

# LIGHT OLEFIN PRODUCTION VIA CATALYTIC, MELT, ELECTRIFIED PYROLYSIS OF POLYETHYLENE

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## Highlights

- We introduce a low-temperature, electrified, and intensified catalytic melt-pyrolysis reactor for recycling low-density polyethylene into polyolefin monomers.
- We employ a mesoporous solid acid catalyst and achieve a light olefin (C<sub>2</sub>-C<sub>4</sub>) selectivity of ~32% at high conversion.
- Higher temperatures favor light olefin production. Varying the N<sub>2</sub> flow rate can tune the product distribution toward heavier or lighter products.
- Reactor modifications allow the recirculation of heavier products to increase their residence times, allowing them to crack into lighter products and increase light olefin yields.

## 1. Introduction

Plastic waste has become a huge burden on our environment, with less than 10% being recycled and the remaining incinerated or thrown into landfills<sup>1</sup>. Most recycled plastic is mechanically recycled. This process cannot handle mixed plastics. Catalytic pyrolysis is an appealing method for plastic deconstruction as it can be feedstock agnostic. However, converting plastic into light olefins (C<sub>2</sub>-C<sub>4</sub>) is challenging, sometimes requiring a two-step process<sup>2</sup>.

Here, we introduce an electrified catalytic melt pyrolysis slurry reactor that operates at low temperatures to produce a narrow distribution of light olefins at high yield. Increasing the operating temperature increases the selectivity of light olefins (C<sub>2</sub>-C<sub>4</sub>). We demonstrate an optimum flow rate to tune product distributions. We also explore reactor optimization via process intensification to further control light olefin yields and present simulations to understand and optimize the process.

## 2. Methods

All reactions were conducted in a tubular reactor with a quartz frit. Low-density polyethylene (LDPE) and a solid acid catalyst were loaded into

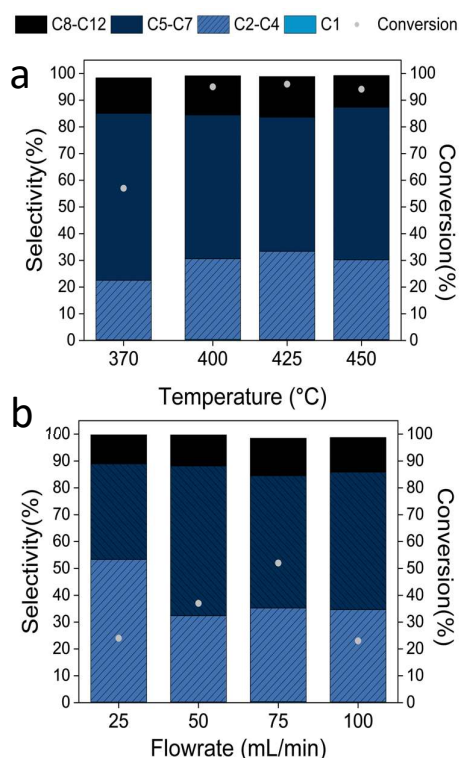
the reactor with a silicon carbide monolith to enhance heat and mass transfer. An upward N<sub>2</sub> flow was used to enhance transport and entrain the products. A thermocouple was used to measure the internal temperature, and a PID controller was used to control the heating. The reactor was placed inside heating coils and ceramic tubes. A Tedlar gas bag was attached to the rear end of a condenser to collect all gaseous products produced. Upon completion of a reaction, the reactor was quickly cooled to room temperature, and liquid products were extracted from the distilling receiver. We varied the mesoporous acid catalysts and the reactor design to tune the product distribution further.

## 3. Results and discussion

At 370 °C and 100 mL/min of N<sub>2</sub>, the LDPE conversion was 58% with 22% and ~100% selectivity to C<sub>2</sub>-C<sub>4</sub> and C<sub>2</sub>-C<sub>12</sub> olefins, respectively. Figure 1a shows that as the temperature increases to 400 °C, the conversion and selectivity toward C<sub>2</sub>-C<sub>4</sub> light olefins increase to nearly 100% and 32%, respectively. The depolymerization reaction begins at approximately 370 °C and is completed after around 200 seconds. At 400 °C, the overall yield to olefins of ≤C<sub>12</sub> is a remarkable ≤ 90+%. This

slate of products is very valuable because light olefins are used for various products like lubricant base oils, cosmetics, etc. For subsequent studies, a temperature of 400 °C was chosen.

The effect of N<sub>2</sub> flowrate on light olefin selectivity at 400 °C at low conversion is shown in Figure 1b. Decreasing the flowrate increases the residence times of the heavier products in the reaction zone, leading to deeper cracking and a higher selectivity toward lighter products. At low flowrates, conversions are low due to ineffective mixing, causing inefficient heat and mass transfer in the slurry reactor. Hence, an optimal flowrate exists for light olefin production and high conversion. Additionally, as temperatures increase, the reaction rates increase and to prevent secondary reactions, good mixing during the reaction is essential, achieved at higher flowrates. Further insights into the transport phenomena are obtained using computational fluid dynamics (CFD) simulations conducted in COMSOL.



**Figure 1.** a) Selectivity and conversion over different temperatures at 100 mL/min of N<sub>2</sub>. b) Selectivity and conversion over various N<sub>2</sub> flowrates at 400 °C.

To tune the product distribution, we introduce an intensified hybrid setup to recirculate heavy

products and further improve the yield to light olefins. This was achieved by introducing a condenser on top of the reactor. As the polyethylene reacts, the products are carried up by the flowing N<sub>2</sub>. A condenser enables heavier products to condense back into the reaction zone to react further. We have found that once the products are light enough, such that they cannot be further condensed, they exit the reaction zone. We will also present results on the effect of acid catalyst.

#### 4. Conclusions

We introduced catalytic melt pyrolysis at relatively low temperatures to depolymerize plastics into a mixture of monomers, closing the loop in the circular economy of plastics. With an electrified slurry reactor with enhanced transport media, we were able to achieve increased yields of light olefins due to enhanced heat and mass transfer at a residence time of seconds. Increasing the temperature increases selectivity toward light olefins and changing the flowrate tunes the product distributions. By introducing a condenser, we further enhanced the selectivity toward light olefins. CFD simulations provided insights into the mixing, heat, and mass transfer in the system. Finally, we will present data for various acid catalysts to elucidate the effect of active site and methods to reduce the residence time to milliseconds and improve the light (C<sub>2</sub>-C<sub>4</sub>) olefin yield to >60%.

#### References

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#### Keywords

Plastic Waste; Catalytic Pyrolysis; Process Intensification; Process Electrification;