Pyrolysis of end-of-life tyres coupled with catalytic vapor upgrading

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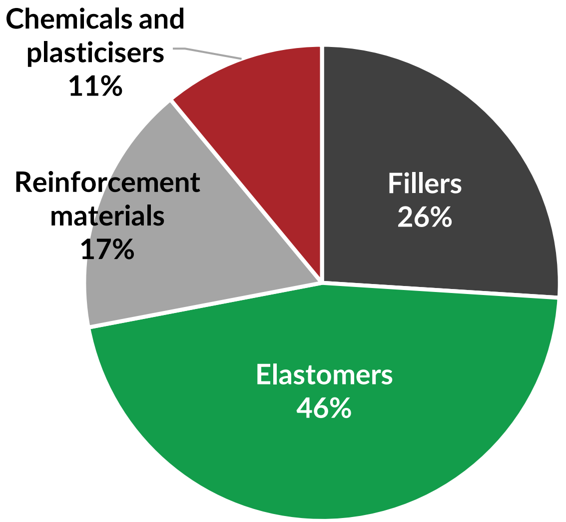
End-of-life tyres

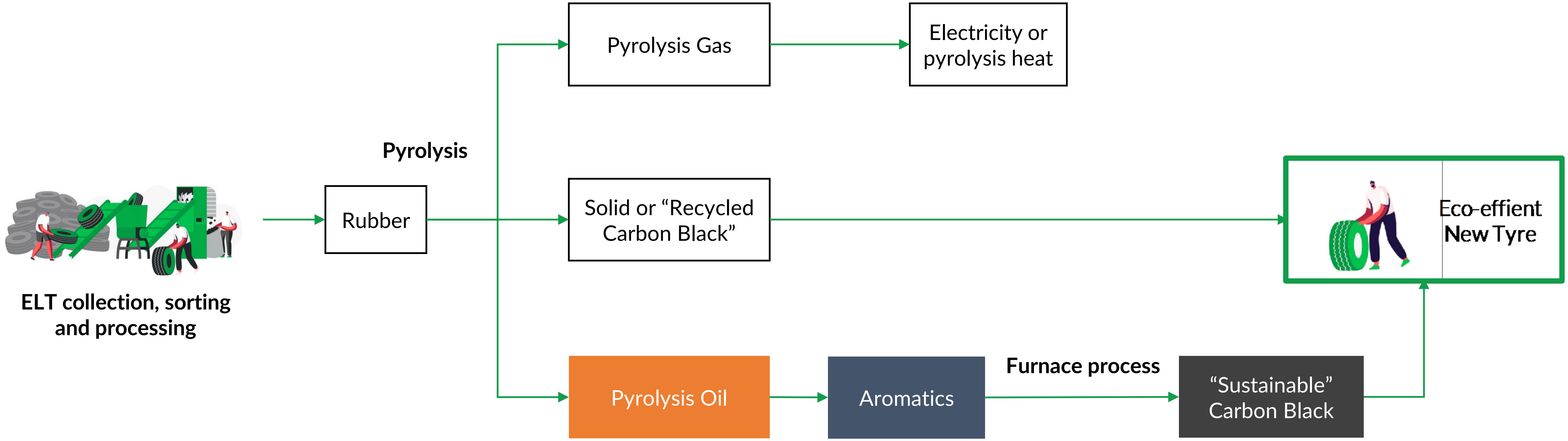
- Tyres are composed mostly of non-renewable and non-recycled components
  - <30% sustainable materials in tyres
- 1.6 billion annual tyre sales worldwide
  - Increasing 3% annually due to demand of vehicles
- Roughly equal number of tyres enter the end-of-life tyre (ELTs) category
  - Large, untapped potential for material recovery
- Recycled ELTs find applications in civil engineering or are used as a fuel substitute
  - Oversupply of ELTs, 50% do not find recycling applications
  - ELT recycling is not circular – raw materials produced are not re-used in new tyres



Average raw material composition of a tyre

Circular economy in the tyre industry: the BlackCycle project

BlackCycle aims at addressing the technological barriers to transform ELTs into high quality raw materials that can be used by the tyre industry.



Aims of this work

Overaching aim

To produce **highly aromatic pyrolysis oils** that will be used as feedstock for Sustainable Carbon Black production.

Objectives

- Investigate catalytic upgrading of ELT pyrolysis vapours to produce pyrolysis oils with increased aromatics content and C/H molar ratio.
    - Screen catalysts for their effect on the pyrolysis oil composition
    - Thoroughly characterise pyrolysis oils
    - Compare thermal vs. catalytic pyrolysis oil composition and yields
    - Process scale-up

Materials

Feedstocks

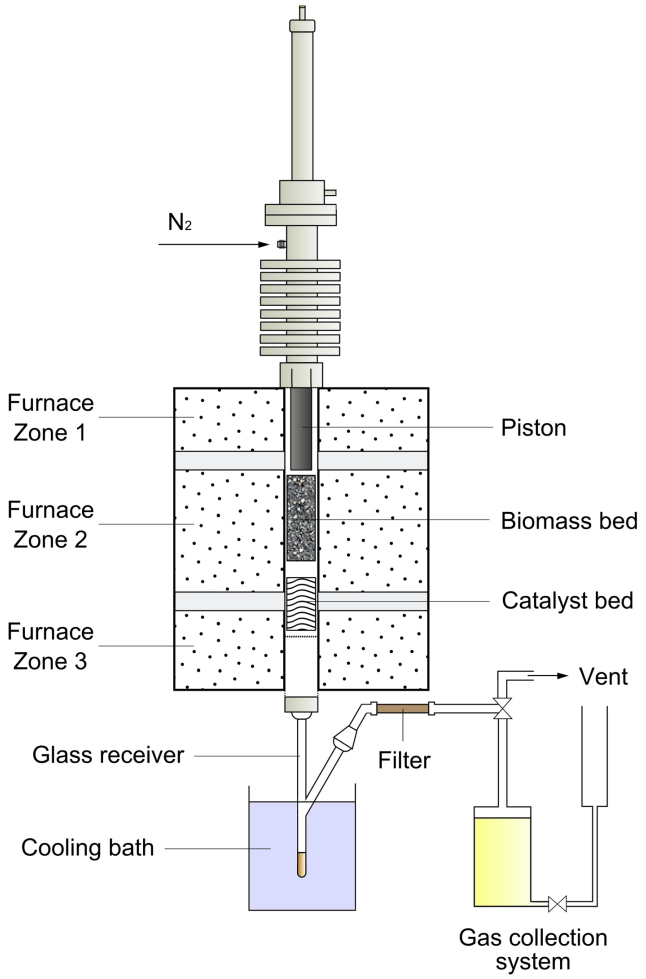
Feedstock	ELT1	ELT2
Provided by	ALIAPUR	MICHELIN
Description	Granules of multi-brand truck tyres	Granules of multi-brand all tyre
Particle size, µm	1000-3000	200-800
Moisture, wt.%	1.0	0.5
Ash, wt.%	8.0	6.1
Carbon, wt%	80.7	81.2
Hydrogen, wt%	7.6	7.7
Sulfur, wt%	1.1-3.6	1.2
Oxygen, wt% (by diff.)	0.1-2.6	3.8
GHV, MK/kg	38.3	37.5

Catalysts

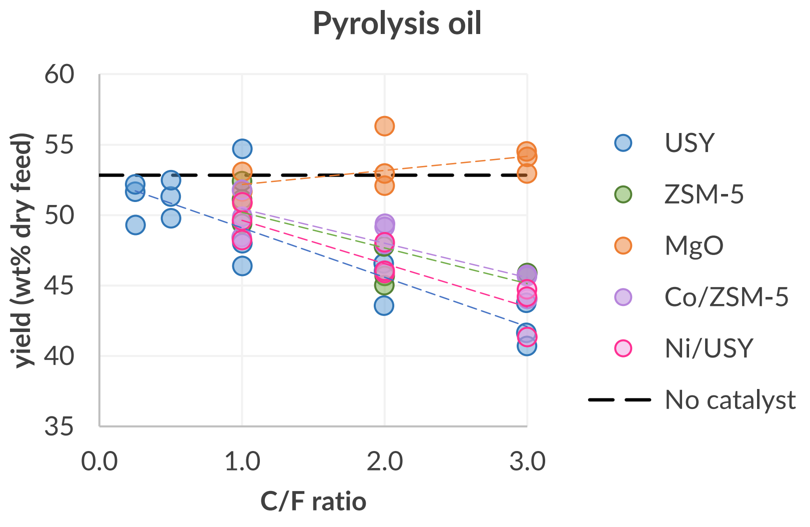
Catalyst	USY	Ni/USY	ZSM-5	Co/ZSM-5	MgO
BET SSA, m^2/g	188	145	138	131	20
Total pore volume, cm^3/g	0.235	n.d.	0.108	0.118	0.179
Average pore size, nm	5.0	n.d.	4.0	3.6	21.2
Brønsted acid sites, µmol pyridine/g	8.8	n.d.	36.5	17.3	-
Lewis acid sites, µmol pyridine/g	14.4	n.d.	18.1	45.9	-
Basic sites, µmol CO_2/g	-	-	-	-	85.9
Ni, wt%	<0.01	1.6	-	-	-
Co, wt.%	-	-	-	5.5	-

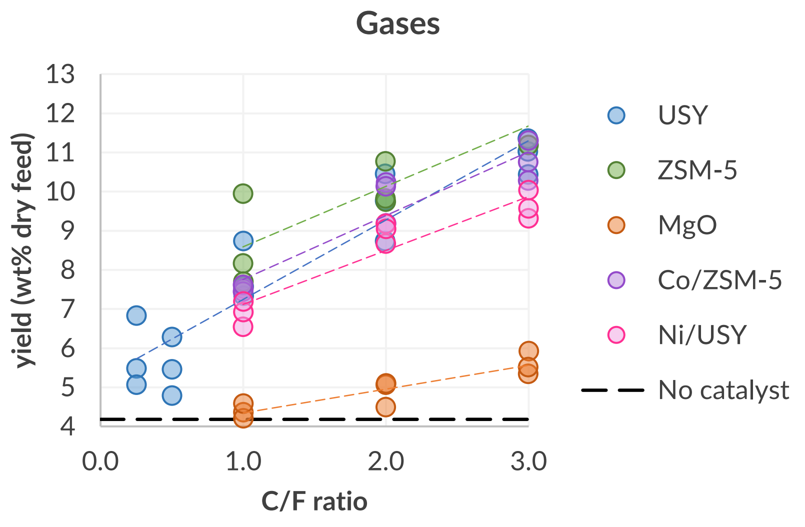
Bench-scale experimental setup for catalyst pre-screening

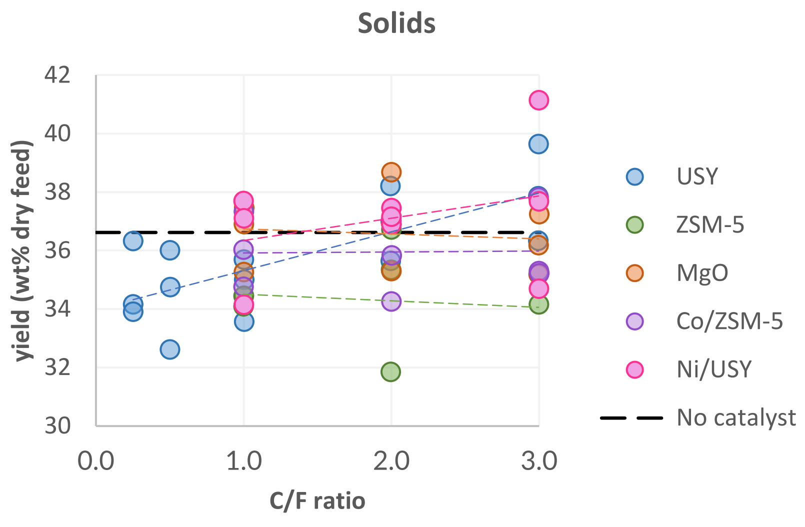
- Fixed bed batch reactor
- Feedstock: **ELT1**
  - 2.8 g feed per batch
- Experiment temperature:
  - 500 °C (pyrolysis and catalytic upgrading)
- Catalysts tested:
  - USY, ZSM-5, MgO, Ni/USY, Co/ZSM-5
- Catalyst-to-feed (C/F) ratios:
  - 0.25, 0.5, 1, 2, 3

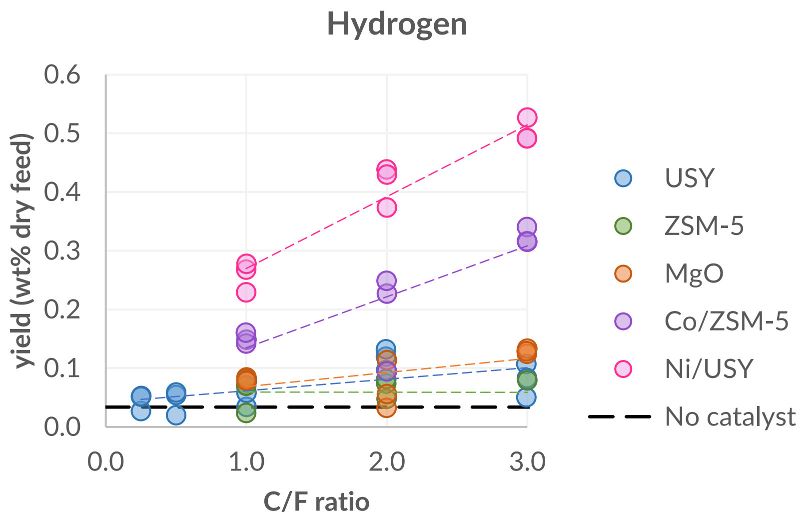


Pre-screening results: pyrolysis product yields



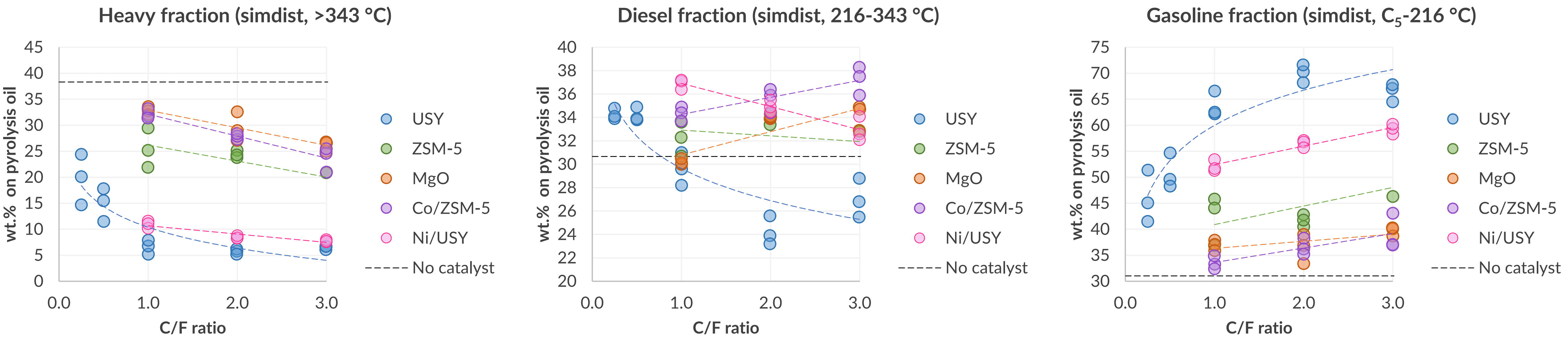






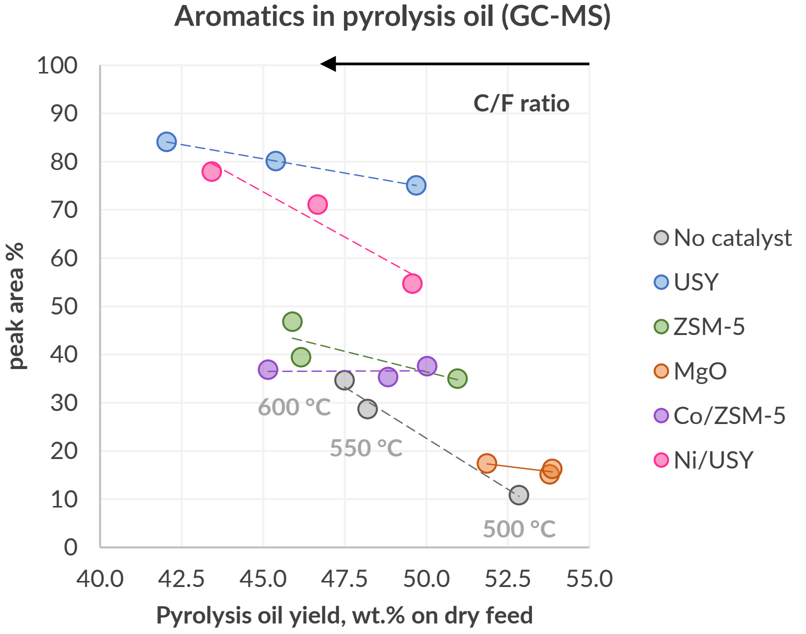
- Non-catalytic pyrolysis yields ~53 wt% pyrolysis oil
- Catalytic upgrading of pyrolysis vapours: increases gas yields at the expense of pyrolysis oil
- Increasing C/F ratio further increases gas yields at the expense of pyrolysis oil
- Zeolite catalysts more active than MgO
- Transition metal-modified catalysts enhanced dehydrogenation reactions

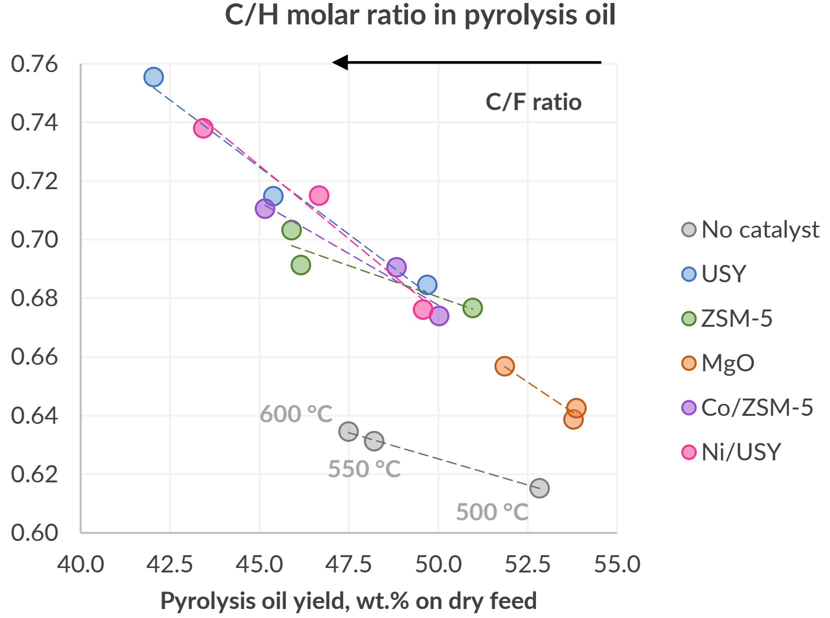
Pre-screening results: composition of pyrolysis oil

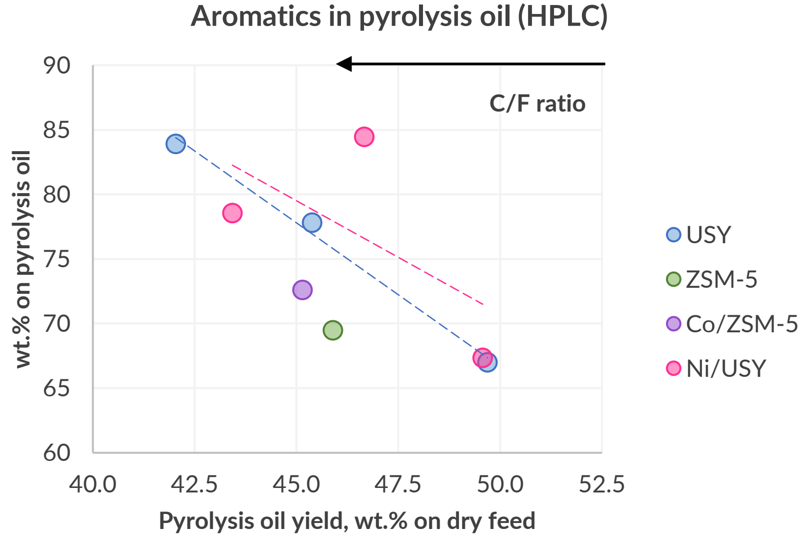


- Non-catalytic pyrolysis yields a heavy pyrolysis oil
  - ~38 wt.% > 343 °C
- Catalytic upgrading of the pyrolysis vapours cracks heavy fraction towards diesel- and gasoline-range molecules
- Increasing C/F ratio ➔ reduction of heavy fraction - increase of gasoline fraction
- Catalyst selectivity towards lighter fractions: USY > Ni/USY > ZSM-5 > Co/ZSM-5 ≈ MgO

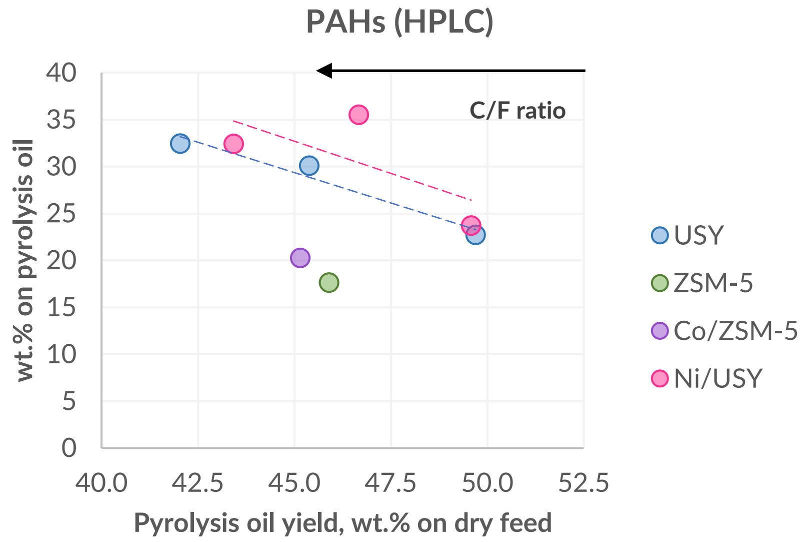
Pre-screening results: pyrolysis oil aromaticity vs. yield





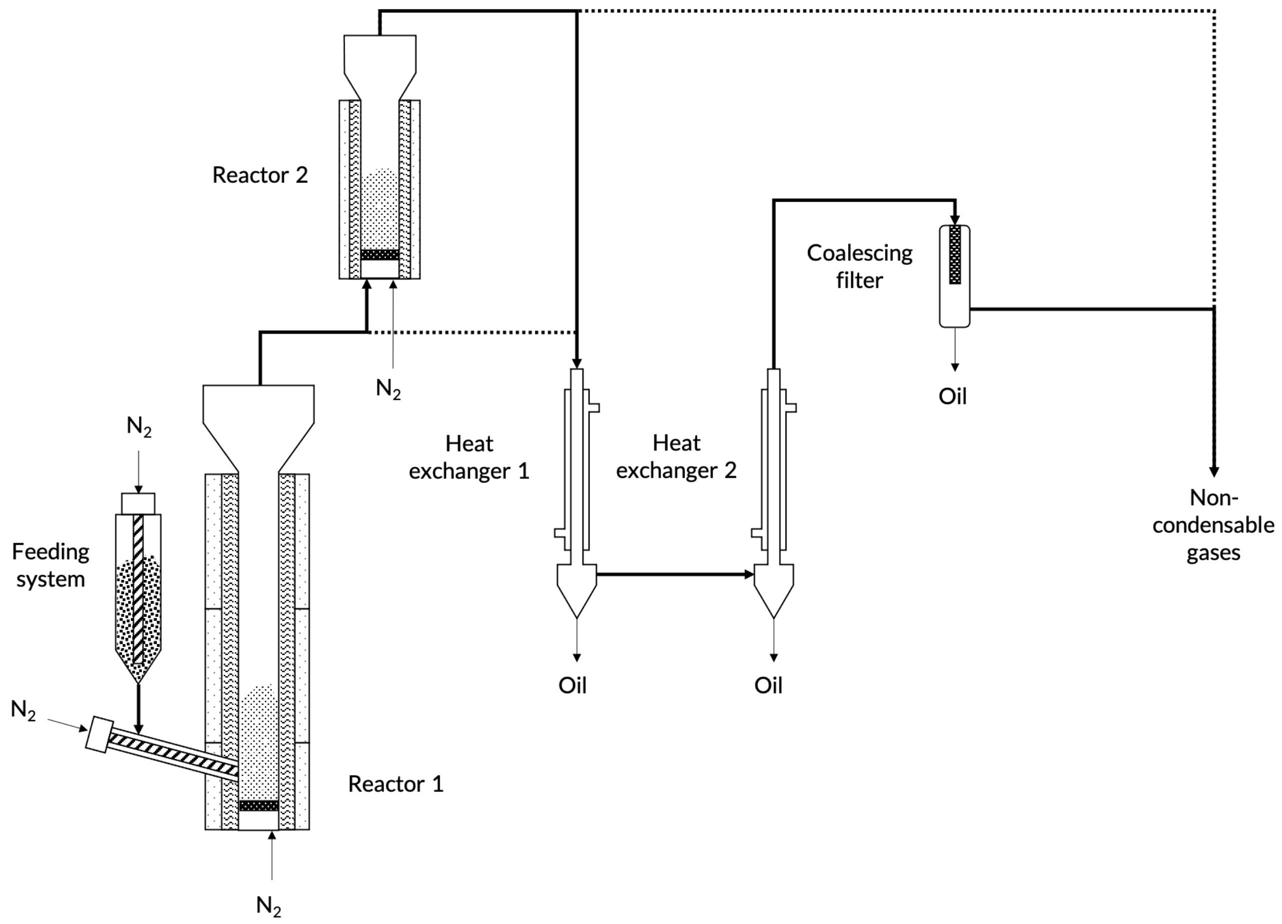


- Increasing thermal pyrolysis temperature to 550 and 600 °C results in a more aromatic pyrolysis oil with increased C/H ratio
  - Accompanied by reduction in pyrolysis oil yield
- Pyrolysis and catalytic upgrading of the pyrolysis vapours at 500 °C:
  - achieved similar pyrolysis oil yields to high-temperature pyrolysis
  - with significantly higher aromatics-content and C/H ratio
- Promising catalysts: USY > Ni/USY > Co/ZSM-5 ≈ ZSM-5
  - MgO also promising in terms of C/H ratio, but exhibited very low activity

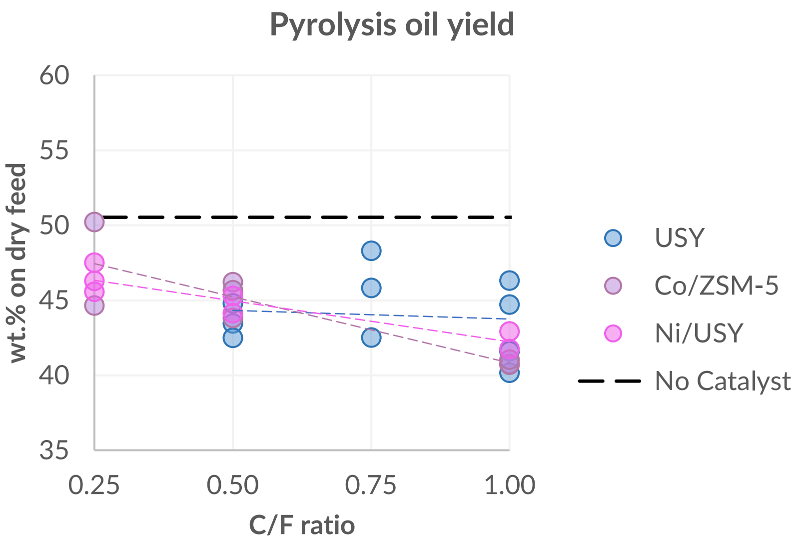


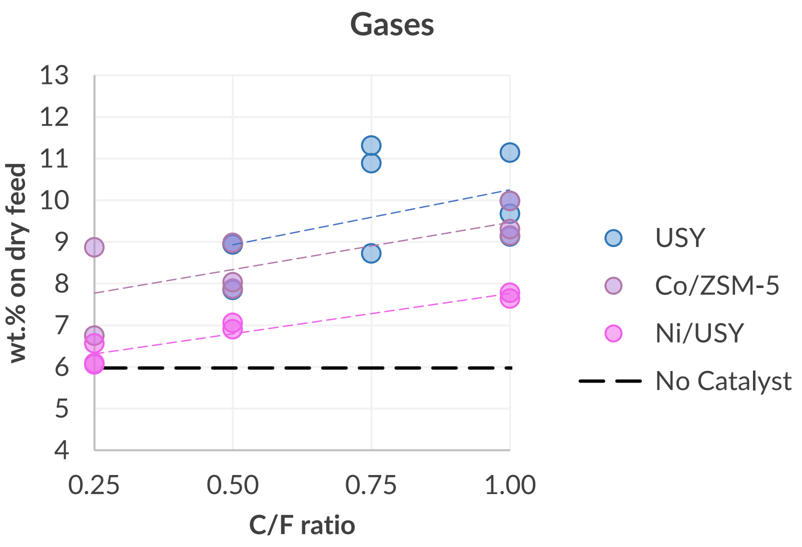
Scale-up to medium-scale: Experimental setup

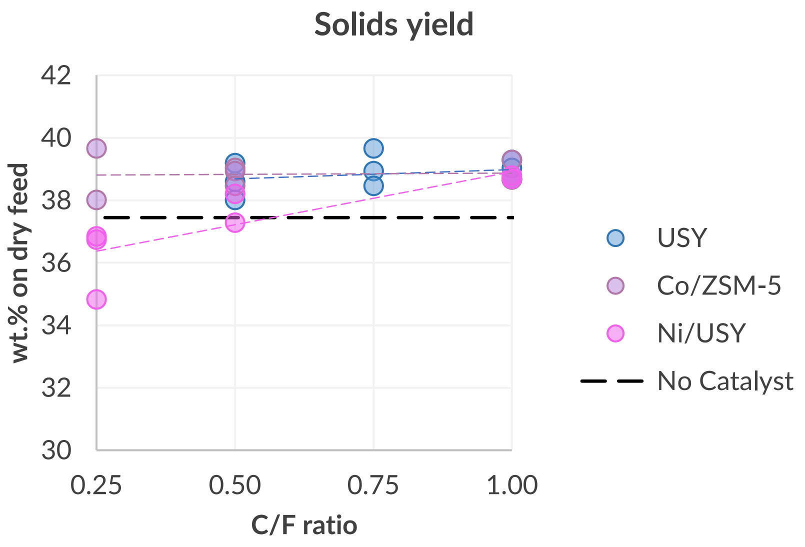
- Continuous cascading bubbling bed reactors
- Feedstock: **ELT2**
  - 5 g/min feeding rate
- Experiment temperature:
  - 500 °C (pyrolysis **and** catalytic upgrading)
- Catalysts tested:
  - USY, Co/ZSM-5, Ni/USY
- Catalyst-to-feed (C/F) ratios:
  - 0.25, 0.5, 0.75, 1

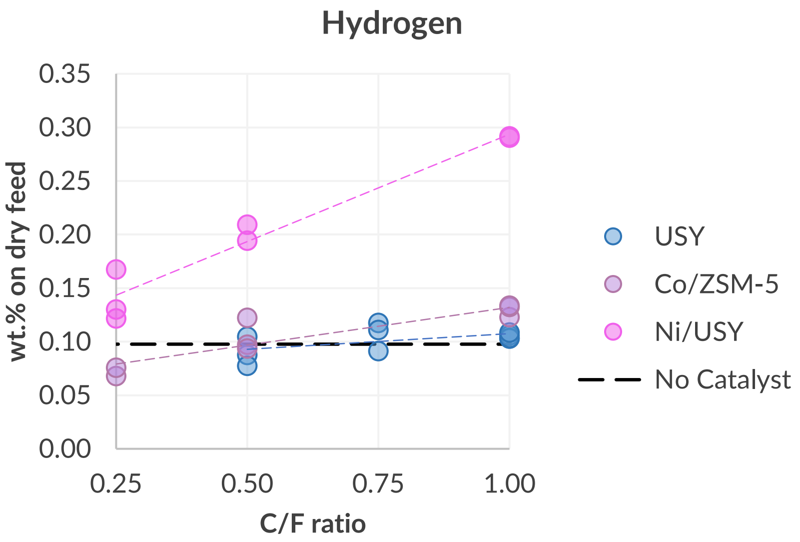


Medium-scale testing: pyrolysis product yields



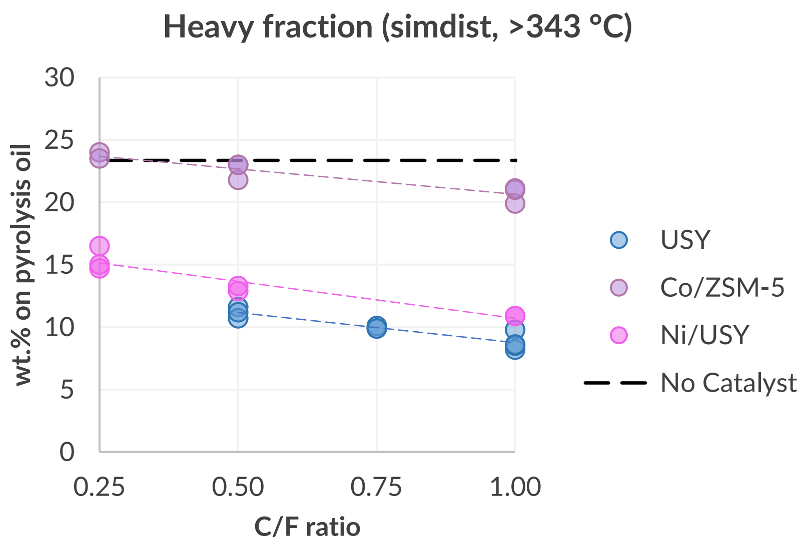


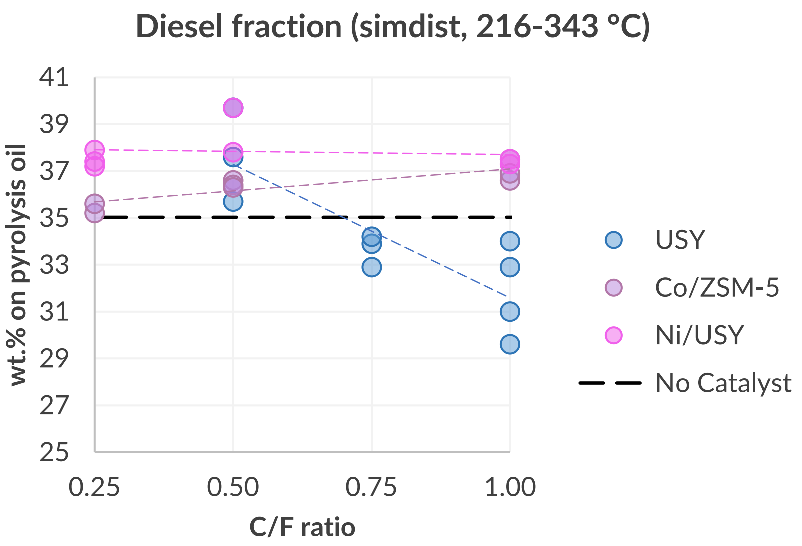


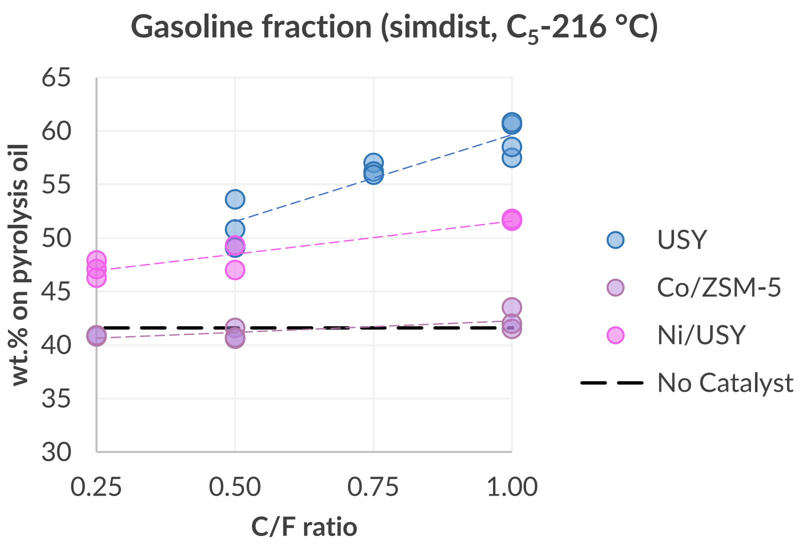


- Non-catalytic pyrolysis yields ~51 wt% pyrolysis oil
- Catalytic upgrading of pyrolysis vapours increases gas yields at the expense of pyrolysis oil
- Increasing C/F ratio further increases gas yields at the expense of pyrolysis oil
- Ni/USY enhanced dehydrogenation reactions
- Trends in agreement with pre-screening tests

Medium-scale testing: pyrolysis oil composition

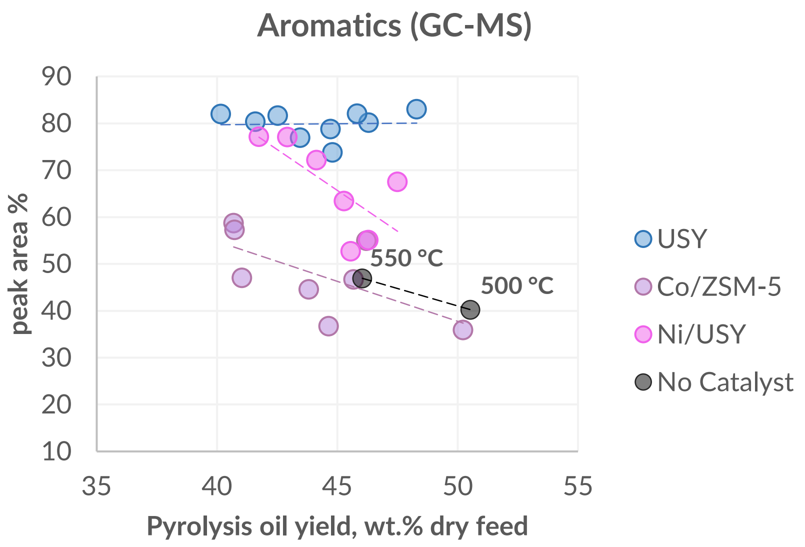


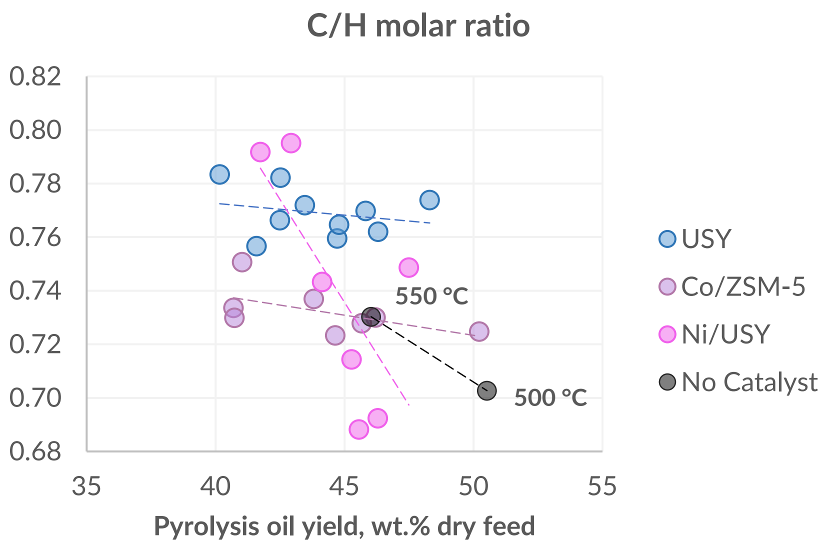


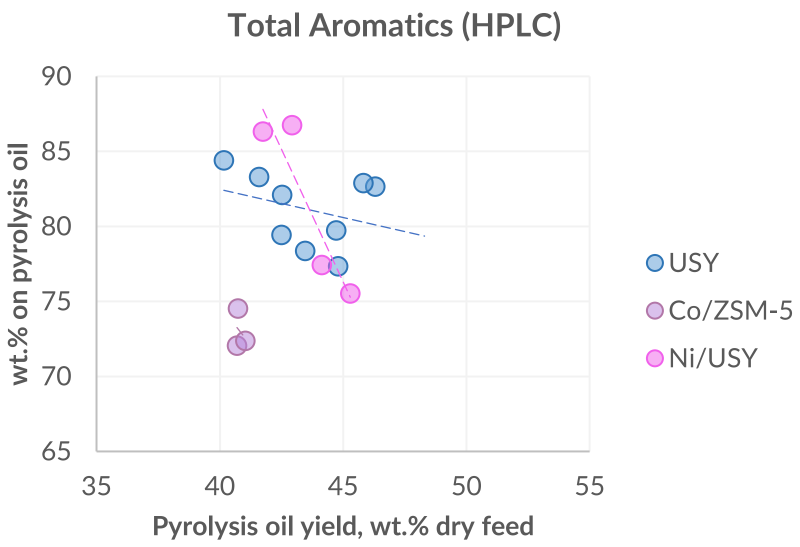


- Non-catalytic pyrolysis contains ~23 wt.% heavy fraction
  - Significantly lower compared to pre-screening tests. Attributed to longer residence times.
- Catalytic upgrading of the pyrolysis vapours cracks heavy fraction towards diesel- and gasoline-range molecules
- Increasing C/F ratio ➔ reduction of heavy fraction - increase of diesel and gasoline fractions
- Catalyst selectivity to lighter fractions: USY > Ni/USY > Co/ZSM-5
- Trends in agreement with pre-screening tests

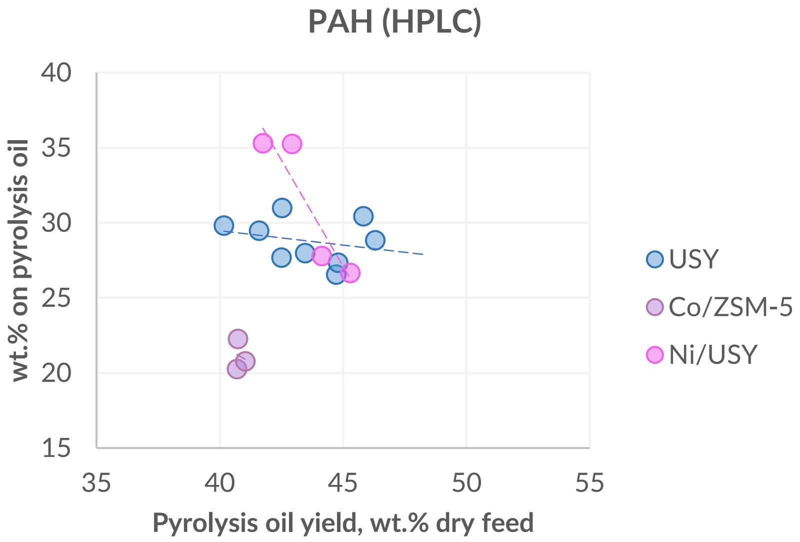
Medium-scale testing: pyrolysis oil aromaticity vs. yield







- Increasing pyrolysis temperature to 550 °C results in a more aromatic pyrolysis oil with increased C/H ratio
  - Accompanied by reduction in pyrolysis oil yield
- Pyrolysis and catalytic upgrading of the pyrolysis vapours at 500 °C:
  - achieved similar pyrolysis oil yields to high-temperature pyrolysis
  - with significantly higher aromatics-content and C/H ratio
- Most effectve catalysts: USY and Ni/USY
  - Ni/USY more selective towards PAHs
  - USY more selective towards monoaromatics
- Higher C/H ratios and total aromatics achieved in the bubbling bed reactor using lower C/F ratios

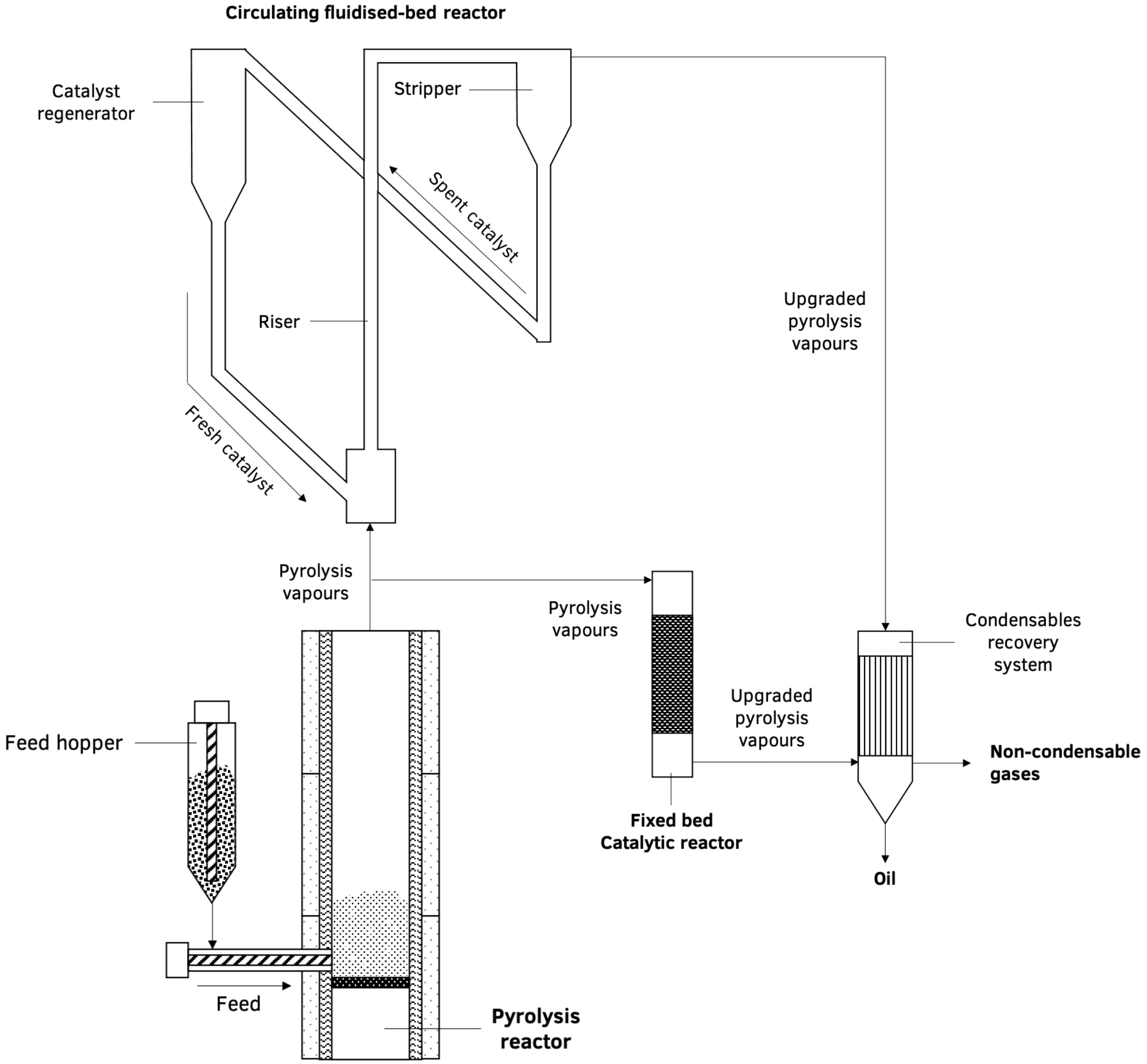


Scale-up to pilot-scale: Experimental setup

- Pilot-scale unit
  - Bubbling bed pyrolysis reactor connected to
  - Circulating-fluidised bed catalytic reactor

  Or
  - Fixed-bed catalytic reactor
  - Feeding rate: 0.5-1 kg/h
- Feedstock: **ELT1**
- Allow production of larger quantities of pyrolysis oil for extensive analysis and distillation trials

Work in progress



Conclusions

- Non-catalytic pyrolysis of ELTs yielded ~50-53 wt% pyrolysis oil with C/H ratios of 0.62-0.64 (fixed-bed) and 0.70-0.73 (bubbling bed)
- Increasing the thermal pyrolysis temperature from 500 °C to 550-600 °C increased the C/H ratio to an extend
- Catalytic upgrading of the pyrolysis vapours at 500 °C produced pyrolysis oils with significantly higher aromatics content and C/H ratios than thermal pyrolysis even at elevated temperatures
- The most effective catalysts were the **USY** and **Ni/USY** catalysts
  - ~42 wt% pyrolysis oil yield with up to 87% aromatics and 0.8 C/H ratio achieved with **Ni/USY**
  - **Ni/USY** was slightly more selective towards PAHs, **USY** was slightly more selective towards monoaromatics
- Experiments in the pilot-scale with a circulating fluidised bed or fixed-bed catalytic reactor with the most optimum catalysts is in progress
  - Production of sufficient amounts of pyrolysis oils for extensive analysis and distillation trials

Acknowledgements

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https://blackcycle-project.eu/