

The VTT logo consists of the letters 'VTT' in a bold, white, sans-serif font, centered within a solid black square.

Catalytic pyrolysis of plastic waste: Opportunities and Challenges

TCBIOMASS 2022

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16/05/2022 VTT – beyond the obvious

Content

- The problem of plastic waste
- Plastic recycling methods
- Catalytic pyrolysis
- Case examples
- Conclusions



Why is plastic relevant?

Employment

**Close to 1.5
million**

Companies

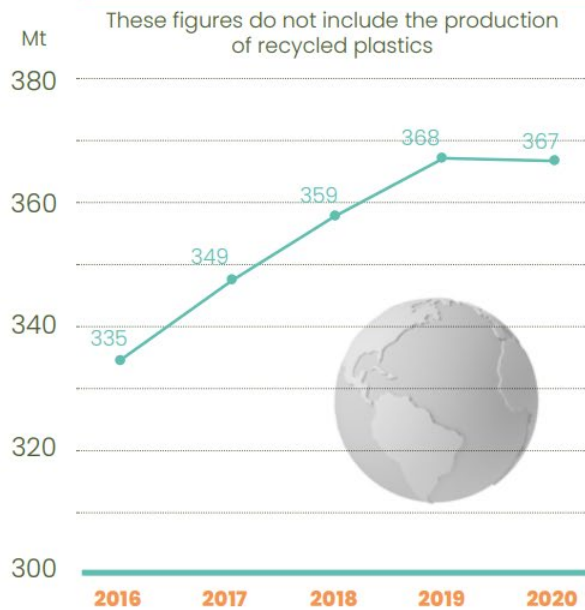
**Close to 52
thousand**

Turnover

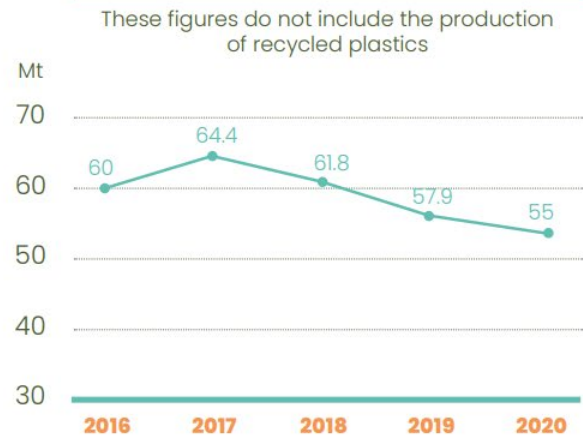
**Close to 33
Billion Eur**

WORLD AND EUROPEAN plastics production evolution

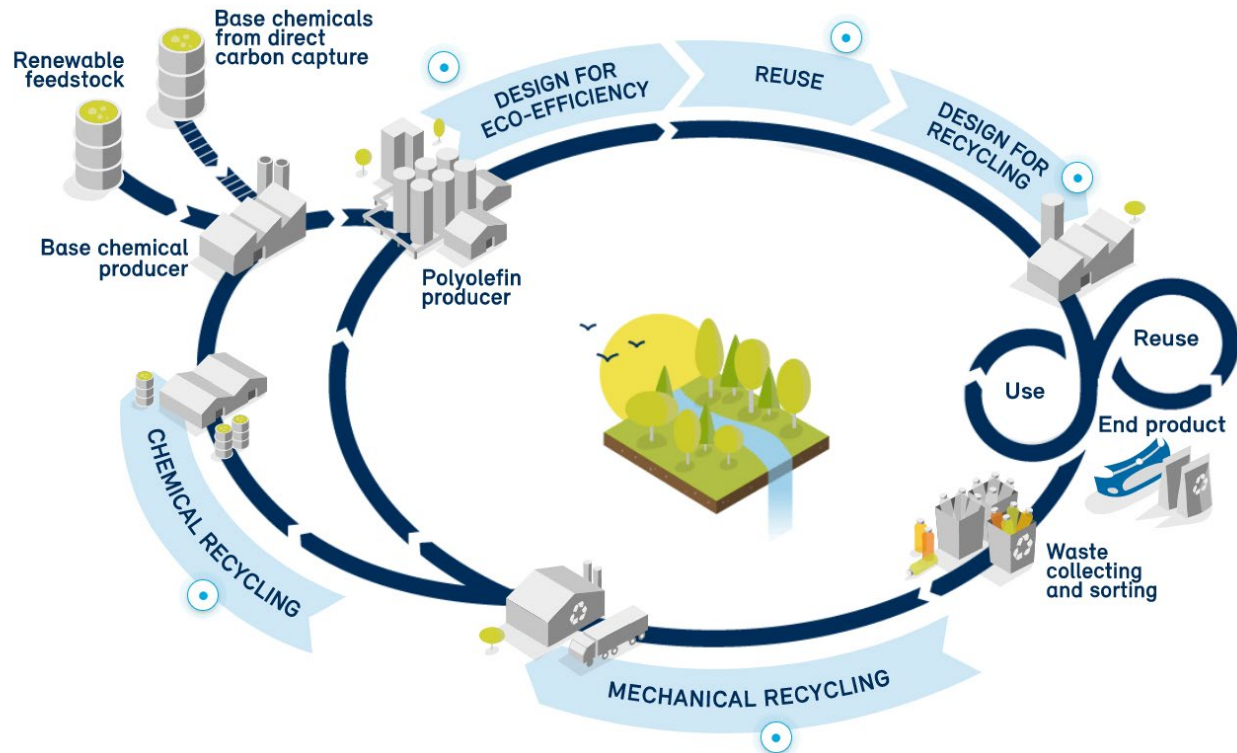
WORLD PLASTICS PRODUCTION



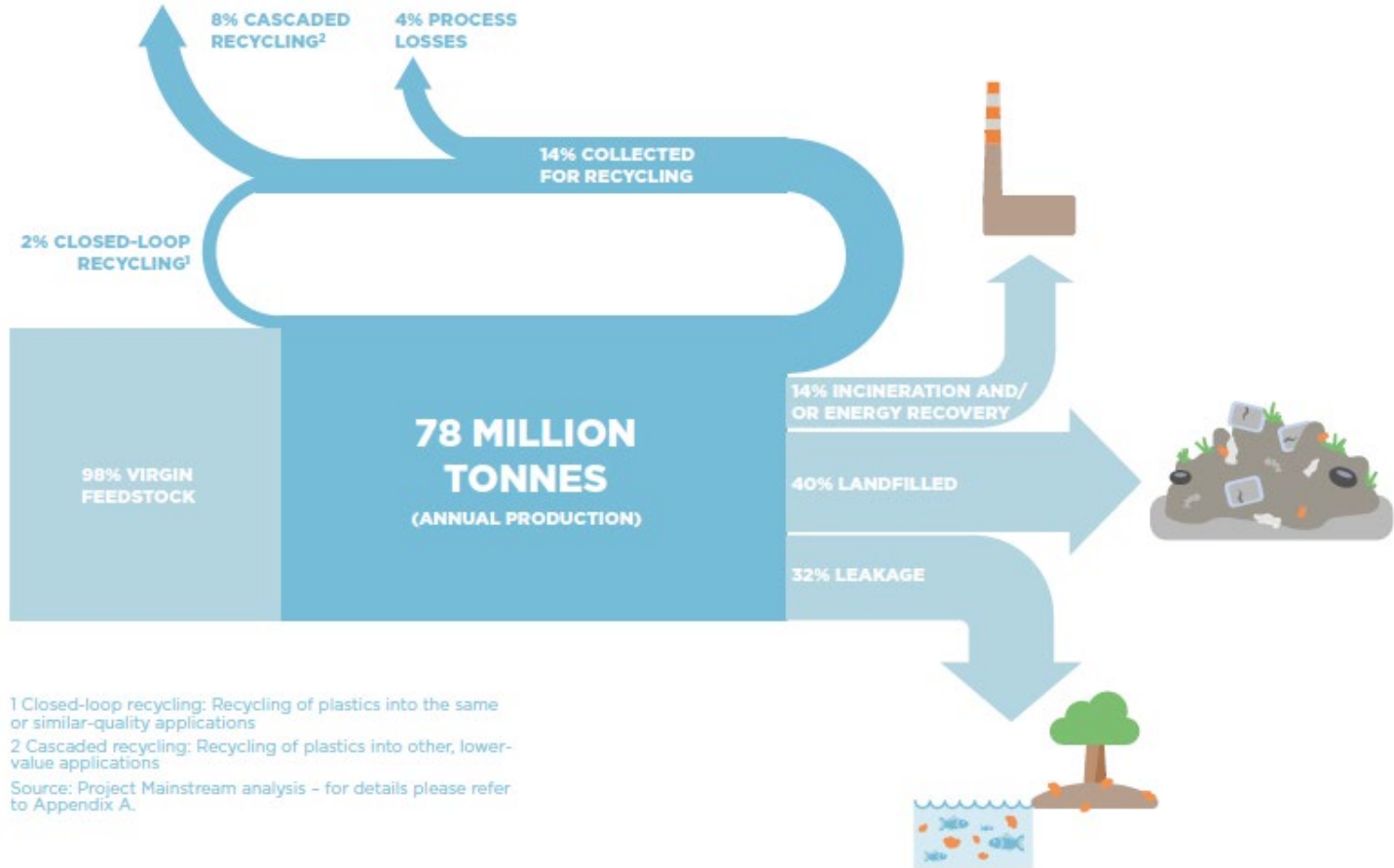
EUROPEAN PLASTICS PRODUCTION



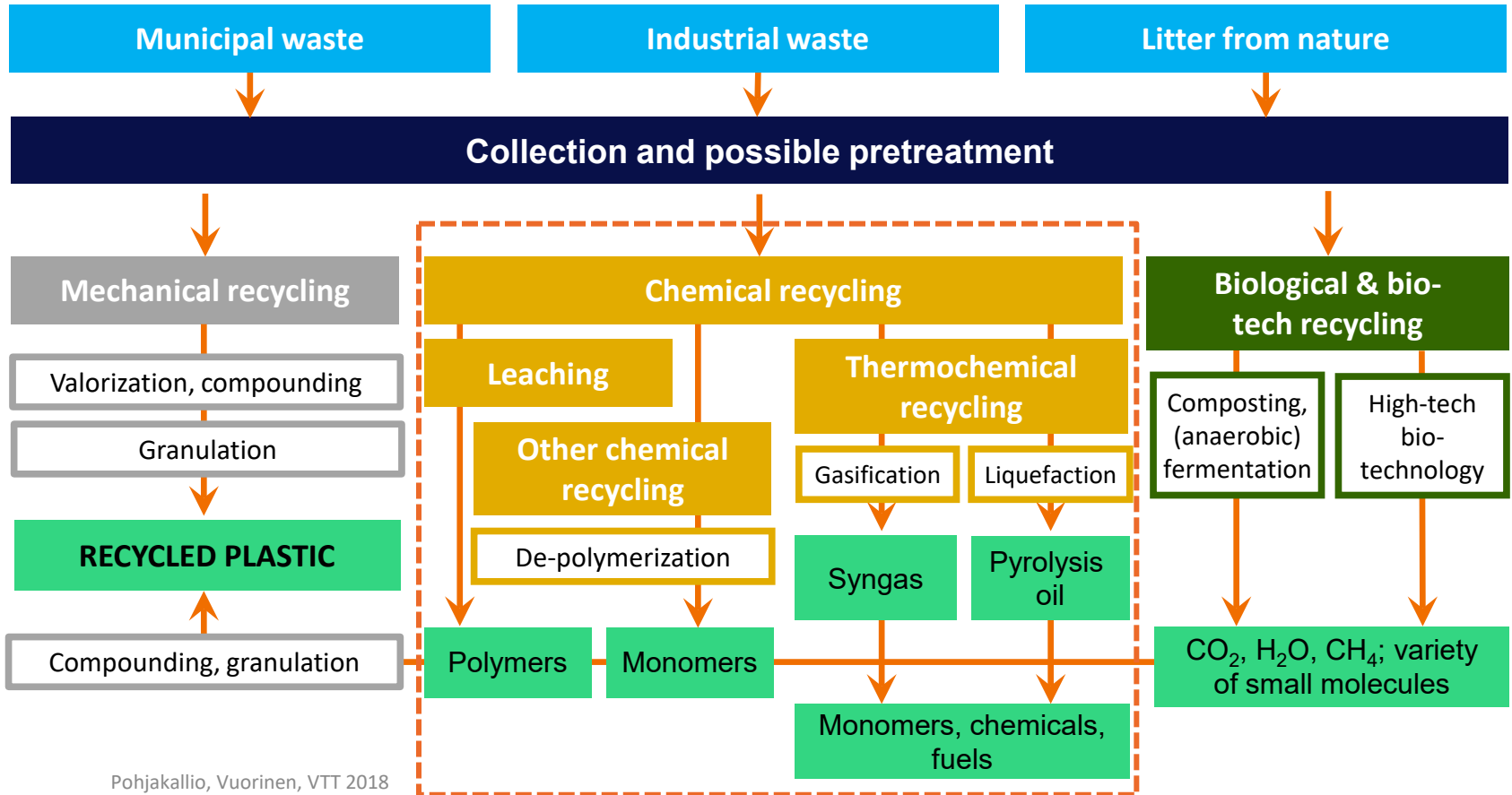
Plastic Circular Economy - Vision



Global flows of plastic packaging materials in 2013



VTT plastic recycling platforms



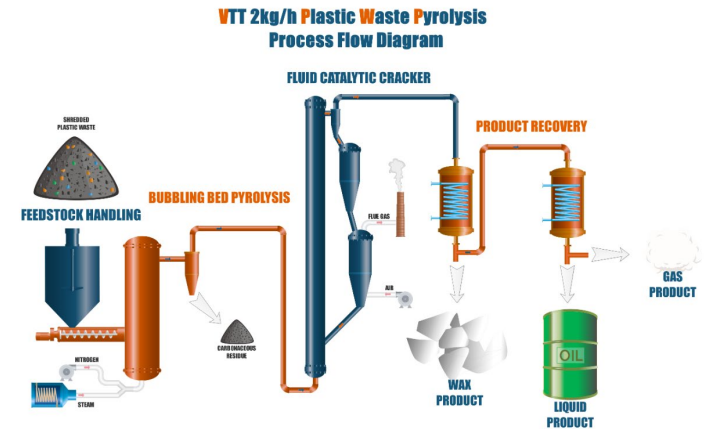
Thermochemical conversion

Pyrolysis

- Thermal degradation of plastics into liquid fuel components
- Suitable to end of life mechanically non recyclable plastics
- Valuable hydrocarbons recovered including monomers for re-polymerization
- Heterogeneous plastics treated
- Selectivity and yield can be optimized with the use of a suitable catalyst
- Mild pretreatment needed
- Energy intensive process – process gas recycled
- Moderately large CAPEX
- Post treatment might be needed depending on the contaminants

Pilot examples

- Agilyx (USA)
- Plastic energy (ES)
- Recycling technologies (UK)
- ResPolyflow (USA)
- PHJK (FI)
- Nexus (USA)



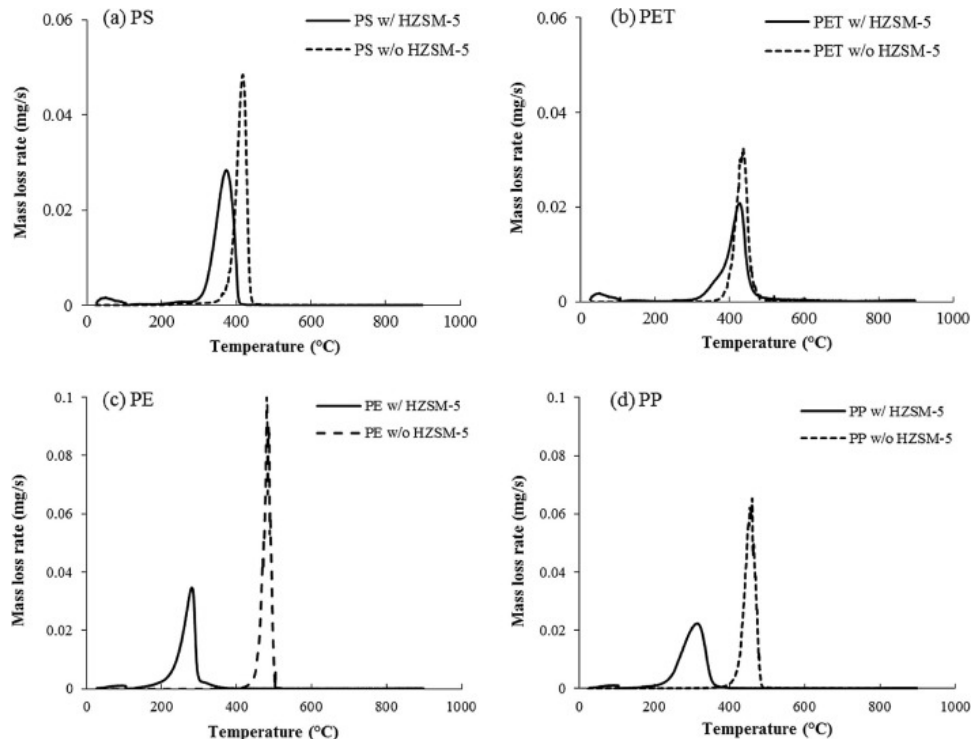
What makes catalytic pyrolysis interesting?

■ Benefits

- Lower operating temperature hence lower energy demand
- High product selectivity
- Tuneable products

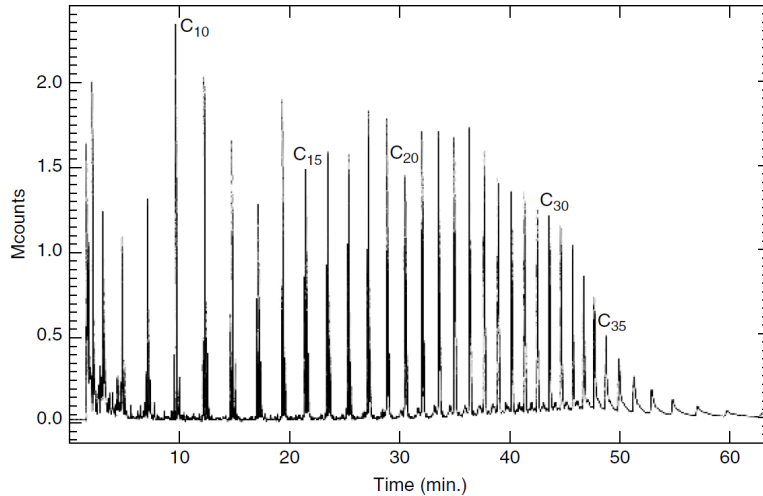
■ Drawbacks

- Coking/poisoning
- Expensive
- Regeneration/replacement required

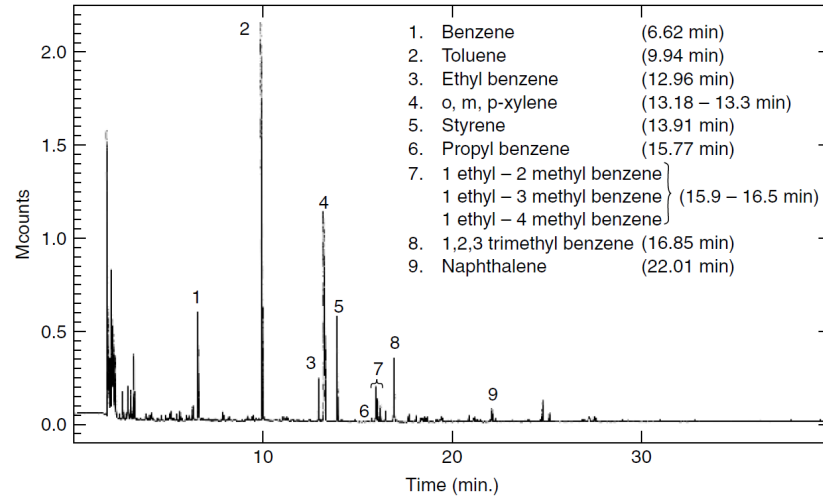


TGA profiles

Thermal vs. catalytic pyrolysis



a



b

GC analysis of the product obtained in the LDPE (a) thermal degradation (b) catalytic degradation over HZSM-5 zeolite

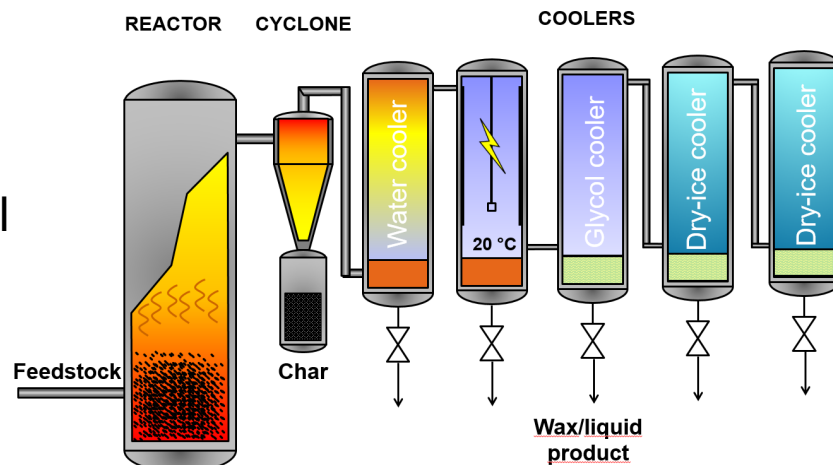
Advantages vs. disadvantages of catalytic cracking

Advantages	Disadvantages
Lowering of the reaction temperature, decrease in energy consumption	Catalysts need regeneration/replacement.
Reaction proceeds faster, bringing about shorter residence times and lower reactor volumes.	Acid solid catalysts can be deactivated by coke deposition and by the occurrence of different cross-linking reactions favoured by the presence of some plastics
Selectivity may be tailored towards different valuable products by a judicious choice of both the catalyst and process conditions in the case of polyolefins, the products derived from the catalytic cracking contain mainly cyclic, branched and aromatic hydrocarbons, which increase the quality of the potential fuels;	The situation is completely different when real polymer wastes are to be degraded. Heteroatoms such as nitrogen, coming from acrylonitrile–butadiene–styrene plastics (ABS) (among other sources), and sulphur, from oils, rubber and some additives, are usually present in plastic wastes, these compounds are known poisons for acid solids catalysts and decrease their activity to a large extent
Inhibition of the formation of undesired products (e.g. chlorinated hydrocarbons), which is a feature especially interesting in the presence of PVC	PVC may cause corrosion problems as well as the formation of toxic chlorine containing compounds

Case examples at VTT

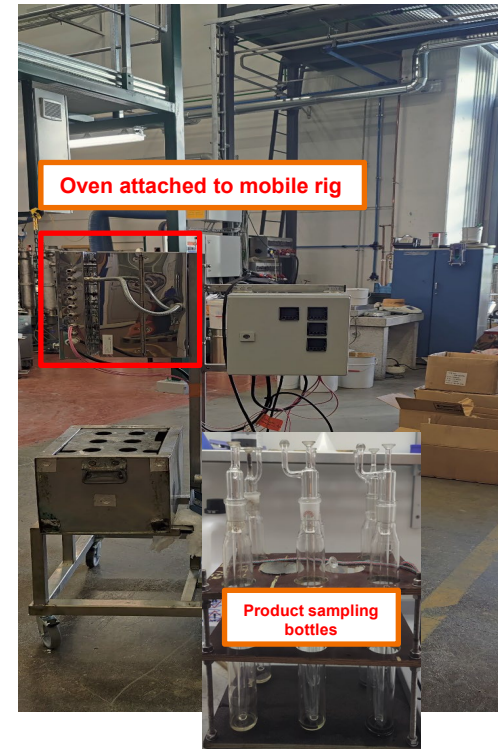
Fast pyrolysis of plastics in bench scale bubbling fluidized bed unit

- Capacity of 1 kg/h
- Temperature up to 650 °C
- Nitrogen or a mixture of steam and nitrogen used to fluidized bed material
- Stage-wise condenstation:
 - Water cooler: 20 °C
 - Electorstatic precipitator: 20 °C
 - Glycol cooler: - 5 °C
 - Dry ice cooler: - 50 °C



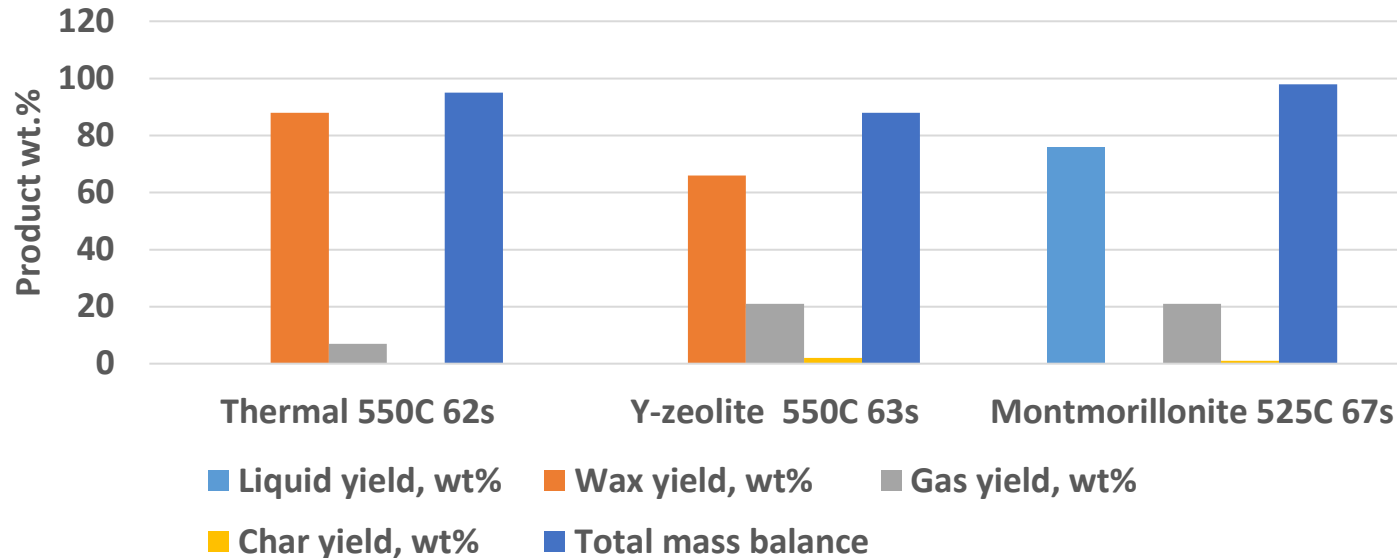
Batch reactor (Lab-scale)

- Batch reactor is heated by an electrical oven that is attached on a mobile rig.
- Batch feeding system uses drop in mechanism of raw materials inside the reactor.
- The rig can be extended to attach another oven and use both batch reactor and a cracking reactor in sequence.

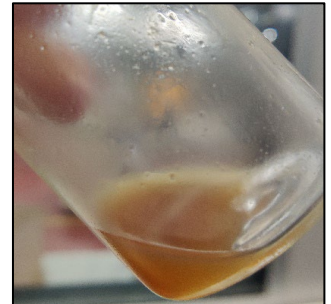
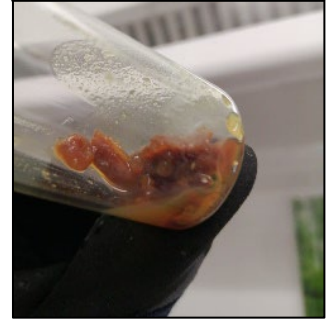


Tuning the product slate

Pyrolysis in a fixed bed reactor (HDPE: LDPE:PP:PS
29:35:22:14)



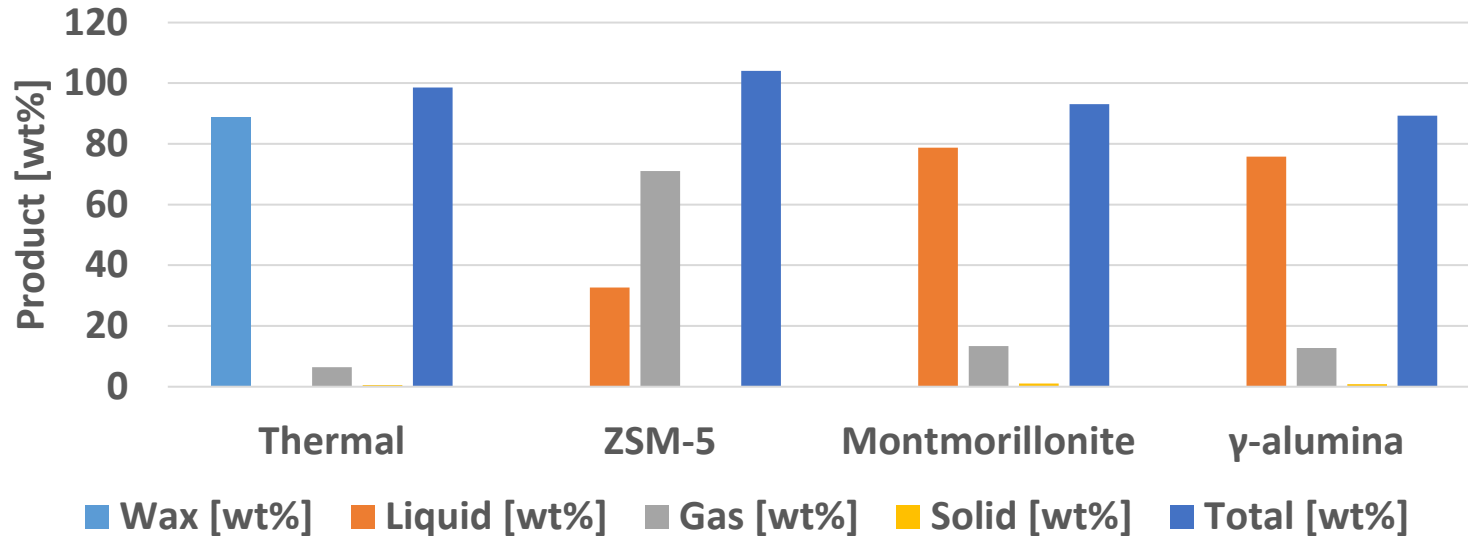
Y-zeolite waxy
product



Montmorillonite
liquid

Comparison of catalyst types

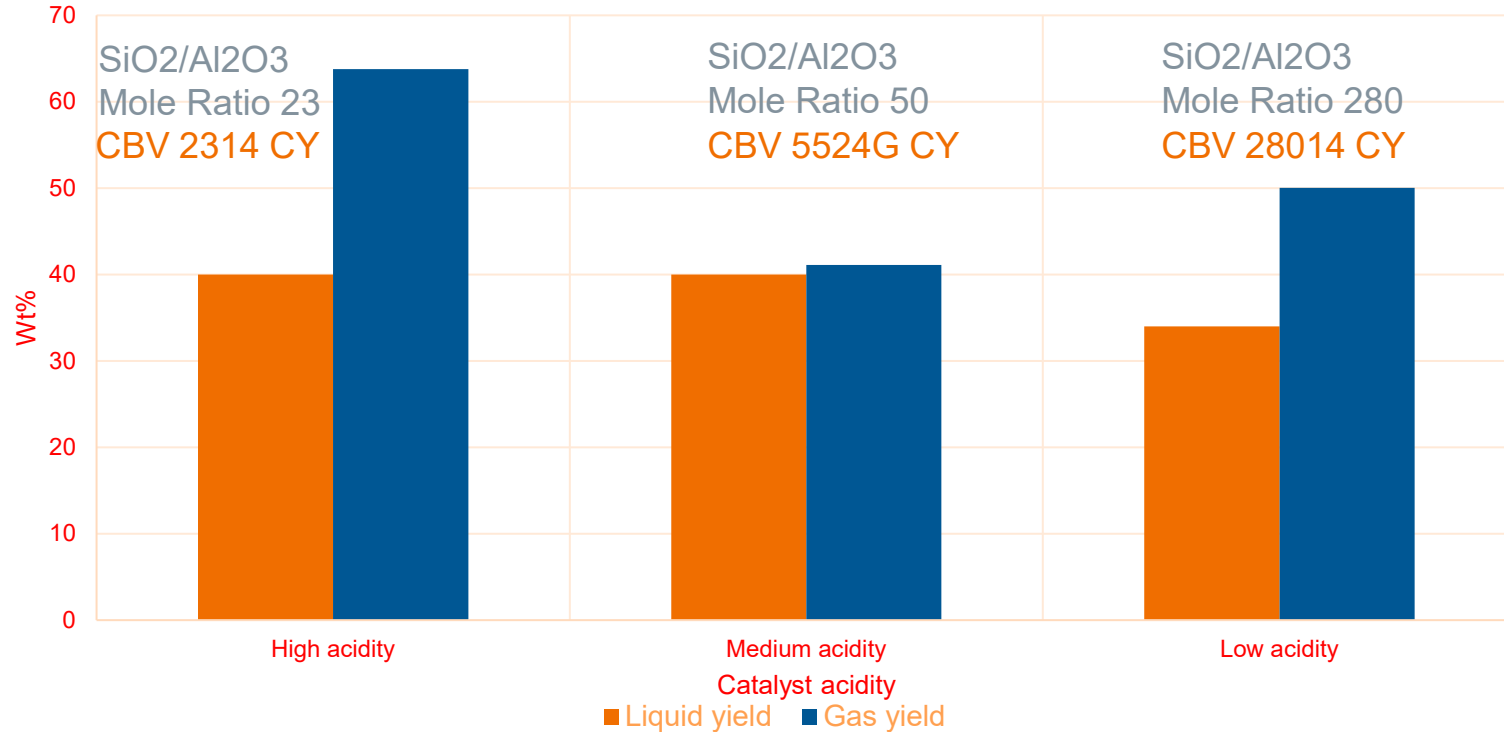
Fixed bed batch pyrolysis at 525 C RT 1min C/F 1:1
HDPE: LDPE:PP:PS 29:35:22:14



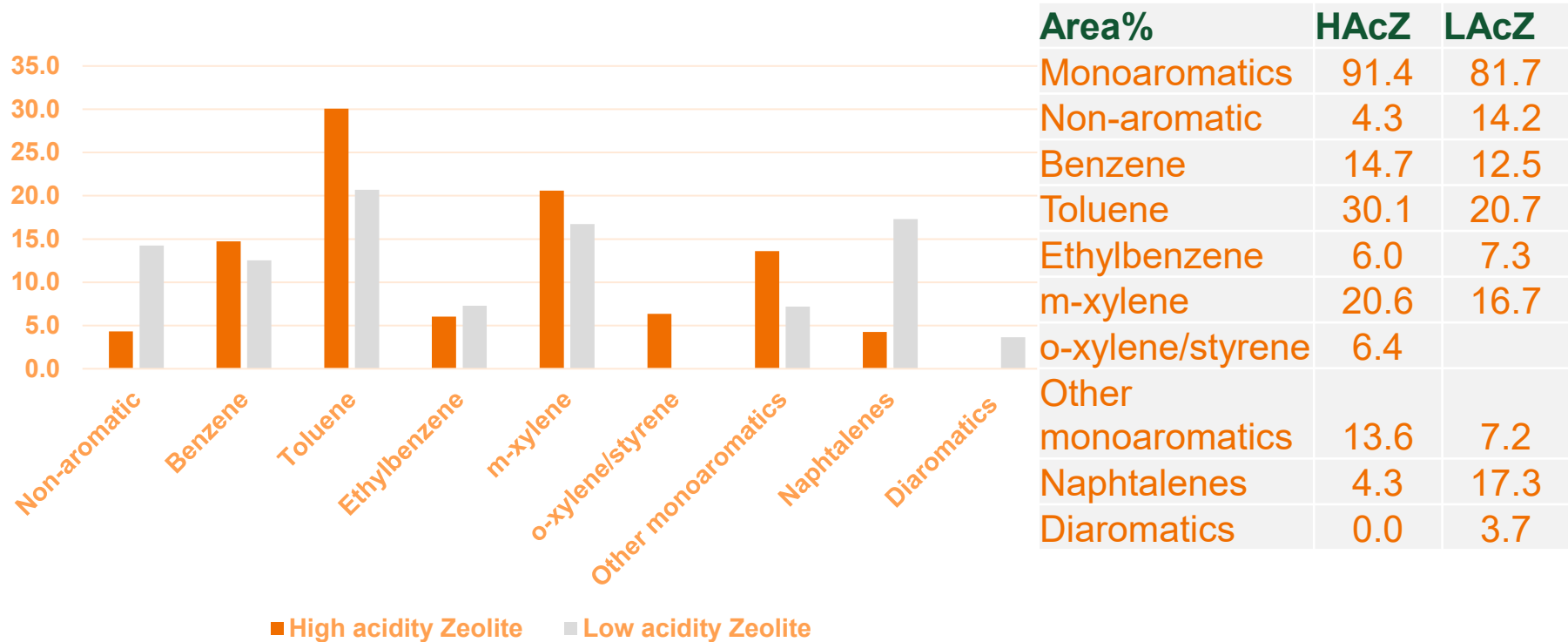
Plastic to Chemicals with catalysts

Effect of zeolite catalyst acidity, comparison at T 550 C

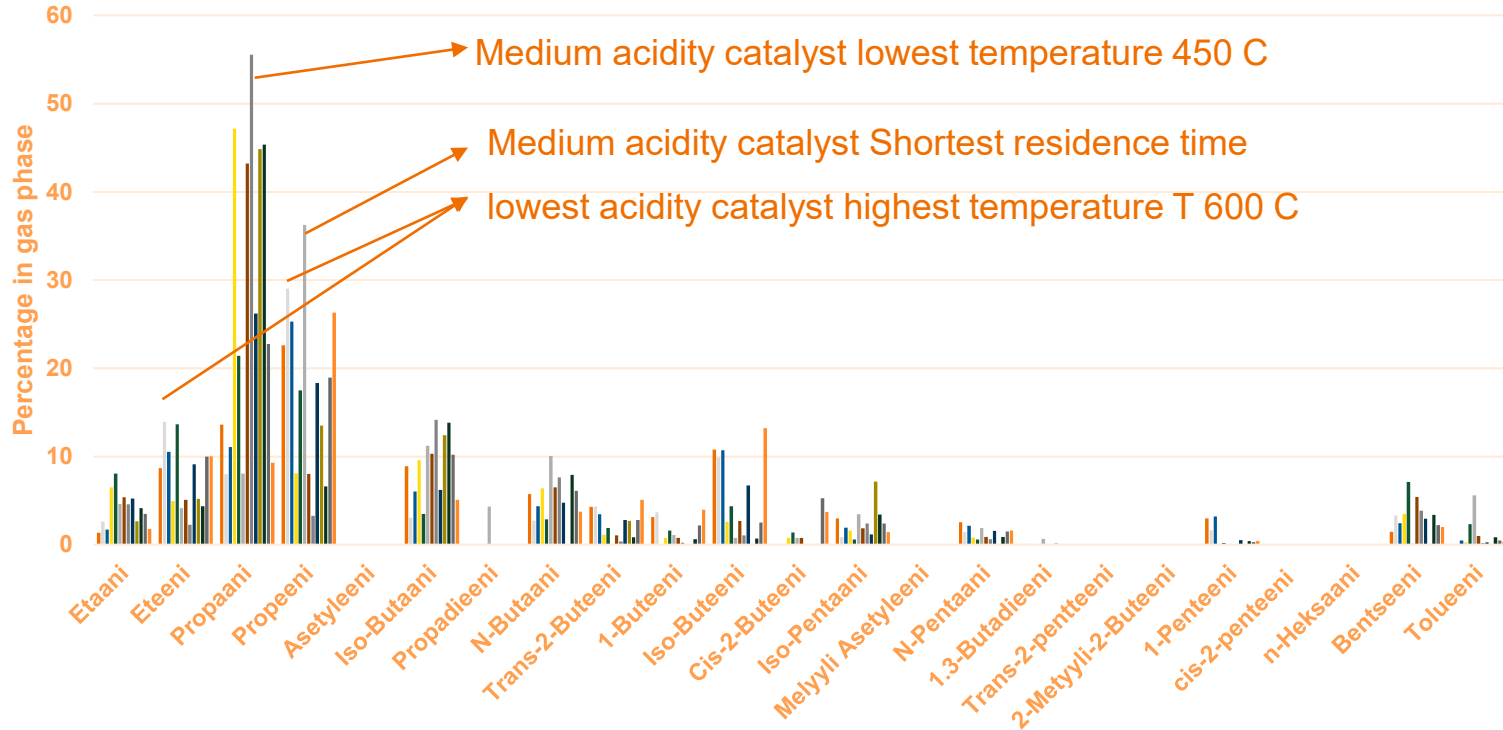
Feedstock (5g) HDPE:LDPE:PP:PS (1.45:1.75:1.1:0.7)



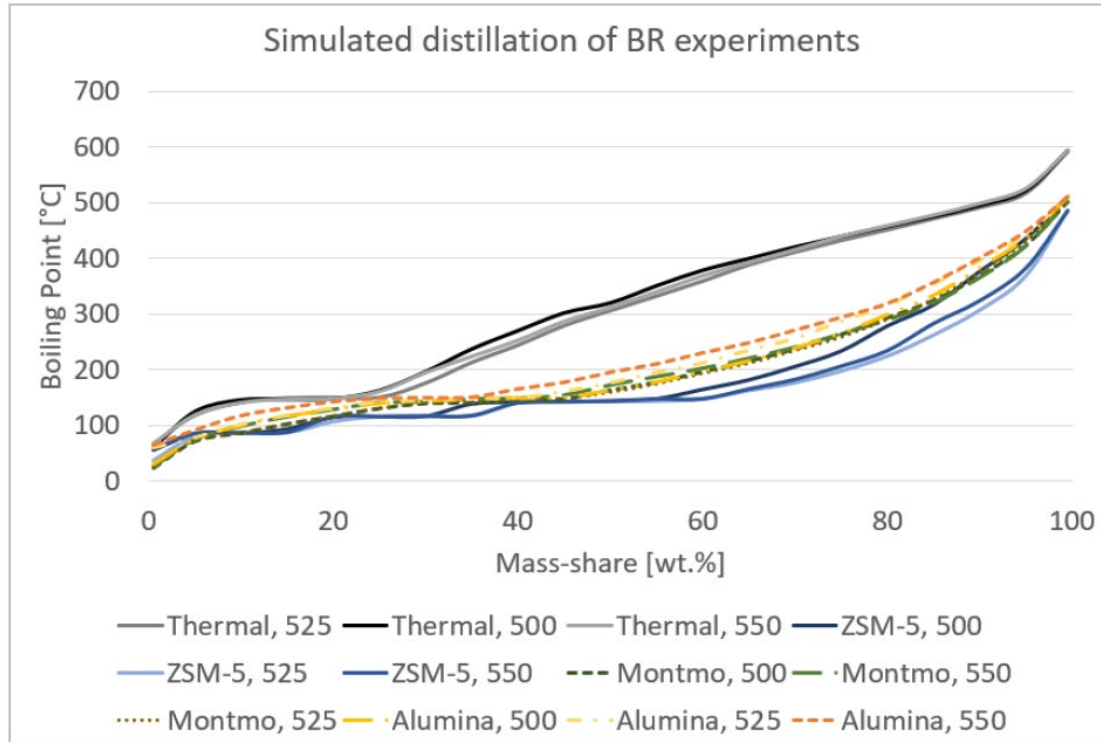
Recovery of highly valuable chemicals



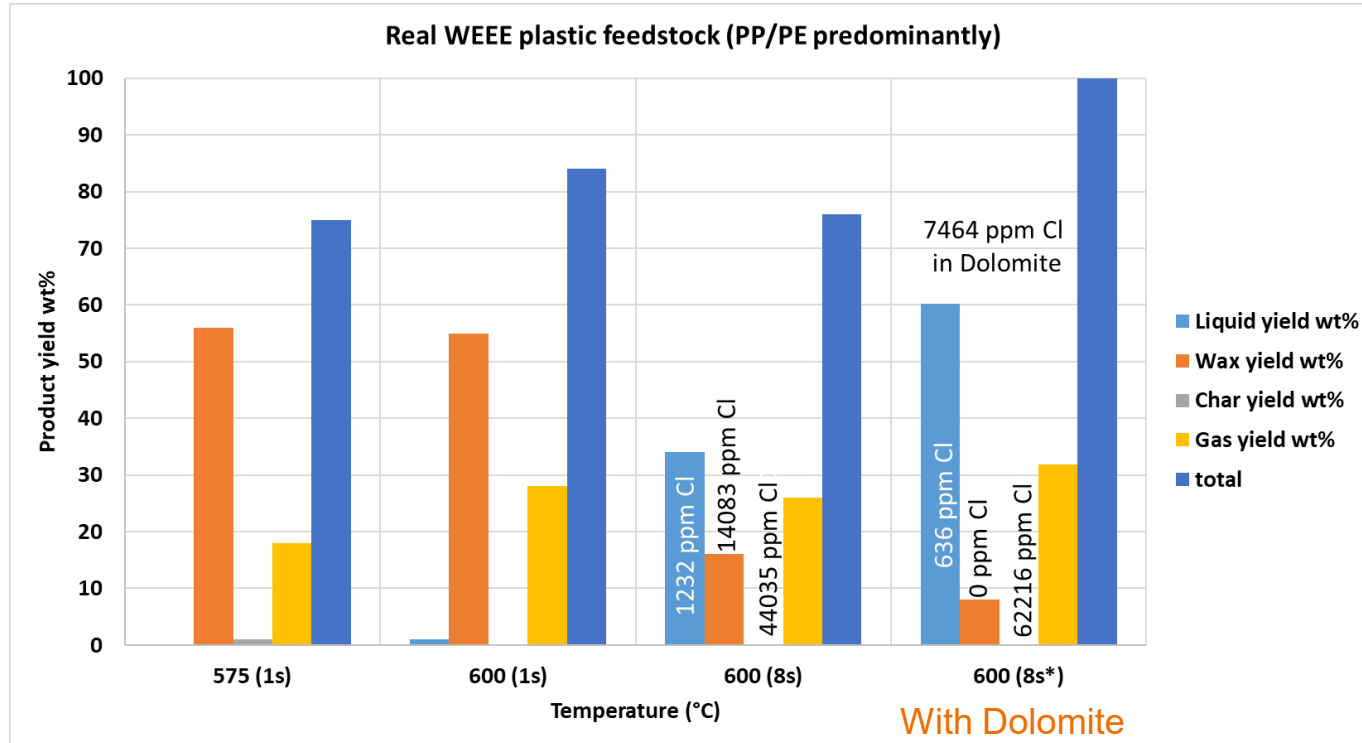
Highly olefinic gas



Boiling point distribution

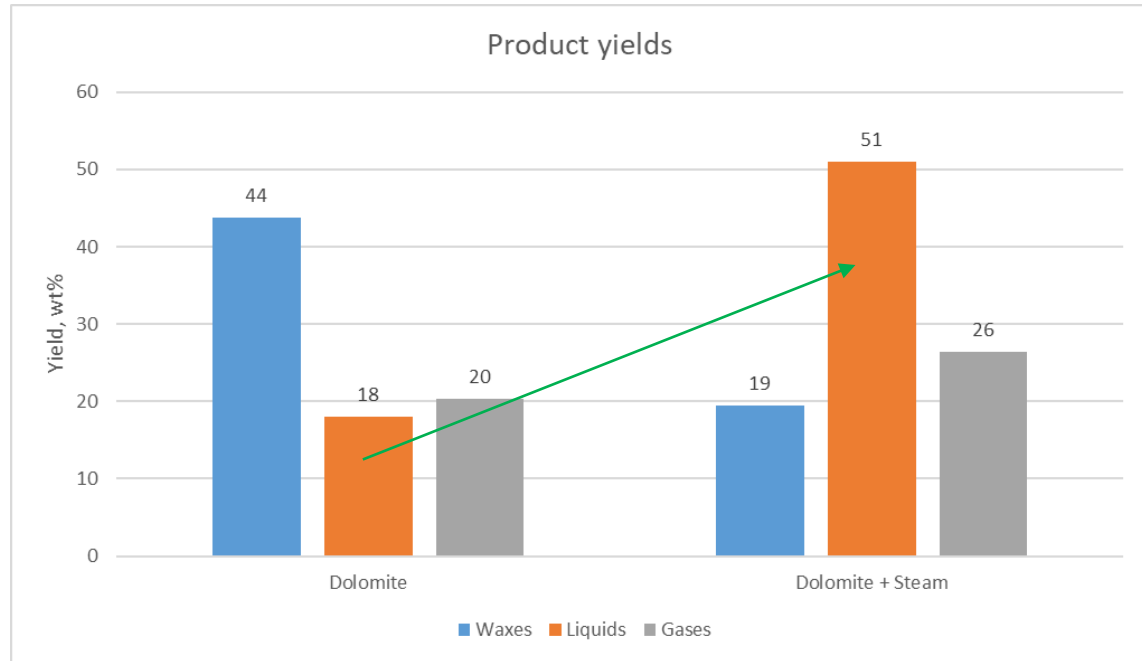


Decontaminating hazardous plastics



Products from catalytic pyrolysis with dolomite

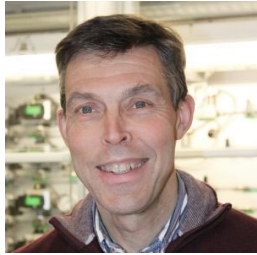
- With dolomite. large increase in the liquid yield was observed with steam addition.
- Addition of steam promotes cracking reactions.



Conclusions

- Pyrolysis process imparts flexibility both towards feedstock and required products.
- The use of a right catalyst enables tuning the pyrolysis oil towards fuels, chemicals and monomers.
- The mode of catalysis (in-situ vs. ex-situ) has an impact on the product and catalyst recovery.
- From the economical point of view, only cheap and robust catalysts can have the place in waste management sector.
- Catalysts are easily poisoned by impurities in plastic waste, therefore long term trials are necessary to validate the extended efficiency.
- Downstream processing of the pyrolysis oil also requires the use of a suitable catalyst.

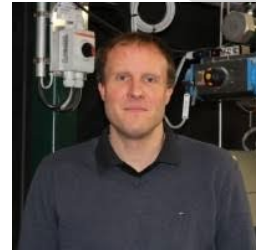
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References

- Image used in the content slide from <https://www.advancedsciencenews.com/global-alliance-to-end-plastic-waste/>
- Slide 2 <https://www.foodnavigator.com/Article/2019/01/24/Waste-experts-gather-in-Davos-There-is-no-silver-bullet-to-the-world-s-plastic-pollution-problem>
- <https://www.globalcitizen.org/en/content/plastic-pollution-facts/>
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the obvious

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