Department of Chemical & Biomolecular Engineering

CHBE TEAM 7

Polytetrafluoroethylene (PTFE)

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Motivation

This project aims to explore the technical and economic feasibility of producing high-performance polymers like polytetrafluoroethylene (PTFE) due to its exceptional chemical and physical properties. PTFE has a complex synthesis that requires high energy inputs, hazardous intermediates, and costly separation units. These challenges pose concerns for efficiency, profitability, and safety for small and medium-scale plants. PTFE, a forever chemical, belongs to the group of per- and polyfluoroalkyl substances (PFAS), which can be dangerous if improperly disposed of. The project uses Aspen Plus to simulate the production of tetrafluoroethylene (TFE) and polymerize it into PTFE, addressing these issues and improving process sustainability.

Test Results

Process Optimization

Sensitivity analyses were performed to refine key reactor parameters: Reactor 4 (PFR) Length Optimization Figure 1 shows that a plug flow reactor (PFR) length sensitivity analysis. Batch Polymerization temperature and pressure in the semi-batch polymerization reactor were. The mass fraction of PTFE peaked at 85 °C—above which side reactions reduced conversion—while pressure remained largely stabilizing, with a maximum yield at 26.34 atm.

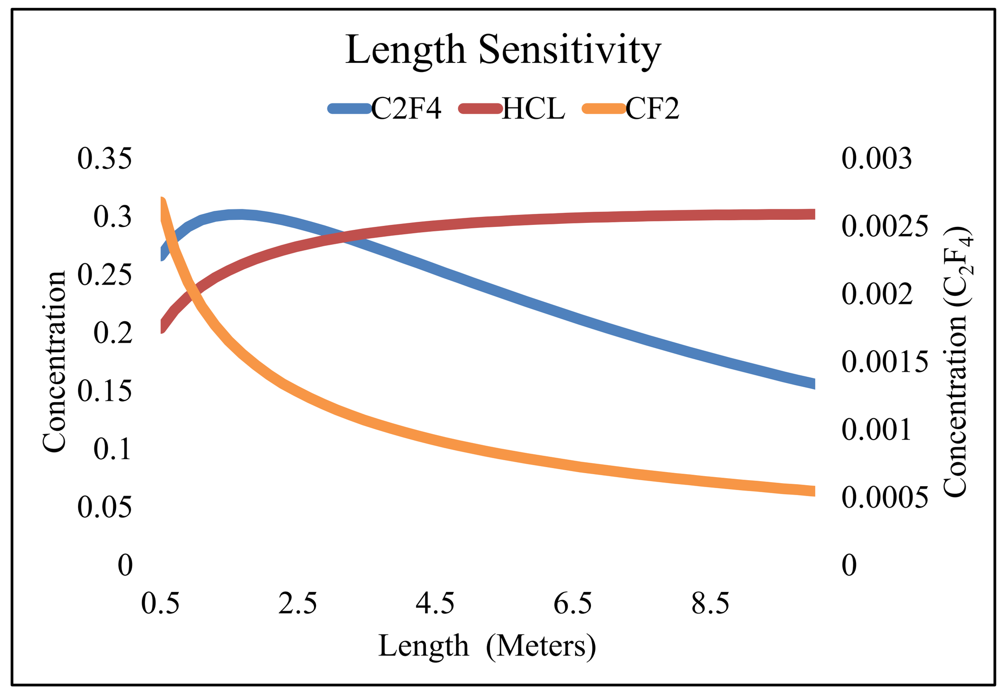

Figure 1 (above). Length of 2.6 m maximizes TFE conversion. This exact length may be impractical at scale, the derived residence time provides a clear design target for scaling up the reactor while maintaining high PTFE yield.

Bells and Whistles

To manage the required cleaning and emptying of the semi-batch reactor at an industrial scale it was proposed that two semi-batch reactors work in parallel—one operating while the other is cleaned—Figure 2. This option, though more expensive, was selected to minimize safety risks associated with TFE storage. Each reactor will operate in 6-hour cycles, allowing sufficient time for cleaning. To support continuous operation, ammonium persulfate is now added at a constant rate of 5 kg/hr instead of being preloaded. At 228.32 kg/hr PTFE output and a density of 2.2 g/cm³, each batch produces 0.6227 m³ of PTFE, setting the minimum volume for each reactor.

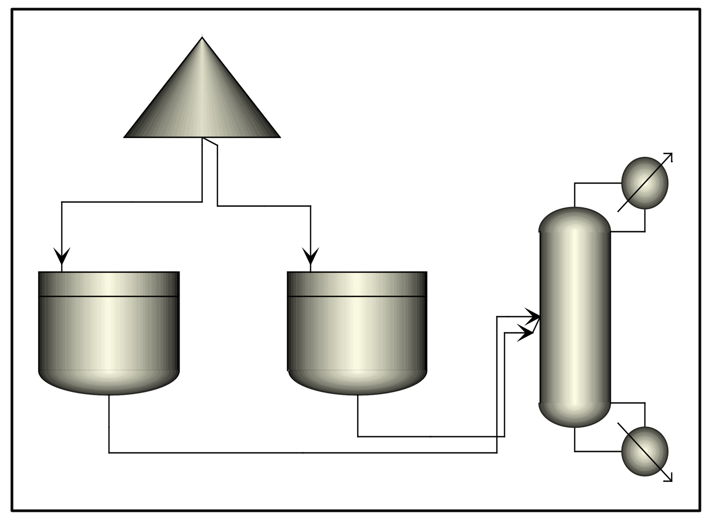

Figure 2 (left). ASPEN Plus representation of a parallel batch reactor unit loading into a separator. This set up allows for continuous PTFE production while one is being cleaned the other is in full operation.

Design Analysis

Reactor 1: Chloroform Synthesis

$CH_4 + 4Cl_2 \rightarrow CHCl_3 + 4HCl$ + byproducts

Chloroform is synthesized by the exothermic gas-phase reaction of methane and chlorine in a continuous tubular reactor

$$reaction\ rate^{species} = \frac{K_c^{species}}{Custom\ Term} * \sqrt{[species]}[Cl_2]$$

Reactor 2: Chlorodifluoromethane Synthesis

$CCl_4 + HF \rightarrow CHClF_2 + HCl$ + byproducts

The proposed reaction mechanism, composed of four assumed-to-be elementary steps, two of which are reversible, follows the path:

(1) $HF + SbCl_5 \rightarrow SbCl_4F + HCl$
(2) $SbCl_4F + CHCl_3 \rightarrow SbCl_5 + CHCl_2F$
(3) $SbCl_4F + CHCl_2F \rightarrow SbCl_5 + CHClF_2$
(4) $SbCl_4F + CHClF_2 \rightarrow SbCl_5 + CHF_3$

Rate Constant	$k_{1,\ forward}$	$k_{1,\ backward}$	$k_{2,\ forward}$	$k_{2,\ backward}$	k_3	k_4
Value	$3.6*10^5$	$8.0*10^5$	$3.2*10^4$	$2.1*10^5$	4680	175

Reactor 3: Pyrolysis

$CHClF_2$ + heat $\rightarrow C_2F_4 + HCl$ + byproducts

The set of elementary steps proposed are shown below, where CF_2^* is a highly reactive radical intermediate.

(1) $CHClF_2 \rightarrow CF_2^* + HCl$
(2) $CF_2^* + HCl \rightarrow CHClF_2$
(3) $2CF_2^* \rightarrow C_2F_4$
(4) $C_2F_4 \rightarrow 2CF_2^*$
(5) $2C_2F_4 \rightarrow C_4F_8$
(6) $C_4F_8 \rightarrow 2C_2F_4$
(7) $C_2F_4 + CF_2^* \rightarrow C_3F_6$
(8) $C_3F_6 \rightarrow C_2F_4 + CF_2^*$
(9) $C_2F_4 + HCl \rightarrow H(CF_2)_2Cl$

Final Design

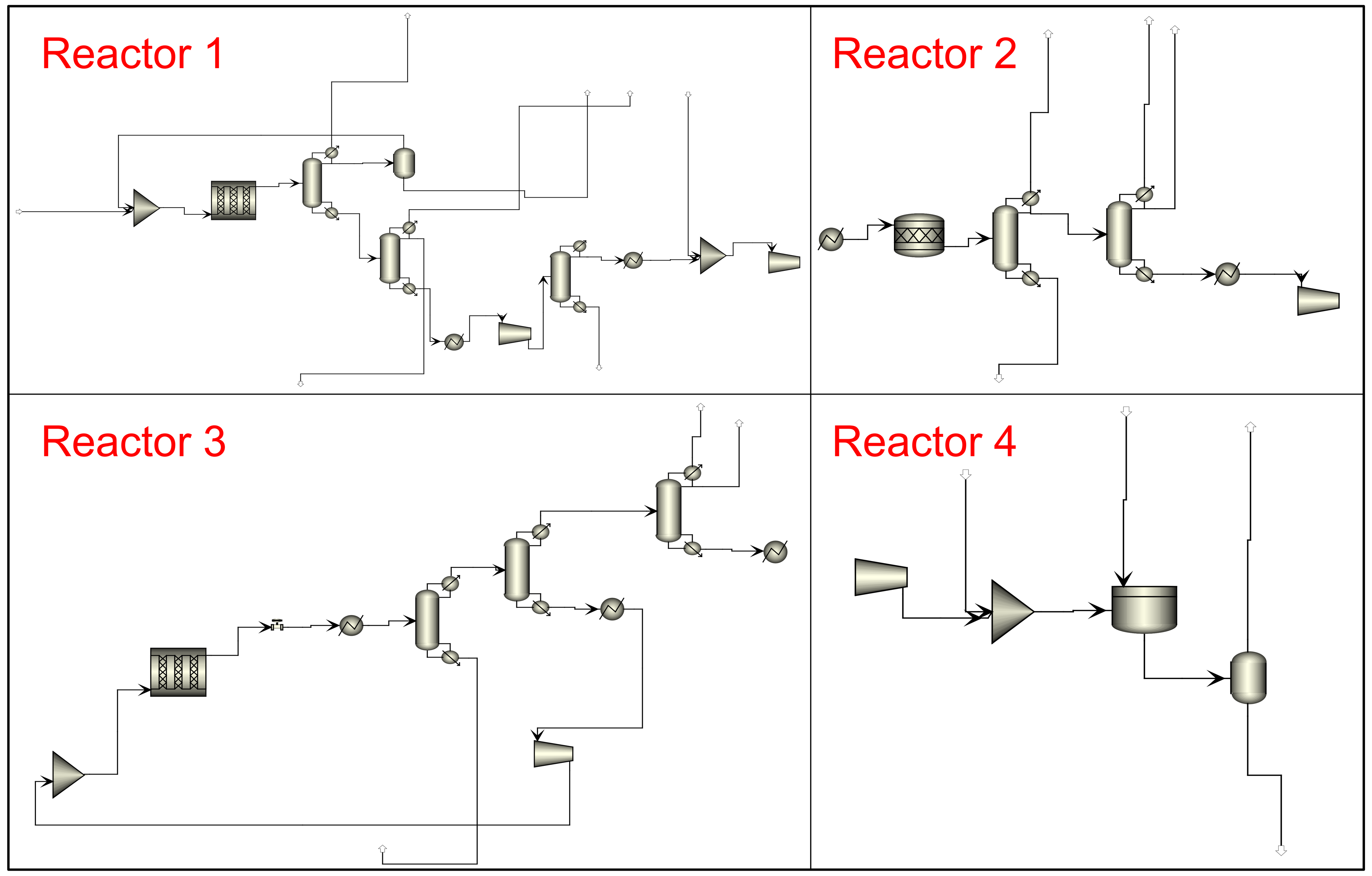

Figure 3 (above): Full process flow diagram of PTFE production developed in ASPEN Plus, including all major unit operations such as reactors, separators, distillation columns, heaters, coolers and compressors. The figure is divided into four quadrants, each representing a major reaction step in the overall PTFE production pathway.

Reactor 4: Polymerization of TFE

The polymerization of TFE to PTFE can be modeled as a suspension radical polymerization. This reaction series can be treated as four reaction phases: chain initiation, chain growth, chain transfer, and chain termination.

Conclusions

In conclusion, the PTFE plant was ultimately not profitable due to the inability to produce the initially intended amount of PTFE and the high cost of raw materials. The process proved to be highly complex, involving numerous unit operations such as reactors, separators, and heaters, each requiring significant optimization. To minimize waste and maximize product purity, additional separators were incorporated, which helped drive reactions to completion with minimal byproduct formation. Energy efficiency was improved through the implementation of a heat exchanger network, resulting in a 31.66% reduction in energy costs. Scaling up the process proved to be more successful with an annual production rate of 5000 metric tons—more than double the original target of 2000 metric tons

References

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