

Chemical recycling of waste plastics: The role of catalysts

Pyrolysis oil from plastics enables the integration of the circular economy for sustainable chemicals and energy

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Background

The mounting issue of plastic waste represents a significant global challenge, calling for the development of creative and enduring solutions for its management. Since the 1960s, the production and use of plastic have escalated dramatically, increasing more than 20 times, mainly due to the demand for single-use packaging. Presently, less than 20% of plastic waste is recycled worldwide. The vast majority ends up in landfills, is incinerated, or unintentionally ends up in natural habitats (Gao, et al., 2022).

Mechanical recycling is often considered the optimal solution for recycling plastics. However, its effectiveness is constrained, especially when dealing with plastics that are mixed or contaminated with unwanted substances like metals, paper, other types of polymers, or fillers. Additionally, the limited number of times that plastics can be mechanically recycled – due to the breakdown of polymer chains during the extrusion process – eventually leads to their disposal as waste, thereby continuing the cycle of environmental contamination. This issue is further aggravated by the predominant use of fossil fuels in plastic production (Musso, et al., 2022).

Due to these limitations, chemical recycling is emerging as a viable alternative, capable of transforming mixed and contaminated plastics into valuable commodities. While there are various chemical recycling techniques, including gasification, pyrolysis, and solvolysis, this work focuses on pyrolysis. In fast pyrolysis, waste plastics are quickly (within a few seconds) heated to around 600°C in the absence of

oxygen. The vapours produced are then condensed to give a dark brown fast pyrolysis oil product. In certain cases, a catalyst, often zeolite-based, might be employed to improve the quality and yield from the pyrolysis process. Ideally, pyrolysis can revert polyolefin plastics to their monomeric forms, which are then utilised within refinery or petrochemical processes. However, the process yields a wide spectrum of products, including gases, naphtha, heavy oils, and waxes.

In the decentralised concept of chemical recycling of plastic through pyrolysis, production of liquids is favoured, given the economic advantage for transportation of liquids over wax or gaseous products. This article investigates two innovative approaches using catalysts to upgrade plastic waste at two different points in the chemical recycling of plastic value chain:

- Maximising naphtha yield in pyrolysis oil through catalytic pyrolysis treatment from waste plastics using BASF's proprietary catalysts.
- Cracking of a waxy fraction produced in the fast thermal pyrolysis of low-density polyethylene (LDPE) using BASF's commercial fluid catalytic cracking (FCC) catalysts.

Catalytic and thermal pyrolysis of waste plastic

The main objective of this work was to increase the amount of condensable vapours generated by the pyrolysis process, particularly in the naphtha range. Pyrolysis was performed in a small-scale unit equipped with two fixed-bed reactors (Stefanidis, et al., 2011) developed by the Chemical Process and Energy Resources Institute (CPERI).

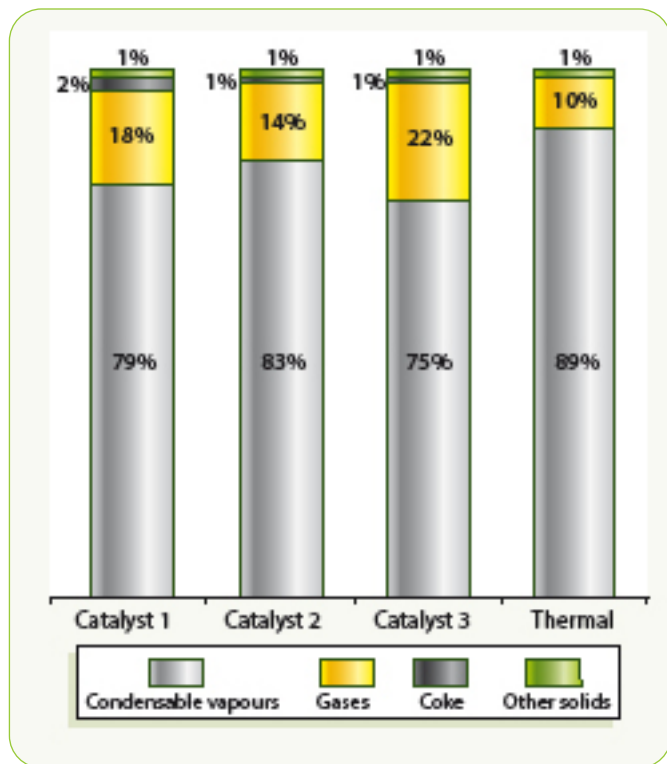


Figure 1 Mass balance after catalytic vs thermal pyrolysis experiments

First, the recycled LDPE and polypropylene (PP) were mixed in a ratio of 65 and 35 wt%, respectively. In the first bed, the mixed plastic feedstock was introduced. Upon heating, the resultant gases were then directed through the second reactor, filled with either inert material ('thermal') or catalyst. The ratio of the introduced feedstock to catalyst was 1 to 1. The feedstock was introduced from ambient temperature into the hot reactor while simulating the following conditions:

- **Conventional pyrolysis:** loaded with inert material ('thermal'), both reactors heated to 600°C.
- **Catalytic pyrolysis:** loaded with BASF's proprietary catalysts (Catalyst 1 to Catalyst 3), both reactors heated to 500°C.

The test without catalyst was performed at 600°C due to high wax formation at lower temperatures. The feedstock composed of LPDE and PP was ground and sieved to 0.4-0.8mm and then was mixed for eight hours in a dry mixer.

The total content of the condensed phase was measured by the gravimetric method. The composition of the pyrolysis oil was studied by simulated distillation. The non-condensed part was studied in the gas collection system.

The total volume of the gases was measured, and a gas sample was collected to analyse its composition by gas chromatography. The solid products were determined by weighing the reactors before and after the runs. The spent catalyst was recovered from the reactor, and its carbon content was determined to assess the coke yield.

The distribution of the final products, including pyrolysis oil, gas, coke, and other solid products, was collected. In **Figure 1**, the results were normalised to 100, and the variation between the total mass balance was 1.4%.

It can be observed in Figure 1 that BASF's catalysts resulted in pyrolysis oil yields between 75% and 83%, while the thermal pyrolysis process resulted in 89% pyrolysis oil. Although the thermal pyrolysis process achieved a higher yield of pyrolysis oil, its quality significantly differed from these catalytic tests due to a higher yield of heavy oil.

The condensed phase from the pyrolysis was investigated using the simulated distillation method. Products with boiling points between C₅ and 216°C were categorised as naphtha, the products with boiling points between 216°C and 343°C were categorised as light cycle oil (LCO), and the rest of the products with boiling points above 343°C were categorised as heavy cycle oil (HCO).

As seen in **Figure 2**, all three BASF catalysts increased the content of the naphtha range products significantly, as high as 84%, while for the thermal process, the naphtha fraction is only 17% of the produced pyrolysis oil. As one of the objectives of this work was to produce a naphtha-rich liquid product to allow for easy transportation, it can be concluded that using the proprietary catalysts from BASF helped to achieve that objective. Proprietary BASF catalysts allowed further cracking of the heavy molecules to produce more naphtha and less heavy oil fractions than the conventional or thermal pyrolysis process. These catalysts can be fine-tuned to further maximise the naphtha fraction in the pyrolysis oil to achieve a product that can be seamlessly integrated into chemical facilities.

This work summarises a comparison of thermal and catalytic pyrolysis processes. While the thermal pyrolysis process is relatively

straightforward and quick to implement, it typically yields a higher fraction of heavy oil products. In contrast, the catalytic pyrolysis process facilitates the formation of lighter fractions, including naphtha.

Upgrading heavy residual waxes from fast thermal LDPE py-oil in the FCC

Many sustainable feedstocks might be considered for co-processing in refinery processes, such as waste plastics, biomass waste, municipal solid waste (MSW), and vegetable oils (see **Figure 3**). Currently, thermo-chemical conversion techniques are required, such as fast pyrolysis or hydrothermal liquefaction (HTL), to convert solids (plastics and biomass) to liquid fuels. For more than 80 years, FCC has been proven valuable for converting heavy, low-value fractions of conventional oil into high-value products, such as gasoline and LPG olefins. The combination of continuous catalyst regeneration and flexible catalyst design makes the FCC process an attractive solution for introducing such renewable and recycled feedstocks. In addition, the FCC as an insertion point for renewable or recyclable feedstocks is economically attractive since no extra hydrogen is required in the unit compared to hydrotreating or hydrocracking processes, which might be problematic when processing feedstocks from biomass.

Co-processing of pyrolysis oils from waste plastics, especially the heavy residual waxes from the thermal process, appears to be a valuable option for FCC units. The main challenges

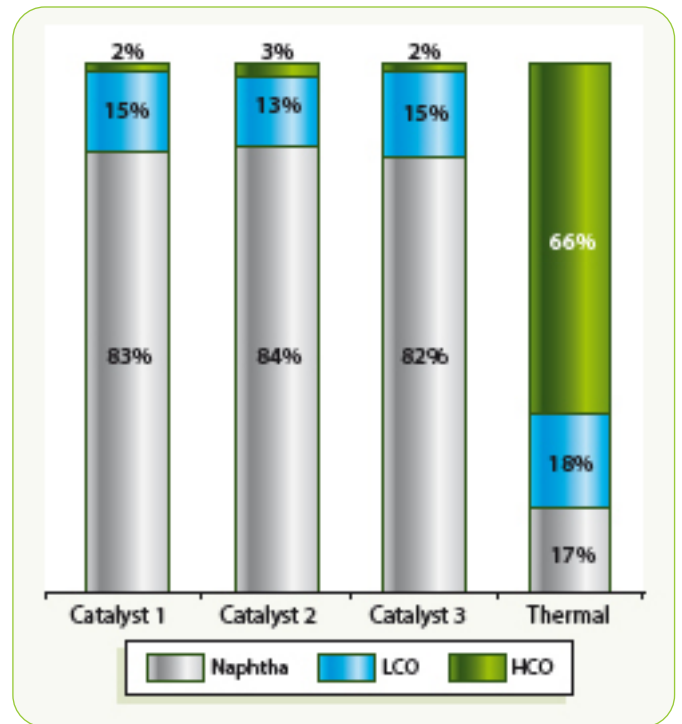


Figure 2 Product distribution of condensed vapours after catalytic vs thermal pyrolysis experiments

associated with pyrolysis oils from waste plastics are residual chlorine from polyvinyl chloride (PVC), trace metals, and variability in terms of composition depending on the raw materials used for producing the pyrolysis oil. The use of polycarbonates or polyethylene terephthalate (PET) might lead to the presence of heteroatoms, such as oxygen, in the resulting py-oil from these waste plastics. Hence, collecting and sorting plastic waste will be an important step in minimising the presence of PVC or PET as raw materials during the pyrolysis process.

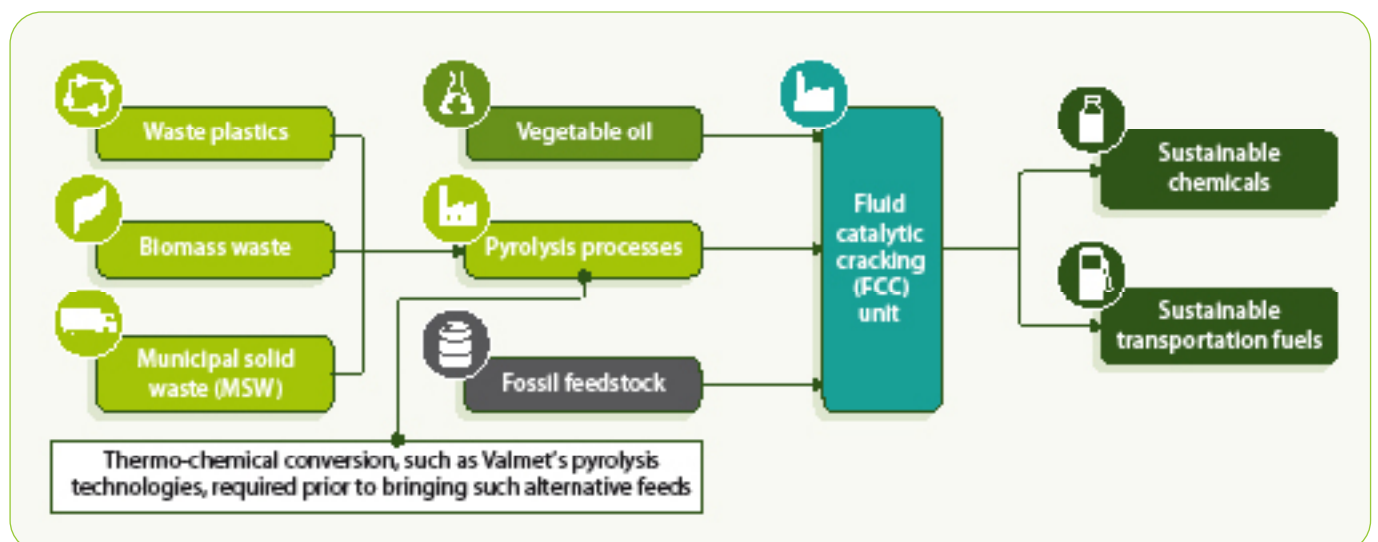


Figure 3 Co-processing feed options through the FCC unit

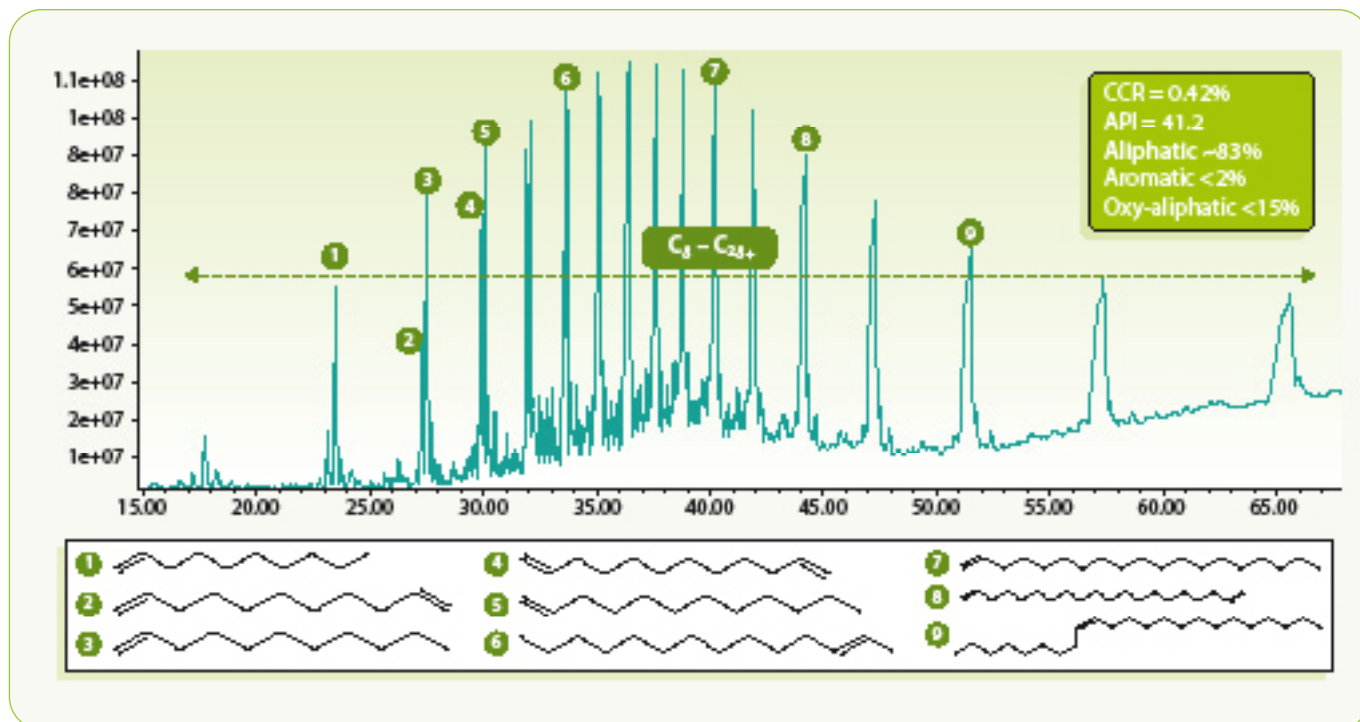


Figure 4 Composition of thermal pyrolysis oil derived from mechanically recycled LDPE, including the major species identified by GC-MS

Polyolefins (PP, LDPE, HDPE) will be the easiest waste plastics for circular manufacturing due to their high effective hydrogen index (EHI) and low Conradson carbon residue (CCR) contents. Valmet provided a py-oil sample originating from mechanically recycled LDPE for further characterisation and testing by BASF. A more detailed analysis of this thermal py-oil using GC combined with mass spectroscopy revealed evidence of olefins and dienes as major substances, resulting in about 83% aliphatic compounds, less than 2% aromatic compounds, and less than 15% oxy-aliphatic compounds (see **Figure 4**). This waxy fraction from thermal py-oil is mainly composed of heavier waxes (>C₂₈), making a suitable feedstock for FCC with or without diluting it with gasoil.

Catalytic measurements were made using an Advanced Catalytic Evaluation (ACE) fluid bed reactor (Kayser, 1997). ACE was introduced in 1997 as a fixed-fluid bed laboratory cracking system, which has rapidly taken over as the industry standard for bench-scale FCC testing compared to fixed-bed MAT units (Clough, et al., 2017). ACE was operated using a steam-deactivated catalyst at a temperature of 550°C, 60-second injection time, 1.125-inch injector height, and constant time on stream protocol to vary catalyst-to-oil ratios between four

and eight. Pyrolysis oil was tested at 100%, although typical commercial application loadings are around 10%. Naphtha product was defined as C₅ to 232°C, LCO as 232°C-360°C, and HCO as 360°C and higher. This waxy LDPE py-oil, containing 10% naphtha, 33% LCO, and 57% HCO, was successfully and fully upgraded to transportation fuels or chemicals, without any dilution with gasoil, through ACE by assessing two commercial BASF catalysts, including:

- ① FCC1 oriented towards naphtha maximisation.
- ② FCC2 oriented towards LPG olefins maximisation.

Table 1 shows results obtained for both catalysts, FCC1 and FCC2, in terms of product yields at a 7.0 catalyst-to-oil ratio after the upgrading of this waxy LDPE py-oil.

Due to the properties of this waxy LDPE py-oil (EHI ~1.9 and CCR ~0.4 wt%), which contains mainly aliphatic compounds, the waxy fraction of the LDPE py-oil was fully converted into valuable products, such as naphtha and LPG hydrocarbons. For FCC2, which is specifically designed for maximising LPG olefins, yields of 45.4 wt% propylene and C₄ olefins can be achieved compared to 25.8 wt% for FCC1, which is specifically designed for naphtha production (Table 1). The olefinicity, which is the ratio of cracking (olefin producing) and hydrogen-

transfer reactions (olefin consuming), is an important metric in FCC analysis. FCC2 has been designed by optimising the acid site density of the base catalyst while introducing ZSM-5 to further boost LPG olefin yields and selectivities.

Given the properties of this py-oil, the coke yield is lower compared to typical gasoil feedstock, with 3.2 wt% and 1.2 wt% for FCC1 and FCC2, respectively (Table 1). Consequently, the FCC unit at a commercial scale might require the addition of fossil-based feedstocks, such as gasoil or resid, to maintain its heat balance and to overcome any shortage of alternative co-feedstocks.

Conclusions

Plastic recycling has gained attention in the circular economy due to its potential for making the plastic lifecycle more sustainable. Chemical recycling is a promising alternative that can overcome the challenges found with mechanical recycling of all plastic waste. Among the different methods of plastic recycling, Valmet advocates pyrolysis as a promising method of converting plastics to their monomers. In scenarios where decentralised processing is advantageous, the liquid products from pyrolysis are often more valuable than other products. Here, the utilisation of the catalyst is crucial.

In the first approach, catalytic pyrolysis optimises the content of pyrolysis oil, and in the second approach, after thermal pyrolysis, the waxes are catalytically degraded to produce oil. In this work, during the catalytic fast pyrolysis of polyolefins, even though the catalyst increased the formation of non-condensable gases from 10% to roughly 20%, the gasoline-range products increased from 15% to approximately 85%. This outcome is particularly noteworthy, as it underscores the potential for generating high-value products from plastic waste.

In the second approach, upgrading the waxy fraction from a thermal pyrolysis process appears to be a valuable option for a co-processing application through the FCC unit. BASF demonstrated that the catalyst can be fine-tuned to either produce more sustainable chemicals, such as LPG olefins, or more transportation fuels, such as gasoline. FCC units appear to be well suited for co-processing alternative feedstocks, where catalysts can be

ACE cracking results of waxy py-oil from LDPE with FCC1 and FCC2 catalysts at a 7.0 cat-to-oil ratio

	FCC1	FCC2
Cat-to-oil ratio, wt%/wt%	7.0	7.0
Conversion, wt%	92.8	93.6
Hydrocarbon yields		
H ₂ , wt%	0.08	0.07
CH ₄ , wt%	1.08	0.48
Ethane, wt%	0.60	0.43
C ₂ =, wt%	1.12	6.17
C ₃ , wt%	1.97	3.02
C ₃ =, wt%	11.2	24.4
n-butane, wt%	1.7	1.4
i-butane, wt%	6.9	3.8
n-butenes, wt%	10.0	12.7
Isobutylene, wt%	4.6	8.3
Naphtha (C ₅ -232°C), wt%	50.4	31.6
LCO (232-360°C), wt%	4.2	3.2
HCO (360°C+), wt%	2.9	3.2
Coke, wt%	3.2	1.2
Calculated values		
Naphtha + total LPG, wt%	86.77	88.42
Total dry gas, wt%	2.88	7.15
Total LPG, wt%	36.37	53.62
LPG olefinicity, wt%/wt%	0.71	0.85
Total C ₄ =, wt%	14.6	21.0
C ₃ olefinicity, wt%/wt%	0.85	0.89
C ₄ olefinicity, wt%/wt%	0.63	0.80

Table 1

fine-tuned to reach refiner objectives while reducing the carbon intensity of the finished products. In a collaborative effort, Valmet and BASF are developing technological solutions to facilitate the commercial-scale integration of circular carbon solutions.

Disclaimer: BASF's contributions to this article were limited to catalyst development and application.

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