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CPERI
Chemical
Process and
Energy
Resources
Institute

Catalytic pyrolysis technologies for the production of fuels from renewable and waste feedstocks

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“Innovations in Advanced Biofuels Production” workshop

Petten, 18 May 2022

Introduction to CERTH

CPERI
Chemical Process and Energy Resources Institute

The national **Centre for Research and Technology-Hellas** (**CERTH**), was established in Thessaloniki in March 2000.

- Non-profit research organization
- Reports to the **General Secretariat of Research and Technology** (GSRT) of the **Ministry of Development and Investments**.

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- INAB – Institute of Applied Biosciences
- iBO (Institute for Bio-Economy and Agri-Technology) – Institute for Bio-Economy and Agri-Technology
- iti – Information Technologies Institute
- Hellenic Institute of Transport (HIT)
- CPERI – Chemical Process and Energy Resources Institute

Introduction to CPERI-LEFH

Chemical Process and Energy Resources Institute (CPERI)

Seven laboratories within CPERI:

1. **Laboratory of Environmental Fuels and Hydrocarbons (LEFH)**
   (Environmental Fuels-Biofuels and Hydrocarbons, Catalytic Processes)
2. Polymer Production Processes
3. Natural Resources Utilization
4. Environmental Processes
5. Advanced Materials and Nanotechnologies
6. Aerosol and Particle Technology
7. Electrochemical Processes

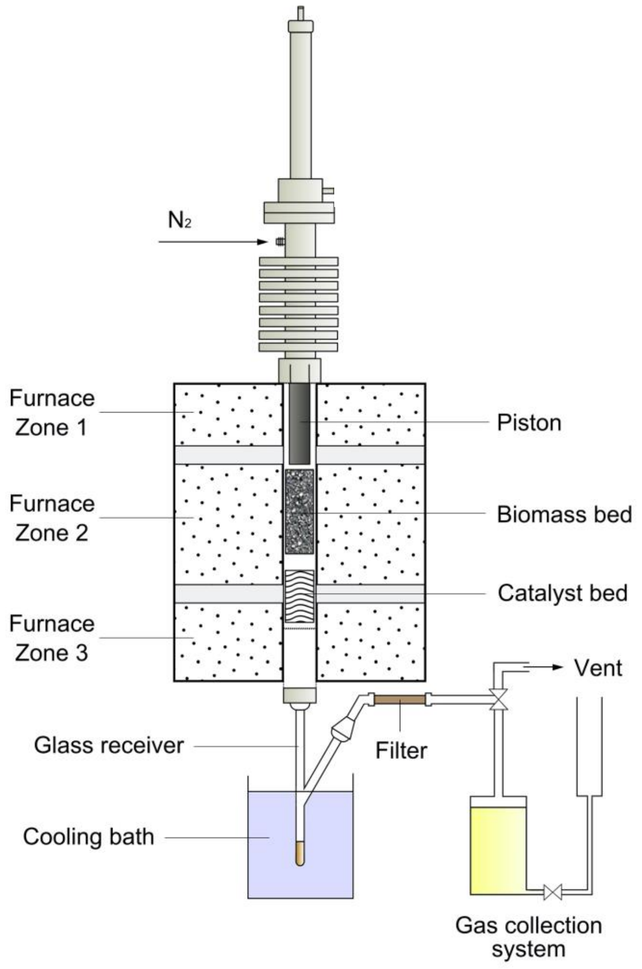
Laboratory of Environmental Fuels and Hydrocarbons (LEFH)

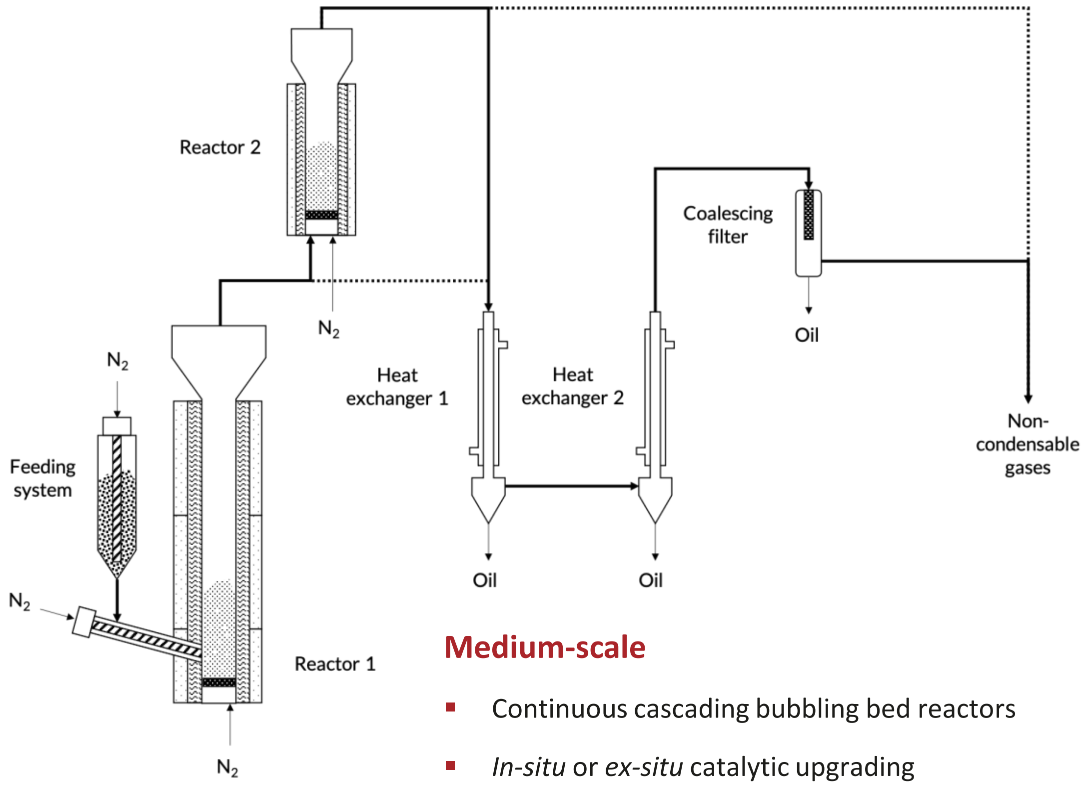
- Catalytic reaction engineering lab, carrying out research in:
  - Refining technologies
  - New conventional fuels
  - Biofuels
  - New catalytic materials
  - Environmental catalytic processes like DeSOx, DeNOx from flue gases
- Technical support to petroleum industry
- Focus on various processes and especially on
  - Fluid Catalytic Cracking (FCC)
  - Hydrodesulfurisation (HDS)
  - Isomerization
  - Alkylation
  - Pyrolysis
  - Bio-fuel Upgrading
  - Selective Catalytic Reduction (SCR)

Facilities – Bench- and medium-scale

Bench-scale

- Batch, fixed bed reactor
- Pyrolysis & catalytic upgrading temperatures:
  - Up to 650 °C
- Typically, 3 g feed/batch
- Typically, up to 8 g catalyst
- Measurement and collection of all pyrolysis products
- Full mass balance calculation
  - Typically, 91-95%
- Ideal for catalyst pre-screening





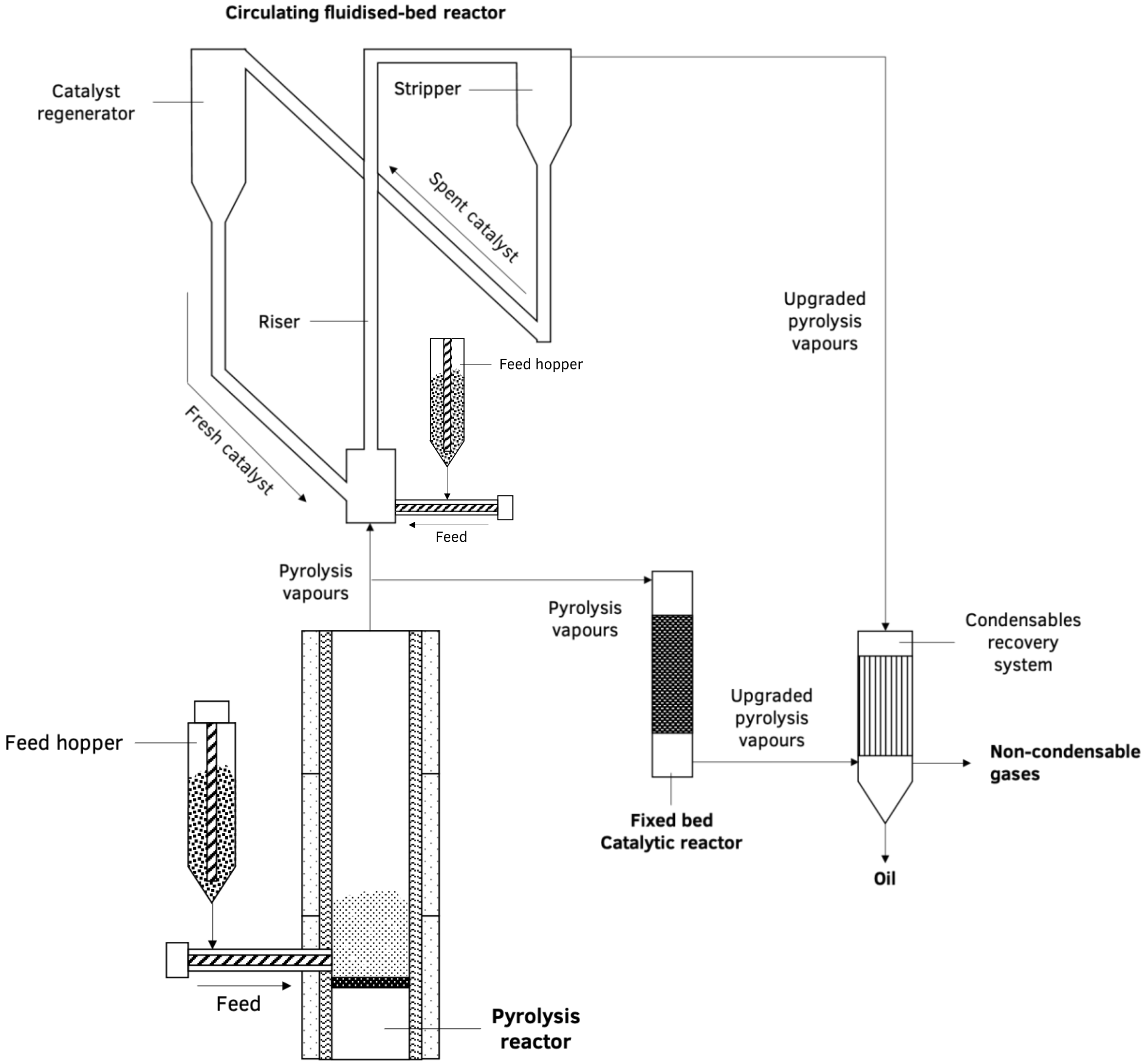
Medium-scale

- Continuous cascading bubbling bed reactors
- *In-situ* or *ex-situ* catalytic upgrading
- Independent temperature control
  - Reactor 1 up to 700 ºC
  - Reactor 2 up to 600 °C
- 300 g/h feed rate
- Up to 150 g catalyst capacity
- Collection of all pyrolysis products, 92-95% typical mass balance

Facilities – Pilot-scale

Pilot-scale

- Modular setup, *in-situ* or *ex-situ* catalytic upgrading
  - *In-situ*: pyrolysis and upgrading in circulating fluidised bed reactor OR in bubbling bed reactor
  - *Ex-situ*: pyrolysis in a bubbling bed reactor connected to a circulating fluidised bed OR a fixed bed reactor for catalytic upgrading
- >10 kg catalyst inventory for circulating fluidised bed
- 200-400 g catalyst for fixed bed reactor
- 1 kg/h feed rate
- Pyrolysis and catalytic upgrading temperature up to 650 °C
- Collection of all pyrolysis products, typically 92-95% mass balance



Facilities - Analytical

Fuel and Biofuel characterisation

- C, H, N, S elemental analysis
- GC-FID/TCD
- GC-MS
- GCxGC-ToFMS
- HPLC
- Ion chromatography for sugar analysis
- FTIR
- XRF

Catalyst characterisation

- N_2 physisorption methods
- XRD
- TPR/TPD/TPO
- ICP
- SEM microanalysis
- TEM
- TGA-MS
- FTIR for catalyst acidity
- Particle size analysis
- ABD
- Attrition resistance
- Grinding/Sieving

Feedstock experience

Biomass

- Clean wood (beech, pine, oak)
- Agricultural, forestry and animal residues
  - Wheat straw, barley straw[1]
  - Olive mill byproducts[2]
  - Poultry waste[3], etc
- Energy crops
  - Miscanthus, eucalyptus[1]
- Lignin[4]

Wastes

- Refuse Derived Fuel (RDF)
- Solid Recovered Fuel (SRF)
- Plastics
  - LDPE, HDPE, PP, polycarbonate, polystyrene, brominated WEEE)[5,6]
- End-of-life tyres

Feedstock pre-treatment

- Removal of inorganics in biomass by water and acid leaching[1]
  - Maximisation of liquid yield and anhydrosugar selectivity
- Acid-free organosolv pre-treatment for fractionation
  - Production of cellulose rich pulp, hemicellulose sugars, lignin[7]

[1] Stefanidis, S.D. et al. *Biomass and Bioenergy* **83**, 105–115 (2015).
[2] Christoforou, E.A. et al. *Waste and Biomass Valorization* **9**, 301–313 (2017).
[3] Kantarli, I.C. et al. *Waste Management and Research* **37**, 157–167 (2018).
[4] Kalogiannis, K.G. et al. *Journal of Analytical and Applied Pyrolysis* **115**, 410–418 (2015).
[5] Antonakou, E.V. et al. *Waste Management* **34**, 2487–2493 (2014).
[6] Charitopoulou, M.A. et al. *Sustainable Chemistry and Pharmacy* **26**, 100612 (2022).
[7] Kalogiannis, K. G. et al. *Bioresource Technology* **313**, 123599 (2020).

Catalyst experience

- **Commercial catalysts**
  - FCC catalysts, ZSM-5 additives[1]
  - Acidic zeolites (Y, ZSM-5, Beta, Mordenite)[2,3]
  - Metal oxides (alumina, silica-alumina, zirconia, titania)[2]
- **Low-cost catalysts**
  - Natural zeolites
  - MgO from natural magnesite[4]
- **Laboratory-synthesized catalysts**
  - Metal-promoted zeolites[5]
  - Mesoporous aluminosilicates (MCM-41, SBA-15, MSU)[6,7]
  - Nano-sized zeolites[8]
  - Hierarchical zeolites[8]
  - Hydrotalcites
  - Metal oxides, mixed metal oxides

Catalyst deactivation experience

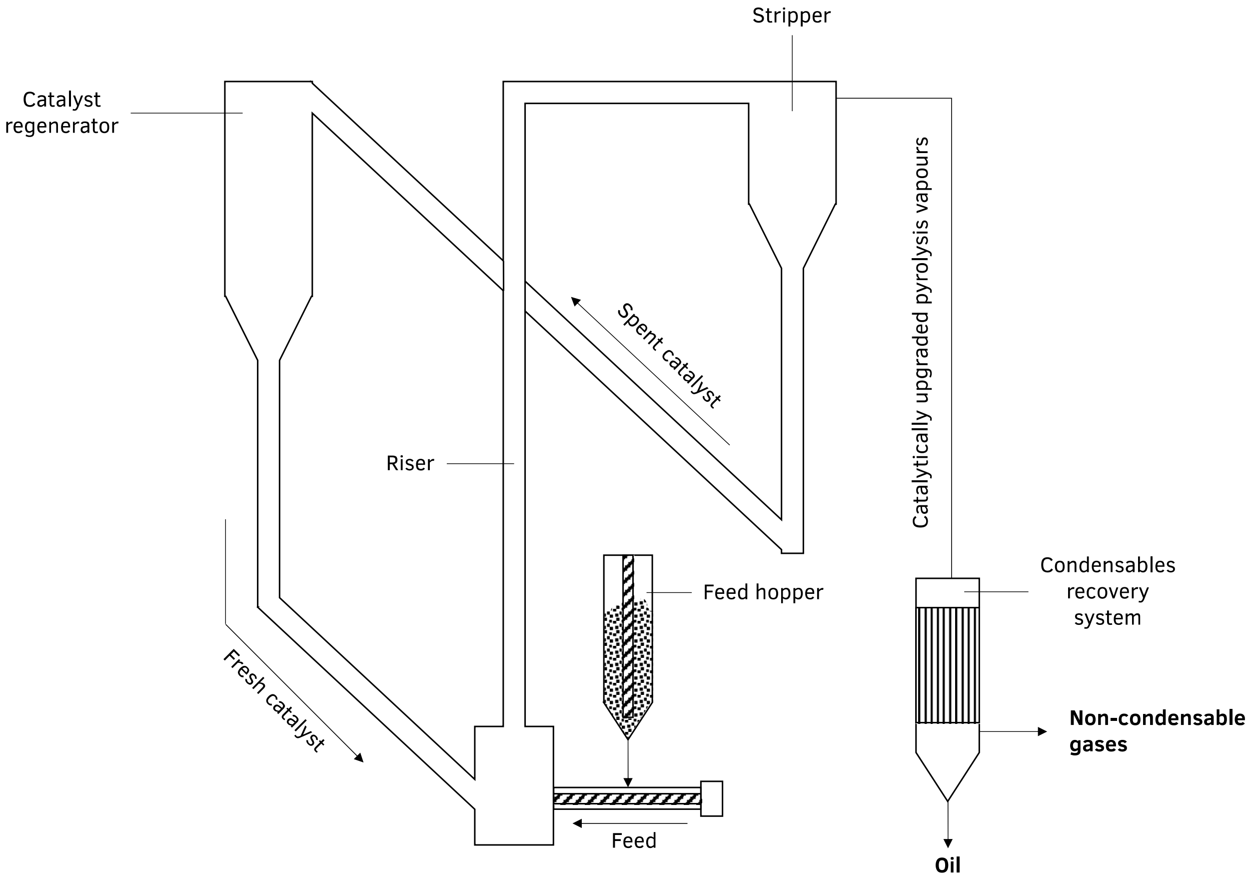
- Hydrothermal deactivation[9]
- Catalyst poisoning from biomass metals during in-situ and ex-situ catalytic pyrolysis[9,10]
- Accelerated deactivation

[1] Lappas, A. A. et al. *Fuel* **81**, 2087–2095 (2002).
[2] Stefanidis, S. D. et al. *Bioresource Technology* **102**, 8261–8267 (2011).
[3] Stefanidis, S. et al. *Green Chemistry* **15**, 1647–1658 (2013).
[4] Stefanidis, S. D. et al. *Applied Catalysis B-Environmental* **196**, 155–173 (2016).
[5] Iliopoulou, E. F. et al. *Green Chemistry* **16**, 662–674 (2014).
[6] Antonakou, E. et al. *Fuel* **85**, 2202–2212 (2006).
[7] Triantafyllidis, K. S. et al. *Microporous And Mesoporous Materials* **99**, 132–139 (2007).
[8] Hernández-Giménez, A. M. et al. *Chemcatchem* **13**, 1207–1219 (2021).
[9] Stefanidis, S. D. et al. *Catalysis Science & Technology* **6**, 2807–2819 (2016).
[10] Kalogiannis, K. G. et al. *Fuel Processing Technology* **186**, 99–109 (2019).

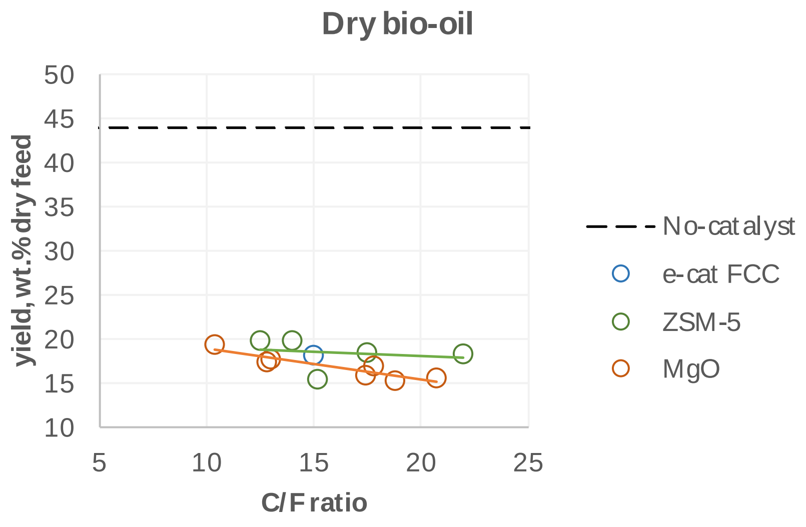
Case study 1: Catalytic pyrolysis of biomass with acidic and basic catalysts

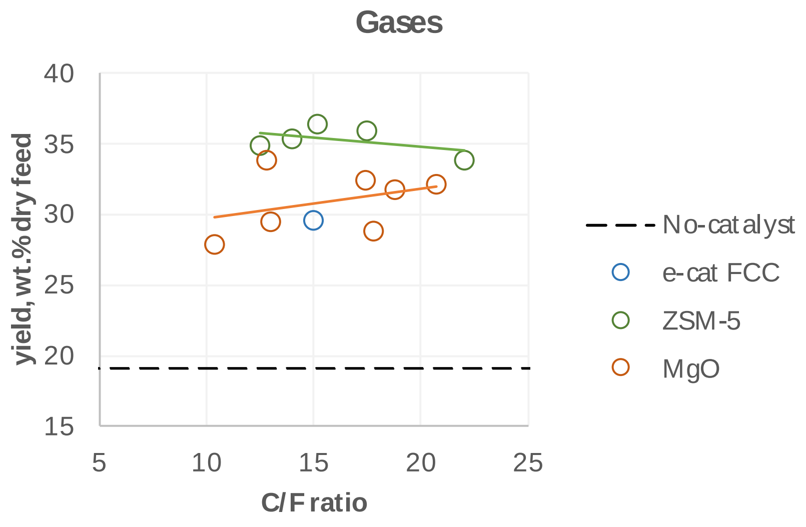
Aim: In-situ deoxygenation of the pyrolysis vapours to produce a bio-oil with reduced oxygen content and improved stability

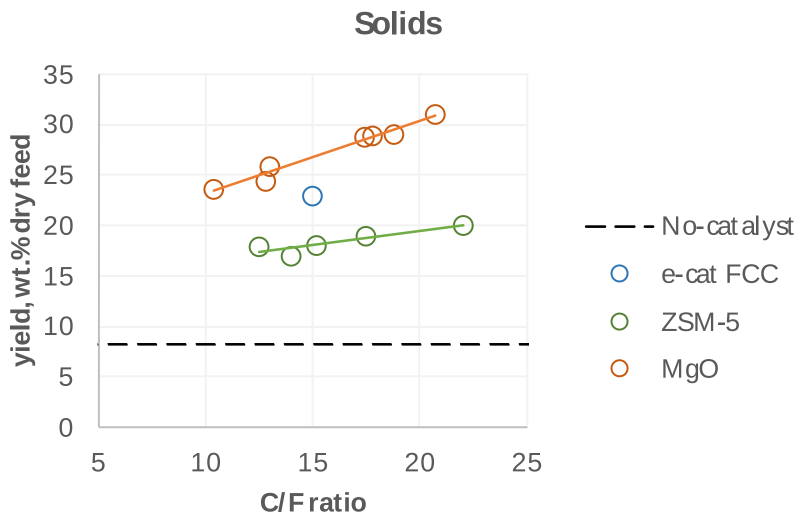
- Feedstock: Lignocel
  (commercial beech wood sawdust)
- Feed rate: 0.6 kg/h
- Pyrolysis & Upgrading temperature: 500 °C
- Catalyst-to-feed ratio: typically, 10-20
- Catalysts:
  - Silica Sand (inert)
  - FCC
  - ZSM-5
  - MgO

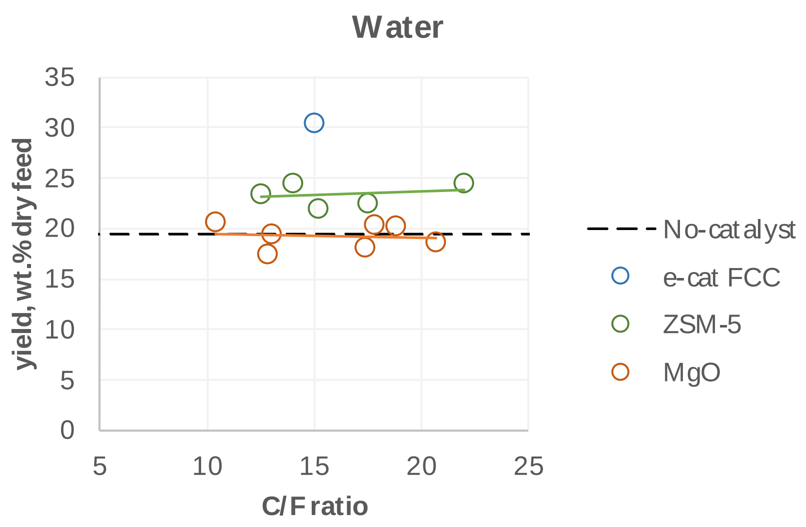


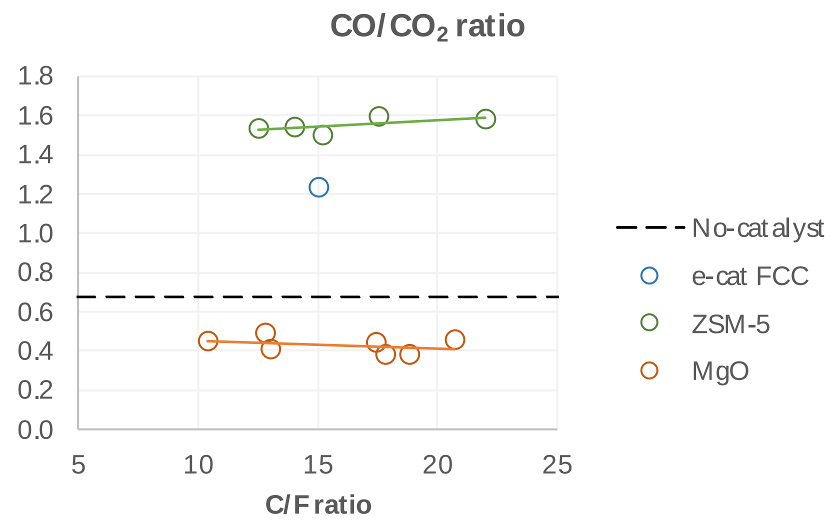
Case study 1: Catalytic pyrolysis of biomass – Effect of different catalysts on product yields



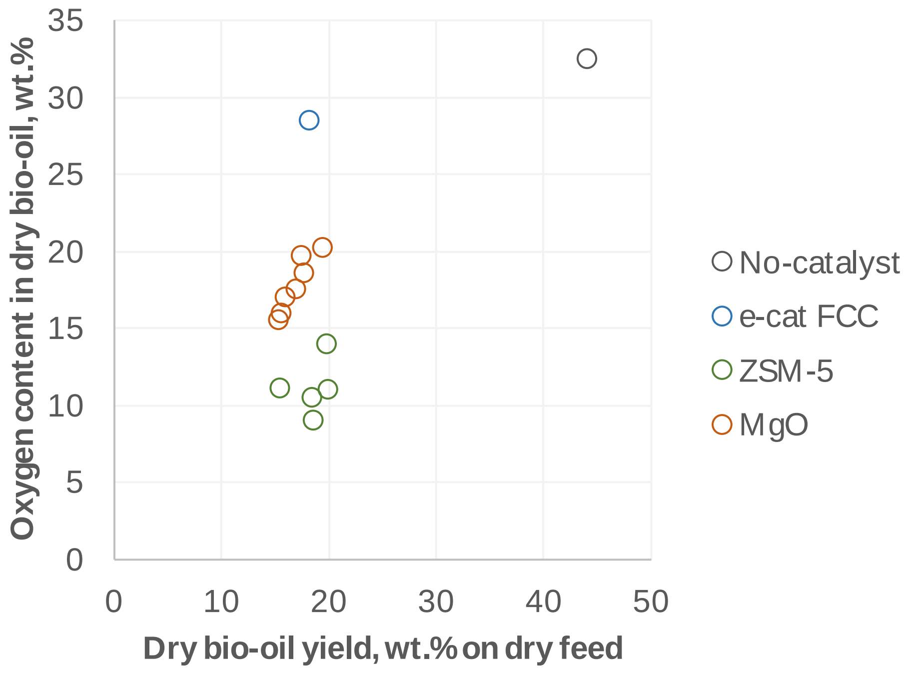








Case study 1: Catalytic pyrolysis of biomass – Effect of different catalysts on the quality of the bio-oil



- Significantly reduced oxygen content compared to non-catalytic pyrolysis
  - Improved stability
- Significant oxygen remains (10-20 wt.%)

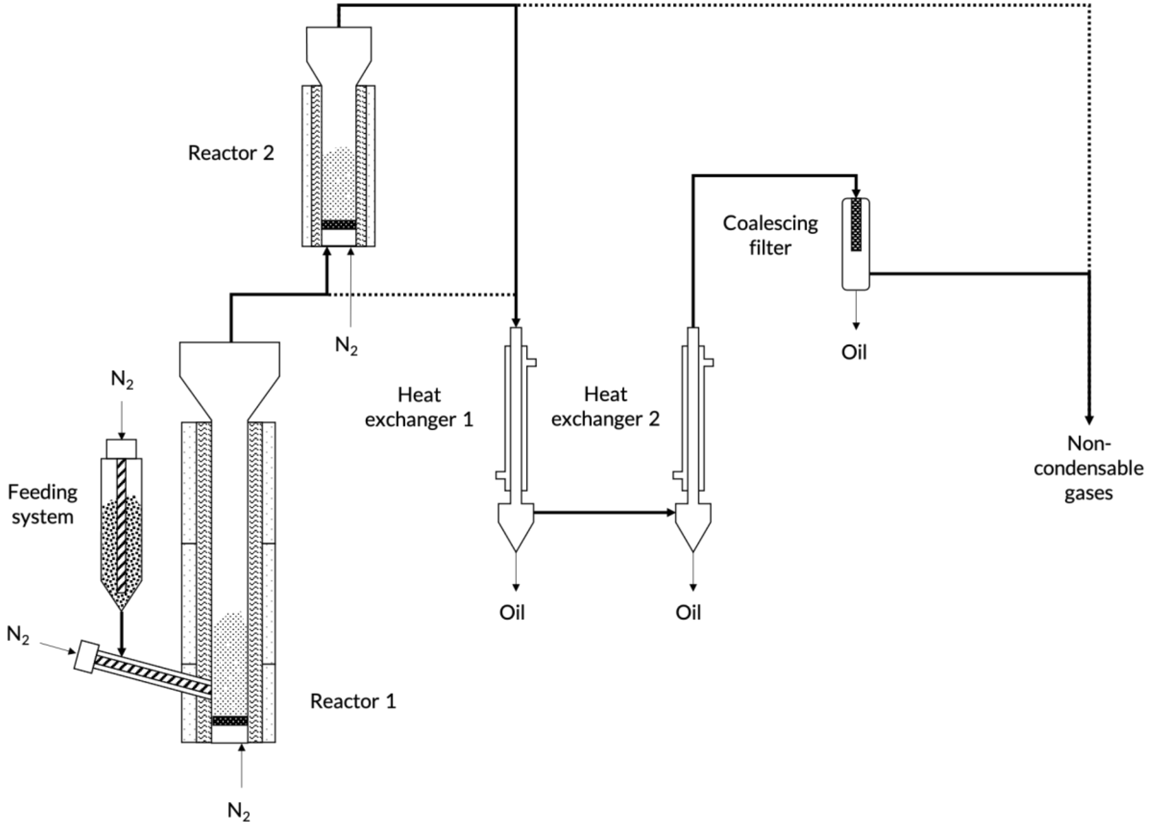
Application of Catalytic Pyrolysis Oils (CPO)

- Improved stability favours co-processing with petroleum feeds in refinery processes
  - Fuel Catalytic Cracking
  - Hydrotreating
  - Utilisation of existing refinery infrastructure
  - Incorporation of renewable carbon in petroleum products
- Upgrading by hydrodeoxygenation
  - Can achieve near complete removal of oxygen

Case study 2: Pyrolysis of end-of-life tyres (ELTs) coupled with catalytic vapour upgrading

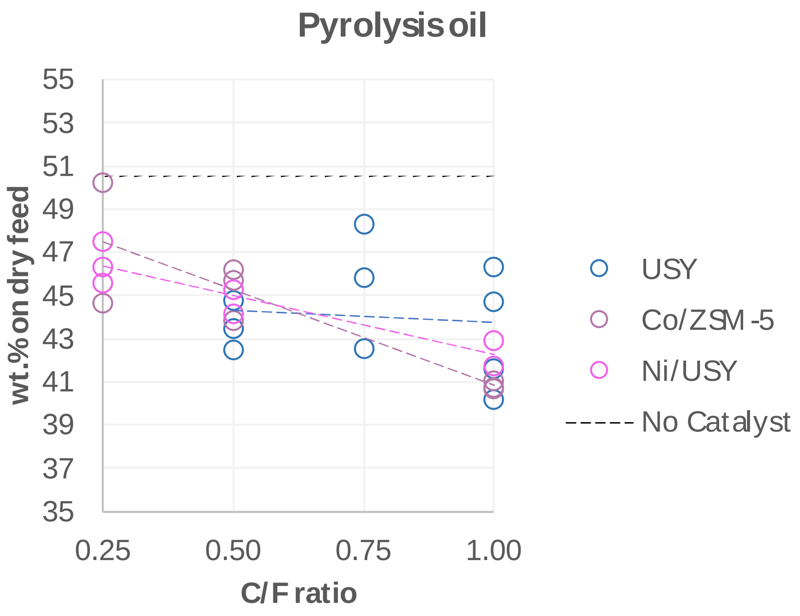
Aim: Produce highly aromatic pyrolysis oils from end-of-life tyres

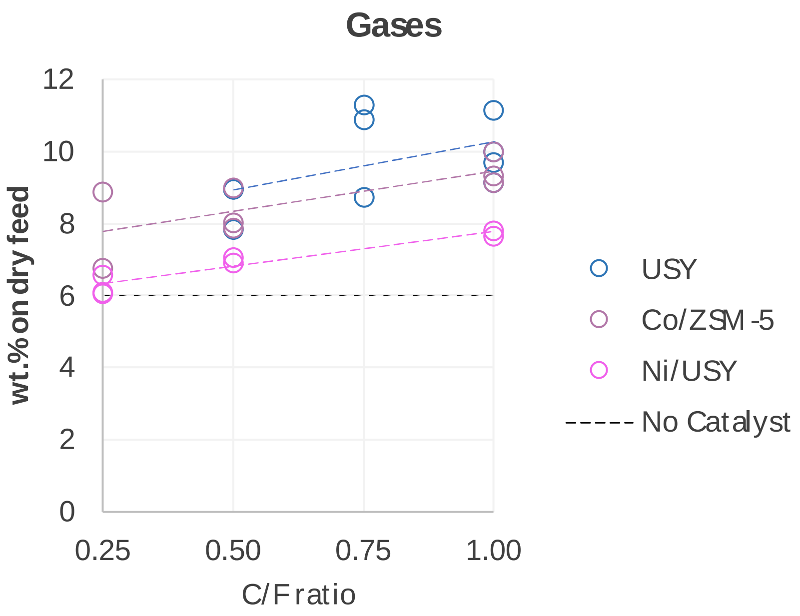
- Continuous medium-scale unit
- Pyrolysis in bubbling-bed reactor (Reactor 1)
  - 500 °C (also, 450-550 ºC for thermal effect)
  - 300 g/h feed rate
- Catalytic upgrading of vapours in bubbling-bed reactor (Reactor 2)
  - 500 °C
  - USY, Ni/USY, Co/ZSM-5 catalysts
  - C/F = 0.25 – 1.00
- Collection of all pyrolysis products

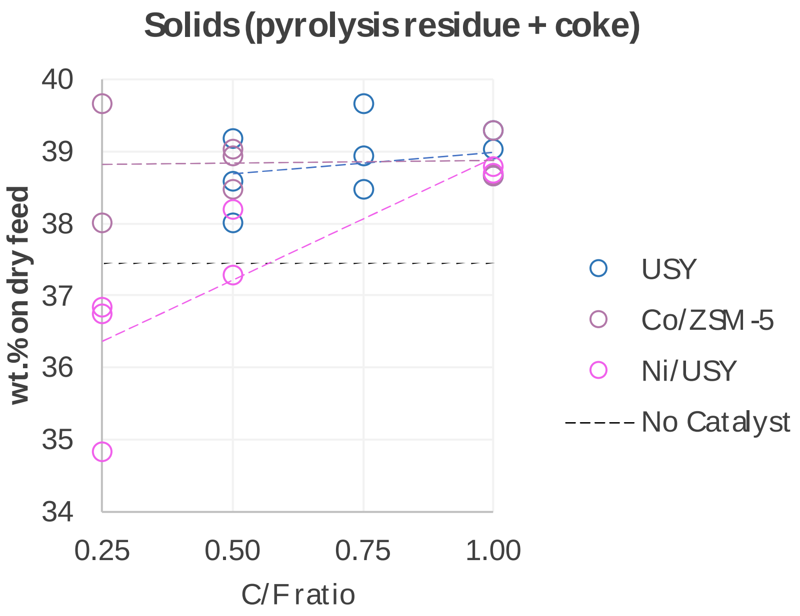


Feedstock	Particle size, µm	Moisture, wt%	Ash, wt%	C, wt%	H, wt%	S, wt%	O, wt%	GHV, MJ/kg
Granules of multi-brand all tyre	200-800	0.5	6.1	81.2	7.7	1.2	3.8	37.5

Case study 2: Pyrolysis of ELTs – Product yields

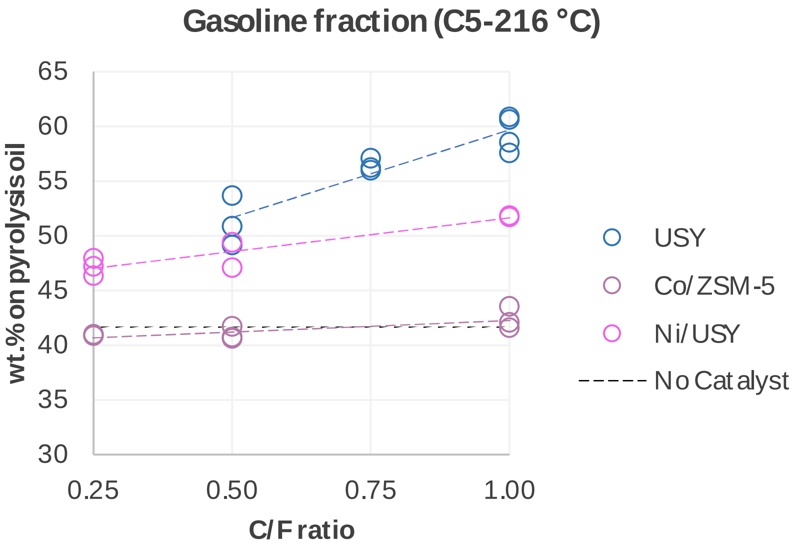


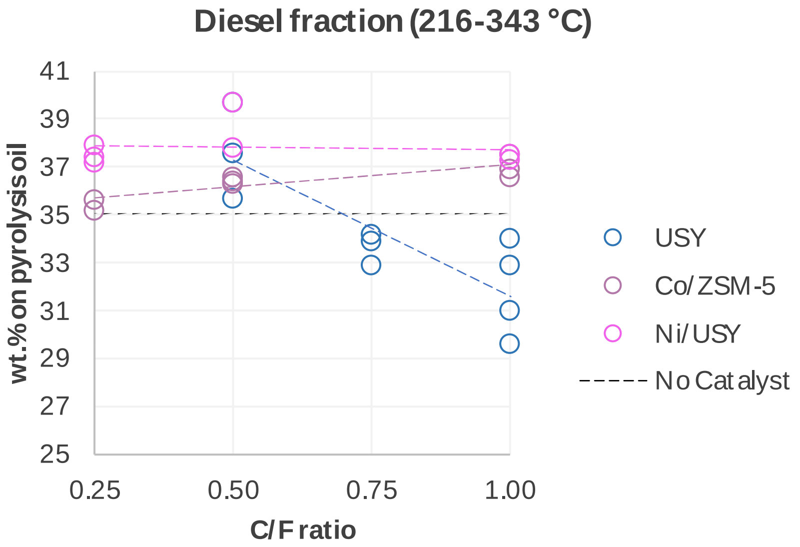


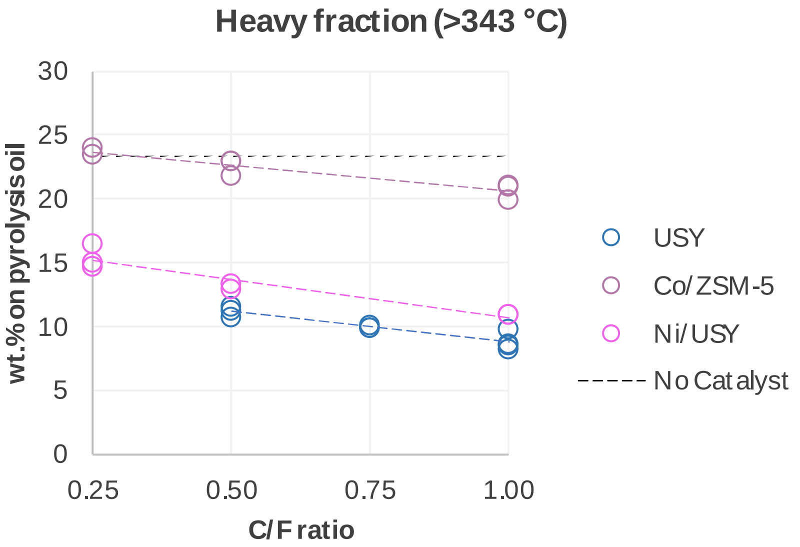


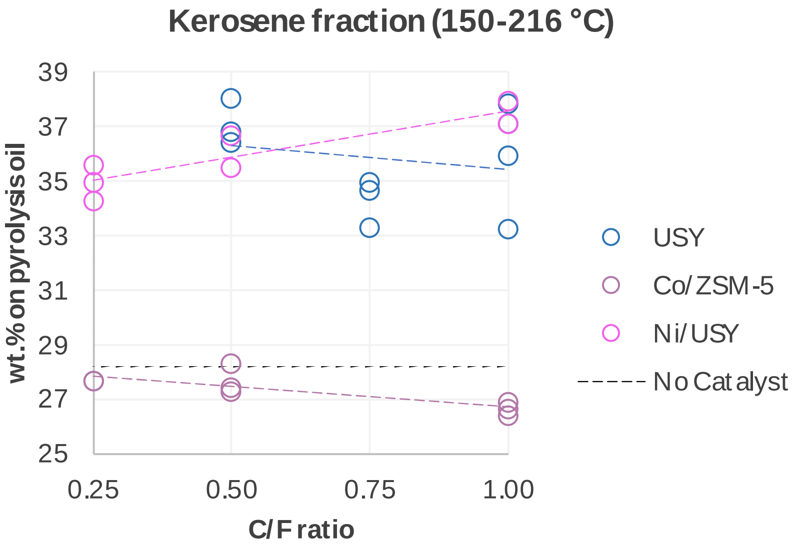
- Thermal pyrolysis yields ~51% liquid product
- Catalytic vapour upgrading moderately reduces oil yield to 40-47% in favour of gases and solids

Pyrolysis of ELTs – Liquid product composition



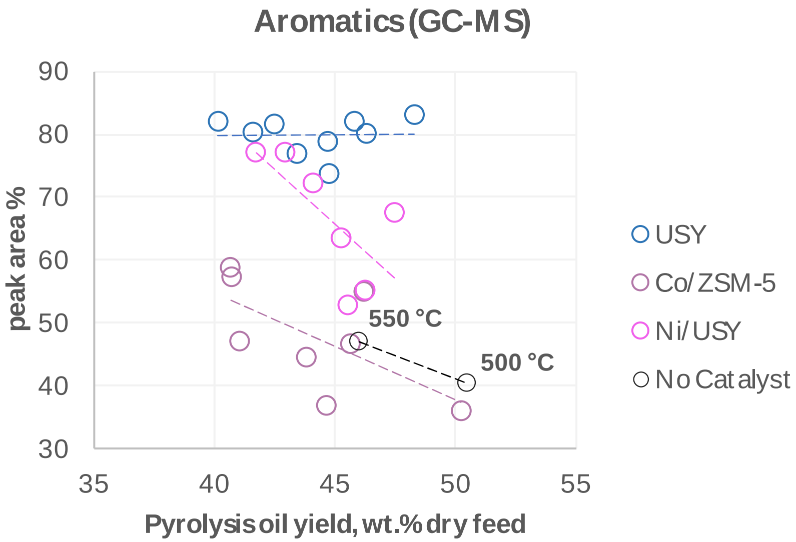


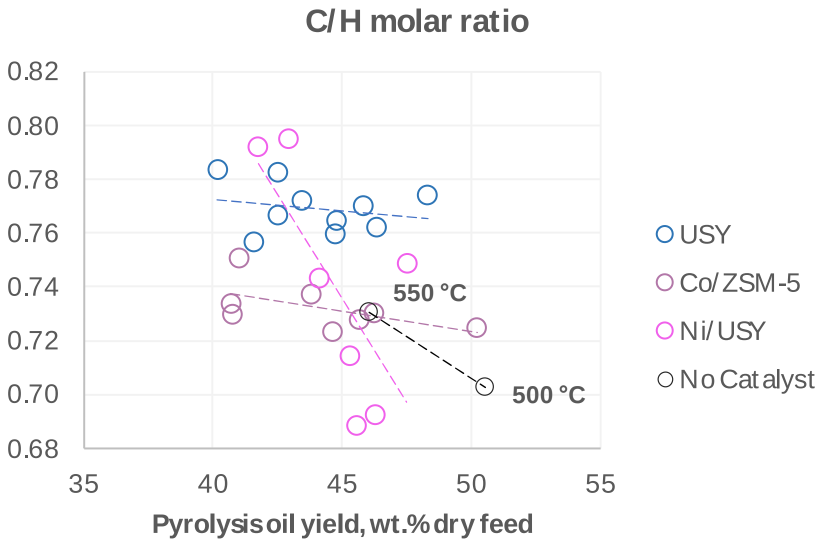


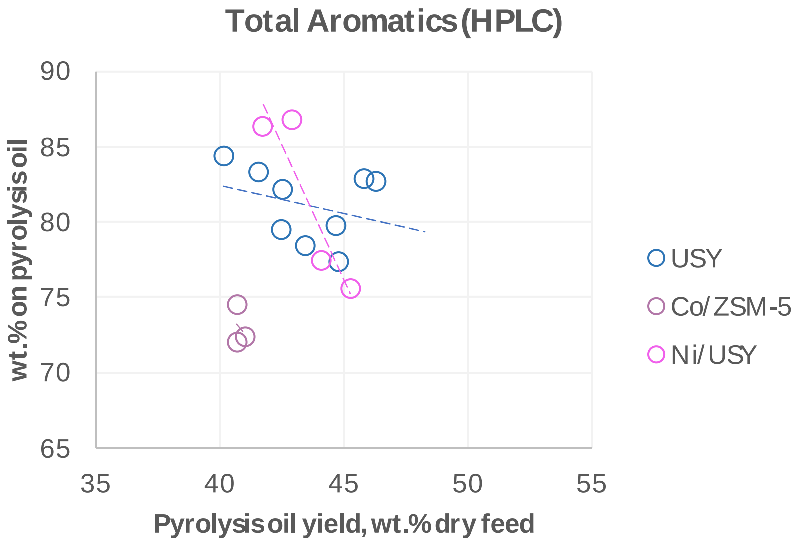


- Thermal pyrolysis oil contains ~25% heavy fraction (>343 °C)
- Catalytic vapour upgrading cracks the heavy fraction to diesel-, gasoline- and kerosene-range components.

Pyrolysis of ELTs – Production of aromatics





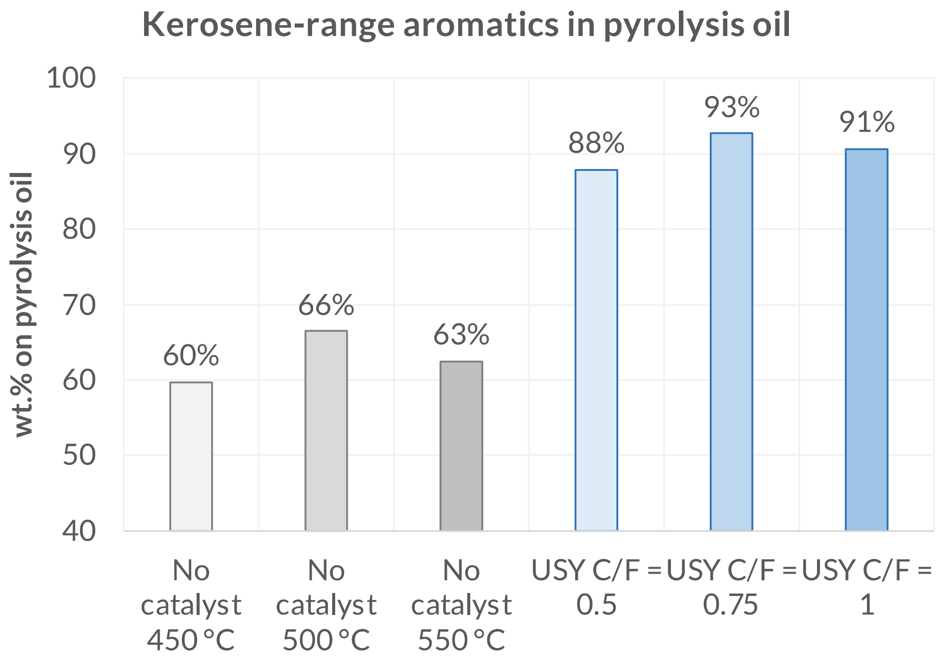


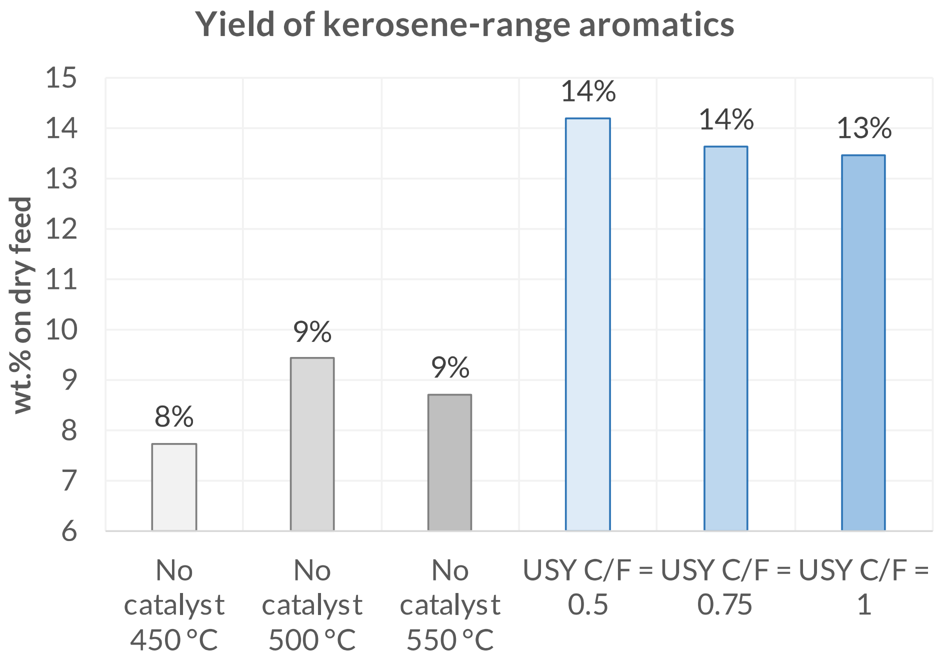
- Catalytic upgrading increased the GC-detectable aromatics in the pyrolysis oil

- Catalytic upgrading increased the C/H ratio of the pyrolysis oil
  - Indicator of overall aromaticity

- Up to 88 wt% aromatics content with 42-43% pyrolysis oil yield achieved

Pyrolysis of ELTs – Effect of catalytic upgrading on the production of kerosene-range aromatics





- Aromatics are key components of aviation fuels, 8-25 vol.%
  - Promote the lubricity of the fuel
  - Ensure elastomeric seal compatibility
  - Push the density to the desired specification range
- Methods for SAF production do not yield aromatics

Thank you for your attention!

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