



Recovering value-added hydrocarbons from pyrolysis of end-of-life tires: fractioning the derived oil in a pilot scale distillation plant

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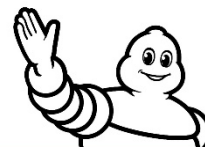
Content

1. Background
2. Materials and methods
 - 2.1 TPO production
 - 2.2 Tire pyrolysis oil (TPO)
 - 2.3 Distillation column
3. Results
 - 3.1 Distillation performance
 - 3.2 Yields and characteristics
4. Conclusions
5. Acknowledgements

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<https://blackcycle-project.eu>



MICHELIN

The BlackCycle project aims at creating, developing, and optimizing a full value chain from ELT feedstock to Secondary Raw Materials (SRMs), with no waste of resources in any part of the chain and a specific attention for the environmental impact



Tire pyrolysis oil (TPO)



Distillation

Light Fraction (LF)

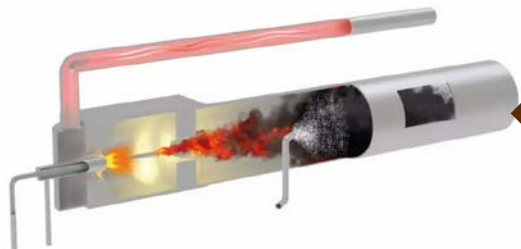


Distillation



BLACK CYCLE
Move to the green revolution

Heavy Fraction (HF) <https://blackcycle-project.eu>



https://www.orioncarbons.com/production_processes



https://www.orioncarbons.com/our_product

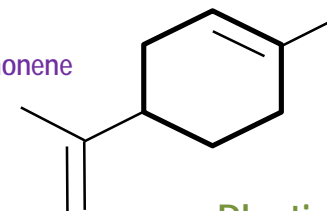
Sustainable carbon black (sCB)

For manufacturing new tires



An ultra-light fraction with very high limonene (↑ 20 wt%)

Limonene

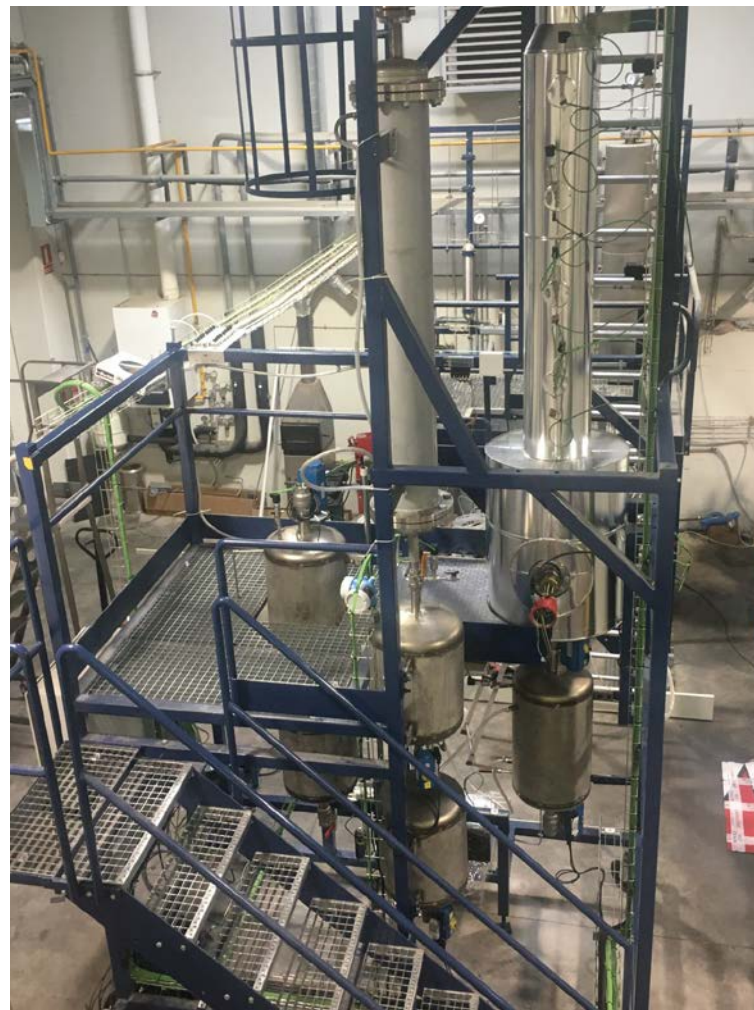


Plasticizer

But, before this, it is necessary:

Designing, building, commissioning
...etc

... “playing” with a “new toy”
(at relevant scale)!

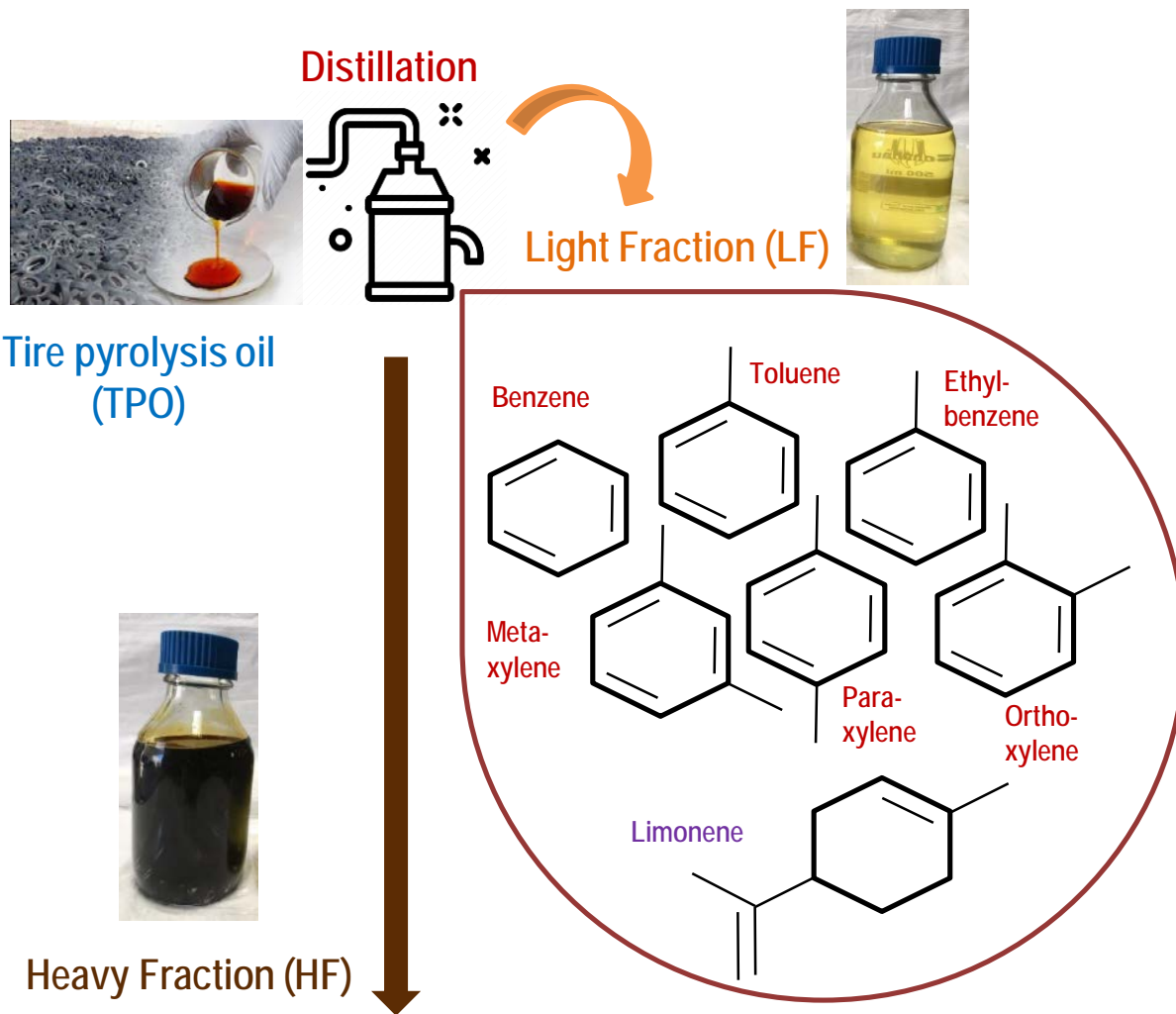


Goal of this presentation?

To show some preliminary experiments aimed at producing:

→ a light fraction (LF) enriched with benzene, toluene, ethylbenzene and xylene (BTEX) as well as limonene,

...using tire pyrolysis oil (TPO) in an industrially relevant conditions packed distillation column



2. Material and methods

2.1 TPO production → semi-industrial plant (TRL-7)



- Feedstock:
Passenger car tires
- Mass Flow rate:
500 kg/h
- Temperature:
From 450 to 800 °C
- Residence time:
15 min

2. Material and methods

2.2 Tire pyrolysis oil (TPO)

An interesting but complex hydrocarbon: $MW_{AVG} = 420 \text{ g/mol}$ (aprox.); $C_6 - C_{55}$



Structure:

HC pure (75%), HC-S1 (14%).

Tri-aromatics (26%), tetra-aromatics (13%) and penta-aromatics (22 and 30%).
HC with S1 → dibenzothiophene (31%) and benzonaphthothiophene (34%).

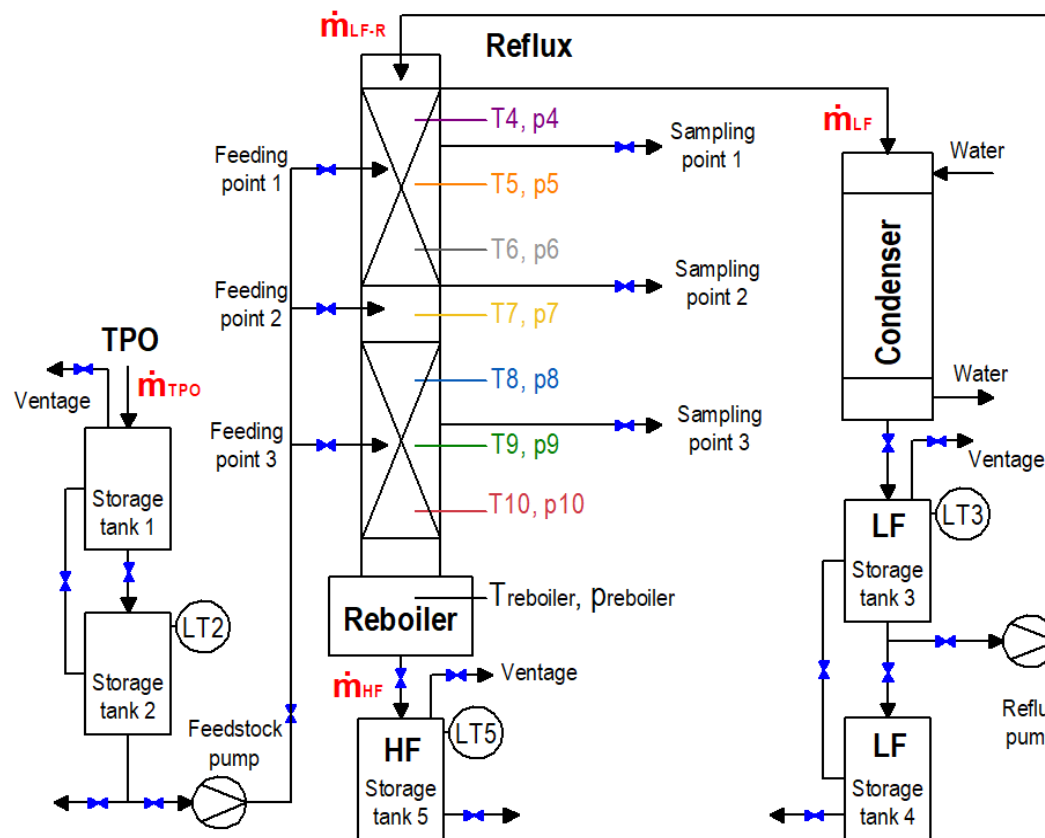
Campuzano et al. (2020). *Energy Fuel*. 34, 12688-12702

Equipment/Method	Parameter	TPO
Thermo Flash 1112, UNE-EN 15307	Carbon (wt%)	88.0
	Hydrogen (wt%)	9.77
	Nitrogen (wt%)	0.9
	Sulfur (wt%)	0.7
From elemental analysis	H/C	1.33
Parr 6400, UNE-EN 15400	HHV (MJ/kg)	42.04
Picnometry	Density @ 20°C (g/ml)	0.98
Brookfield LVDV-E, ASTM D445	Viscosity @ 40°C (cp)	7.5
Crison Titromatic, ASTM E203	Water content (ppm)	153
Grabner Instruments, ASTM D6460	Flash point (°C)	< 25
Mettler Toledo T50	pH (---)	6.4
Mettler Toledo T50	TAN (mgKOH/g)	5.293
Simulated distillation (ASTM D2887)	IBP (°C)	69.0
	T ₅₀ (°C)	243.1
	FBP (°C)	513.9
Gas chromatography (Perkin Elmer Clarus 590) – FID detector and 60-m DB-5ms capillary column (0.25 mm ID and 0.25 μm df)	Benzene (wt%)	2.1
	Toluene (wt%)	6.2
	Ethyl-Benzene (wt%)	1.0
	(p+m)-Xylene (wt%)	5.0
	o-Xylene + Styrene (wt%)	1.8
	Total BTEX (wt%)	16.2
	Limonene (wt%)	2.7

2. Material and methods

2.3 Distillation column (TRL5)

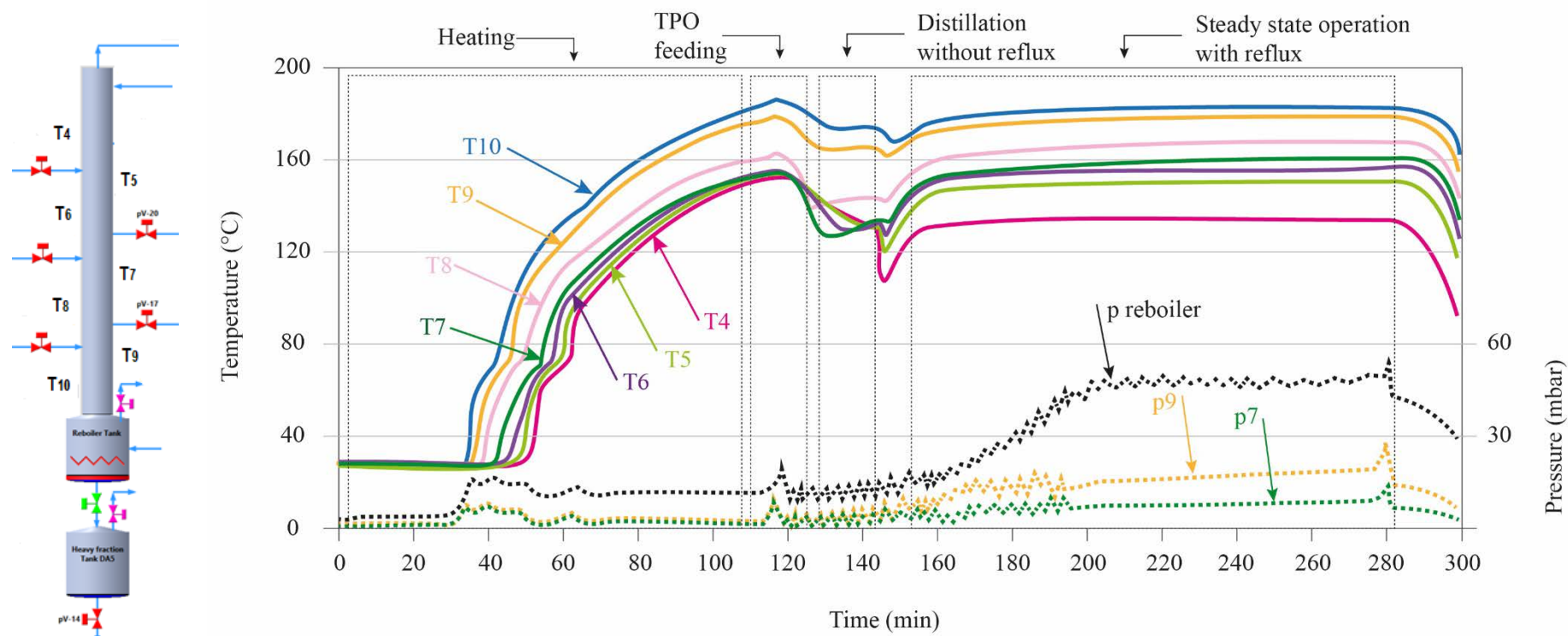
Nominal capacity: 20 kg/h; reflux ratio: 1-3; packing: pall rings
1 in size, h: 4 m; Øi: 110 mm; equilibrium stages: 8



3. Results

3.1 Distillation performance

Temperature and pressure profile over the operation time for the experiment at 250 °C and 2.4 of reflux ratio

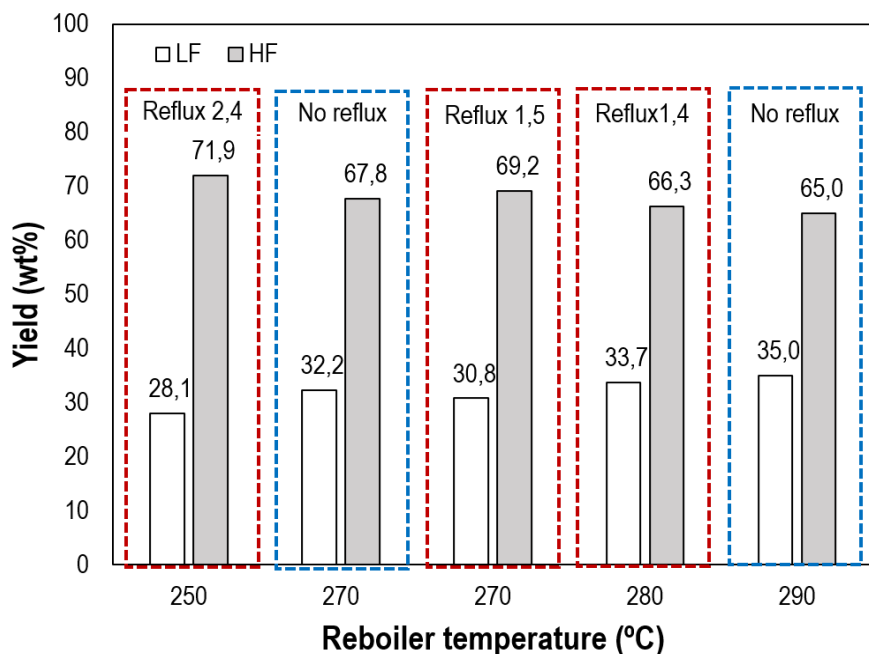


3. Results

3.2 Yields and characteristics

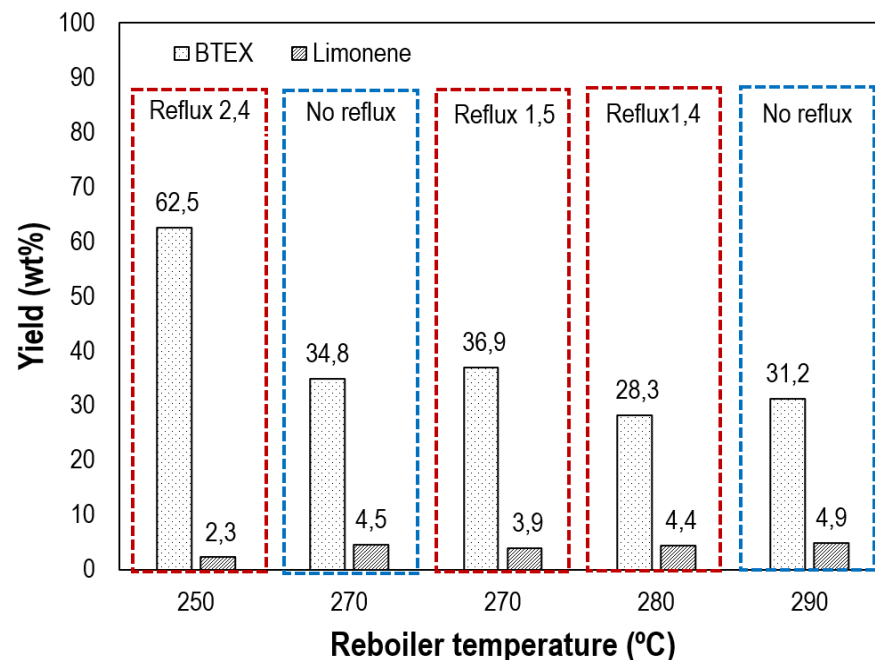
→ LF and HF yields

The higher the reboiler temperature, the higher the yield of the LF, and the lower the yield of the HF



→ BTEX and limonene concentration in the LF

The lower the reboiler temperature, the higher the BTEX, and the lower the limonene concentration in the LF



4. Conclusions

- The temperature and pressure profile along the distillation column were found to be very stable over the operation time, and suggest no accumulation of the TPO inside the column.
- Under the experimental conditions used in this work, the LF was between 27 wt% and 35 wt%, while the HF was between 65 wt% and 73 wt%.
- The highest BTEX concentration in the LF was 62.54 wt%, when the temperature of the reboiler and the reflux ratio were 250 °C and 2.4, respectively.
- The lower the reboiler temperature, the higher the BTEX, and the lower the limonene concentration in the LF.

Acknowledgements



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Interdisciplinary Platform for Sustainable
Plastics towards a Circular Economy

Thank you very much for your
attention!

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