Karlsruhe Institute of Technology

Institute for Technical Chemistry

# Evaluating the technical integration of catalytic pyrolysis for polyolefin-rich waste recycling into light olefins

$11^{th}$ International Freiberg Conference on Circular Carbon Technologies – Towards a Net-Zero Carbon Economy

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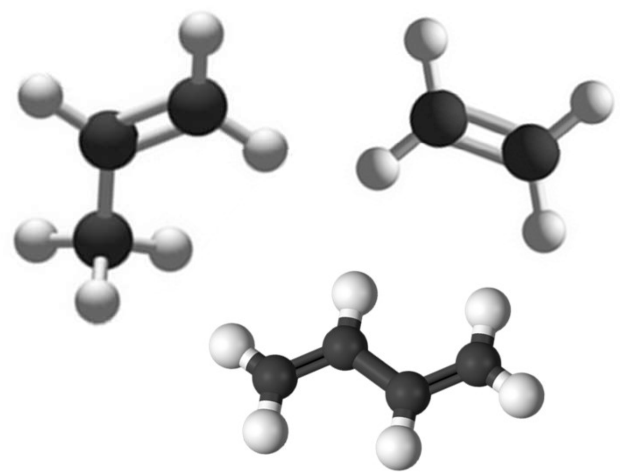
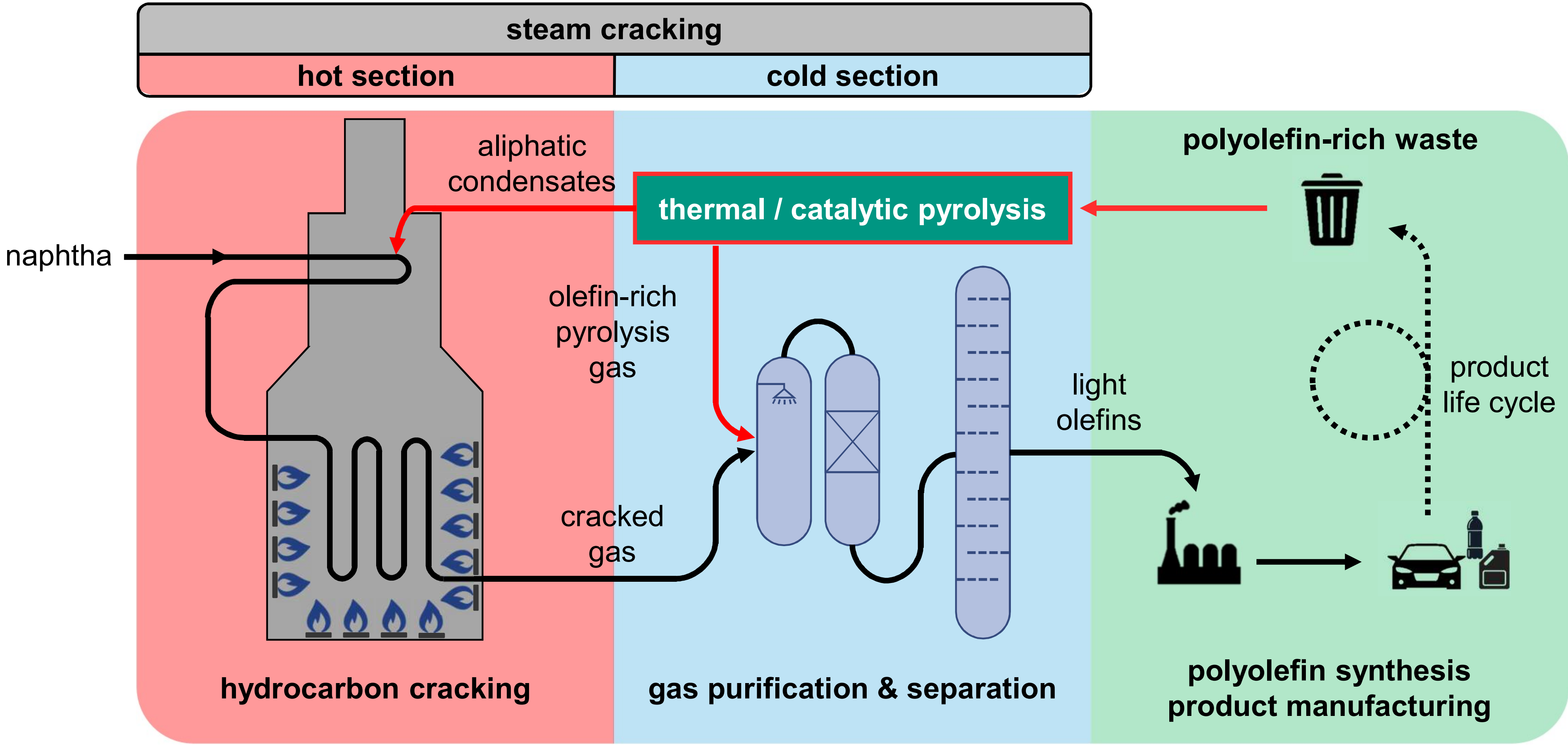


# Chemical recycling: Polyolefinic waste to light olefins



# Pyrolysis database – experimental setup

| | |
|---|---|
| PIW | Post-industrial plastic waste |
| PCW | Post-consumer plastic waste |

**Auger-type screw reactor**

- Sand-supported process
- Continuous tests in pilot-scale
- Mass and energy balance
- Online gas analysis subsequent to integrated hot gas filtration and condensation unit

**Over 170 experiments on influence of:**

- Feedstock composition (virgin polyolefins, PIW, PCW)
- Catalyst type
- Catalyst preparation
- Virgin and regenerated catalyst
- Process parameters (e.g. temperature, solid residence time)

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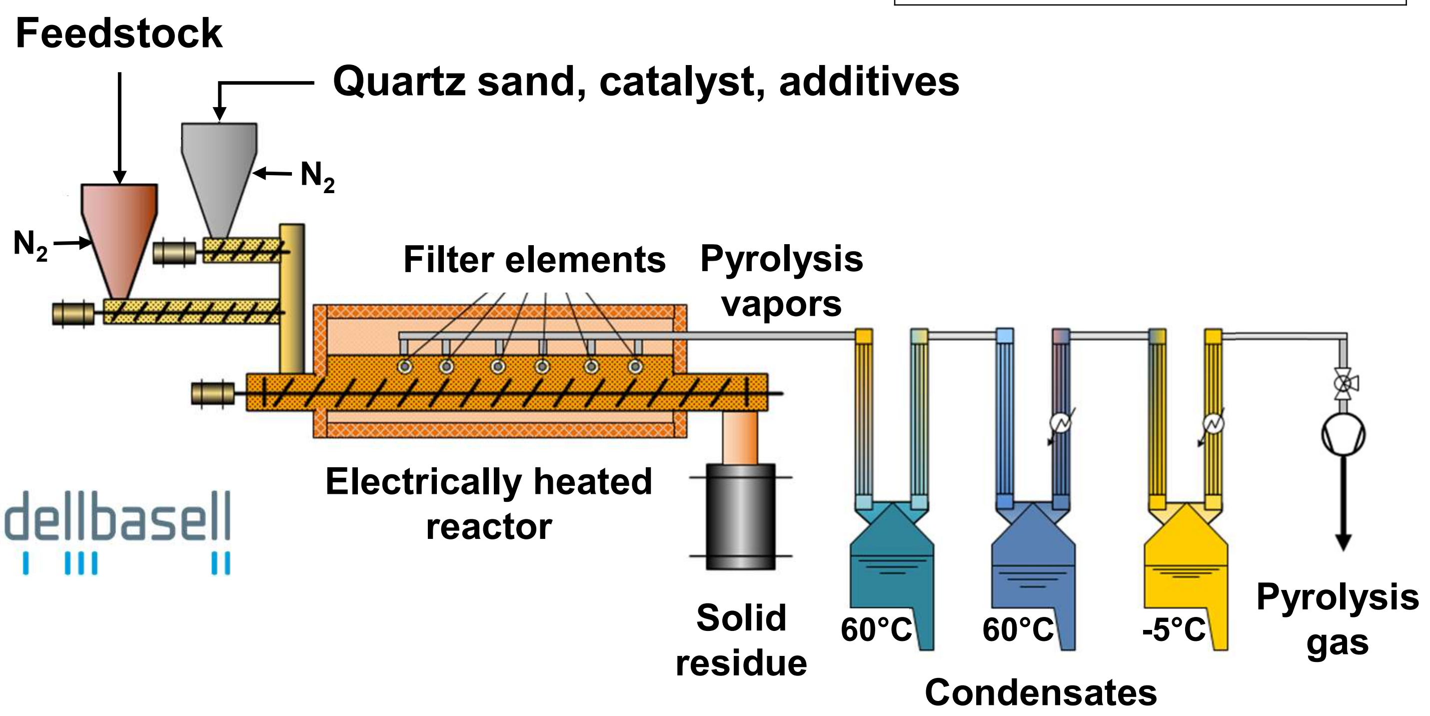


$\dot{m}_{Feed}$ ≈ 1 kg/h $\quad \frac{Sand}{Feed} \approx \frac{4\ kg}{1\ kg} \quad \frac{Catalyst}{Feed} \approx \frac{80\ g}{1\ kg} \quad \tau_{Solids}$ = 30-60 min $\quad T_{Reactor}$ < 600 °C

# Pyrolysis database – mass balance & product composition

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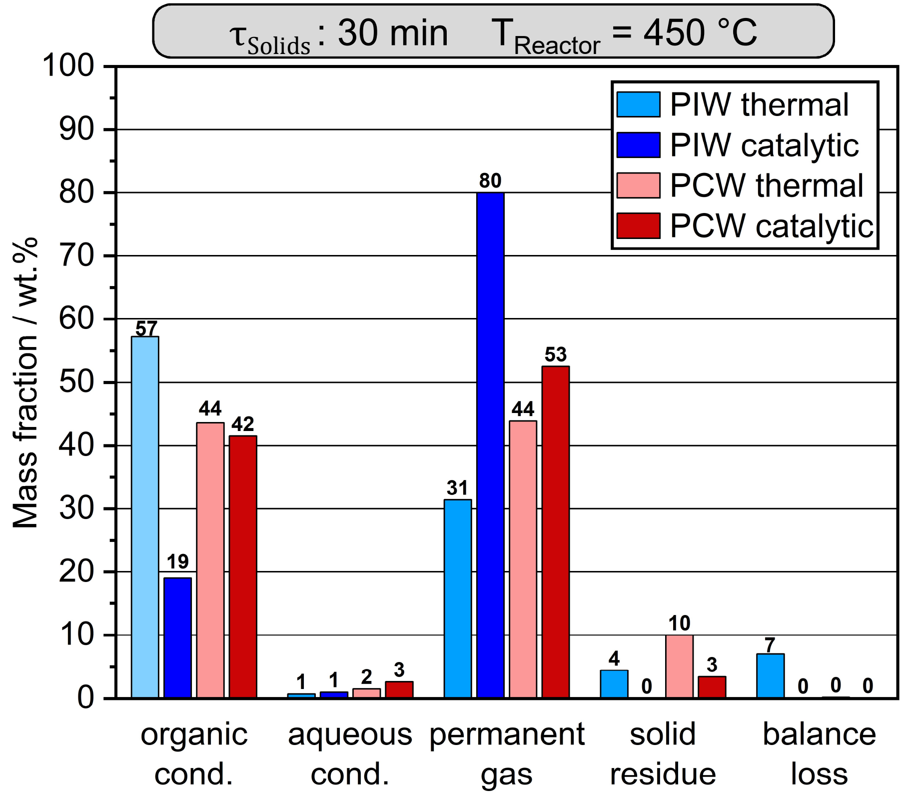
Netsch et al. 2023. *Chem Ing Tech*, 95 (8), pp. 1305-1313

| | **PIW** in wt.% | **PCW** in wt.% |
|---|---|---|
| Material | Waste agricultural LDPE films | Residue from sensor-based PCW-sorting |
| Moisture | 0.0 | 0.0 |
| Ash | 2.4 | 2.1 |
| C | 81.5 | 74.7 |
| H | 13.2 | 10.1 |
| N | < 0.1 | 0.4 |
| Cl | < 0.01 | 0.1 |
| O [1)] | 2.9 | 12.6 |

1) Calculated as difference to 100 wt.%

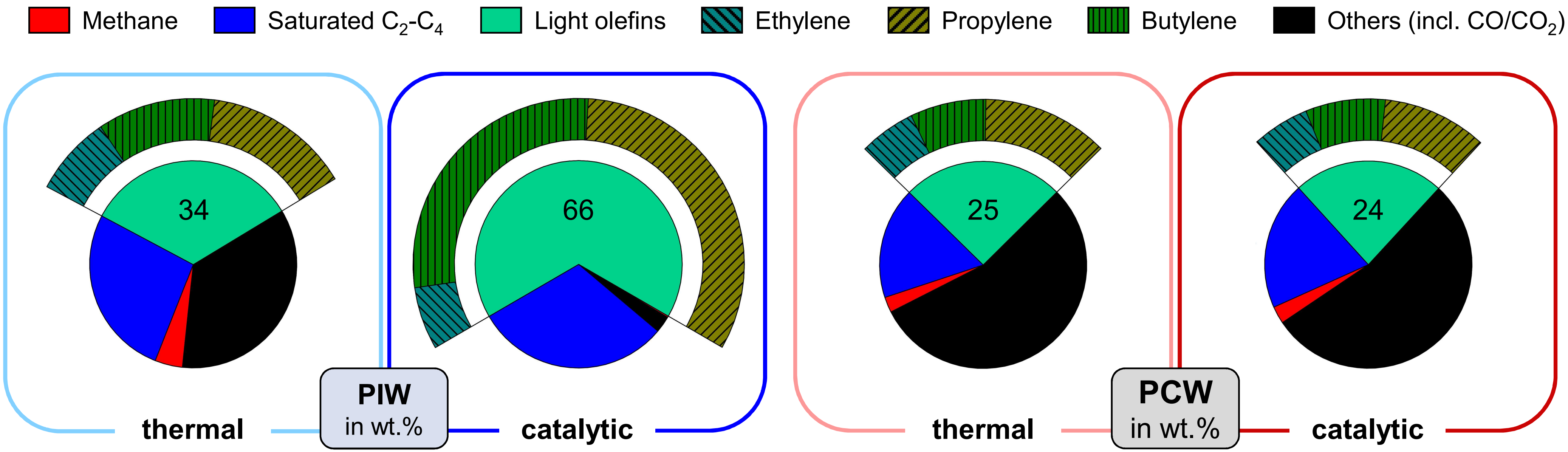



→ Catalysts enable shift from liquid to gaseous products

→ Catalytic effect impaired by heteroatom impurities

# Pyrolysis database – mass balance & product composition

$\tau_{Solids}$ : 30 min $T_{Reactor}$ = 450 °C

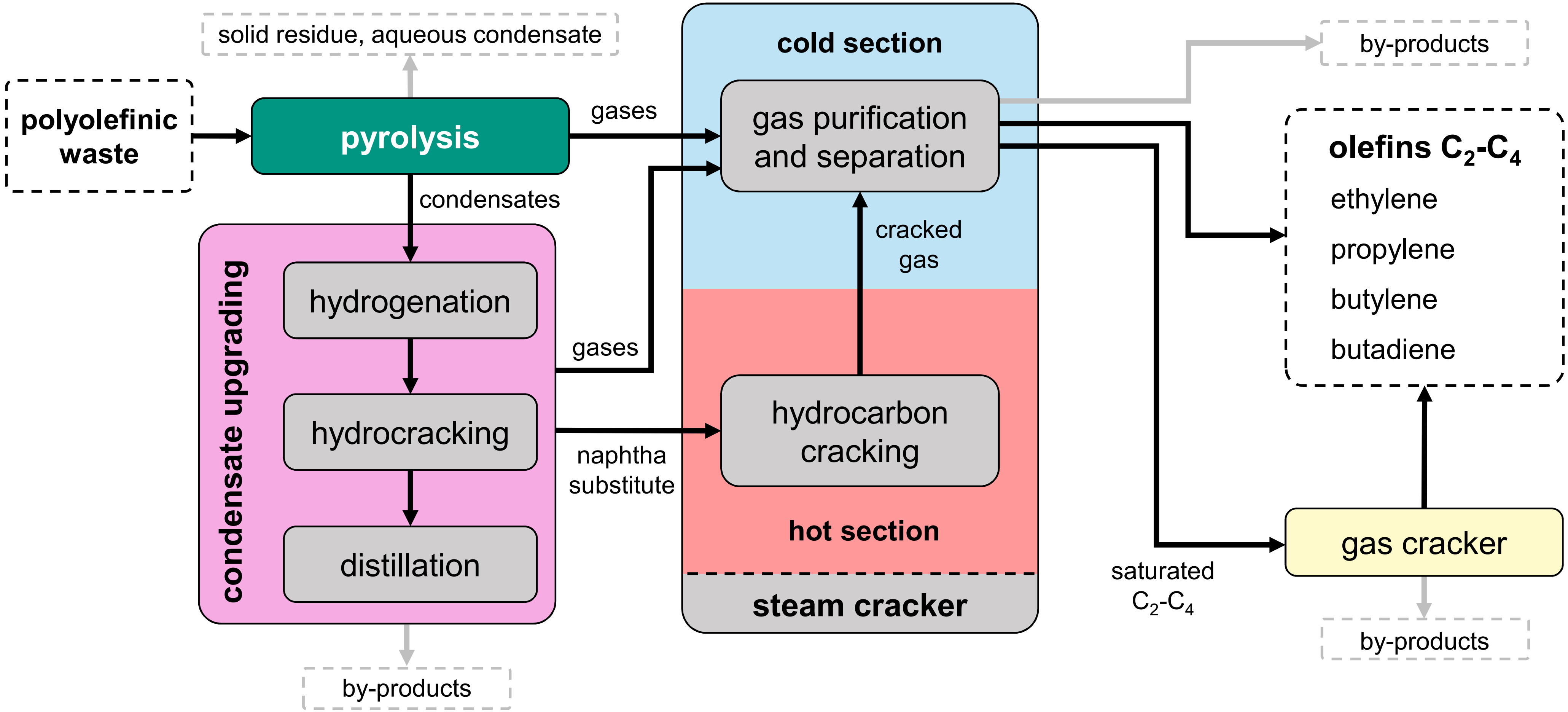



→ Catalytic treatment enhances light olefin formation when pyrolyzing high-quality feedstock

→ Light olefin purification by gas separation necessary

→ Heteroatom removal required (Cl, O, N, etc.) to meet naphtha specification

# Evaluated recycling pathway

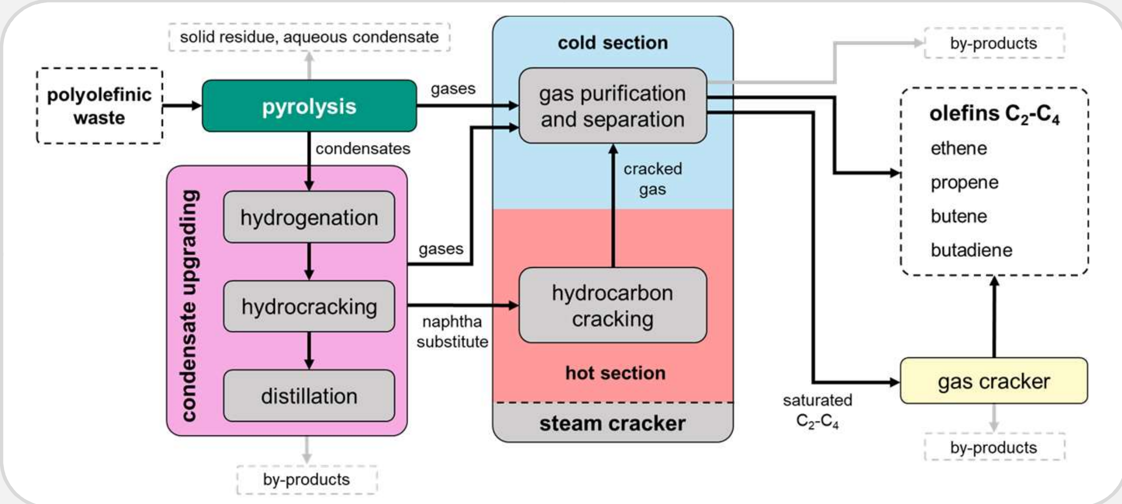


# System calculation

## Pyrolysis

- Experimental database
- Mass balance, condensate composition, and gas distribution
- Complete separation of solids and aqueous phase

Netsch et al. 2023. *Chem. Ing. Tech.*, 95 (8), pp. 1305-1313




## Condensate upgrading

- Experimental database
- Removal of heteroatom containing hydrocarbons
- Hydrocracking and distillation considered depending on boiling range

Neuner et al. 2022. *Reactions*, 3 (3), pp. 352-373

## Steam cracking and gas purification & separation

- Cracker yields based on literature data and adapted to composition of naphtha substitute
- Ideal gas separation

Kusenberg et al. 2022. *Waste Manage.*, 141, pp. 104-114

Kusenberg et al. 2022. *Sci. Total Environ.*, 838, 156092

## Gas cracker

- Cracker yields adapted to feed composition (25% Ethane, 35% Propane, 40% Butane)

Van Damme et al. 1975. *AIChE Journal*, 21 (6), pp. 1065-1073

Froment et al. 1976. *Ind. Eng. Chem. Process. Des. Dev.*, 15 (4), pp. 495-504

Froment et al. 1977. *AIChE Journal*, 21 (6), pp. 1065-1073

# Mass balance evaluation

**Product fraction in $100 \cdot kg_{Fraction}/kg_{Feedstock}$**

| PIW thermal | PIW catalytic | PCW thermal | PCW catalytic |
|---|---|---|---|

**Polyolefinic waste**

## Olefins $C_2$-$C_4$

| | PIW thermal | PIW catalytic | PCW thermal | PCW catalytic |
|---|---|---|---|---|
| **Olefins $C_2$-$C_4$** | **54** | **73** | **32** | **34** |
| → Ethylene | 26 | 21 | 15 | 16 |
| → Propylene | 17 | 29 | 11 | 11 |
| → Butylene & butadiene | 11 | 23 | 6 | 7 |

## Other hydrocarbons

| | PIW thermal | PIW catalytic | PCW thermal | PCW catalytic |
|---|---|---|---|---|
| BTX-aromatics | 4 | 3 | 8 | 7 |
| LPG | 3 | 3 | 2 | 2 |
| Methane | 13 | 8 | 8 | 9 |

## By-products

**Pyrolysis**
Solid residue
Aqueous condensate

**Condensate upgrading**
Off-gas
High boiling distillation residue

**Cracker & gas treatment**
$CO$ & $CO_2$
Long chain hydrocarbons
Others (heteroatom-containing)

→ Significant increase of light olefin yield by catalytic pyrolysis and bypassing steam cracker hot section depending on feedstock quality

→ Feedstock-depended formation of valuable by-products

# Conclusion

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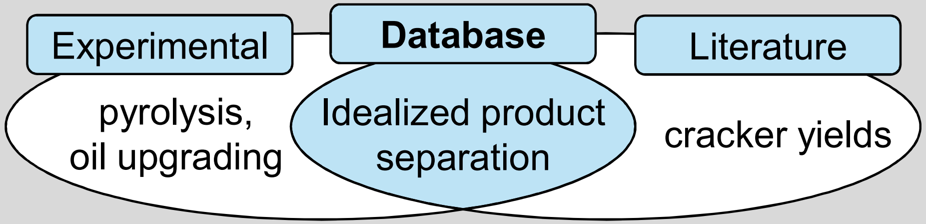
## Summary

- Mass balance of polyolefin-to-olefin recycling pathway evaluated depending on feedstock quality and catalyst




Feed quality: High

- Catalytic pyrolysis increases recycling efficiency

Feed quality: Low

- High heteroatom content and non-polyolefinic plastics
- Thermal cracking und oil upgrading

## Outlook

- Optimizing thermal and catalytic pyrolysis
  → Feedstock dependency
  → Catalyst screening
  → Impurity and contaminant discharge

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- Further investigations to strengthen the data basis for subsequent processes
  → Specification-compliant hydroprocessing of pyrolysis condensates
  → Steam cracking: suitability study and experimental yield determination of upgraded condensates

- Techno-economic and ecological process evaluation

# Literature


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