Systematic screening of conventional and hierarchical zeolites for the catalytic conversion of end-of-life tyre pyrolysis vapours to aromatics

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1 INTRODUCTION

- Tyres are composed mostly (>70%) of non-renewable and non-recycled components
- 1.6 billion annual tyre sales worldwide, 3% increased sales per annum
- Equal number of tyres enter the end-of-life tyres (ELTs) category annually
- Oversupply of ELTs, 50% do not find recycling applications
- ELT recycling not circular – raw materials produced are not re-used in new tyres

The BlackCycle project

Aims to develop technologies to transform ELTs into high quality raw materials that can be re-used by the tyre industry, according to **Fig. 1**.

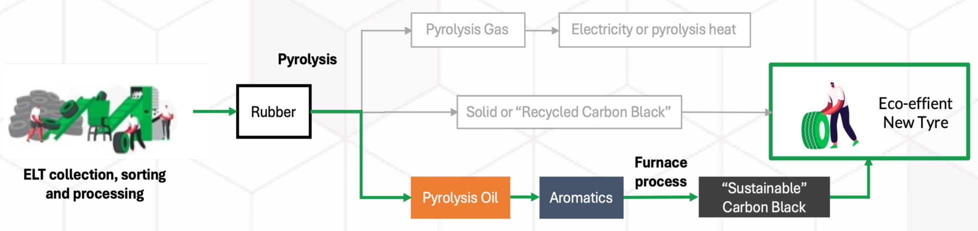


Fig. 1. Flowsheet for the conversion of ELTs to high quality raw materials via pyrolysis.

Objectives of this work

1. Pre-screening of commercial zeolites for the catalytic upgrading of the pyrolysis vapours to increase the aromatic content of the pyrolysis oil.
2. Synthesis of hierarchical zeolites via desilication followed by dealumination and testing of their catalytic performance in comparison to the parent microporous zeolites.

2 EXPERIMENTAL

Feedstock

- ELT feedstock was provided by Aliapur, a tyre collection and recycling company based in France.

Its composition is shown in **Table 1**.

Table 1. Ultimate and proximate composition of the ELT feedstock.

Feedstock	C, wt.%	H, wt.%	N, wt.%	S, wt.%	Ash, wt.%
ELT	21.1	4.2	11.0	0.040	

Catalysts

- Microporous Y, ZSM-5 and beta zeolites with variable silica-to-alumina ratios (SAR) were obtained from Zeolyst.
- Hierarchical zeolites were prepared by desilication and dealumination of Y SAR 30 and ZSM-5 SAR 80 zeolites (denoted with **DS**).

The properties of the catalysts are shown in **Table 2**.

Table 2. Surface and acidic properties of the catalysts used.

Catalyst	Surface area, m²/g	Micropore surface area, m²/g	Brønsted acid sites, μmol pyridine/g	Lewis acid sites, μmol pyridine/g
Y SAR 5	918	882	385.1	146.2
Y SAR 30	847	622	184.4	82.8
Y SAR 30 **DS**	1,007	223	68.7	22.4
ZSM-5 SAR 80	451	330	171.2	23.7
ZSM-5 SAR 80 **DS**	476	248	165.4	76.4
Beta SAR 25	609	423	179.6	210.1

Catalytic pyrolysis experimental setup

Non-catalytic and catalytic pyrolysis of the ELT was carried out in a lab-scale fixed bed reactor (**Fig. 2**).

- Non-catalytic pyrolysis runs T: 500, 550, 600 °C
- Catalytic pyrolysis runs T: 500 °C
- Catalyst-to-feed (C/F) ratio varied by changing the amount of catalyst in the reactor

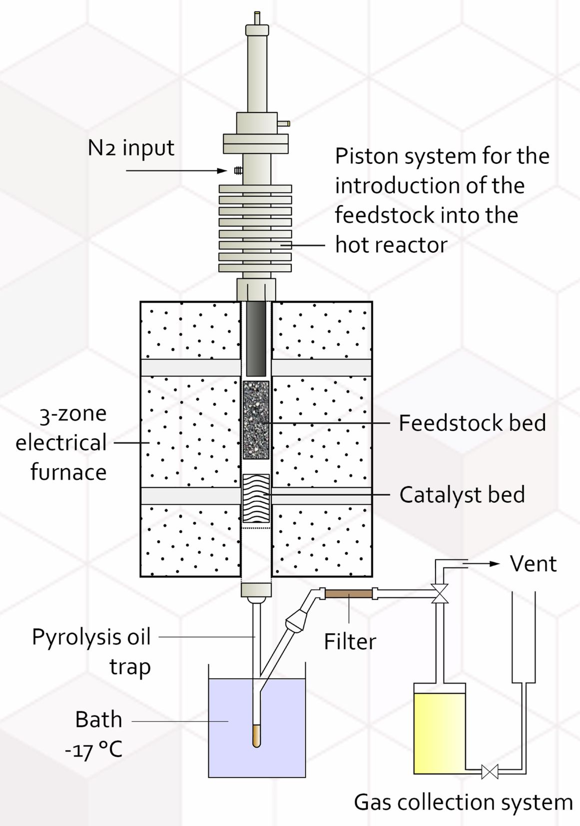


Fig 2. Schematic representation of the catalytic pyrolysis experimental setup.

Analysis methods

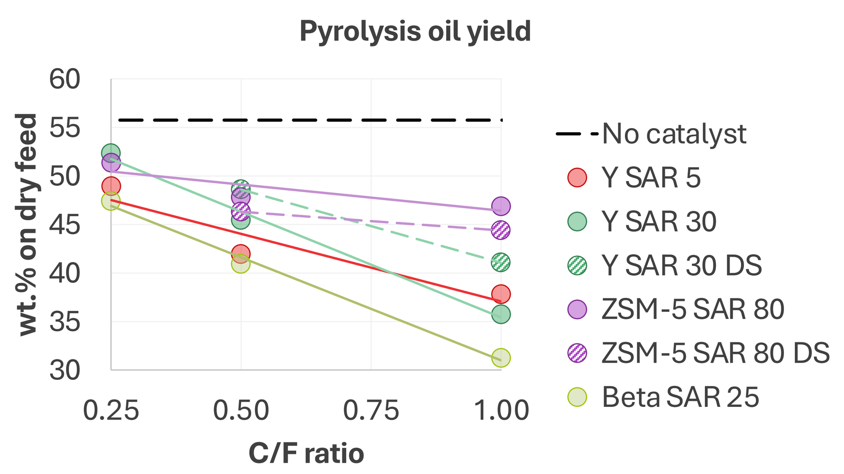
Catalysts: N_2 sorption-desorption and FTIR with in-situ pyridine adsorption.

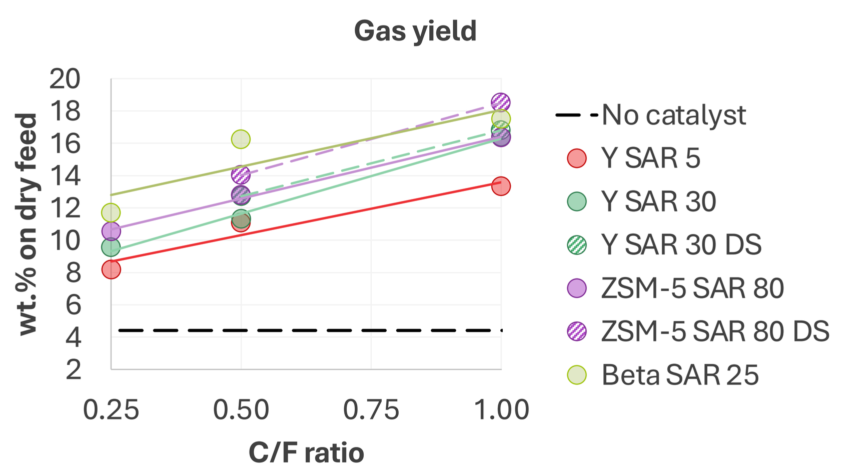
Pyrolysis oils: Elemental composition (C, H, S), H2O, GC-MS, simulated distillation, PIONA

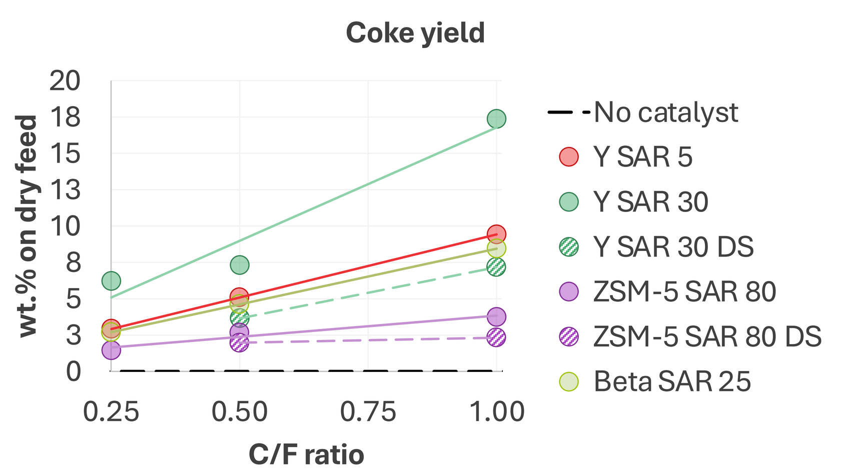
Pyrolysis gases: GC-TCD/FID

3 RESULTS

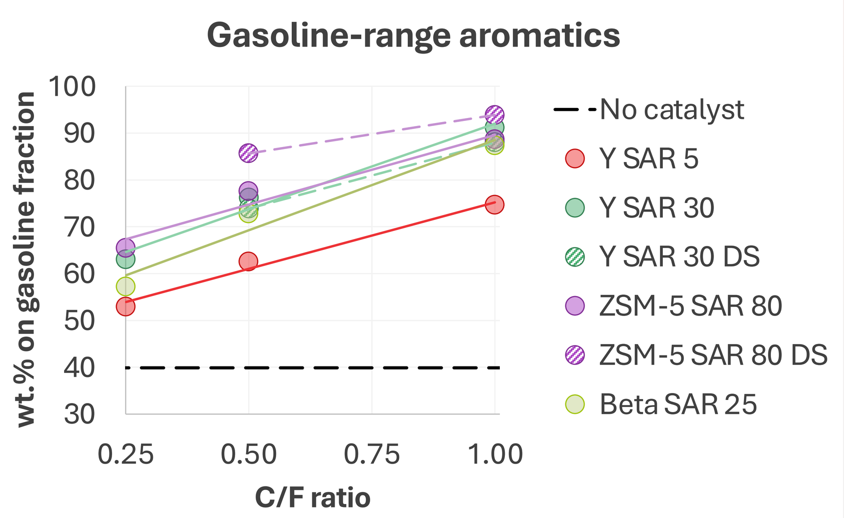
Catalyst effect on pyrolysis product yields

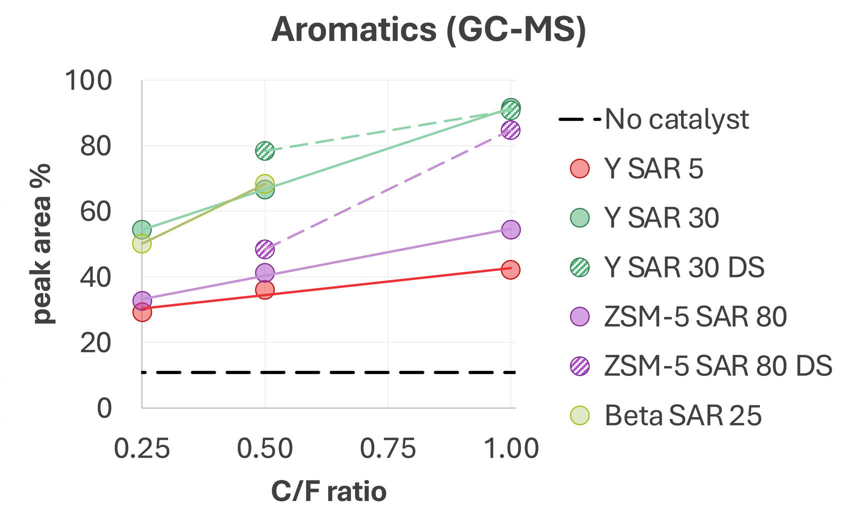


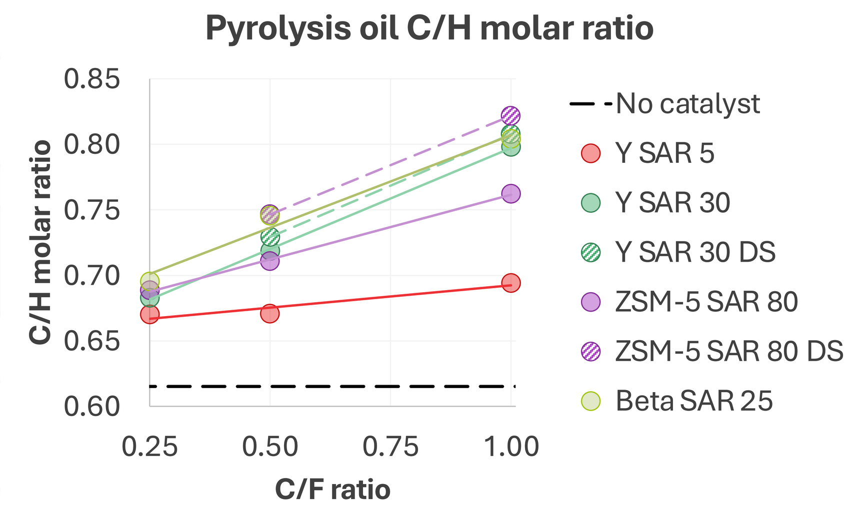




Catalyst effect on the pyrolysis oil composition

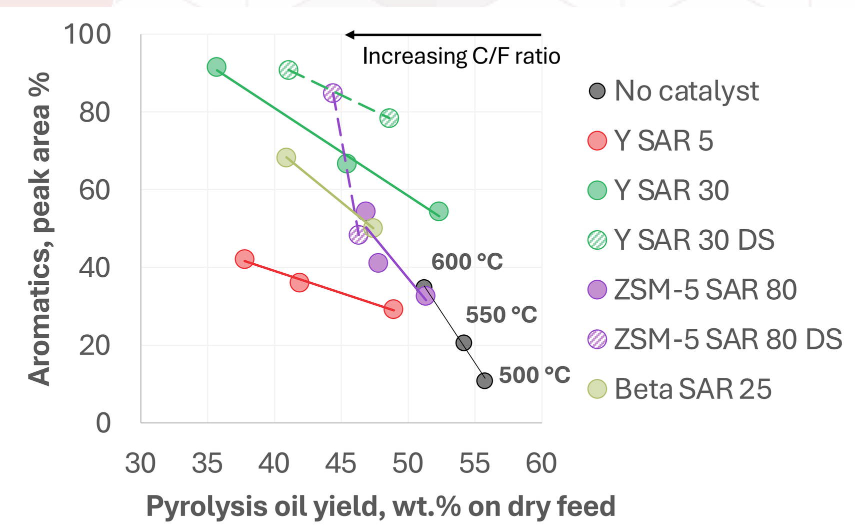


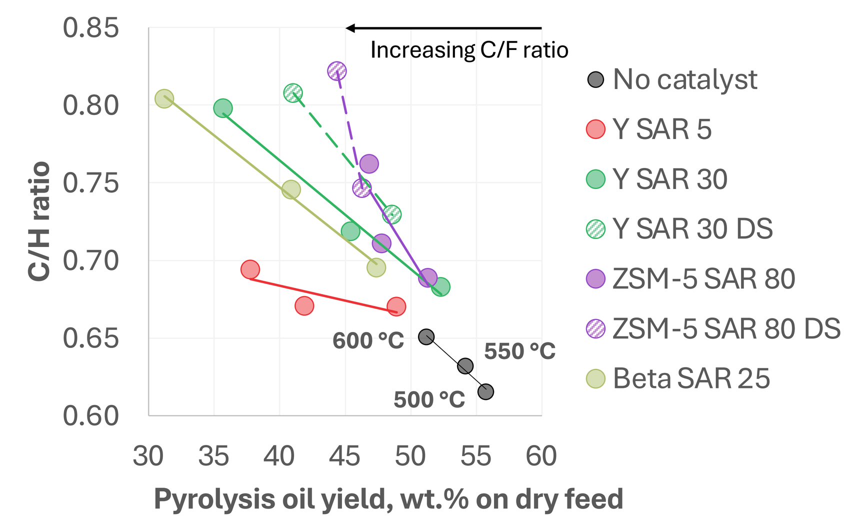




- Catalytic pyrolysis increased the aromatics in the pyrolysis oil, evident from GC-MS and elemental analysis (higher C/H ratio → higher aromaticity).
- Activity: ZSM-5 SAR 80 **DS** > Y SAR 30 **DS** ≈ Beta SAR 25 > Y SAR 30 > ZSM-5 SAR 80 > Y SAR 5

Aromaticity of the pyrolysis oil vs. pyrolysis oil yield





- Compared to thermal pyrolysis (500-600 °C), catalytic pyrolysis at 500 °C can produce oils with increased aromaticity and small oil yield penalty.
- Most efficient catalysts: ZSM-5 SAR 80 **DS**, Y SAR 30 **DS**

4 CONCLUSIONS

- Catalytic pyrolysis of ELTs at 500 °C yielded pyrolysis oils with increased aromatics content compared to thermal pyrolysis at 500-600 °C.
- Hierarchical Y and ZSM-5 zeolites exhibited significantly improved performance compared to their microporous counterparts, achieving higher yields of pyrolysis oils with high aromatics content.

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