

PYROLYSIS OF POLYSTYRENE IN A GAS-SOLID VORTEX REACTOR

Sangram Roy, Sepehr Madanikashani, Robin John Varghese, Mehrdad Seifali Abbas-Abadi, Tom Verspeelt, Yi Ouyang, Geraldine J. Heynderickx, Kevin M. Van Geem*

¹Laboratory for Chemical Technology (LCT), Ghent University, Technologiepark 125, 9052 Zwijnaarde, Belgium

*Corresponding author: Kevin.VanGeem@ugent.be

ABSTRACT

Pyrolysis is one of the promising routes for the chemical recycling of polystyrene. However, the challenge lies in developing optimal contacting patterns to enhance the yield of liquid products (styrene). The present work demonstrates the applicability of a vortex reactor to effectively pyrolyze polystyrene. Three experiments were conducted at temperatures of 450, 500 and 550 °C, wherein the polystyrene was fed at a rate of 1kg/h. Prior experiments had indicated that such a flow rate ensures a smooth and uniform injection of PS in the reactor. The liquid products obtained were condensed in a system of two condensers. Subsequently, the products were analyzed offline in GC x GC- FID. The analysis showed the significant formation of styrene.

Key Words: Thermal pyrolysis, GC x GC-FID

1 INTRODUCTION

Modern-day lifestyle has led to gradual demand in consumption of plastics. With a nearly twenty-fold surge in plastic products for the past half-century, it is expected to consume 40% of all crude oil by the mid of this century. Such indiscriminate usage of plastics has brought challenges due to vast plastic solid wastes (PSW). However, it has also led to growing concern about the recycling of such products. Presently, the aim is to address this demand by recycling 60% of all plastics in this decade and gradually attain complete recycling by 2040¹⁻³. It is further estimated that the efficient recycling of PSW could save ~3.5 billion barrels of crude, amounting to \$176 billion¹⁻³.

Prior studies have indicated that pyrolysis emerges as a promising alternative to the chemical recycling of plastics. Specifically, high volatile matter (> 86.83 %) and low ash content (<2%) of conventional plastics offer an attractive route to produce liquid oil². However, as PSW are mostly a plethora of plastics, it is pertinent to optimize and design systems for each of them. Among several such plastics, Polystyrene (PS) is a major driver of the demand¹⁻³. Thus, in this study, PS pyrolysis was studied arguably for the first time in an in-house developed vortex reactor.

Typically, pyrolysis of polystyrene is known to propagate through initiation, transfer, decomposition, and termination. It may involve random as well as end chain scissions. Irrespective of temperature, as compared to plastics like polyethene (PE), and polypropylene (PP), PS products are mostly liquid monomers (~80%). It was reported that liquid styrene production is maximized at about ~450- 500 °C.

2 EXPERIMENTAL

For the present study, a novel gas-solid vortex reactor was used to conduct the pyrolysis of PS. Several past studies on the hydrodynamics of such contacting patterns have established its relevance as a process intensification unit^{4,5}. The reactor consisted primarily of 4 sections – a 12-slotted ring gas distributor, a reactor, throat. It was itself stationed inside an electrically heated oven with pressure and temperature sensors mounted to monitor the process conditions. N₂ from portable nitrogen cylinder was supplied through a vaporizer and inline flow heater (Kanthal, Sandvik). The PS was fed from a gravimetric feeder (Coperion K-Tron) with a screw injector. The feeder itself was pressurized to prevent the backflow of hot gases from the reactor and to maintain an inert atmosphere. Silicon oil coolant was flown to maintain in the jacket injector at 15°C to prevent blockage and smooth flow. To initiate an experiment, the gas feeding section and the reactor oven were heated. Hot N₂ at 15 Nm³/h was injected to heat the reactor. The PS from the feeder was started only after it was ensured that the bed reached the desired temperatures of 450, 500 and 550 °C. A drop in pressure in the bed indicated a stable vortex formation in the reactor (Figure 1). Prior experiments established that a feeding rate of 1 kg/h of PS ensures a smooth injection. The pyrolyzate obtained was sent through a system of two U-tube double pipe condensers. The first water-cooled condenser was kept at 70 °C, whereas the second oil-cooled condenser was maintained at 15 °C. The condensable liquid products were collected from the condensers and labelled at regular intervals of 30 min. Whereas the non - condensable gases were vented out through filters. The liquid oil so collected was mixed with 0.5 % of 4-tert-Butylcatechol inhibitor and refrigerated for further analysis. A summary of experiments performed as a part of this study is tabulated in Table 1.

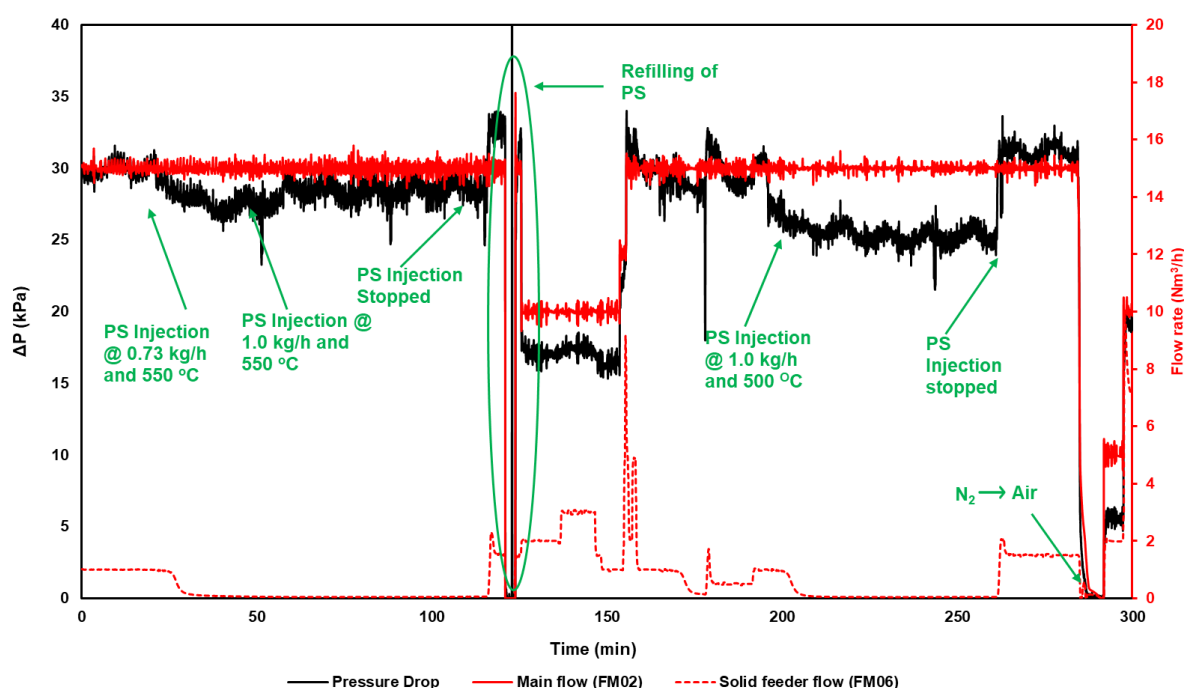


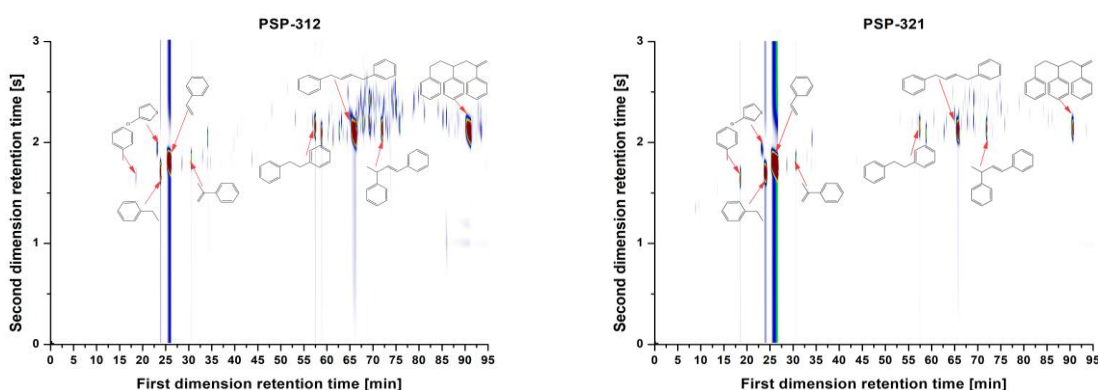
Figure 1. Pressure and temperature profile

Table 1. Summary of conditions studied

PS flow rate [kg/h]	1.0
Primary N ₂ flow rate [Nm ³ /h]	15
Secondary (solid feeder) N ₂ flow rate [Nm ³ /h]	1.5
Average Bed Temperature (Bed and Throat) [°C]	450, 500, 550
Total Injected PS [gm]	1 kg

3 RESULTS AND DISCUSSIONS

The liquid product obtained were analysed in GC x GC-FID. The carbon numbers detected ranged from C₈- C₂₄ and were grouped into – ethylbenzene, styrene, dimers and trimers. Figure 2 below illustrates the detailed GC x GC -FID chromatogram analysis of product oil. The compounds were quantified based on 3-Chlorothiophene as the internal standard, which was sufficiently separated from other compounds. The detailed composition of the oil is summarized in Figure 3. As can be noted, no definite trend was observed in the pyrolysis product of condenser 1. This was largely owing to insufficient condensation of the gases. However, for the second condenser, it can be distinctly noted that about 90% of the liquid product consists of a styrene monomer. Along with it, about 4-6 % of dimer and 1.5% of trimer were also formed. It was also observed that the production of styrene monomer and its trimer showed a marginal drop when the temperature dropped marginally. Similar studies earlier indicated that pyrolysis of PS results in the production of mostly as compared to other plastics². In fact, the recovery of monomers is also in significant proportions. Thus, an optimum temperature of 450 °C was found to be suitable.

**Figure 2. GC X GC -FID chromatogram of (a) first (b) second condenser**

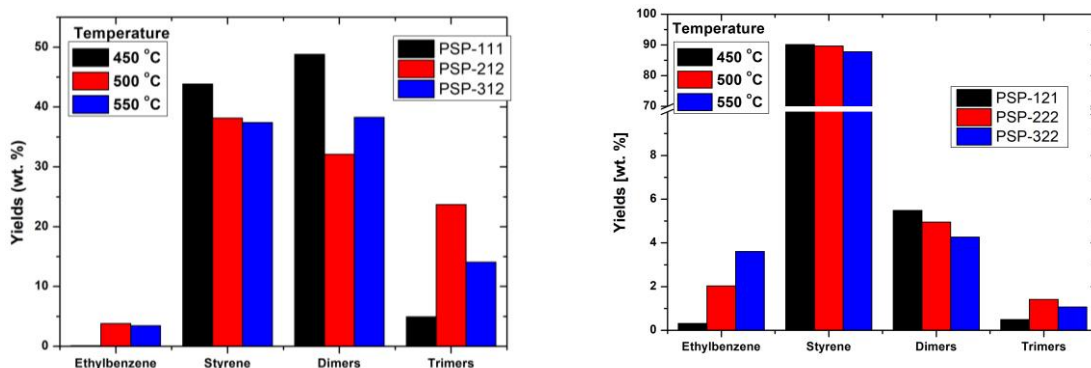


Figure 3. GC X GC -FID chromatogram of (a) first (b) second condenser

4. CONCLUSIONS

The study established a vortex reactor as promising process equipment for the pyrolysis of polystyrene. Product analysis revealed that the styrene was in significant proportions as compared to its dimers and trimers. However, as an improvement in the analysis of the liquid product, online analysis is being developed for simultaneous quantification of liquid (GC x GC-FID) as well as non-condensable gases (RGA).

5. ACKNOWLEDGEMENTS

The authors gratefully acknowledge the funding received from the Fund for Scientific Research Flanders (FWO) and innovation program/ERC grant agreement no.818607 (OPTIMA). This work was also performed in the framework of the Catalisti cluster SBO project WATCH (HBC.2019.0001 "Plastic waste to chemicals") and PREFER (The Plastics Refinery: No More Waste) with the financial support of VLAIO (Flemish Agency for Innovation and Entrepreneurship).

6. REFERENCES

1. A. Zayoud, H.D.Thi, M.Kusenberger, A.Eschenbacher, U. Kresovic, N.Alderweireldt, M. Djokic, and K.M.Van Geem, *Waste Manage.*, 2022, **139**, 85-95.
2. Y.Peng, Y.Wang, L.Ke, L.Dai, Q.Wu, K.Cobb, Y.Zeng, R.Zou, Y.Liu, and R.Ruan, *Energy Convers. Manage.*, 2022, **254**, 115243.
3. W.Kaminsky, *Fuel Commun.*, 2021, **8**, 100023
4. M.N.Manzano, A.G.Quiroga, P.Perreault, S.Madanikashani, L.A.Vandewalle, G.B. Marin, G.J.Heynderickx, and K.M.Van Geem, *J. Anal. Appl. Pyrolysis*, 2021, **156**, 05165.
5. A.Gonzalez-Quiroga, P.A.Reyniers, S.R.Kulkarni, M.M.Torregrosa, P.Perreault, G.J.Heynderickx, K.M.Van Geem, and G.B. Marin, *Chem. Eng. J.*, 2017, **329**, 198-210.