µTeaching ESR 12:
Valorizing pyrolysis gases back to monomers

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C-PlaNeT online NTE 2, December 9th 2020

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CIRCULAR PLASTICS NETWORK
FOR TRAINING

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

Overview

Introduction:

- Plastic waste in Europe: how are we doing today?
- Pyrolysis as a waste-to-resource process
- Cross-metathesis: catalysts and operating conditions for olefin disproportionation

Work outline:

- Thermodynamic analysis
- Synthesis of catalysts
- Characterization
- Screening of catalysts

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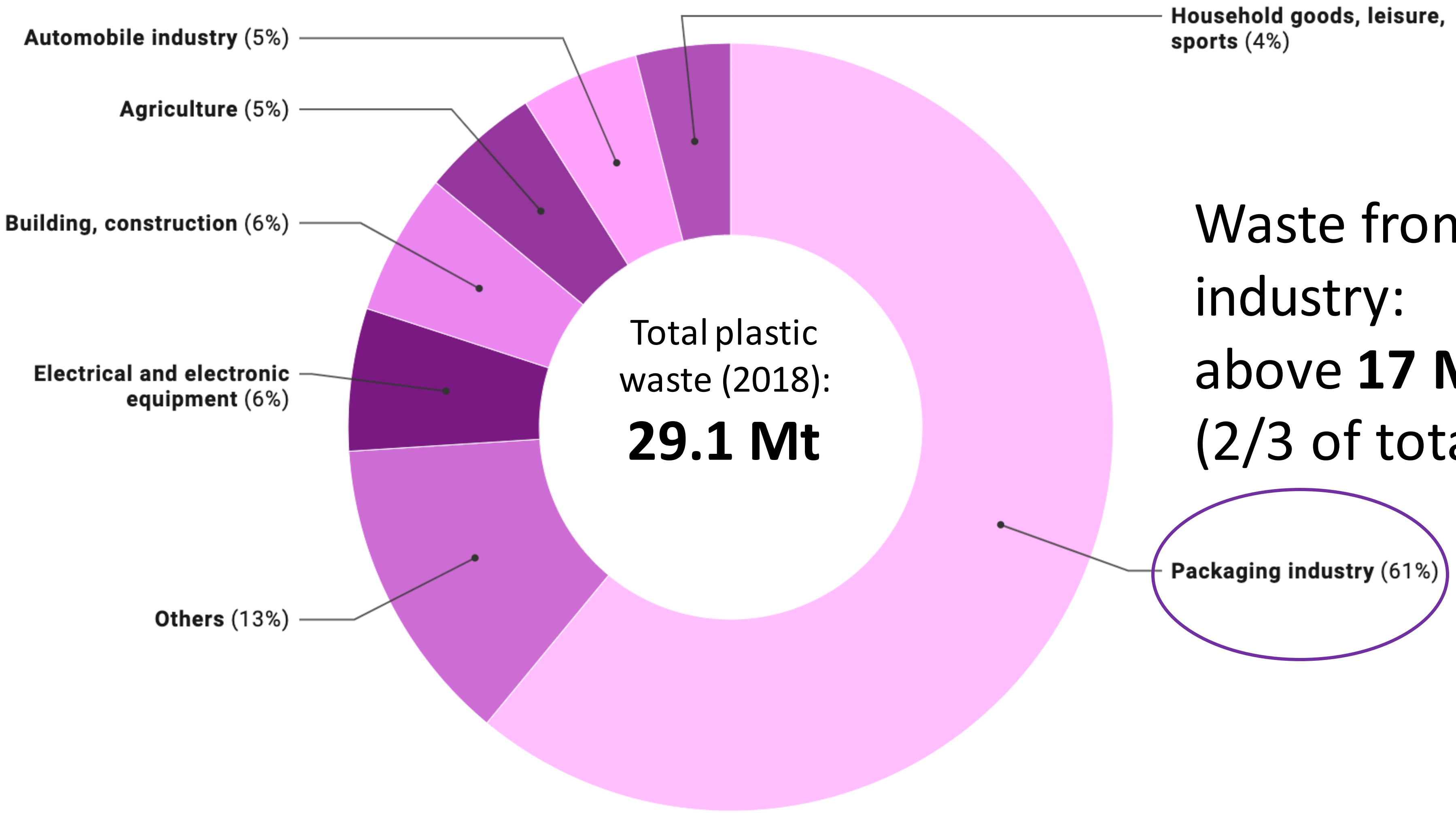
Plastic waste generation in Europe by sector



Waste from Packaging industry:
above **17 Mtonnes**
(2/3 of total plastic waste)

Data source: EU action to tackle the issue of plastic waste, European Court of Auditors 2020
Data visualization: EDJNet, https://www.europeandatajournalism.eu/eng

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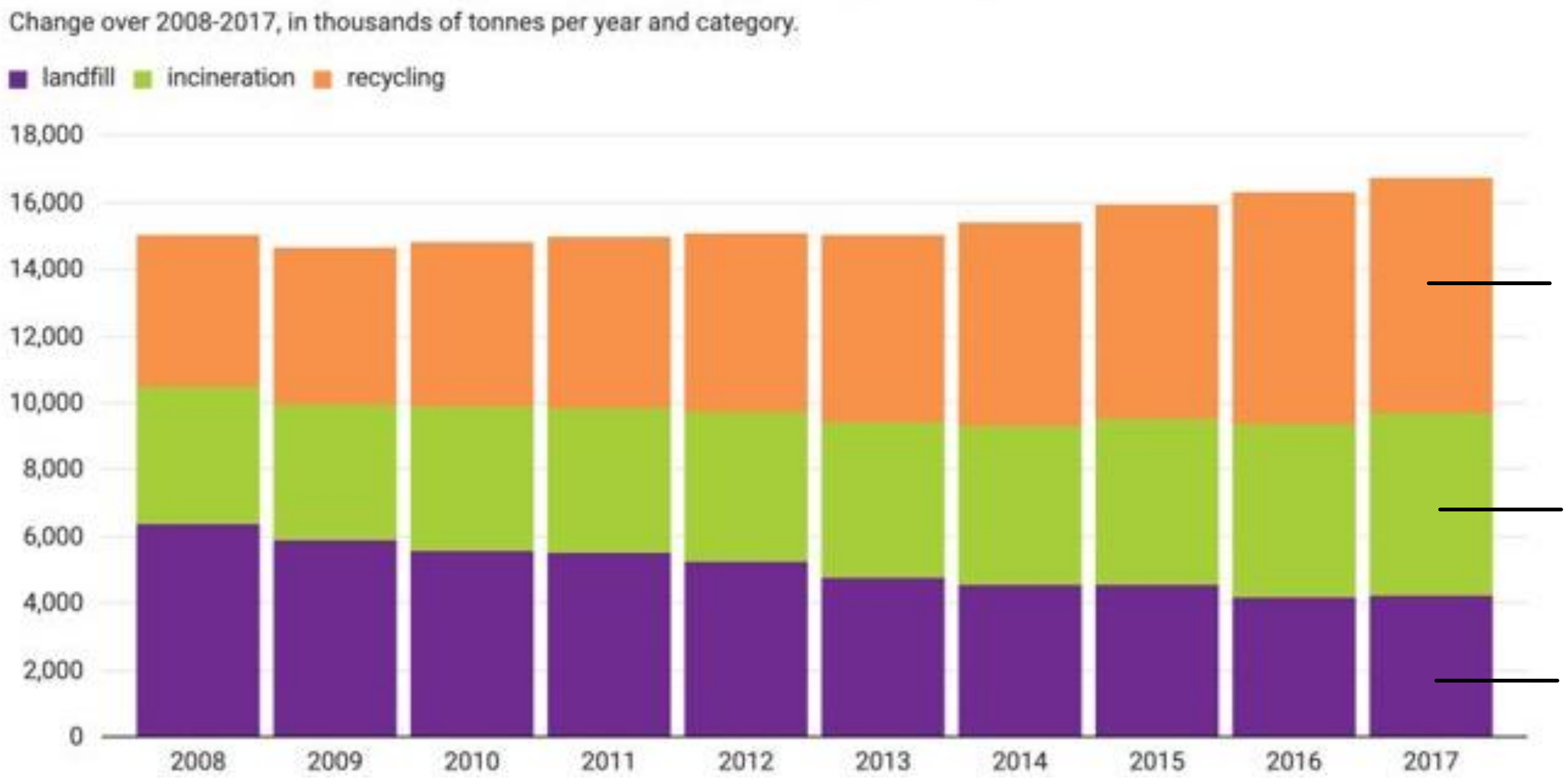
Recycling packaging plastic waste in Europe



42% recycled

33% incinerated

25% landfilled

Data source: EU action to tackle the issue of plastic waste , European Court of Auditors 2020
Data visualization: EDJNet, https://www.europeandatajournalism.eu/eng

58% of 17 Mt = 10 Mt
(1/3 of total plastic waste)

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How much is 1 million tonne?

1 Mt of PET can make

23 billion plastic bottles

23 billion 2L bottles can fill almost

20.000 olympic pools

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Goals and restrictions on plastic waste

Goals:

- 50% recycling rate for plastic packaging waste by 2025
- 55% by 2030

Restrictions:

New amendment from **Basel Convention on hazardous waste** (January 2021)

Limitations to **plastic waste export**: most packaging waste not admitted in the "Green List"

Green list = non-hazardous waste

Recyclable materials must be:

- uncontaminated
- pre-sorted
- free of any non-recyclable material
- prepared for immediate recycling in an environmentally sound manner

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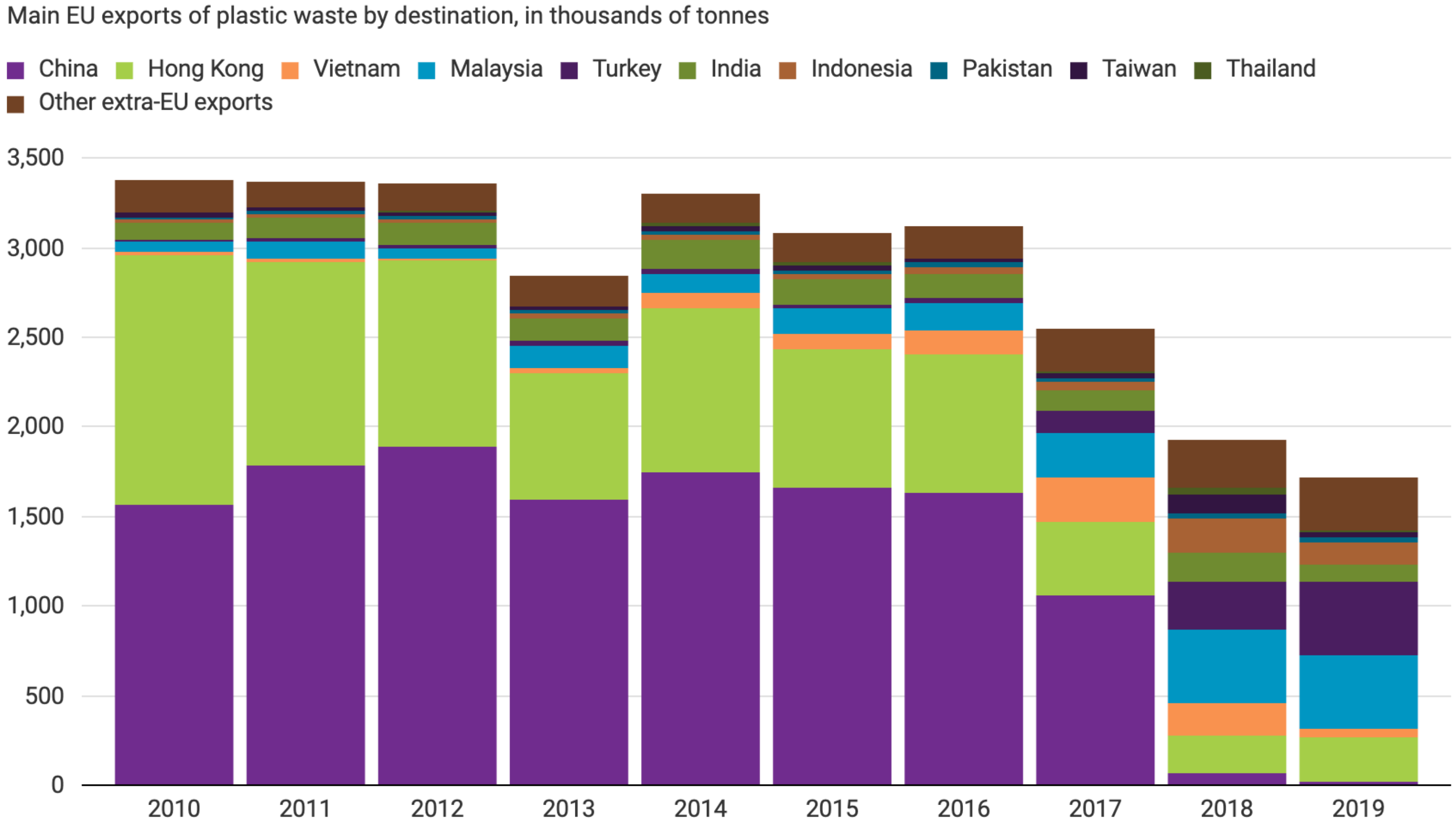
EU exports of plastic waste by destination



Data source: EU action to tackle the issue of plastic waste , European Court of Auditors 2020
Data visualization: EDJNet, https://www.europeandatajournalism.eu/eng

Exporting = Recycling

About **75%** of exported plastic waste is **packaging** (1.9 Mt in 2017)

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Problems in plastic recycling

1/3 of total plastic waste **not recycled** (packaging)

EU goal: increase packaging recycling %

Decrease % of recycled plastics from export

Need of **new technologies** to recycle plastic packaging waste

A promising solution is represented by chemical recycling: **pyrolysis+valorization**

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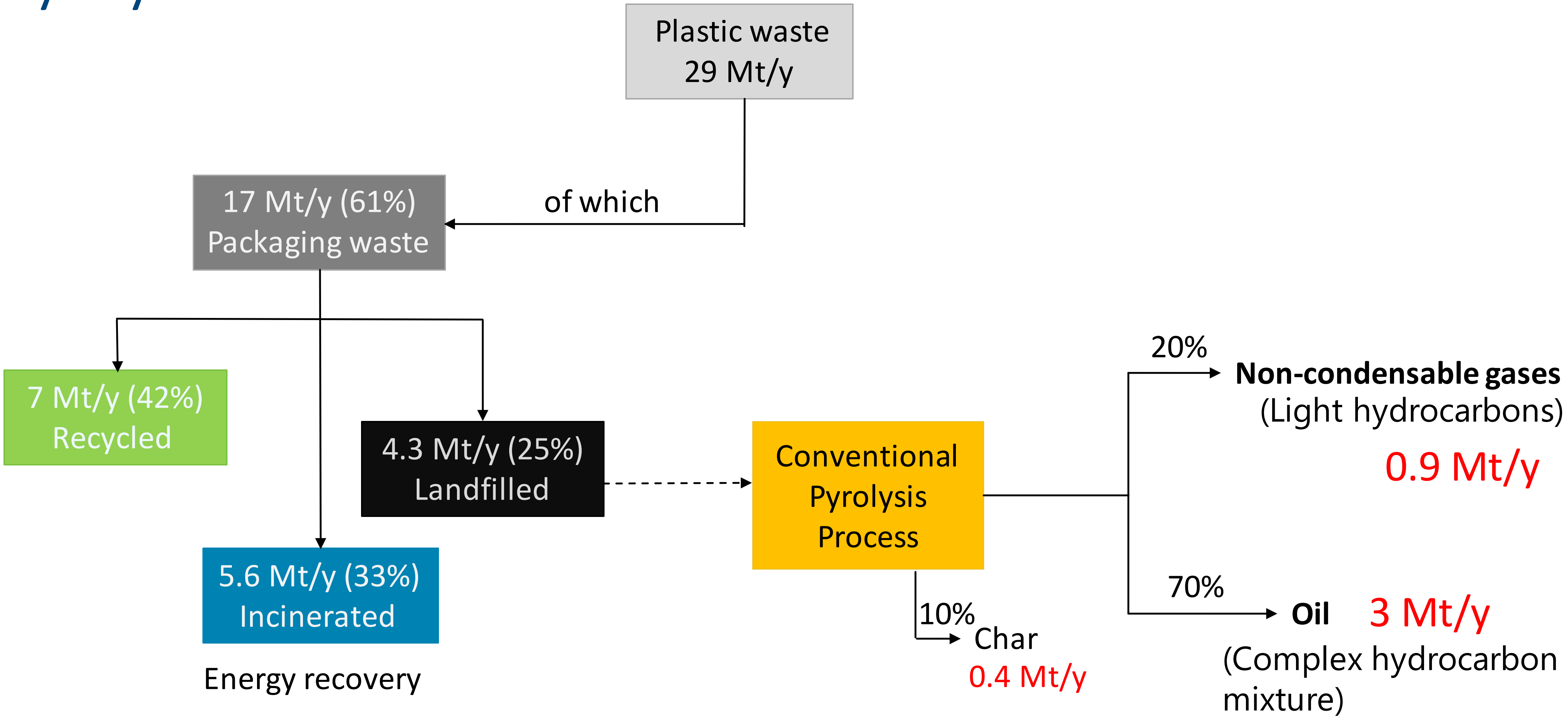
Pyrolysis: short term



Plastic waste
29 Mt/y

of which

17 Mt/y (61%)
Packaging waste

7 Mt/y (42%)
Recycled

4.3 Mt/y (25%)
Landfilled

5.6 Mt/y (33%)
Incinerated

Energy recovery

Conventional Pyrolysis Process

20%

Non-condensable gases
(Light hydrocarbons)
0.9 Mt/y

70%

Oil 3 Mt/y
(Complex hydrocarbon mixture)

10%
Char
0.4 Mt/y

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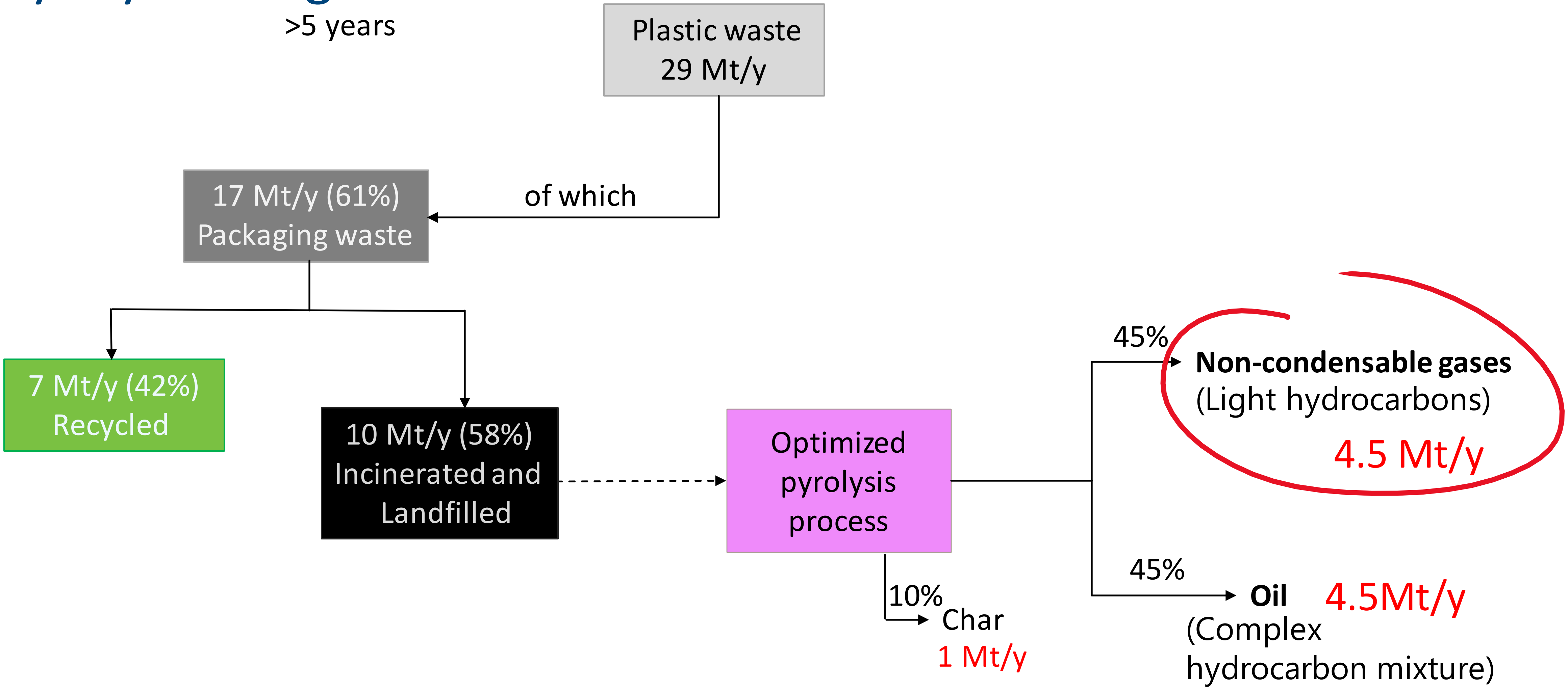
Pyrolysis: long term

>5 years



Plastic waste
29 Mt/y

of which

17 Mt/y (61%)
Packaging waste

7 Mt/y (42%)
Recycled

10 Mt/y (58%)
Incinerated and Landfilled

Optimized pyrolysis process

45%
Non-condensable gases
(Light hydrocarbons)
4.5 Mt/y

45%
Oil 4.5Mt/y
(Complex hydrocarbon mixture)

10%
Char
1 Mt/y

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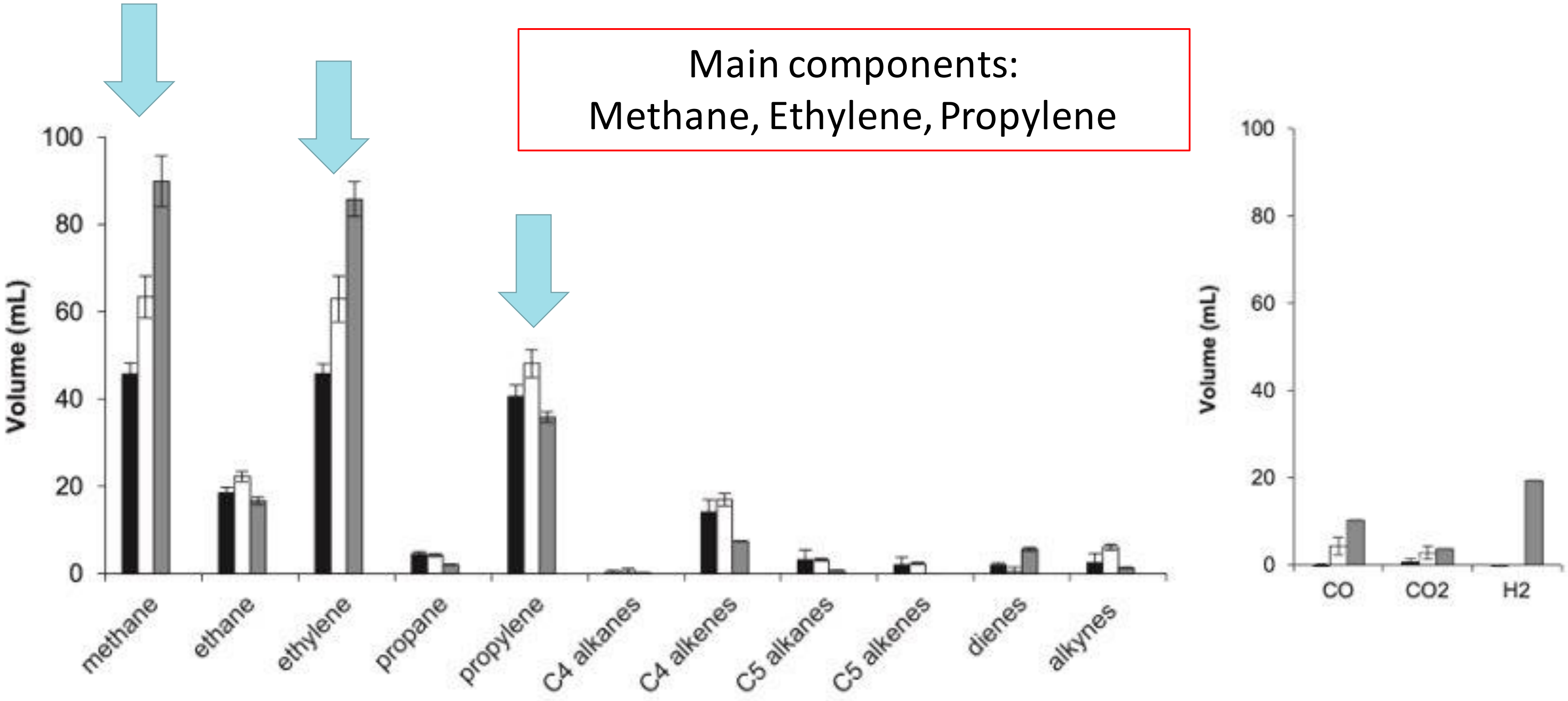
Non-condensable pyrolysis gases

Main components:
Methane, Ethylene, Propylene



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.

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.

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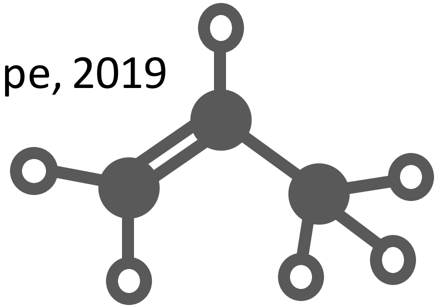
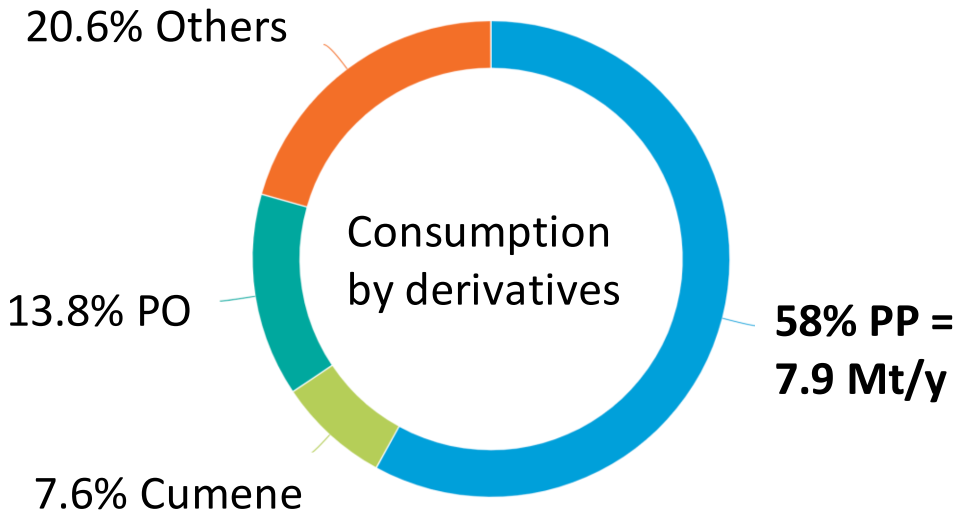
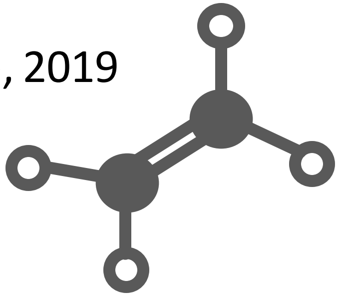
Consumption of olefins in Europe

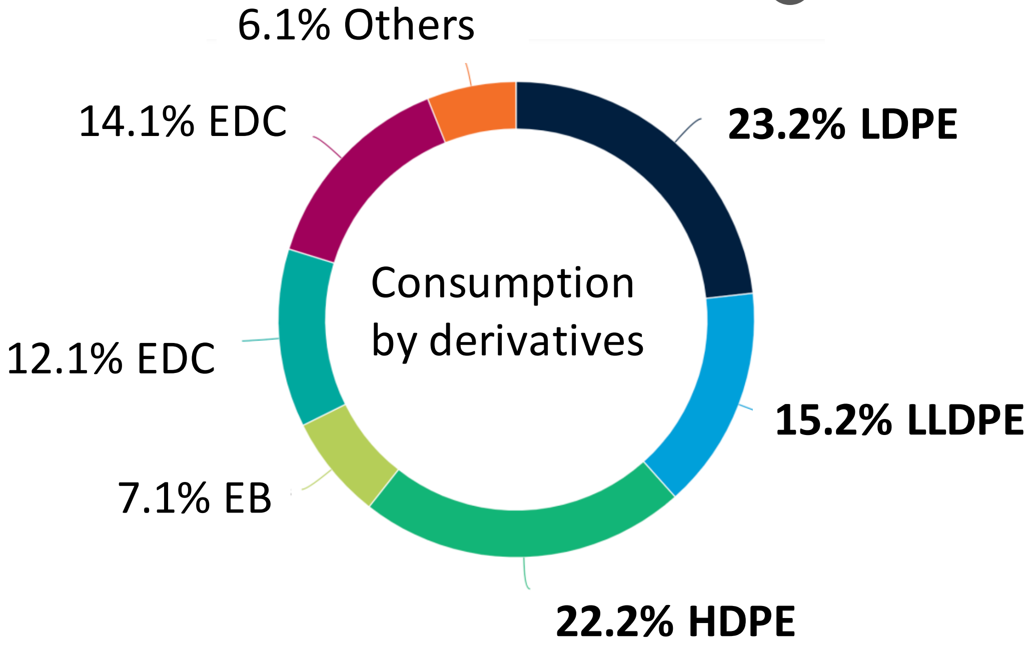
Propylene market in Europe, 2019
Produced: **13.3 Mt**
Consumed : **13.7 Mt**





Ethylene market in Europe, 2019
Produced: **18.4 Mt**
Consumed : **18.5 Mt**





Source: https://www.petrochemistry.eu/about-petrochemistry/petrochemicals-facts-and-figures/european-market-overview/ (visited 27/11/20) based on Cefic, 2019

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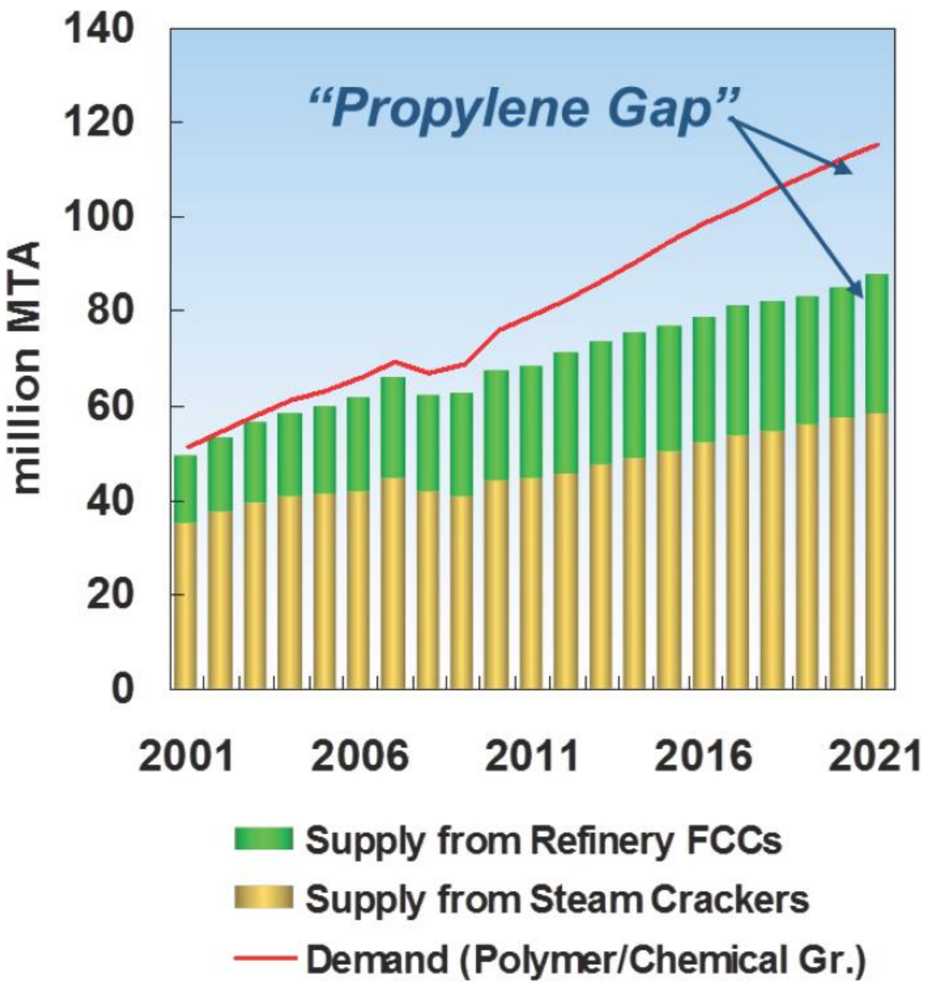
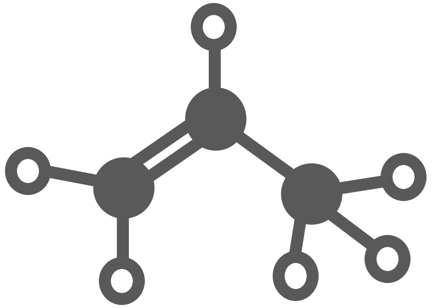
Valorization: bridging the "propylene gap"



"The Changing Landscape of Hydrocarbon Feedstocks for Chemical Production: Implications for Catalysis: Proceedings of a Workshop" at NAP.Edu. https://doi.org/10.17226/23555.

Valorization of non-condensable pyrolysis gases



Increasing propylene content by catalytic process

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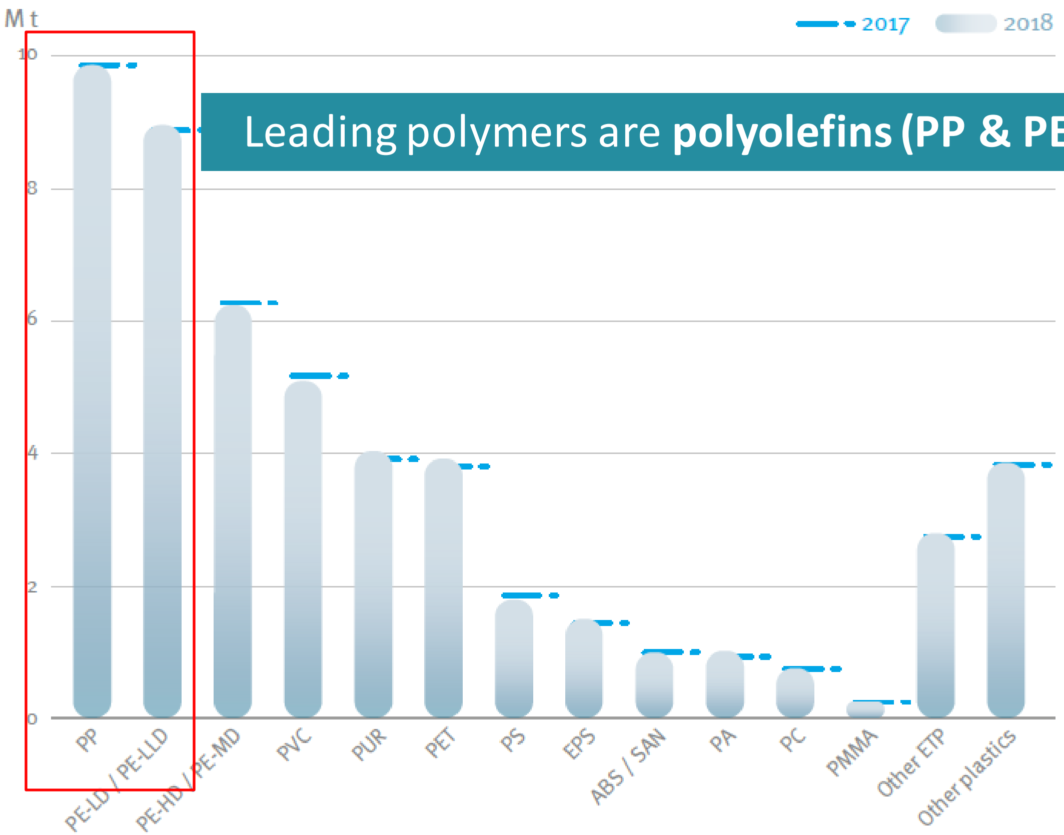
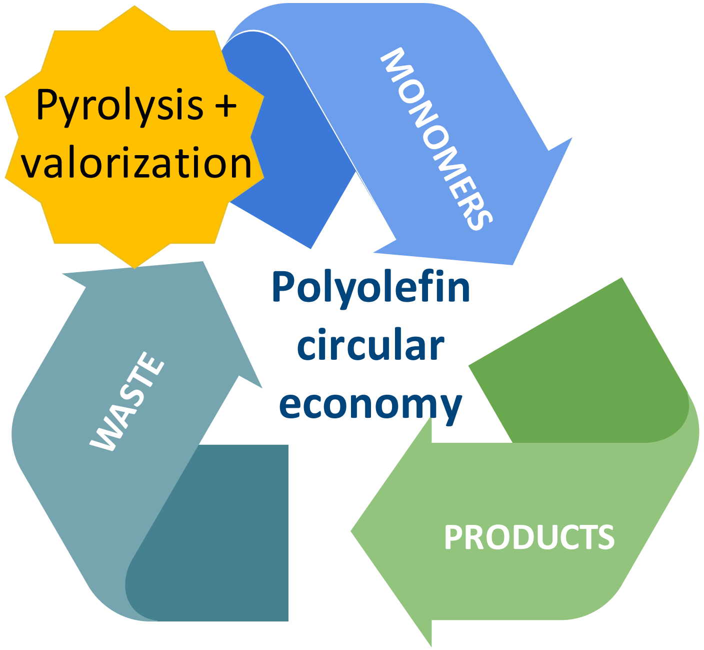
Valorization: a tool for circular economy



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

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



Pyrolysis + valorization

MONOMERS

Polyolefin circular economy

WASTE

PRODUCTS

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A step further in olefin circular economy

Light olefins are important commodity chemicals

+

Gap in the market: consuming is higher

+

Pyrolysis gases are rich in light olefins

+

Catalytic process to increase % propylene

=

Increase in recycling rate

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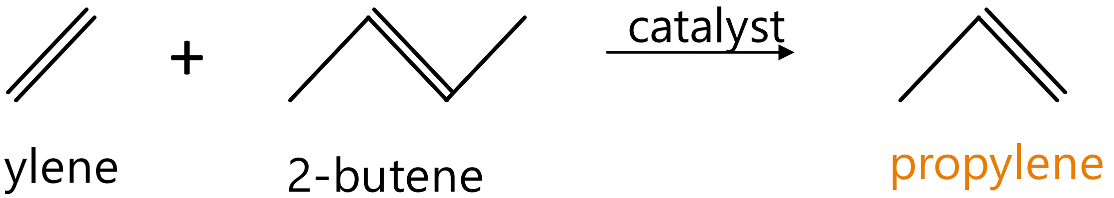
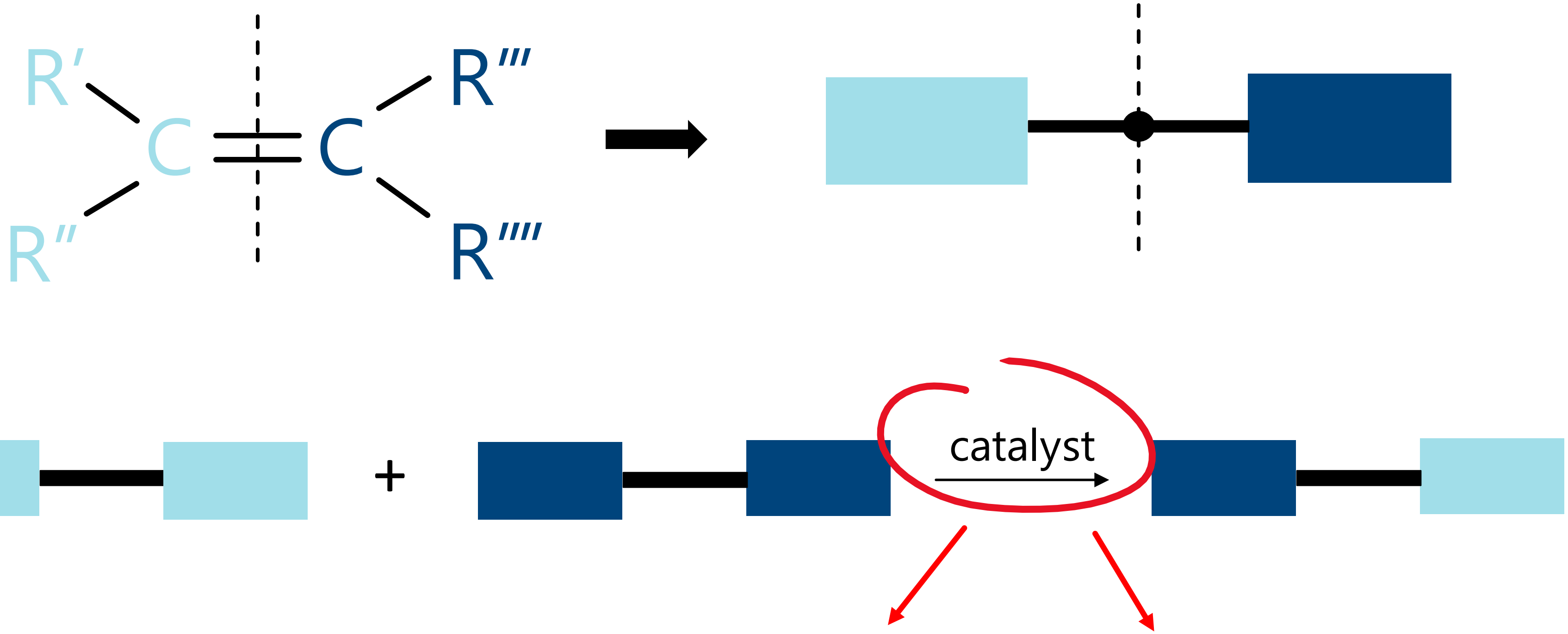
Olefin cross-metathesis

From pyrolysis
non-condensable
gases:



CONCEPTUAL MECHANISM



Homogeneous

Heterogeneous

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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

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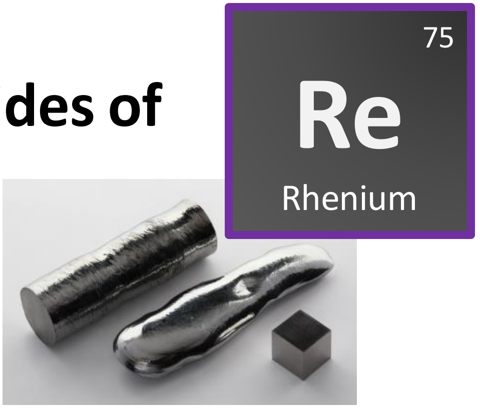
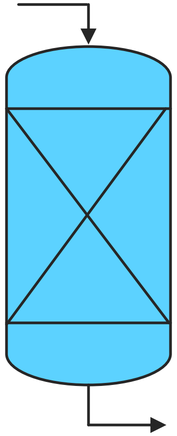
Heterogeneous catalysts for olefin cross metathesis

Metathesis active phase:

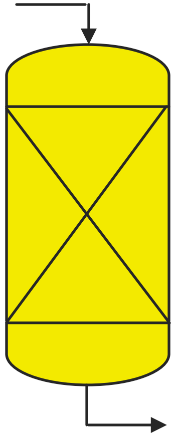
Oxides of



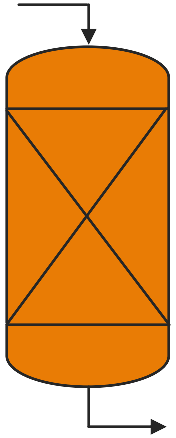
Operating temperature:



Room temperature



Medium temperature



High temperature

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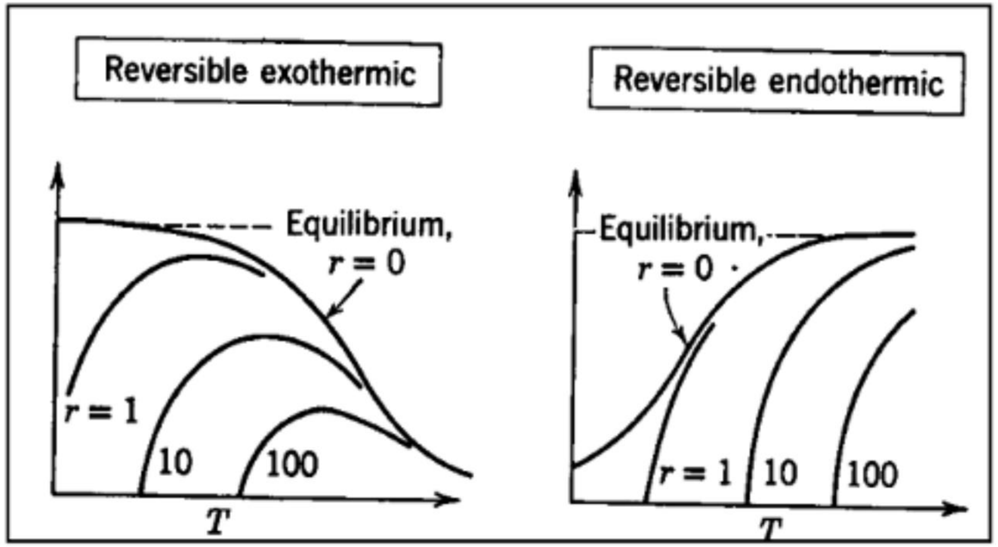
Kinetics and thermodynamics are related

- Catalysis has the role to modify the kinetics of a reaction (speed it up)
- Thermodynamics acts as a gatekeeper
- Equilibrium conversion determined by thermodynamics is the limit



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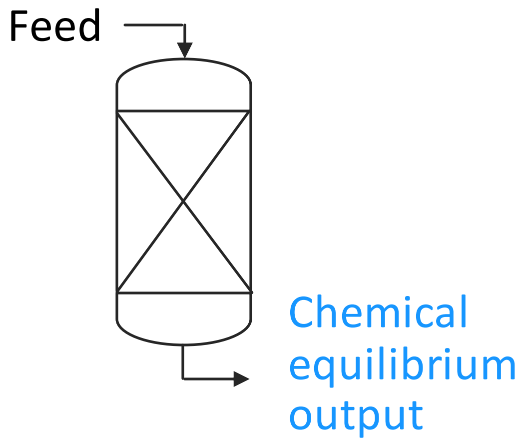
Thermodynamic analysis

Variables:

Temperature **Pressure** **Feed composition**

Aim: determination of effect of variables on
yield of **propylene** and on **ethylene conversion**

Software: Aspen Plus V9
reactor model: REquil



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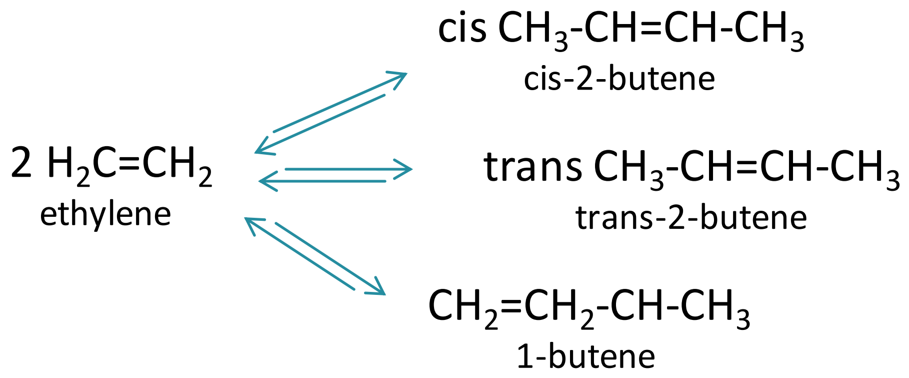
Parallel and consecutive reversible reactions

Ethylene dimerization



2 $H_2C=CH_2$
ethylene

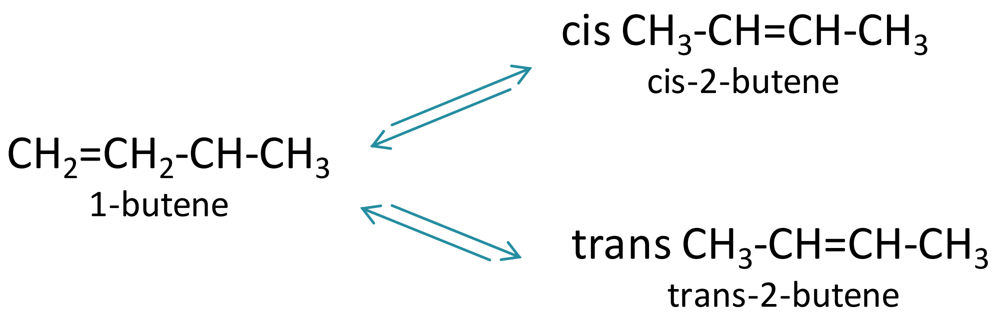
$\rightleftharpoons$ cis CH_3-CH=CH-CH_3
cis-2-butene

$\rightleftharpoons$ trans CH_3-CH=CH-CH_3
trans-2-butene

$\rightleftharpoons$ $CH_2=CH_2$-CH-CH_3
1-butene

ΔrH˚=-50 kJ/mol

Butene isomerization



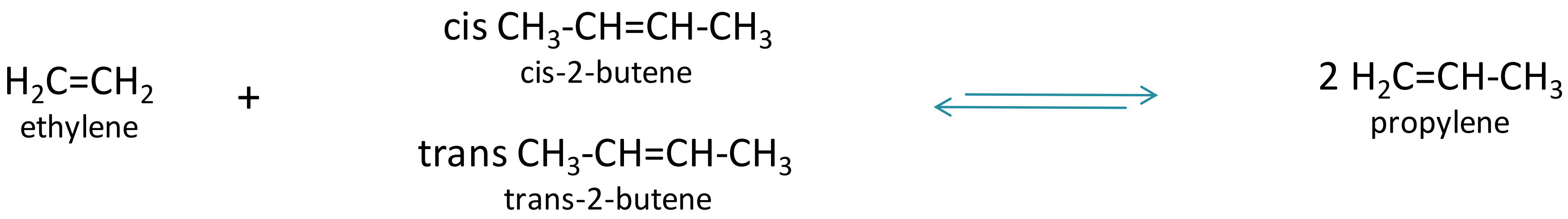
$CH_2=CH_2$-CH-CH_3
1-butene

$\rightleftharpoons$ cis CH_3-CH=CH-CH_3
cis-2-butene

$\rightleftharpoons$ trans CH_3-CH=CH-CH_3
trans-2-butene

ΔrH˚=-12 kJ/mol

Olefin metathesis



$H_2C=CH_2$
ethylene

+

cis CH_3-CH=CH-CH_3
cis-2-butene

trans CH_3-CH=CH-CH_3
trans-2-butene

$\rightleftharpoons$

2 $H_2C=CH-CH_3$
propylene

ΔrH˚=-4 kJ/mol

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Evaluation of reaction performance: yield and conversion

$$\textbf{Product yield } (\%) = \frac{\alpha_j*(F_j^{out} - F_j^{in})}{\sum_k \alpha_k*F_k^{in}} *100 = \frac{\overbrace{3*(F_{propylene}^{out} - F_{propylene}^{in})}^{\text{Generated propylene}}}{\underbrace{2*F_{ethylene}^{in} + 4*(F_{cis2butene}^{in} + F_{trans2butene}^{in} + F_{1butene}^{in})}_{\text{Ethylene and butenes in feed}}} *100$$

Where:

- F_j and F_k are the molar flow of species j and k
- j is the desired product
- k is any molecule considered as reactants
- α is a coefficient equal to the number of C atoms in molecules j and k

$$\textbf{Reactant conversion } (\%) = \frac{F_k^{in} - F_k^{out}}{F_k^{in}} *100 = \frac{\overbrace{F_{ethylene}^{in} - F_{ethylene}^{out}}^{\text{Consumed ethylene}}}{\underbrace{F_{ethylene}^{in}}_{\text{Ethylene in feed}}} *100$$

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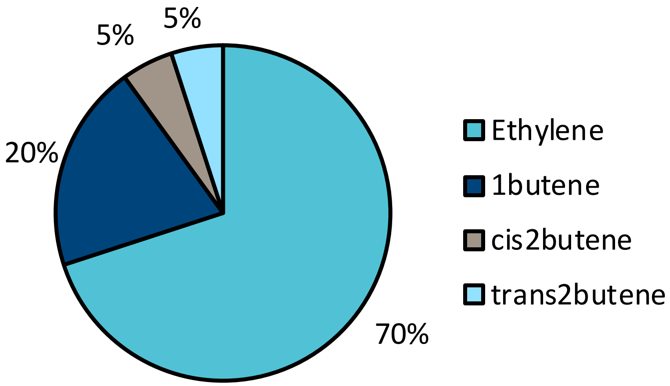
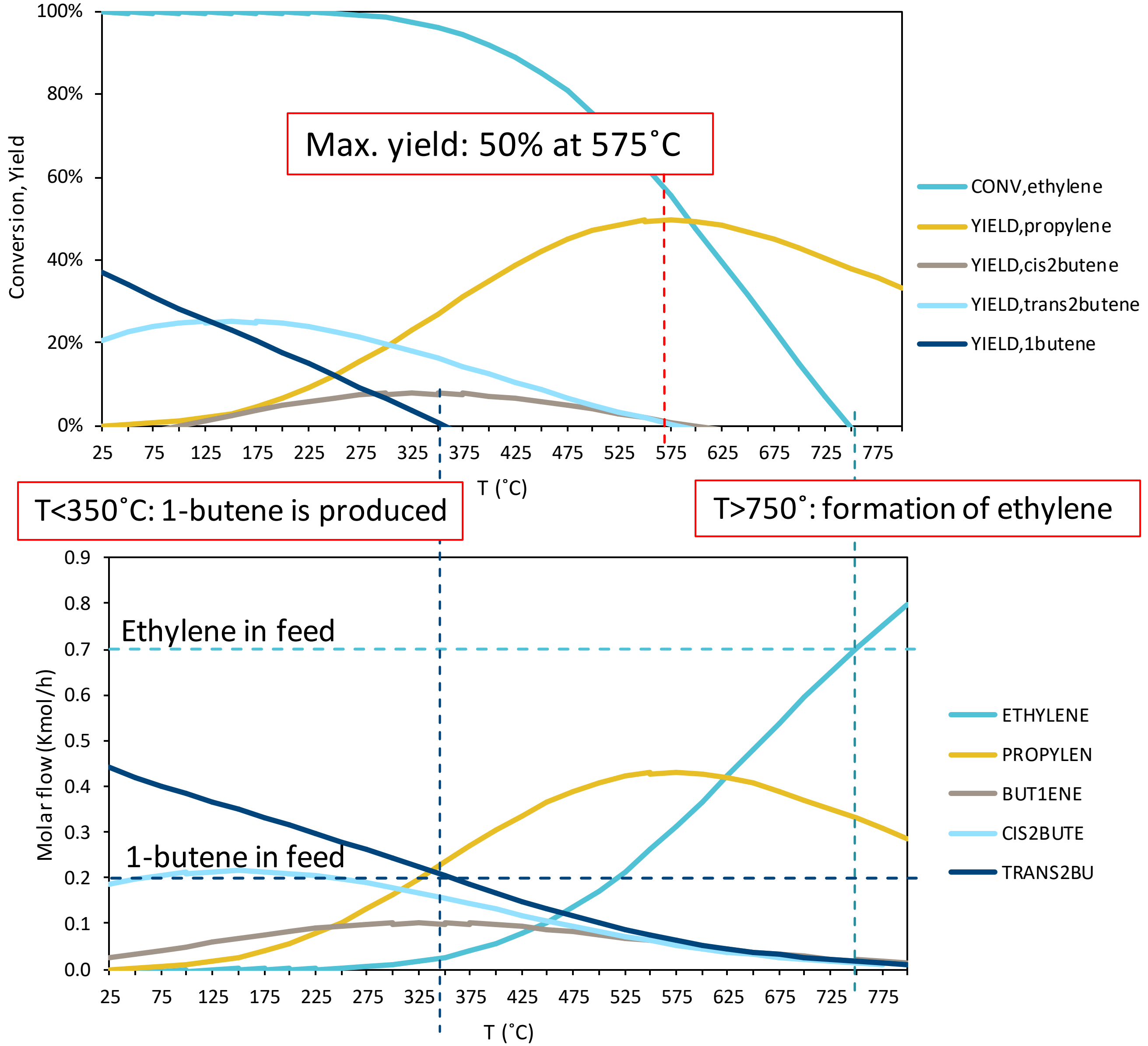
Thermodynamic analysis



Feed:
1 kmol/h
Ptot=1bar
T= variable

Reactions:

- ethylene **oligomerization** to cis- and trans-2-butene
- 1-butene **isomerization** to cis- and trans-2-butene
- **metathesis** of ethylene and cis- or trans-2-butene to propylene



Max. yield: 50% at 575˚C

T<350˚C: 1-butene is produced

T>750˚: formation of ethylene

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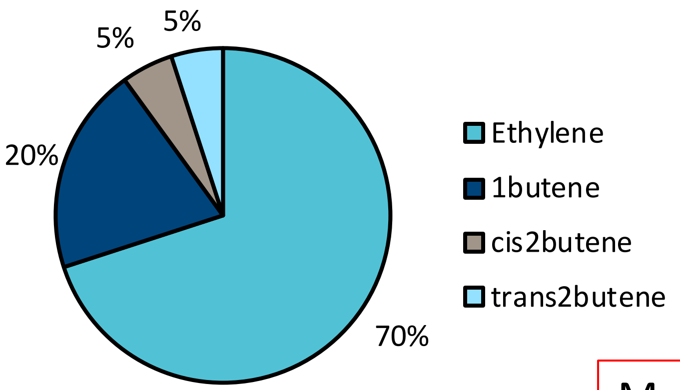
Thermodynamic analysis



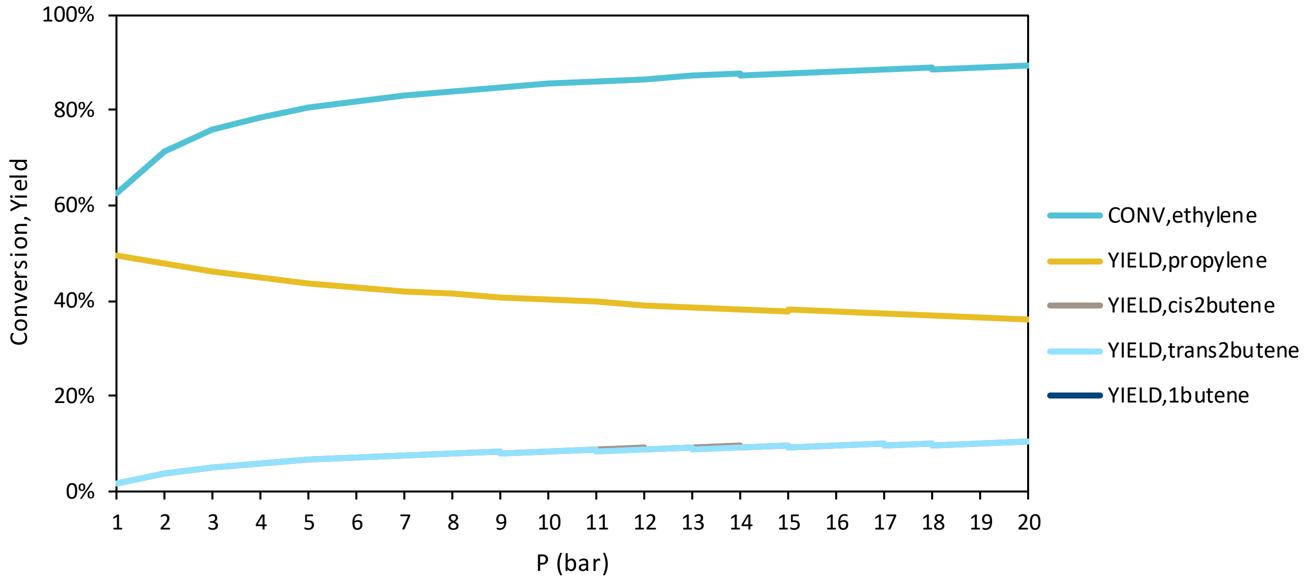
Feed:
1 kmol/h
Ptot= variable
T=550˚C

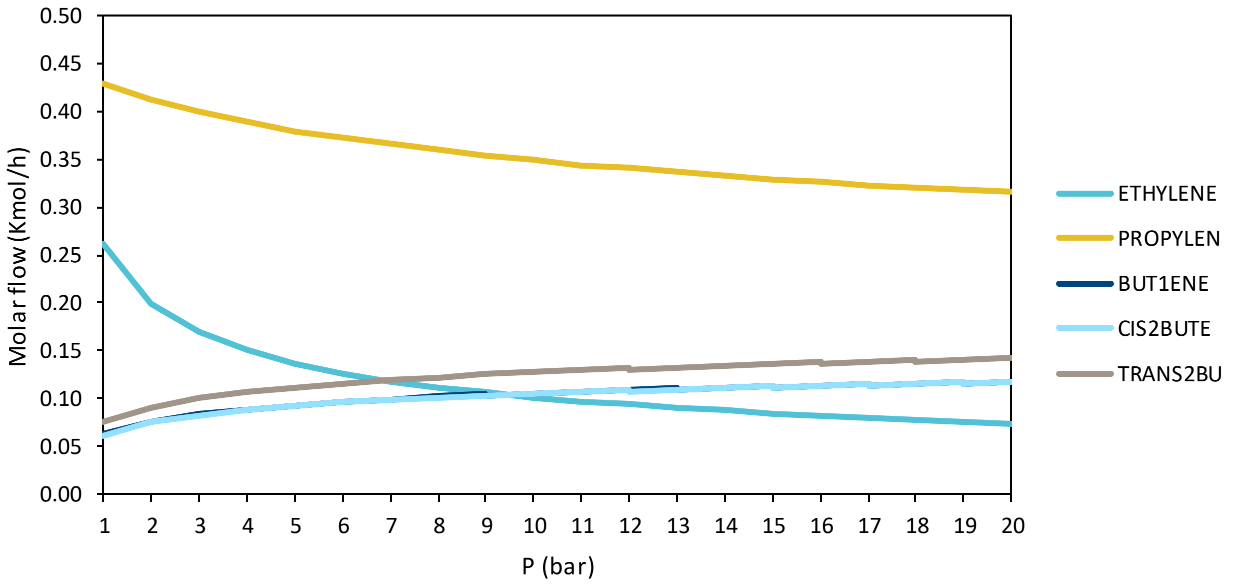
Metathesis is favored at low pressure

Reactions:

- ethylene **oligomerization** to cis- and trans-2-butene
- 1-butene **isomerization** to cis- and trans-2-butene
- **metathesis** of ethylene and cis-
to propylene

Ethylene oligomerization is favored with increasing pressure





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Effect of variables on propylene yield

Temperature:

Maximum yield at T~550˚C.

Window of temperature for propylene production: 400-700˚C.

Pressure:

Atmospheric pressure (1 bar) favors propylene formation.

Feed composition:

Feedstock from 500-600˚C pyrolysis is preferred.

Propylene yield is independent from ethylene:butenes feed ratio.

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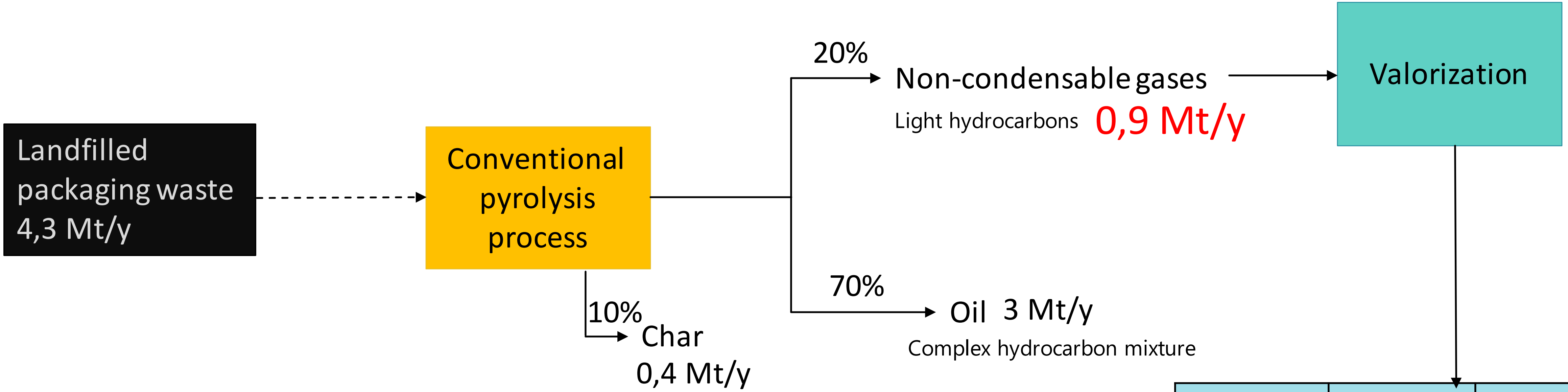
Preliminary calculations - short term scenario



Landfilled packaging waste 4,3 Mt/y

Conventional pyrolysis process

20% Non-condensable gases

Light hydrocarbons 0,9 Mt/y

Valorization

70% Oil 3 Mt/y

Complex hydrocarbon mixture

10% Char 0,4 Mt/y

	Mass fraction	Mass flow (Mt/y)
Ethylene	19%	0.2
Propylene	40%	0.4
Butenes	20%	0.2
Methane	21%	0.2

1% of 2019 production

3% of 2019 production

More than
100 billion
plastic caps

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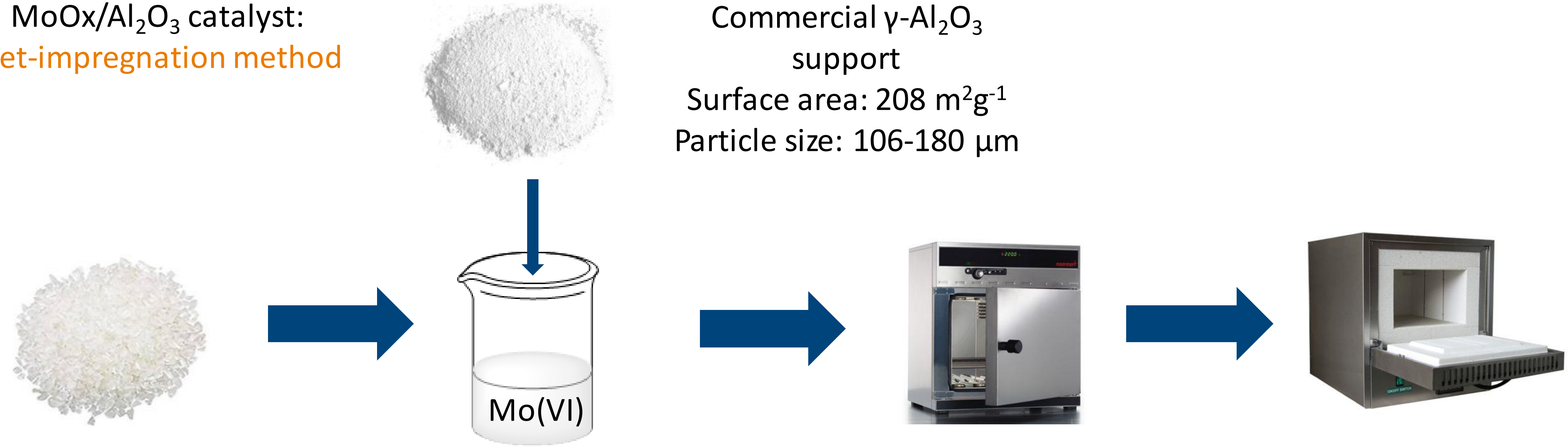
1st generation catalysts

MoOx/Al_2O_3 catalyst:
Wet-impregnation method



Commercial γ-Al_2O_3
support
Surface area: 208 m^2g^{-1}
Particle size: 106-180 µm

$(NH_4)_6Mo_7O_{24}$
precursor

Solvent: H_2O

Drying
(overnight, 105°C)

Calcination
(4h at 600˚C)

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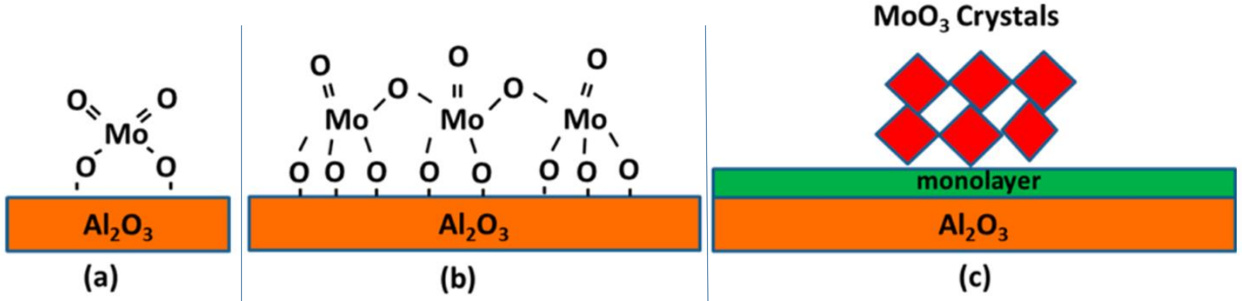
1st generation catalyst: strategy



Atoms/nm^2: 1 5

Increasing Mo coverage

20% monolayer monolayer

Below monolayer Monolayer Multilayer

Sample	**A**	**B**	**C**	**D**	**E**
Mo atoms/nm^2	0,5	1	2,5	5	7

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

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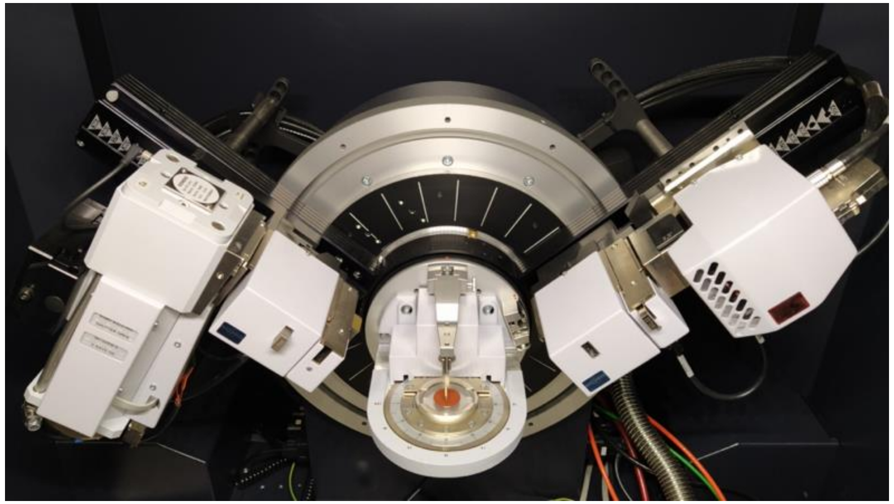
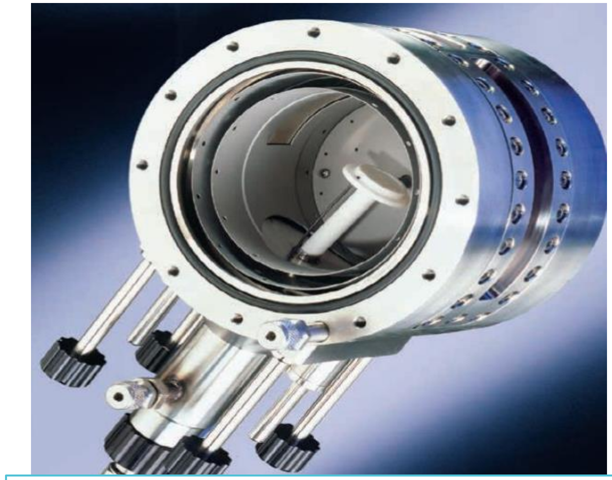
Characterization techniques

X-ray Photo-electron Spectroscopy (XPS): valence state of Mo, interaction with support

At the Physics Department of AUTh
https://www.physics.auth.gr/en

X-Ray Diffraction spectroscopy (XRD): crystalline phase, size of crystallite





Stage for *in situ* and *operando* XRD

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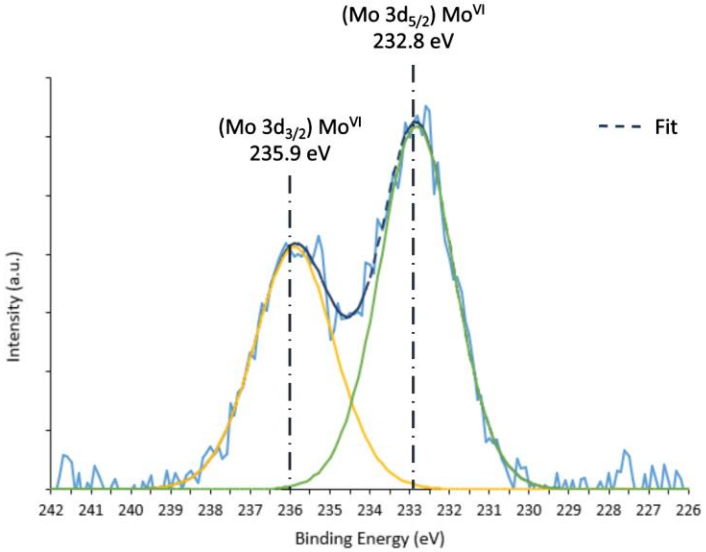
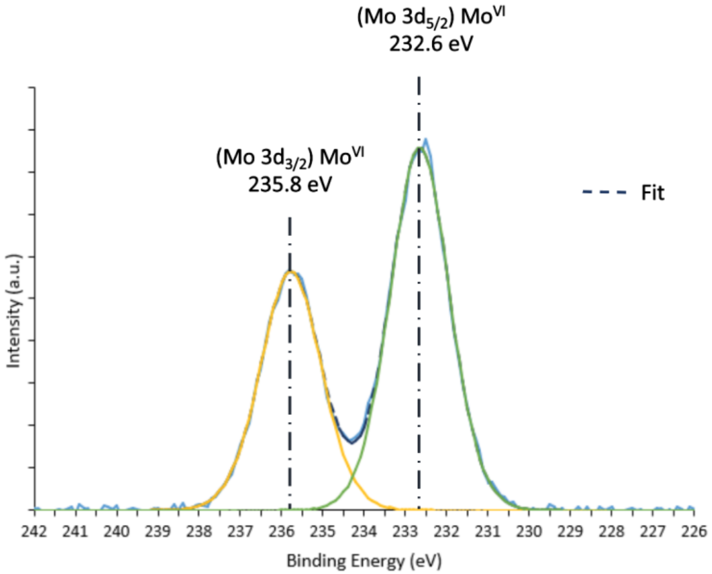
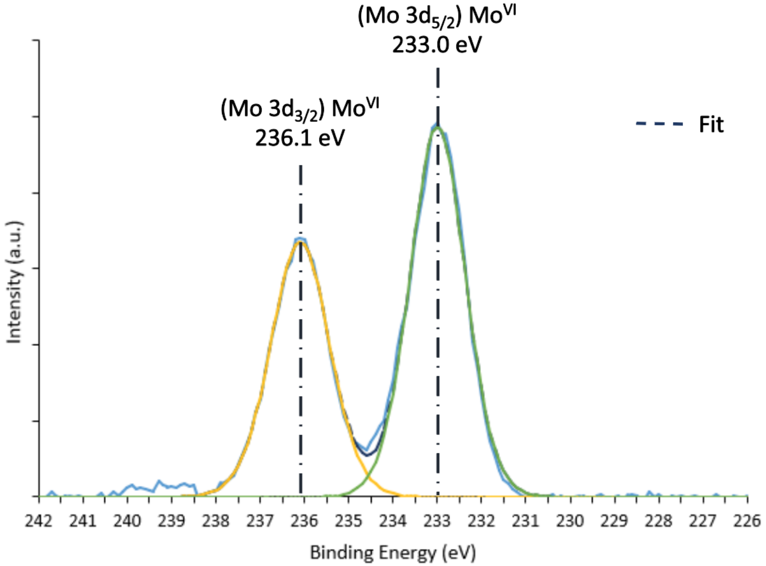
XPS: Molybdenum valence state



4.7w% MoO_3/Al_2O_3
0.5 Mo atoms/nm^2
Below monolayer



19.9w% MoO_3/Al_2O_3
5 Mo atoms/nm^2
Monolayer



25.8w% MoO_3/Al_2O_3
7 Mo atoms/nm^2
Multilayer

The Mo 3d peaks observed in the XPS assigned to Mo(VI)
Only one valence state observed

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XPS: Mo3d and Al2p peaks – shift and interaction

Shift from pure MoO_3

	Mo3d 5/2 (eV)	Al2p (eV)	Mo/Al	
Pure Al2O3*	-	74.1	-	
4,7% MoO_3/Al_2O_3	232.8	74.4	0.03	Below monolayer
19,9% MoO_3/Al_2O_3	232.6	74.2	0.14	Monolayer
25,5% MoO_3/Al_2O_3	233.0	74.7	0.21	Multilayer
ref. pure MoO_3 **	233.1	-		
ref. pure MoO_2**	229.5	-		
ref. pure Al_2O_3**	-	74.6		

*no thermal treatment

** from Thermoscientific XPS database

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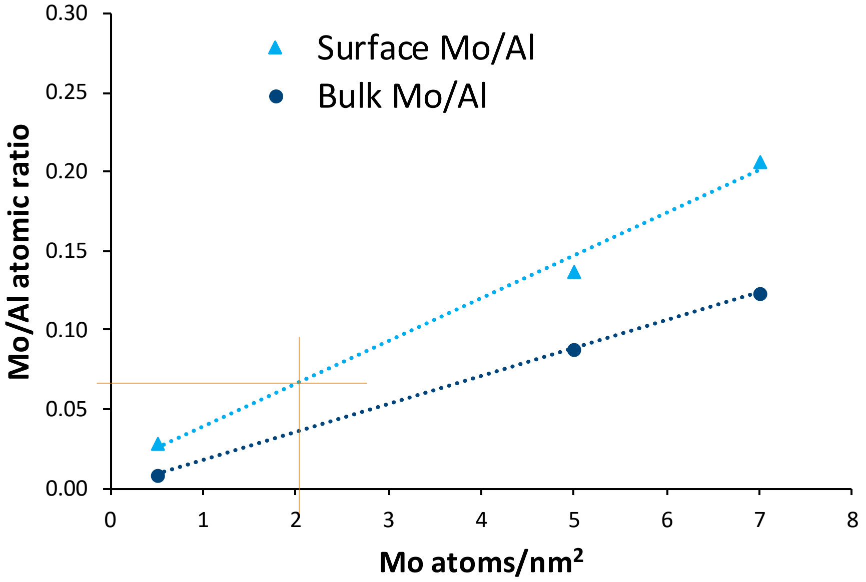
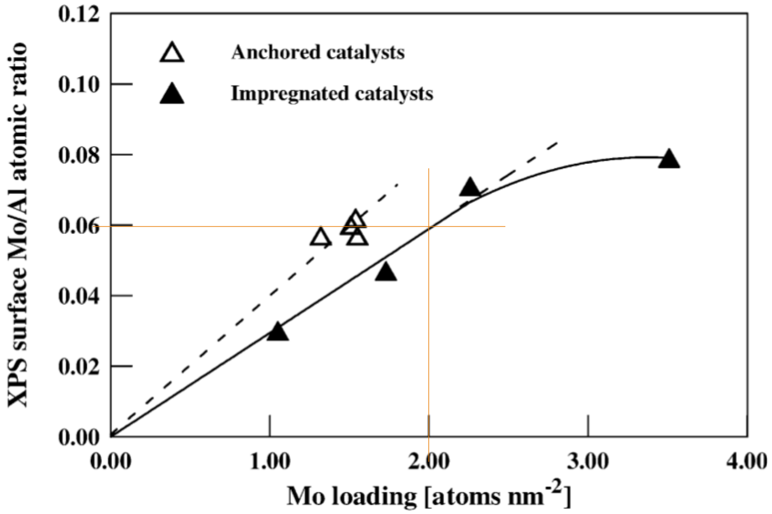
Mo/Al surface atomic ratio





- Mo enrichment of surface
- Linear dependence of Mo/Al ratio = high Mo dispersion

Slope of Mo/Al surface atomic ratio is comparable to literature

Handzlik, J.; Ogonowski, J.; Stoch, J.; Mikołajczyk, M. *Applied Catalysis A: General* **2004**, *273* (1), 99–104

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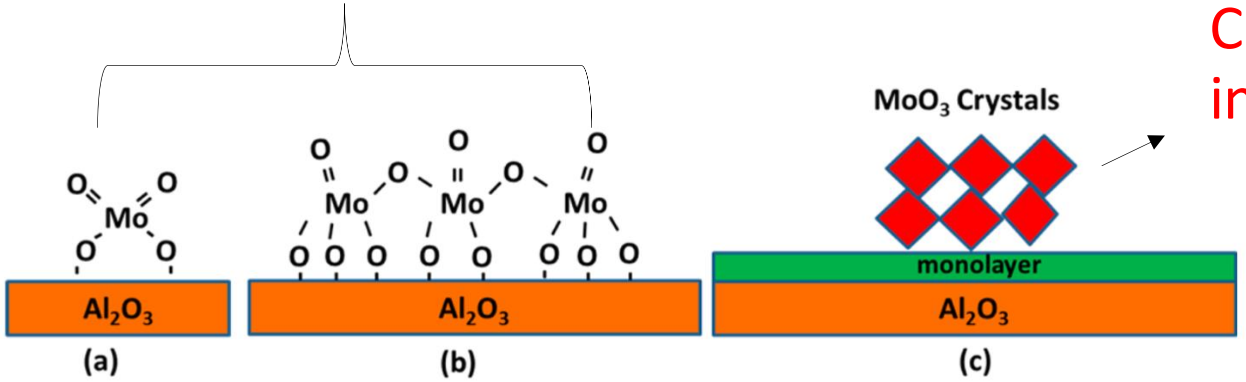
Structure-activity relationship

Debate over active sites



Catalytically inactive

- Open debate on identity of active species and valence state
- Convergence of opinion on MoO_3 and $Al_2(MoO_4)_3$ crystalline phases not active for metathesis
- Mo dispersion is considered a crucial parameter for good catalytic activity

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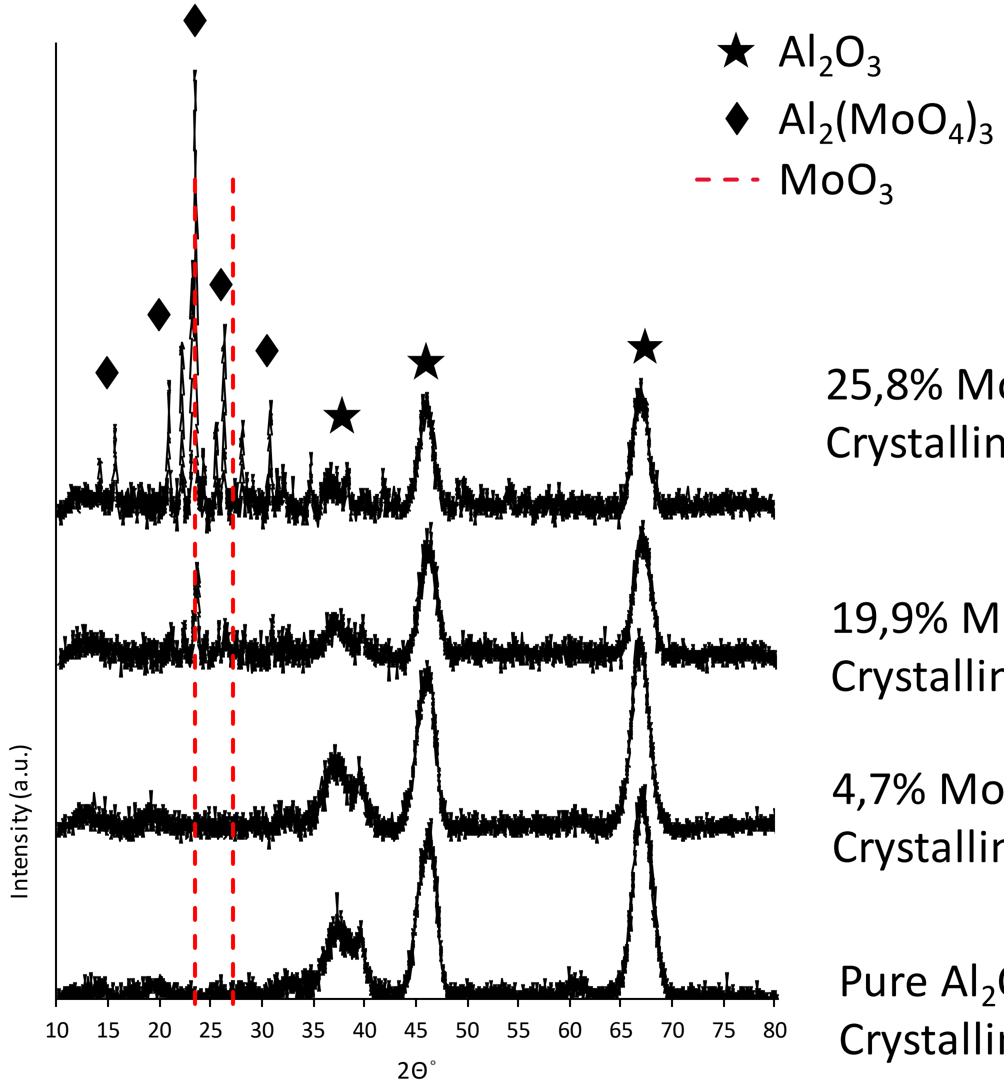
Characterization: XRD



25,8% MoO_3 /Al_2O_3
Crystallinity: 30,7%

19,9% MoO_3/Al_2O_3
Crystallinity: 28,5%

4,7% MoO_3/Al_2O_3
Crystallinity: 33,8%

Pure Al_2O_3
Crystallinity: 39,8%

At high MoO_3 loading:
$Al_2(MoO_4)_3$ crystalline phase

At low MoO_3 loading:
No MoOx crystalline phase detected

Signal/noise ratio is low
Low crystallinity of support

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Catalyst screening

Catalytic

Factors

Selectivity, Conversion, Stability
Normalized reaction rate
Deactivation rate

Conditions

Intrinsic kinetics in continuous flow reactor

Aim

Correlation of catalyst formulation with catalytic activity/performance

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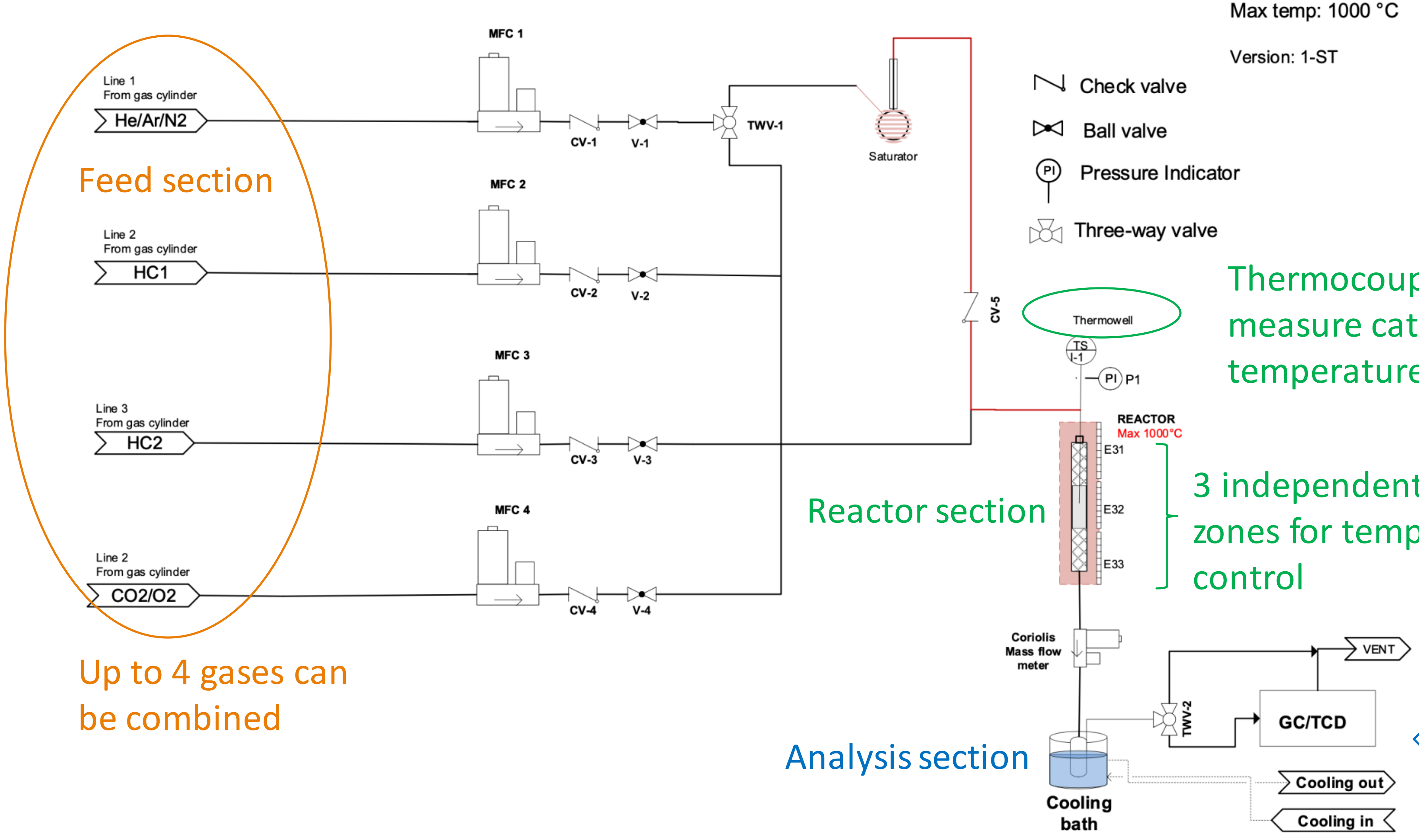
Reactor unit at LPT



Feed section

Up to 4 gases can be combined

Thermocouple to measure catalyst bed temperature

Reactor section

3 independent oven zones for temperature control

Analysis section

+ Mass Spectrometer (MS) can be added

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Catalyst screening: kinetics

- Intrinsic kinetics
  - ❖ not affected by transport phenomena
  - ❖ well defined process conditions

- scale
  - ❖ pellet scale: internal & external gradients (C, T)
  - ❖ reactor scale: plug flow / perfectly mixed flow
    integral / differential operation

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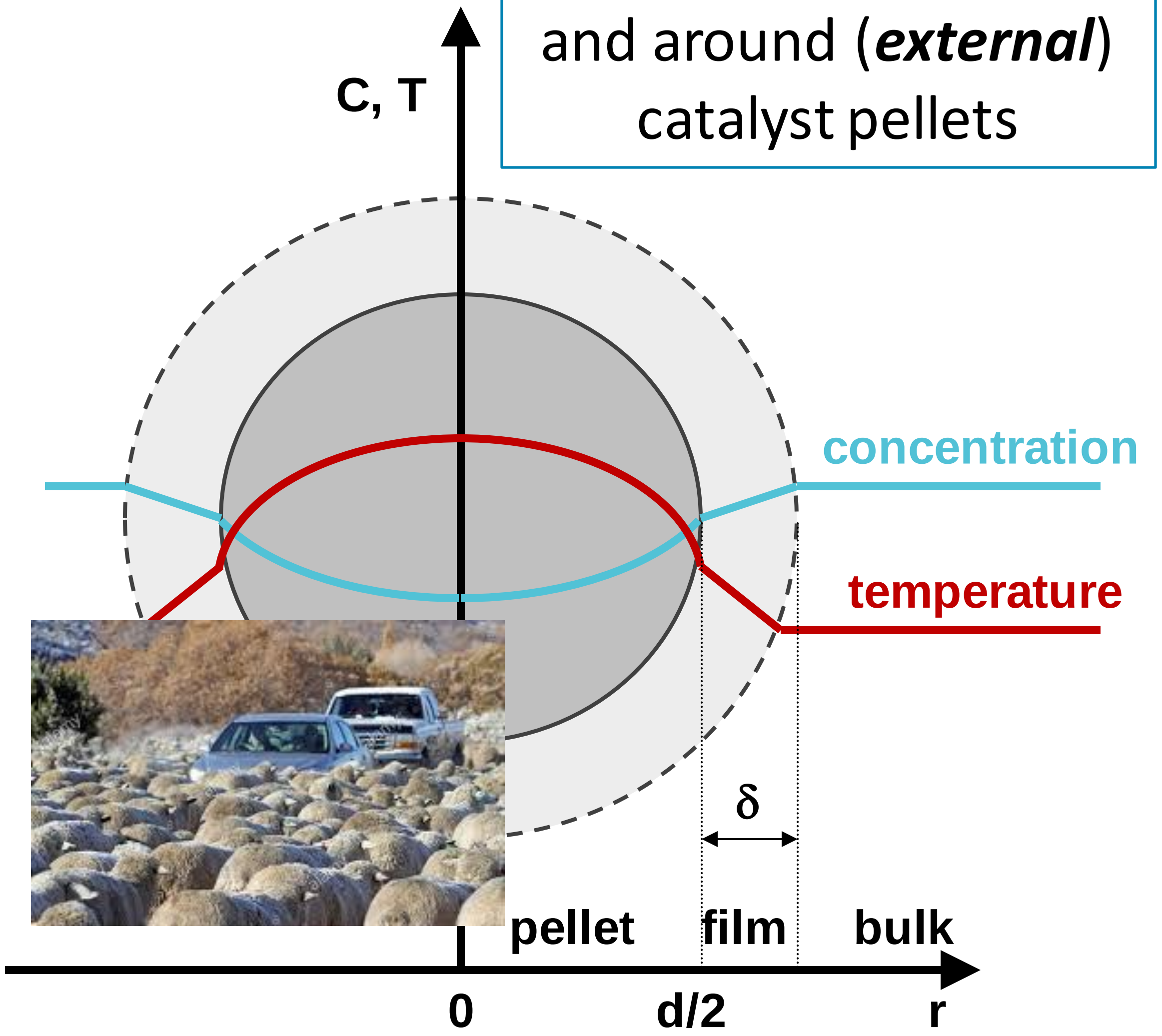
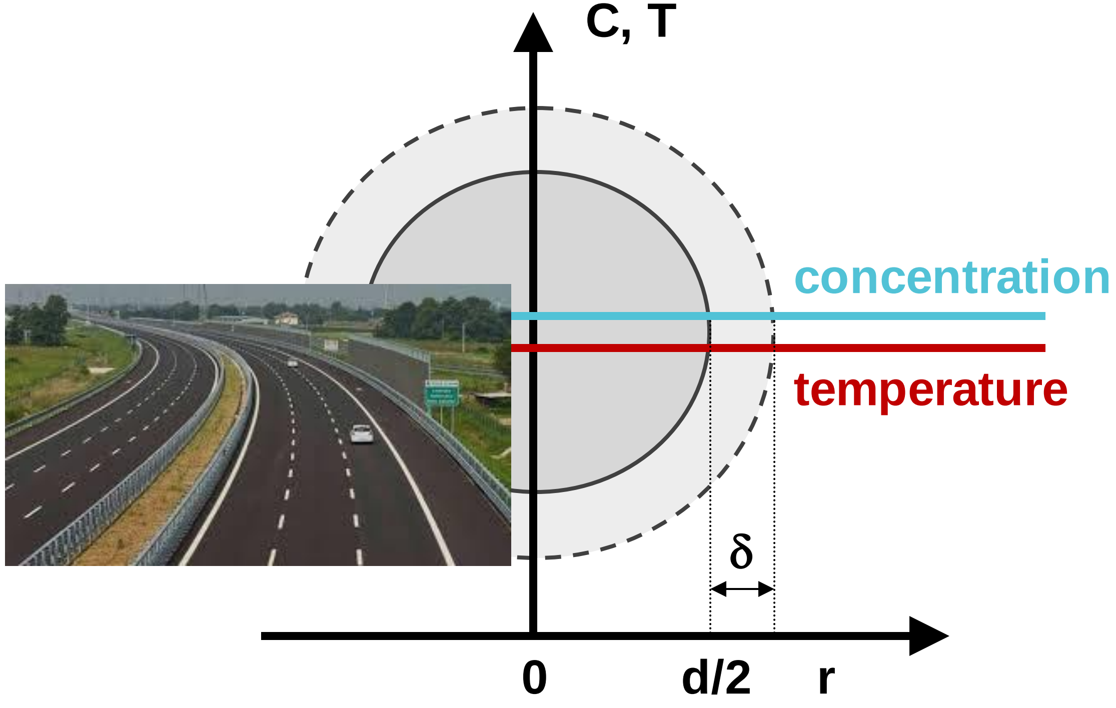
Pellet scale transport phenomena and gradients

Gradients in (***internal***) and around (***external***) catalyst pellets



Intrinsic kinetics

Avoid gradients



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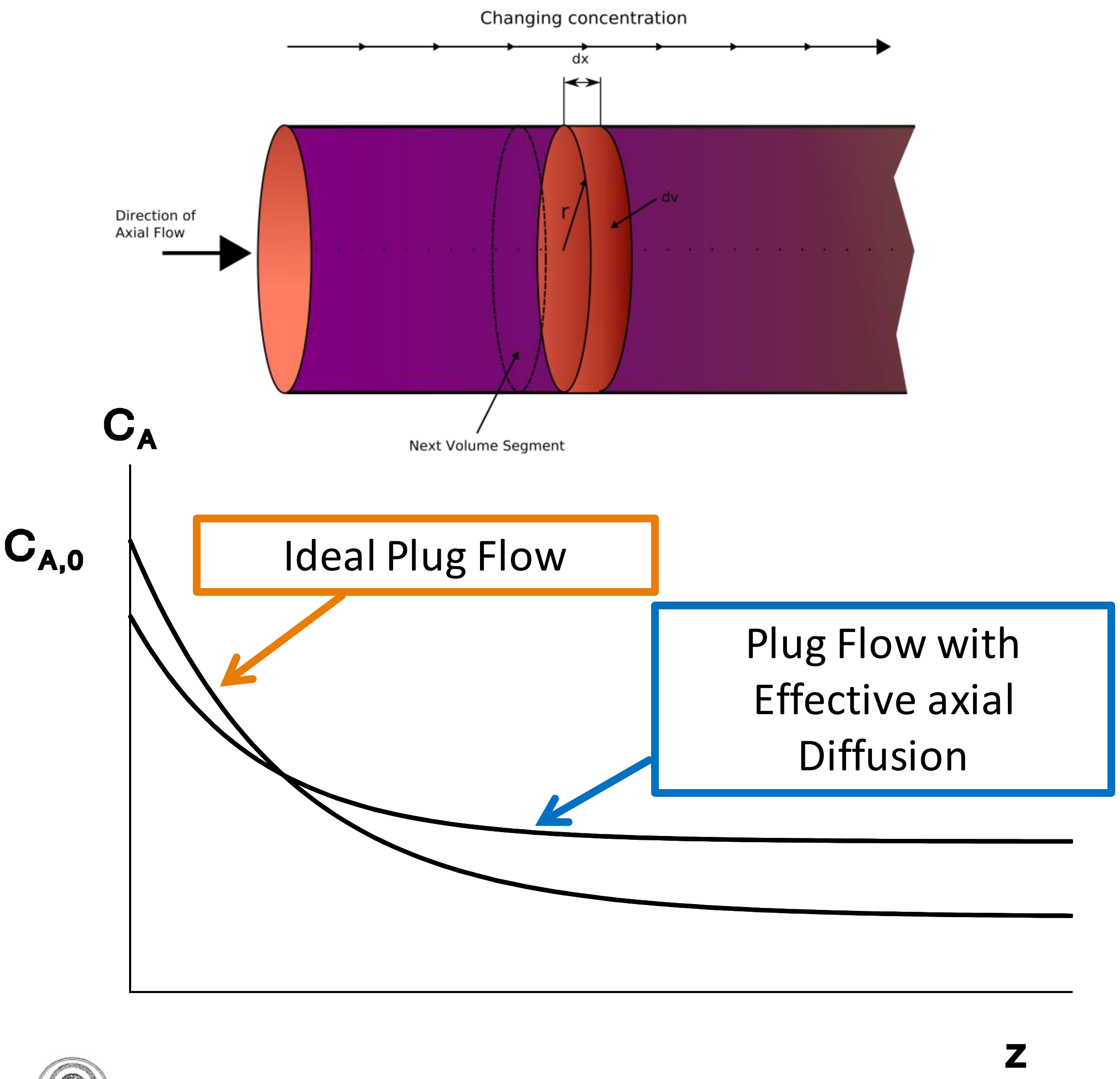
Reactor scale transport phenomena



- absence of axial diffusion
- absence of radial gradients

Ideal Plug Flow Regime

$\tau_0 < \tau_0$

$L_p < L$ required reactor length (for a given conversion) is smaller

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Future work (6 months)

Further **synthesis** of 1st generation catalysts (WOx- and ReOx-based)

Catalyst screening with high purity feedstock

Further **characterization** of fresh and spent catalyst

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Conclusions

Catalyst screening methodology was illustrated and will be part of future work

1st generation Mo-based catalysts were synthesized and characterized with XPS and XRD

Favorable thermodynamic conditions for propylene metathesis were determined by simulation

Valorization of gases from pyrolysis to **recycle olefins** from plastic waste and **reduce carbon footprint** of polymer industry

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μTeaching ESR 12: Valorizing pyrolysis gases back to monomers

Thank you for your attention!

Francesca Martelli, Dr. Stavros Theofanidis, Prof. Angeliki Lemonidou

You can find me at: fmartelli@cheng.auth.gr
http://lpt.cheng.auth.gr/en

Laboratory of Petrochemical Technology, Chemical Engineering Department,
Aristotle University of Thessaloniki

C-PlaNeT online NTE 2, December 9th 2020

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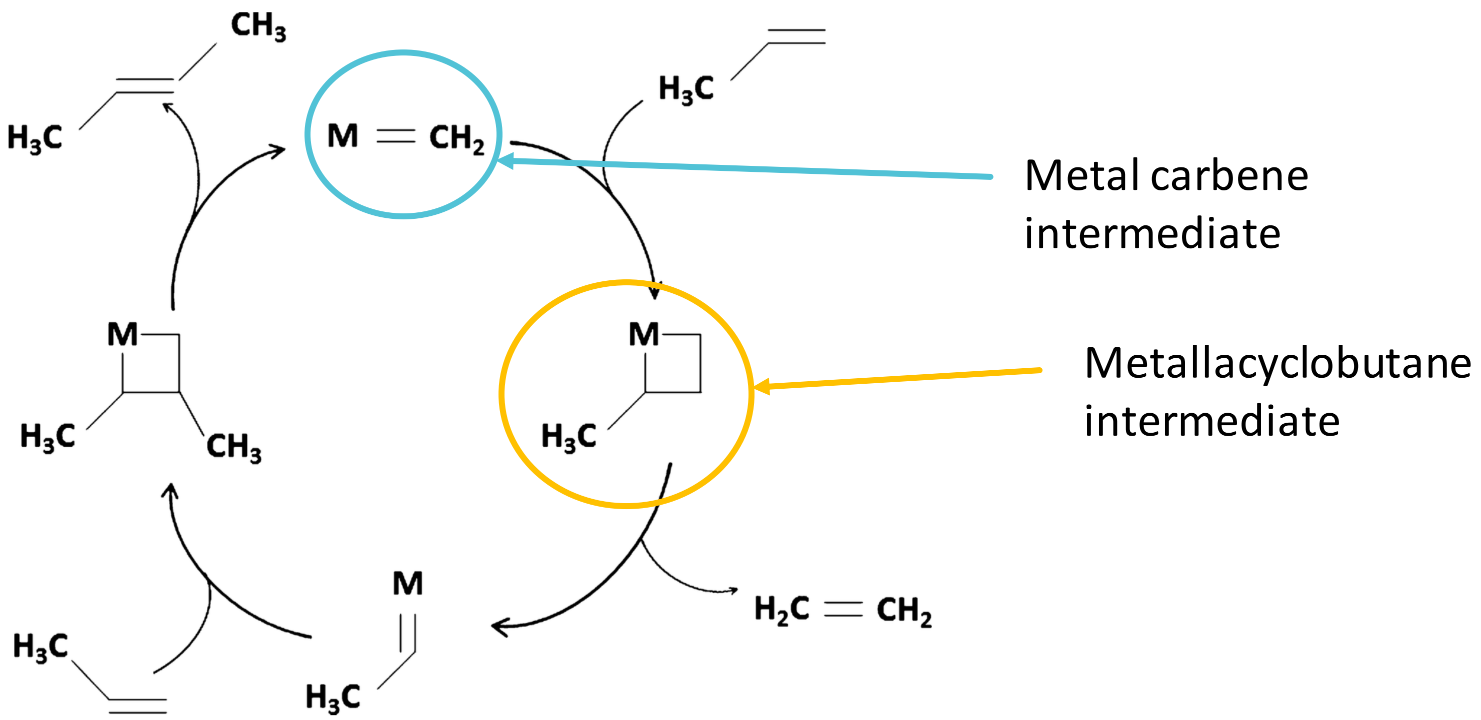
Chauvin's mechanism for Olefin Metathesis

Self-metathesis of propylene to ethylene and 2-butene



Metal carbene intermediate

Metallacyclobutane intermediate

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

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