

ESR 12: Valorizing pyrolysis gases back to monomers

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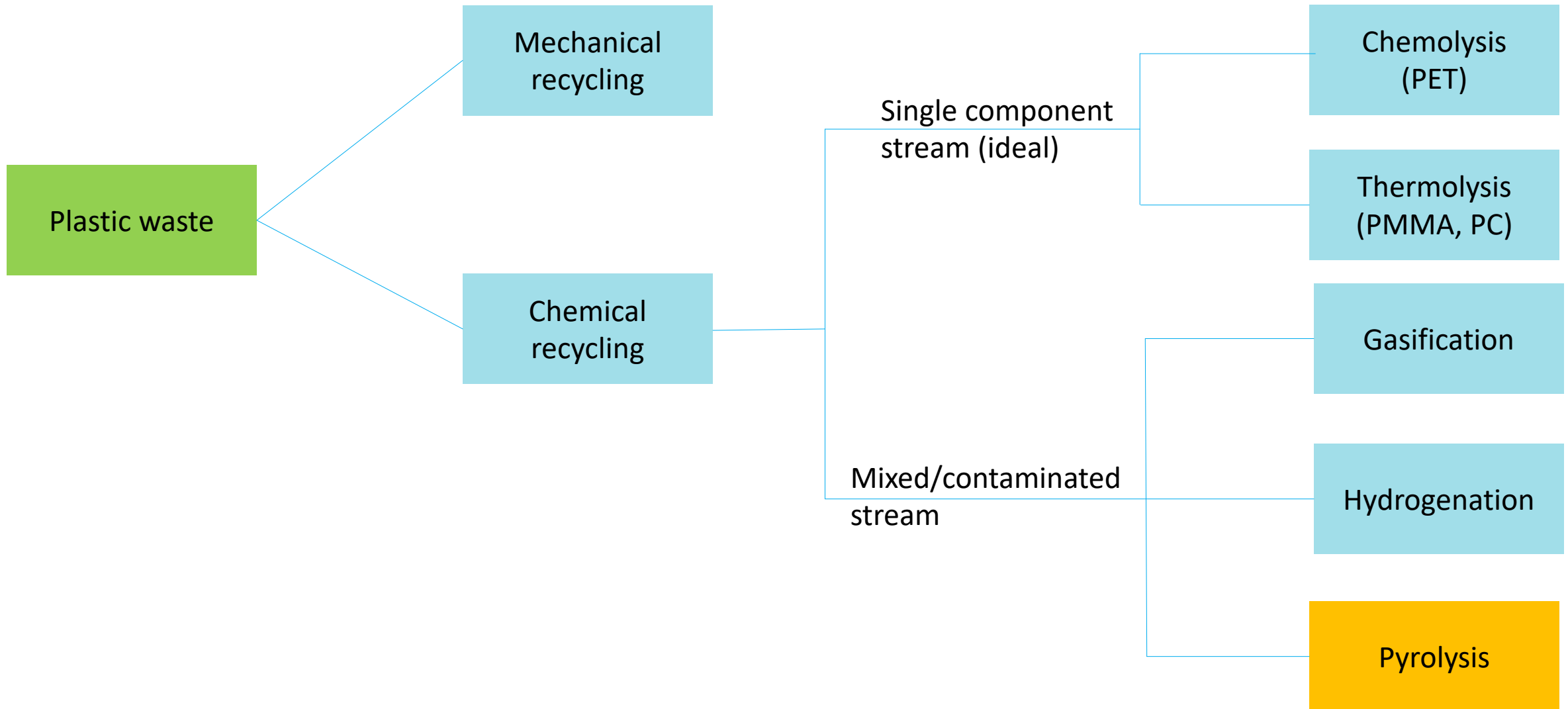
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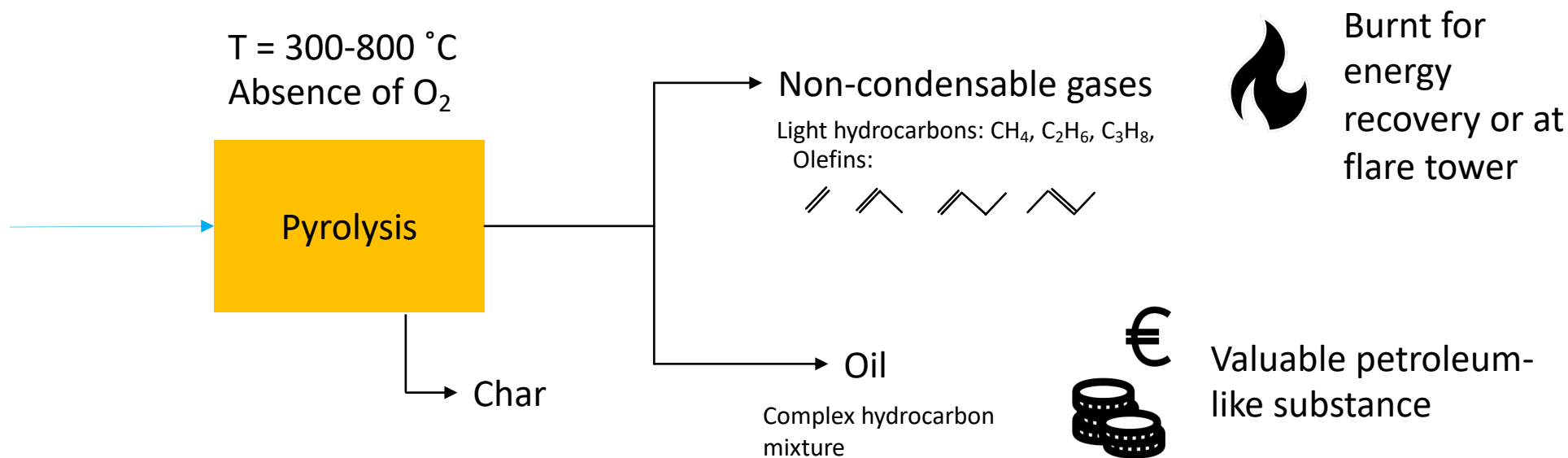


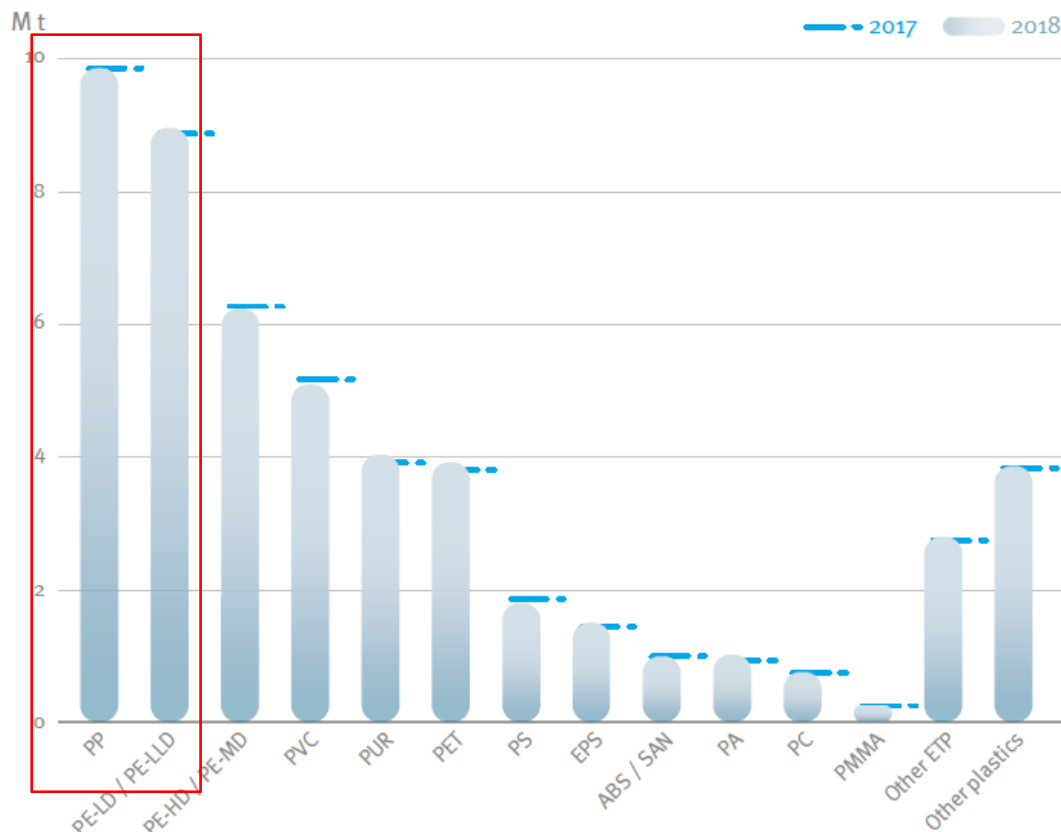
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CIRCULAR PLASTICS NETWORK
FOR TRAINING

This Project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 859885

CHEMICAL RECYCLING OF PLASTICS







SOURCE: PlasticsEurope Market Research Group (PEMRG) and Conversion Market & Strategy GmbH

Distribution of European (EU28+NO/CH) plastics converters demand by resin type in 2018

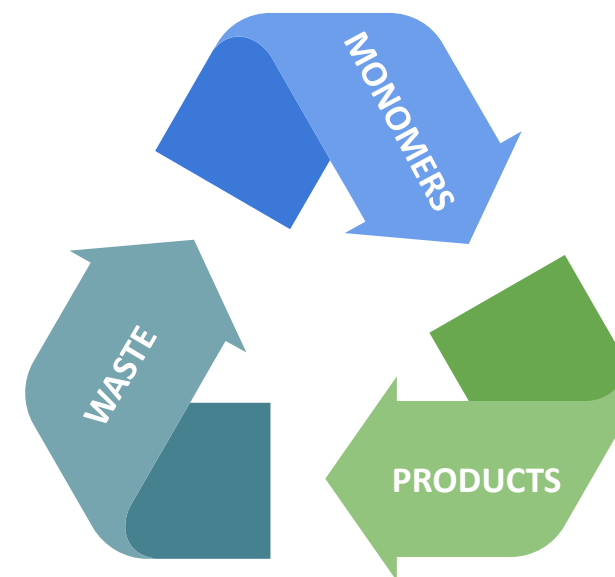
Leading polymers are **polyolefins (PP & PE)**.

Valorization of non-condensable gases



MONOMERS:
a valuable product

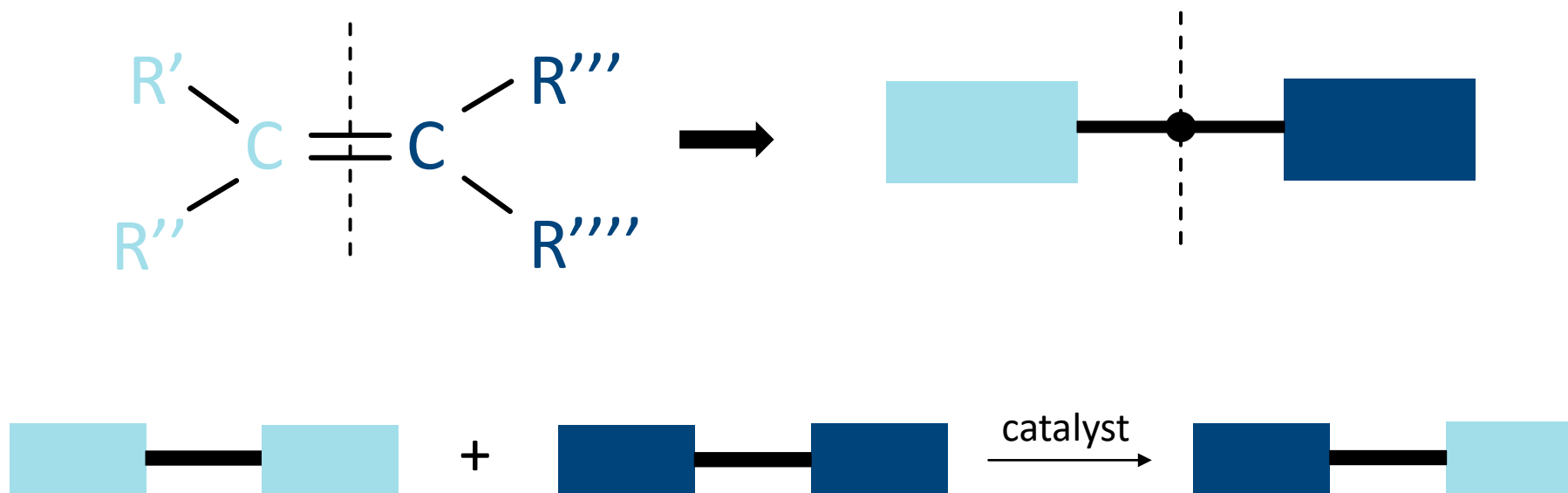
Circular economy for polyolefins



From pyrolysis non-
condensable gases:



CONCEPTUAL MECHANISM



Catalytic Olefin Cross-Metathesis reaction – HISTORY



Discovered in 1964 by researchers from Phillips industries



Breakthrough discoveries during the early 1990 decade spark interest for organic synthesis



2005 **Nobel Prize for Chemistry** awarded to Y. Chauvin, R. R. Schrock and R. H. Grubbs “**for the metathesis method in organic synthesis**”



Photo: U. Montan
Yves Chauvin



Photo: R. Paz
Robert H. Grubbs

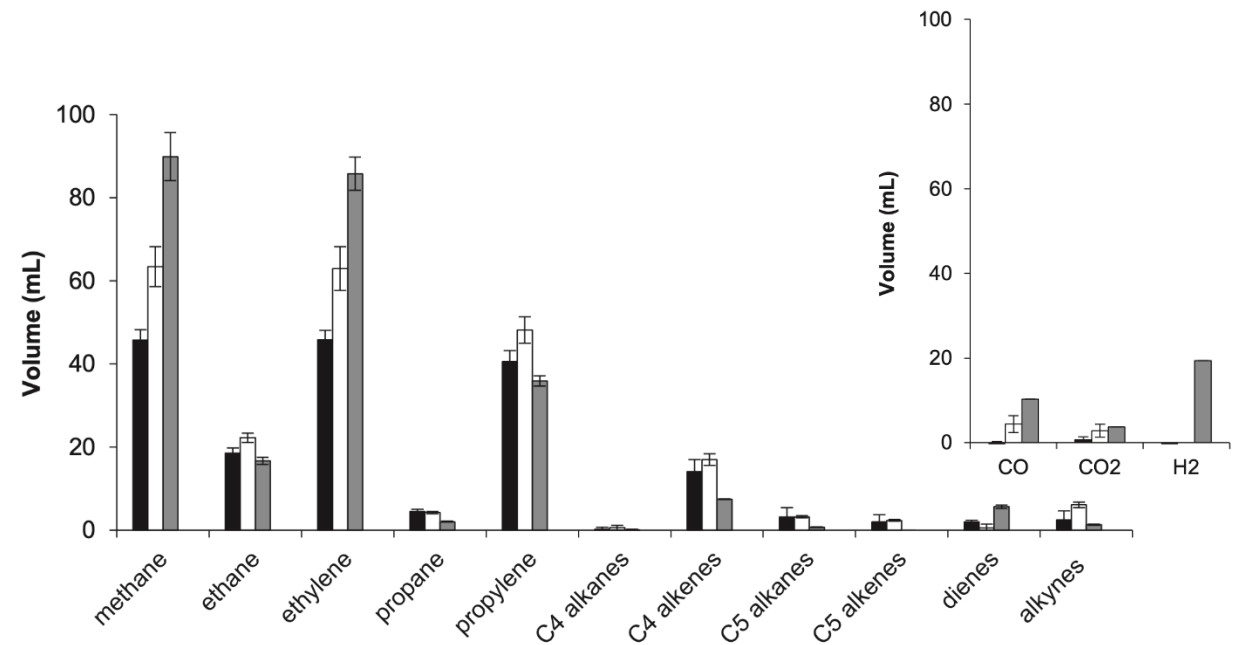


Photo: L.B. Hetherington
Richard R. Schrock

Pyrolysis non-condensable gases valorization: CHALLENGES

- **Pyrolysis gases as feedstock:** complex and varying **composition** influenced by pyrolysis feedstock and process conditions (particularly temperature)
 - Presence of short chain alkanes (CH_4 , C_2H_6 , C_3H_8), C2-C4 alkenes, CO_2 , CO , H_2 , and **HCl**
- Evaluation of catalyst performance in **realistic conditions** (investigation of impurities effect over **activity** and **selectivity**)
- Development of **de-chlorination** step

Example: Composition of non-condensable gases from mixed plastic waste pyrolysis at **500°C (black)**, **600°C (white)**, and **700°C (gray)**. Plastic mixture: 40% LDPE - 40% PP -10% PS- 10% PVC. Source: Veksha et al, 2018.



Veksha, A.; Giannis, A.; Oh, W.-D.; Chang, V. W.-C.; Lisak, G. Upgrading of Non-Condensable Pyrolysis Gas from Mixed Plastics through Catalytic Decomposition and Dechlorination. *Fuel Processing Technology* **2018**, 170, 13–20.

Catalysts for olefin cross-metathesis

- **Multifunctional** catalysts (MoO_x/WO_x/ ReO_x as active phase) to obtain propylene from **ethylene pure feed** (dimerization + metathesis) (Hulea, 2019)

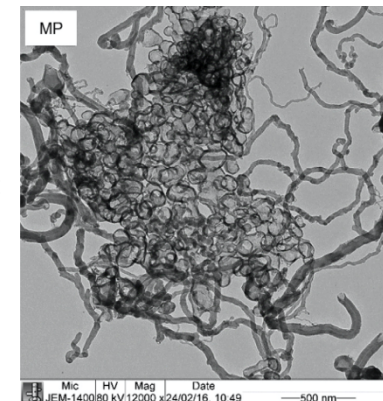
In this project:

- A complex feed is used for methatesis reaction
- Pyrolysis gases are used as a source of monomers

Valorization of pyrolysis gases from plastic waste

- Used as **replacement of natural gas** as fuel: purification technologies for dechlorination and elimination of olefins (Veksha et al, 2018)
- Conversion to **carbon nanotubes** (CNTs) with a Nickel-based catalyst, study of feedstock composition effect over CNTs morphology (Veksha et al. 2017)

TEM image of carbon material produced at 500°C from mixed plastic pyrolysis non-condensable gases (40% PE, 40% PP, 10% PET, 10% PS)



Hulea, V. Direct Transformation of Butenes or Ethylene into Propylene by Cascade Catalytic Reactions. *Catal. Sci. Technol.* **2019**, 9 (17), 4466–4477.

Veksha, A.; Giannis, A.; Chang, V. W.-C. Conversion of Non-Condensable Pyrolysis Gases from Plastics into Carbon Nanomaterials: Effects of Feedstock and Temperature. *J. Anal. Appl. Pyrolysis* **2017**, 124, 16–24.

Veksha, A.; Giannis, A.; Oh, W.-D.; Chang, V. W.-C.; Lisak, G. Upgrading of Non-Condensable Pyrolysis Gas from Mixed Plastics through Catalytic Decomposition and Dechlorination. *Fuel Processing Technology* **2018**, 170, 13–20.



Development of highly active and selective catalysts using pyrolysis gases as feedstock


- Catalyst formulations based on reducible metal oxides / immobilized homogeneous catalysts
- Identification of operating condition for maximizing propylene yield



Advanced catalyst characterization



Mechanistic and kinetic studies



Dechlorination to remove Cl impurities at KU Leuven under the supervision of prof. Dirk de Vos

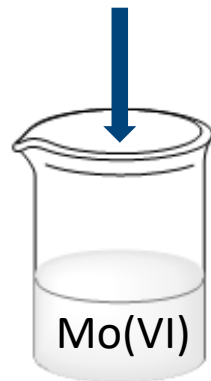
MoOx/Al₂O₃ catalyst:
Wet-impregnation method



(NH₄)₆Mo₇O₂₄
precursor



Commercial γ -Al₂O₃
support
Surface area: 208 m²g⁻¹
Particle size: 106-180 μ m



Solvent: H₂O

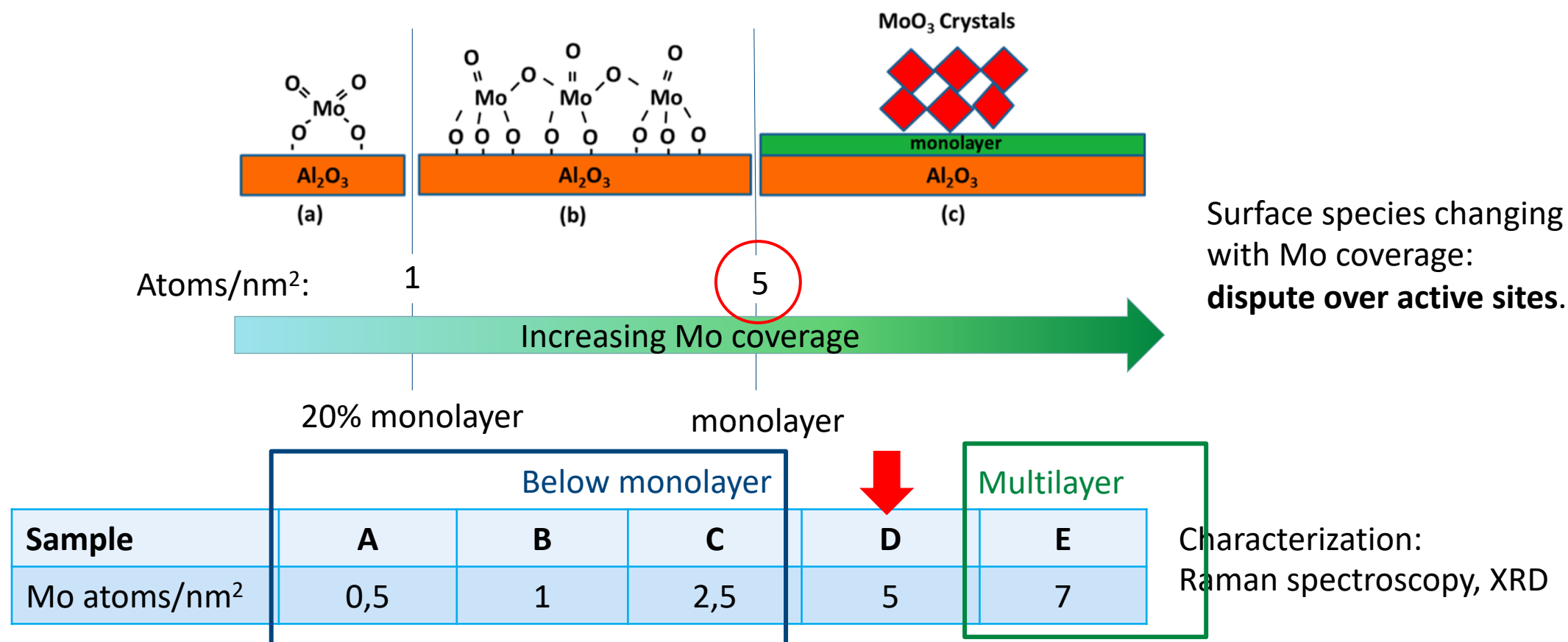


Drying
(overnight, 105°C)



Calcination
(4h at 600°C)

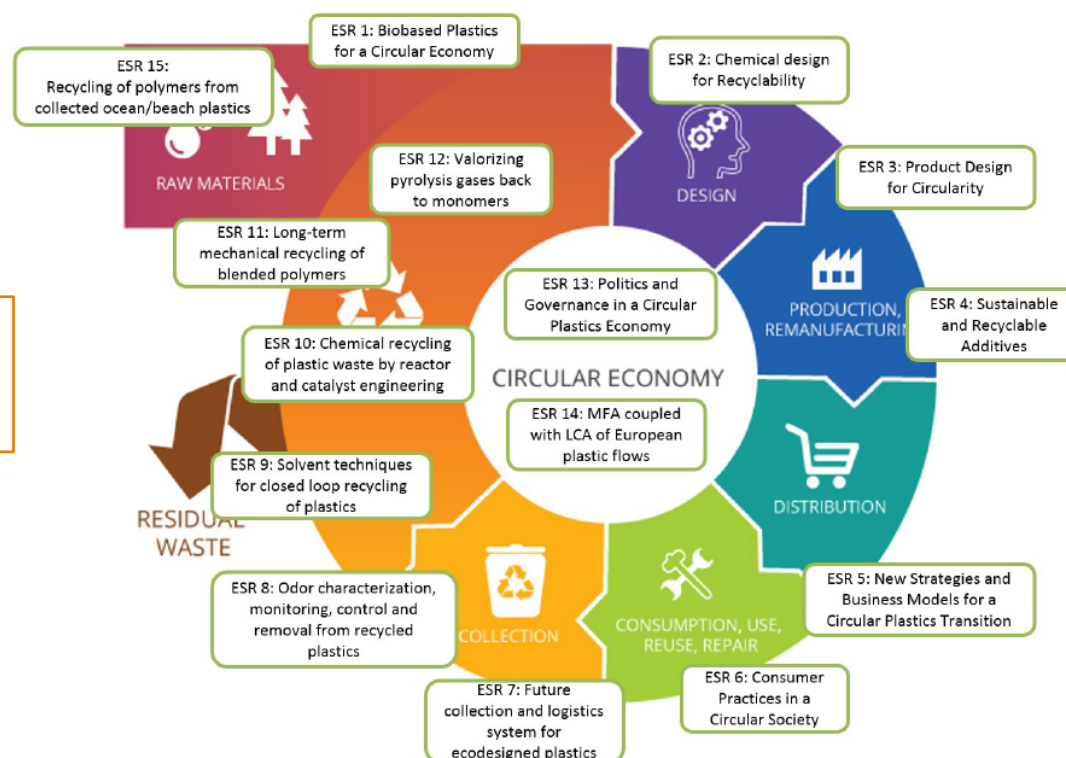
Structures of surface MoO_x species on Al_2O_3 . (a) Isolated dioxo MoO_4 , (b) oligomeric mono-oxo MoO_5 , and (c) crystalline MoO_3 NPs on surface MoO_x monolayer (Lwin&Wachs, 2014).



Lwin, S.; Wachs, I. E. Olefin Metathesis by Supported Metal Oxide Catalysts. *ACS Catal.* **2014**, 4 (8), 2505–2520

ESR 10: operating conditions that favor non-condensable gases

ESR 15: beach/ocean collected plastics as possible feedstock



And many more to find...

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Thank you for your attention!

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