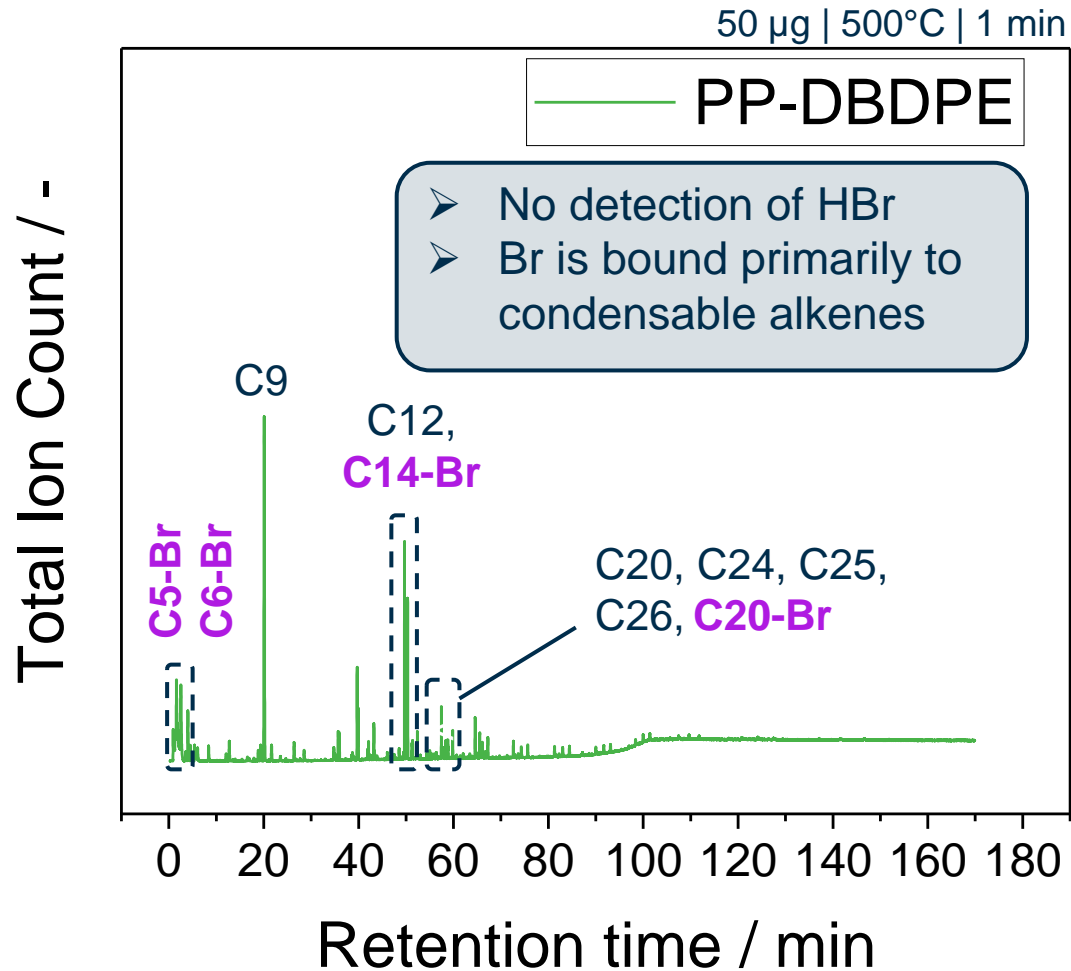


Decomposition behavior

In which chemical form is bromine released?



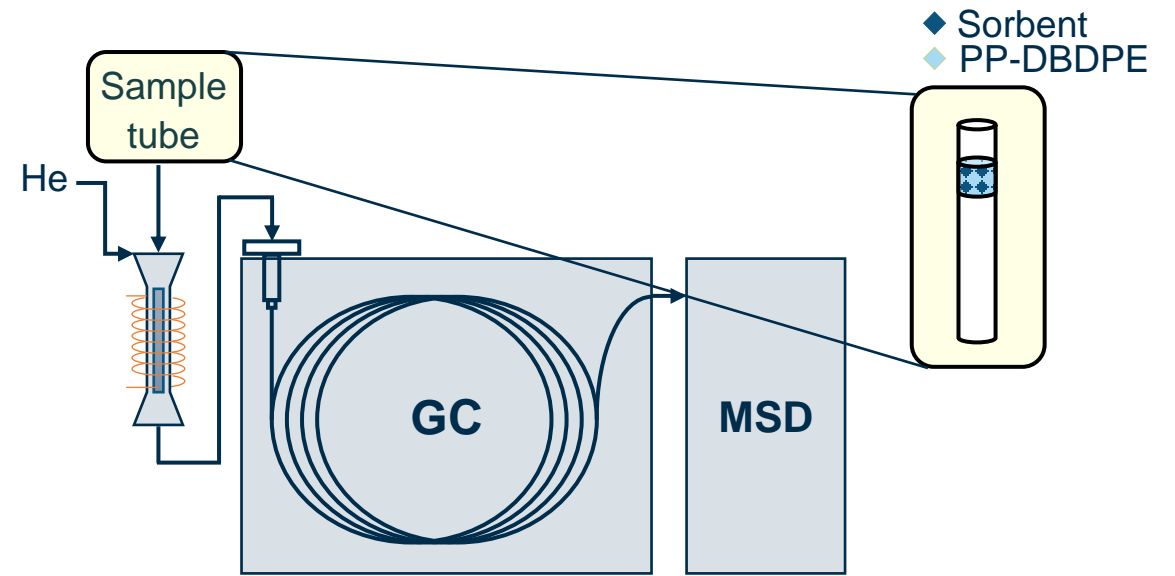
Effect of Ca-based sorbents



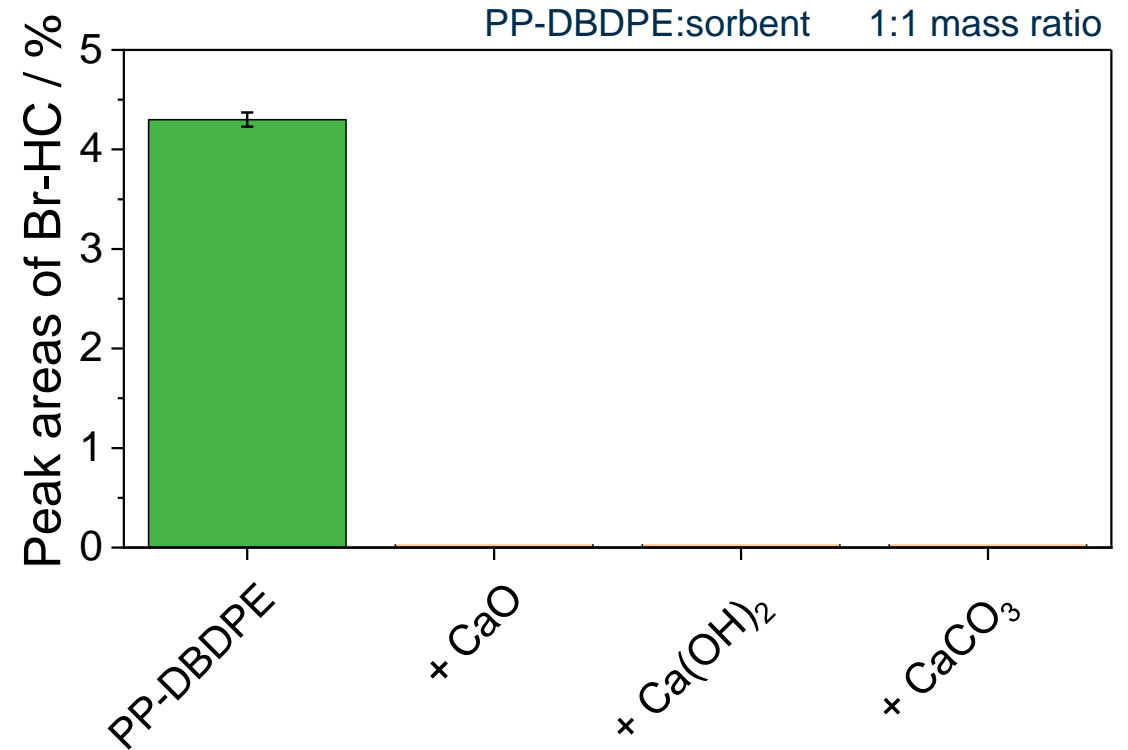
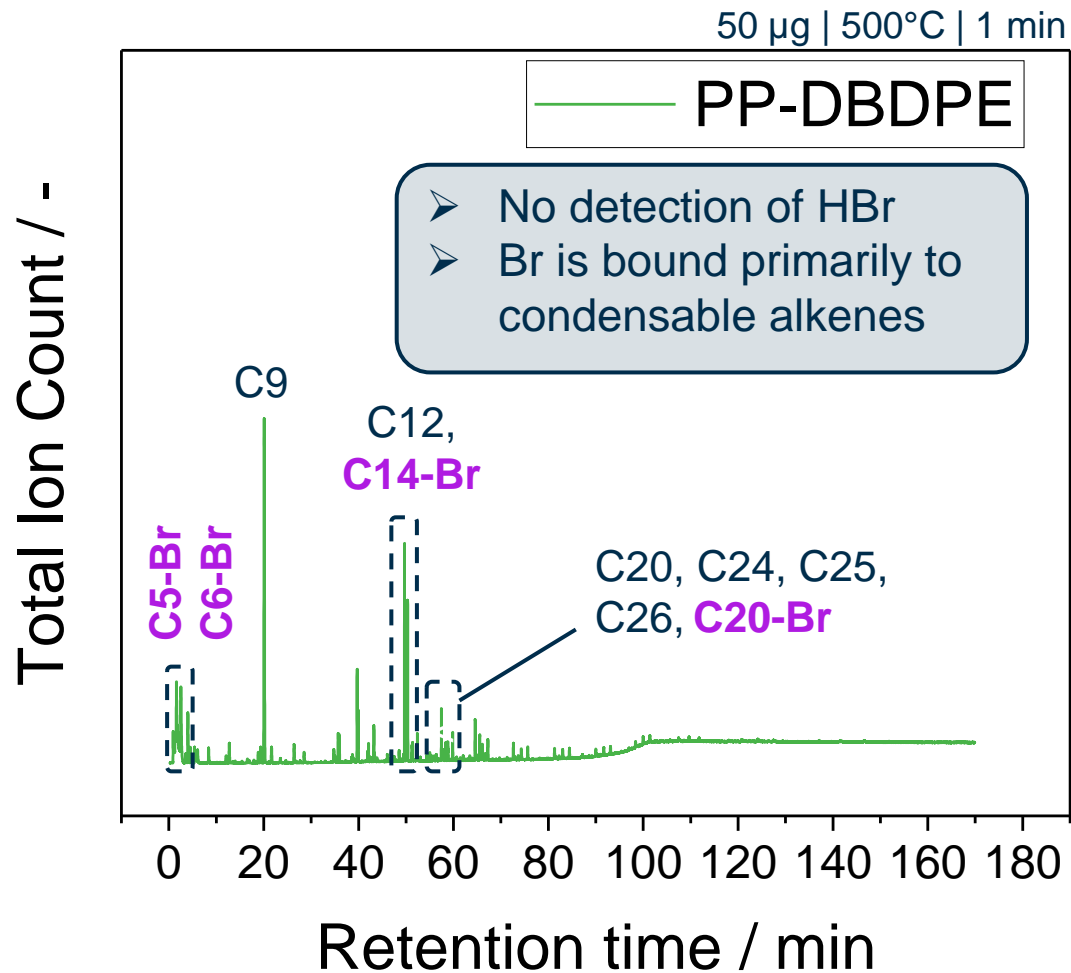
Reducing Br in the oils

Use of Ca-based sorbents:

- $\text{Ca}(\text{OH})_2$
- CaO
- CaCO_3

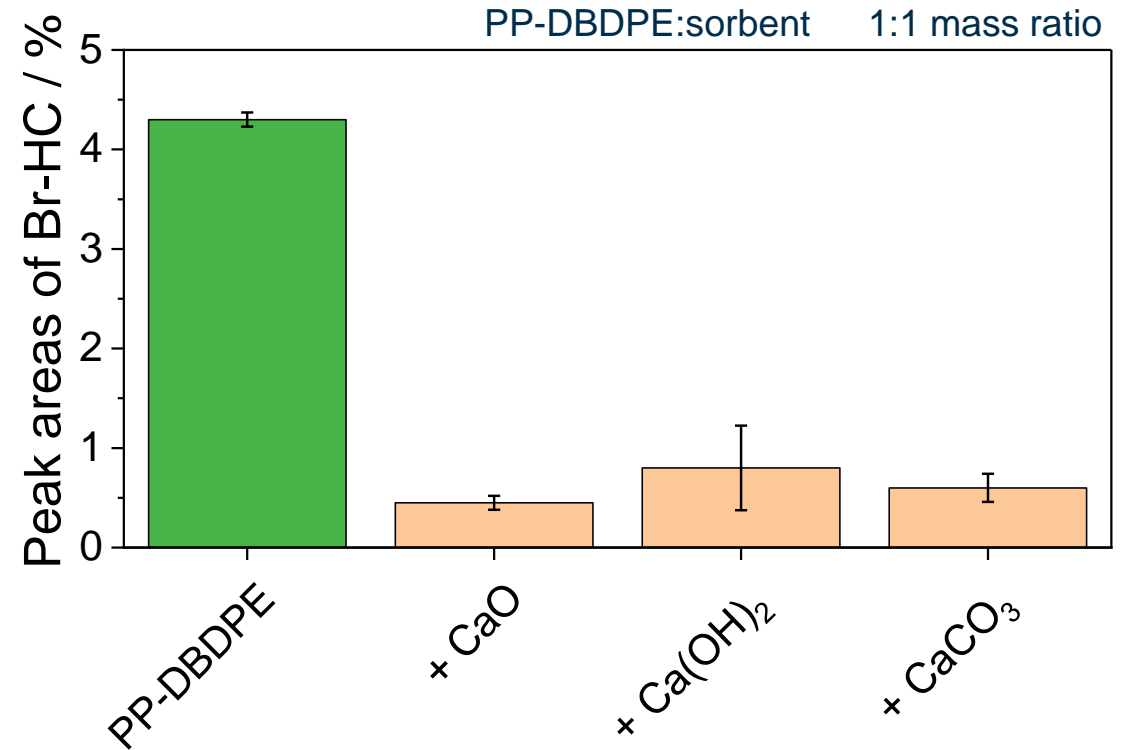
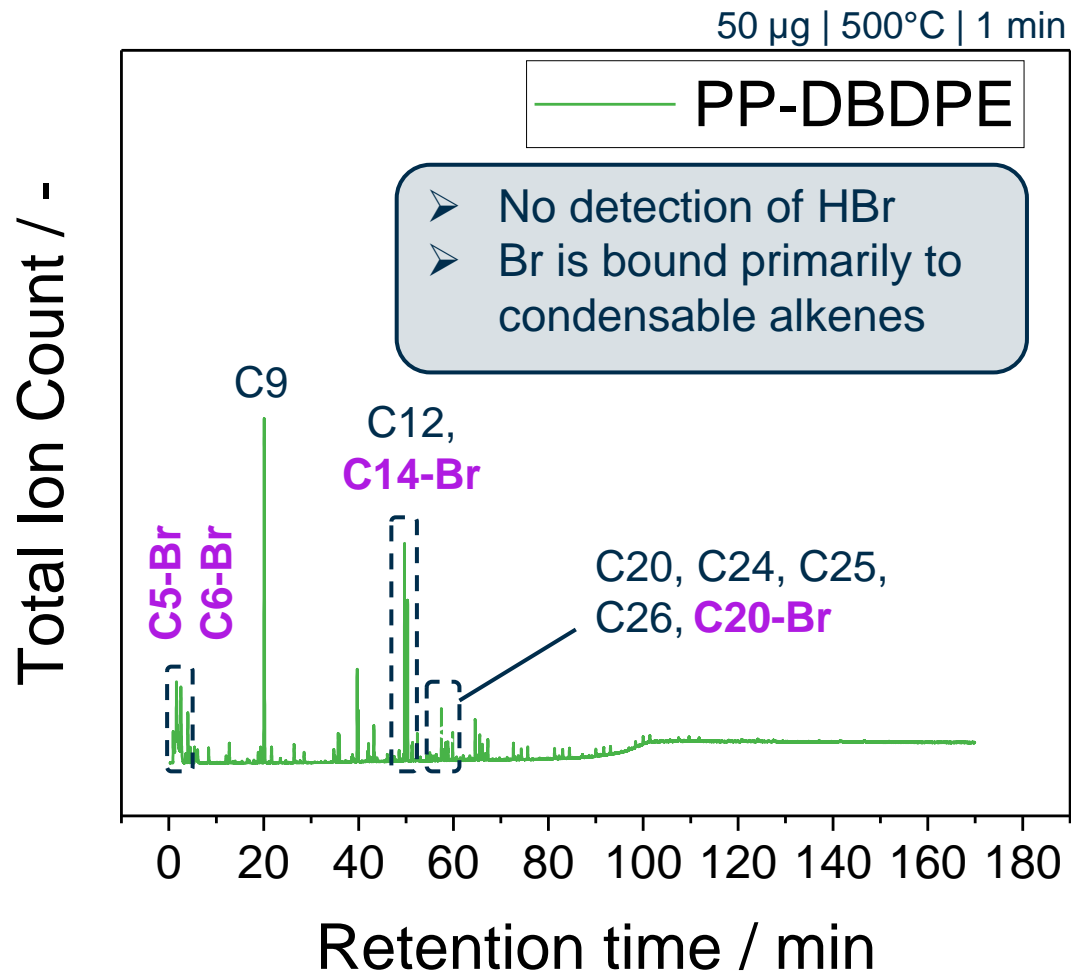


Effect of Ca-based sorbents



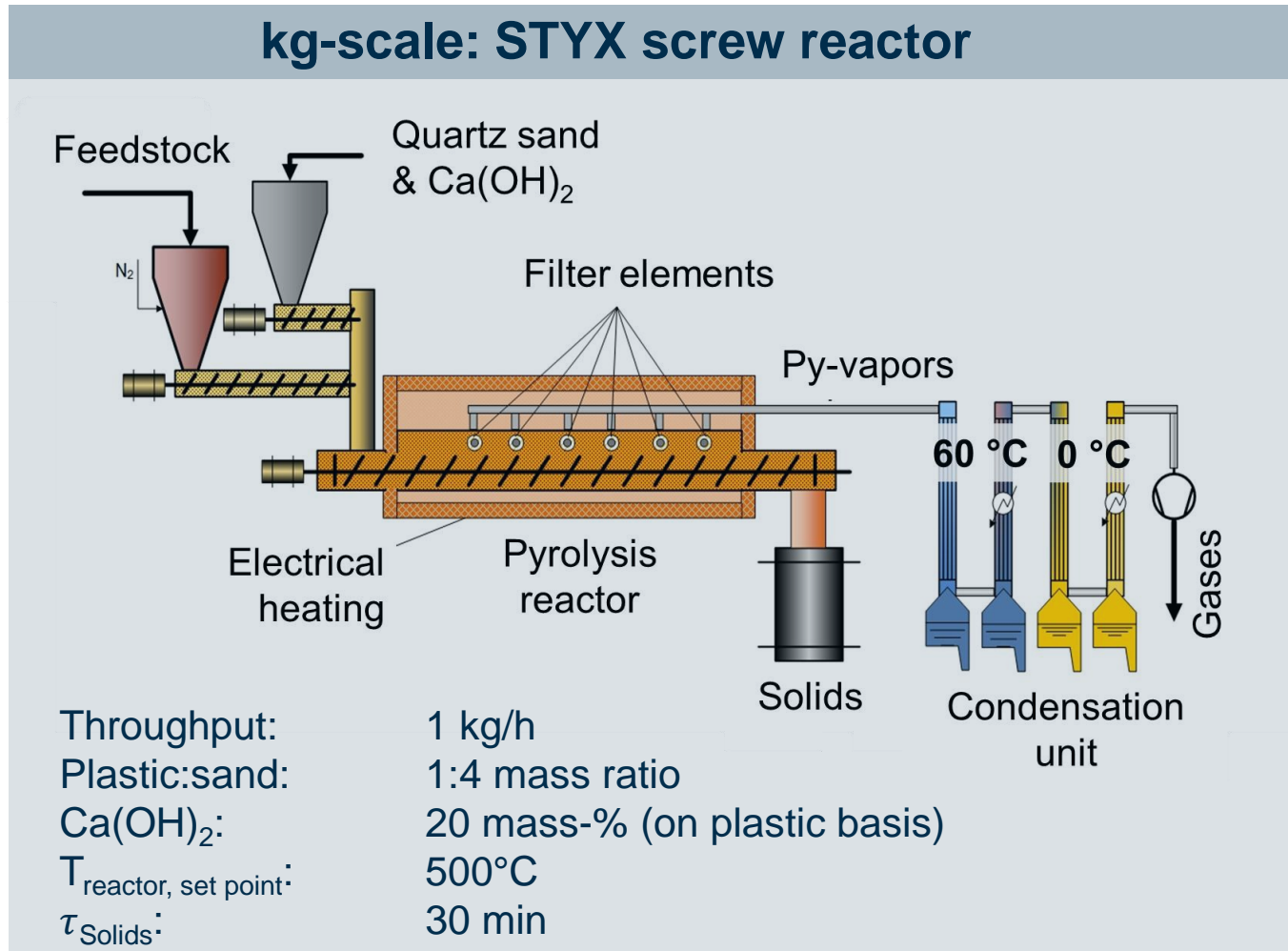
- Ca-based sorbents reduce the peaks areas of detected brominated hydrocarbons (Br-HC) in the pyrolysis vapors

Effect of Ca-based sorbents



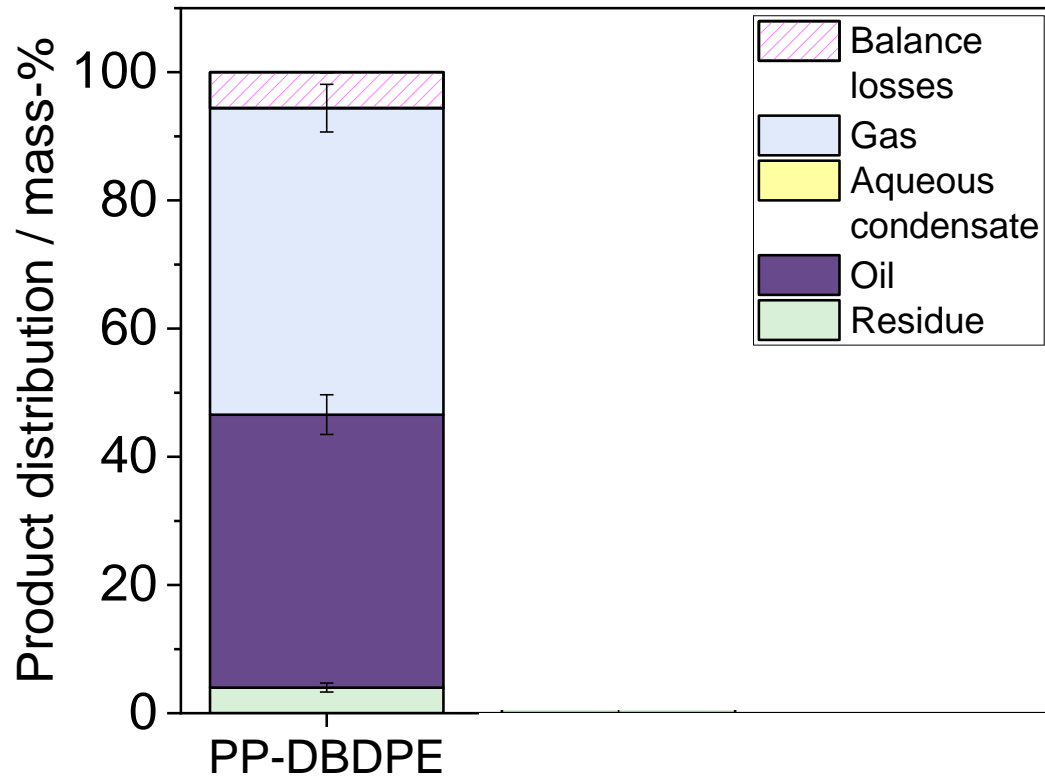
- Ca-based sorbents reduce the peaks areas of detected brominated hydrocarbons (Br-HC) in the pyrolysis vapors

Effect of Ca-based sorbents



- ✓ Separation of product fractions
- ✓ Analysis of products
- ✓ Mass balancing
- ✓ Bromine balancing

Pyrolysis behavior with Ca-based sorbents



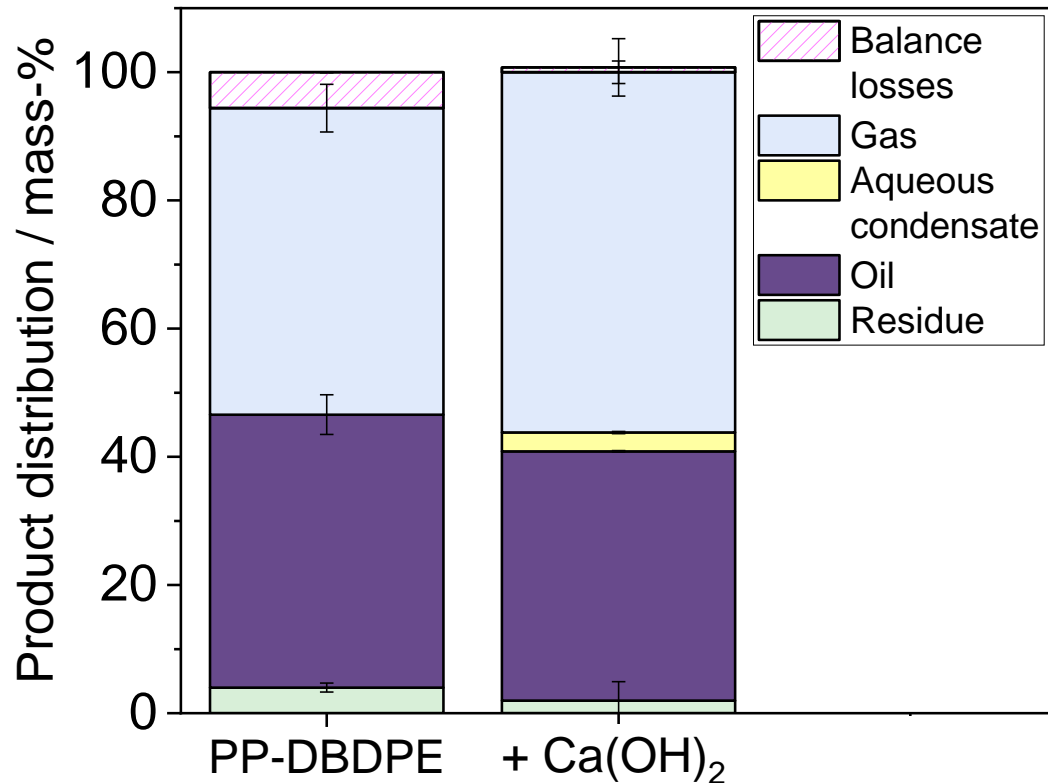
➤ PP-DBDPE primarily decomposes into oil and gas

Bromine content in the oil in mass-% Br

PP-DBDPE

35.3

Pyrolysis behavior with Ca-based sorbents



➤ **+ Ca(OH)₂:** PP-DBDPE primarily decomposes into oil and gas

Bromine content in the oil in mass-% Br

PP-DBDPE	+ Ca(OH) ₂
35.3	16.5

➤ **+ Ca(OH)₂:** Br content in the oil drops due to a shift from the oil to other product fractions

Summary and conclusion

PP-DBDPE:

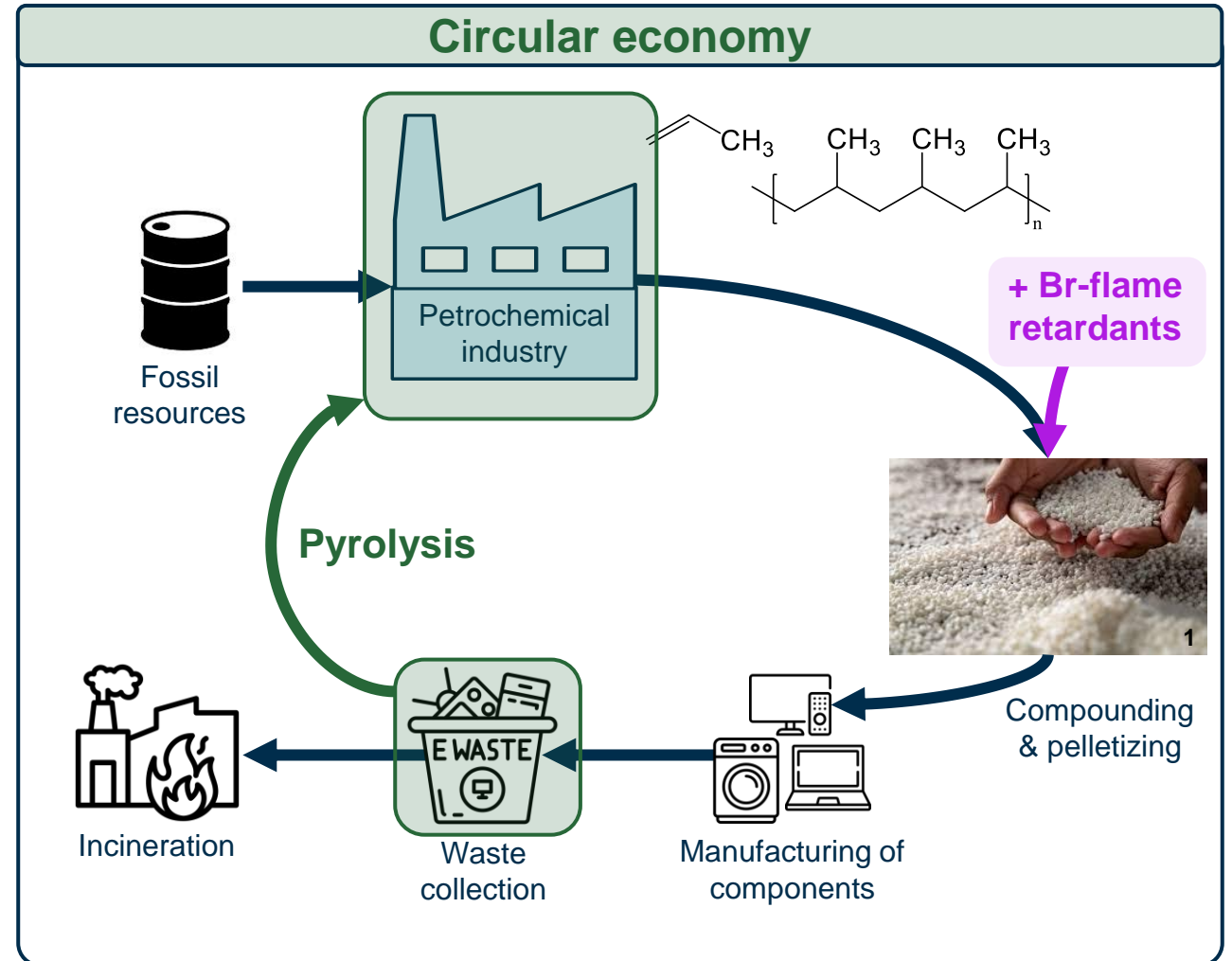
- Br is primarily bonded to condensable hydrocarbons

PP-DBDPE + sorbents:

- **Reduced** detectable condensable brominated hydrocarbons
- **Decreased** bromine content in the oil
- **Shifted** bromine-loading from the oil to other product fractions

Need for further investigation:

- Optimization of technical pyrolysis for sorbent application to enhance bromine reduction potential



¹ <https://www.goodfishgroup.com/general-purpose-polystyrene-gpps/close-up-of-plastic-polymer-granules-hand-hold-polymer-pellet>, accessed on 27.05.2025

Thank you for your attention.

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