

# Selective catalytic cracking of plastic waste for naphtha-like pyrolysis oil production

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### Significance and Relevance

This study examines the in-situ catalytic upgrading of plastic waste pyrolysis oil into naphtha-range hydrocarbons, highlighting the impact of catalyst properties such as acidity and porosity on product composition and distribution. Through the systematic investigation of aluminosilicate catalysts, the work identifies critical factors driving the selective production of  $C_5-C_{12}$  hydrocarbons, suitable for direct use (or after mild hydrotreatment) in existing steam cracking units. The findings provide valuable mechanistic insights to guide the subsequent design of advanced catalytic systems for efficient plastic waste valorization, facilitating the conversion to fossil-based raw material and effectively closing the plastics lifecycle loop.

*Preferred topic:* 1<sup>st</sup> Circular economy, 2<sup>nd</sup> Sustainable and clean energy production and transport *Preferred presentation:* Poster preferred or short oral

### **Introduction and Motivations**

Plastic waste constitutes nearly 13% of global solid waste, with over 70% either landfilled or incinerated, leading to the the loss of its hydrocarbon-rich polymeric structure. While mechanical recycling is a promising approach, it is often hindered by the heterogeneous and complex nature of real mixed plastic waste streams <sup>1,2</sup>. In contrast, chemical recycling, particularly pyrolysis, offers an alternative by converting plastics into crude py-oils. A critical challenge, however, is upgrading these oils into refined, high-value fractions, like naphtha, capable of reintegration into the plastic production chain <sup>1-3</sup>. The present study addresses this challenge by examining the in-situ catalytic upgrading using aluminosilicate materials to enhance the yield, quality, and selectivity of the resulting py-oils.

#### **Materials and Methods**

A fixed-bed reactor was employed under fast pyrolysis conditions (450-700 °C, contact time <1s, N<sub>2</sub> flow: 100 ml/min, plastic/catalyst mass ratio of 10:1) for both thermal and catalytic pyrolysis of LDPE, the major component of real plastic waste streams. The resulting py-oils were analyzed using GC-MS/FID, while gaseous products were collected and analyzed offline via GC-TCD/FID. A broad range of aluminosilicate materials with varying pore sizes, structures, and Si/AI ratios was tested, resulting in differing acidic properties, including variations in the abundance and strength of Brønsted and Lewis acid sites. Catalysts included highly Brønsted acidic microporous crystalline zeolites, like ZSM-5, alongside other zeolitic materials (MOR, FER, Beta, USY, etc.) and mildly acidic mesoporous mixed oxides, such as silica-alumina, which primarily exhibits Lewis acidity, thereby covering a wide range of catalytic properties. Additionally, natural zeolites were evaluated as cost-effective and potentially competitive alternatives. Fresh and spent catalysts were extensively characterized using XRD, FTIR-pyr, N<sub>2</sub> sorption, TGA, elemental analysis, and other complementary techniques.

# **Results and Discussion**

Thermal pyrolysis of LDPE primarily produced heavy waxes (>70 wt%), predominantly consisting of  $C_{20+}$  hydrocarbons at temperatures up to 600 °C, with minimal formation of gaseous products and pyoil (both <5 wt%). The introduction of catalysts notably reduced waxes fraction while significantly enhancing both py-oil and gaseous products yields.

Notably, the strongly acidic ZSM-5 (SAR=11.5) demonstrated exceptional catalytic cracking performance, with its small tubular micropores facilitating extensive overcracking. This resulted in over



70 wt% gaseous products at 450 °C, with propylene accounting for up to 20 wt%, underscoring ZSM-5's potential for low-temperature monomer recovery applications. In contrast, zeolites such as Beta, FER, and MOR, despite having similar SAR values, exhibited moderate cracking activity, limiting overcracking and achieving higher py-oil yields of up to 50 wt%. While all catalysts effectively converted heavy waxes into lighter fractions, the balance between wax conversion towards py-oil or gases was strongly influenced by the specific physicochemical properties of each catalyst.

The py-oils produced predominantly fell within the naphtha range, yielding substantial amounts of  $C_5-C_{12}$  hydrocarbons (Figure 1). Catalyst acidity was a key determinant in directing the cracking and reforming pathways of pyrolysis vapors. Variations in acid site type and abundance significantly affected product distribution, with Brønsted acidic catalysts favoring paraffin formation and Lewis acid sites promoting olefin production. The aromatic content of py-oils remained consistently low (<10 wt%), a desirable property for steam cracking applications, as aromatics are prone to coke formation. The olefin to paraffin ratio was notably high, with iso-olefins in the  $C_5-C_7$  range dominating the composition. While the high olefinic content makes these oils unsuitable for direct steam cracking, they can be effectively hydrotreated under mild conditions to produce a highly saturated naphtha feedstock. This downstream hydrotreatment step provides a more efficient pathway to high-quality naphtha production, minimizing the need for severe hydrocracking of crude py-oils and enhancing the overall efficiency of plastic waste conversion into valuable hydrocarbons.



Figure 1 Detailed hydrocarbon analysis of py-oils obtained from different zeolites.

# References

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