# Enhancing Polystyrene Recycling: Temperature-Responsive Pyrolysis in a Vortex Reactor

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### Highlights

- Polystyrene was pyrolysed in a vortex reactor with high styrene recovery
- Vortex reactor minimized the secondary reactions.
- High temperature increased the styrene recovery while decreasing dimer and trimer selectivity

### 1. Introduction

The accelerated degradation of polystyrene (PS), prominent at lower temperatures, coupled with its impressive conversion rate of over 60% into styrene monomers under normal conditions, has propelled advanced recycling via pyrolysis into the forefront as a promising recycling route [1]. Polystyrene, owing to its lower thermal resistance compared to polyolefins, demands less energy for degradation and monomer recovery. Additionally, its molecular structure facilitates higher styrene monomer recovery rates with limited secondary reactions compared to other polymers such as polyolefins. However, maximizing styrene recovery through optimizing reaction conditions and selecting a suitable reactor can further enhance the economic viability of polystyrene pyrolysis [2].

The widely accepted view in terms of the degradation mechanism of polystyrene predominantly follows an chain scission and unzipping process. Thus, the primary products of polystyrene pyrolysis include styrene oligomers, comprising the styrene monomer, dimer, and trimer, constituting over 80 wt.% [2]. The primary target of PS pyrolysis is the production of styrene monomers. However, dimers, trimers, and more stable aromatics such as benzene, toluene, ethylbenzene, xylene (BTEX) are unavoidable byproducts that can diminish the purity of the pyrolysis oil. Choosing a suitable reactor capable of reducing residence time to prevent secondary reactions becomes crucial [3]. In this context, the vortex reactor emerges as a viable candidate. The design and concept of the vortex reactor aim to minimize the residence time of produced gas to few milliseconds. Furthermore, the concept of the vortex regime suggests that the residence time of compounds in the reactor varies. Due to centrifugal force, heavier compounds exhibit a higher tendency to linger in the reactor compared to lighter species. Consequently, there is an increased probability of conversion of dimers, trimers, and heavier oligomers to styrene monomers and BTEX [4].

#### Methods

Virgin general purpose polystyrene (GPPS) granules were provided from Total Energies. Coperion ZSK 18 Ml twin screw extruder were used to inject melt polystyrene at 280°C into the vortex chamber while N<sub>2</sub> as carrier gas enters the vortex chamber tangentially through the sides to facilitate the vortex regime. The product gases were then allowed to exit through the diverging exhaust at the center of the vortex chamber. A small tube connected to a pump was placed at the center of the exhaust to collect gas samples in facilitating the analysis. The analysis section comprises of a refinery gas analyzer (RGA) and a two-dimensional gas chromatography (GCXGC) equipped with atomic emission detector (AED) for better detection and accurate quantification of the compounds.

The experiments were conducted at three temperatures 500°C, 600°C, and 700°C under atmospheric pressure while  $N_2$  gas flow and PS extruder feeding flow were kept constant throughout all the experiments at 15 Nm<sup>3</sup>/h and 2.186 kg/h, respectively.

## 3. Results and discussion

At 700°C, styrene monomer yield reached  $\approx 90$  %, significantly higher compared to other reactors such as CSBR [1]. Increasing the temperature led to higher styrene monomer recovery and lower selectivity of dimer and trimer (Figure 1). At 500°C, the selectivity of styrene trimer, compared to styrene dimer, was higher. The elevated temperature favored the production of styrene monomer while concurrently inhibited the formation of styrene trimer, while selectivity of styrene dimer showed no significant alteration with changes in pyrolysis temperature. However, at 700 °C, almost no dimer and trimer were produced primarily from the higher conversion of dimer and trimmer to lighter aromatic compounds such as styrene and BTEX compounds and not due to less monomer recombination at higher temperatures.. Moreover due to reduced secondary reaction, it can be concluded that styrene dimer and trimer are not formed through the recombination of monomers but through hydrogen transfer and  $\beta$ -scission [2].

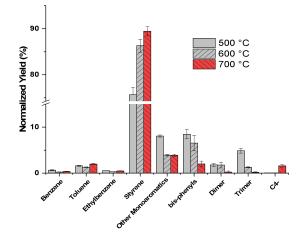


Figure 1. Product yields of GPPS pyrolysis in vortex reactor at different temperatures.

# 4. Conclusions

Based on the findings, it can be concluded that increasing the temperature during the pyrolysis process leads to a higher recovery of styrene monomer and a reduction in the selectivity of dimer and trimer. Moreover it was showed that the formation of styrene dimer and trimer do not follow monomer recombination but through hydrogen transfer and  $\beta$ -scission. The pyrolysis of polystyrene in a vortex reactor has demonstrated a high potential for the recovery of styrene monomer, with a yield reaching approximately 90% at 700°C. This promising result surpasses the performance of other types of reactors, indicating the effectiveness of the vortex reactor in achieving a high yield of styrene monomer from polystyrene pyrolysis.

# References

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# Keywords

Vortex reactor, Polystyrene, Pyrolysis, Styrene oligomers