Investigation of a Microchannel Reactor for the Synthesis of Low Molecular Weight K-Type Perfluoropolyether Methyl Esters

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Abstract

This study demonstrates the synthesis of perfluoropolyether (PFPE) acyl fluoride from hexafluoropropylene oxide (HFPO) using a microchannel reactor. The reaction was conducted under low-temperature conditions with diethylene glycol dimethyl ether as the solvent and tetramethylethylenediamine (TMEDA) as the catalyst. The resulting acyl fluoride was esterified with methanol at room temperature to obtain K-type PFPE methyl ester, and its molecular weight was determined. The polymerization degree of the product was precisely regulated by systematically varying the microchannel length, HFPO flow rate, and reaction temperature. Compared to traditional systems, the microchannel reactor offers enhanced control over reaction parameters and can be seamlessly integrated into continuous production lines, underscoring its strong potential for the scalable synthesis of low-molecular-weight K-type PFPEs.

Keywords

Hexafluoropropylene Oxide; Microchannel Reactor; Polymerization; Esterification; K-type PFPE Methyl Ester.

1. Introduction

Low molecular weight perfluoropolyether (PFPE) are characterized by very low surface tension, minimal thermal expansion, exceptional chemical inertness, and high dielectric strength, non-flammability[1]. In recent years, low molecular weight PFPEs has great potentiality as a heat transfer fluids[2, 3] and solvents[4, 5] in the industrial field. Furthermore, low-molecular-weight PFPEs serve as key intermediates[6]. For instance, dimeric acid fluorides react with carbonates to yield the critical monomer, perfluoroisopropyl vinyl ether (PPVE). Likewise, trimeric and tetrameric acid fluorides can be further derivatized to produce a range of oxygenated fluorocarbon surfactants[7].

According to their synthetic processes and monomer constituents, commercially available PFPEs are broadly classified into four main types: PFPE Z, PFPE Y, PFPE K and PFPE D[8]. The PFPE Z and PFPE Y are produced via photocatalytic polymerization, whereas the PFPE K and PFPE D are synthesized through anionic polymerization[9]. While the current PFPE market is dominated by highly polymerized forms, the expansion of the fluorine industry is driving a rising demand for low-molecular-weight versions. This growing demand creates an urgent need to overcome technical hurdles, refine production technologies, and reduce manufacturing expenses.

Catalytic cracking represents a key industrial process for the preparation of low molecular weight PFPEs with high yield. The cleavage of medium molecular weight PFPE is facilitated by Lewis acids, such as AICI3, Al_2O_3, or AIF3, at temperatures between 150 and 380 °C, resulting in a PFPE acyl fluoride of low number-average molecular weight[10, 11]. However, this approach requires a two-step reaction sequence, and the removal of catalyst residues poses a significant challenge.

An alternative synthesis employs the photo-oxidation of hexafluoropropylene (HFP) with oxygen. This reaction yields a product characterized by a broad molecular weight distribution, which must be fractionated to obtain PFPE of specific polymerization degrees[12]. The resulting product consists predominantly of medium molecular weight PFPE, resulting in low availability of low molecular weight PFPE. Researchers accomplished the single-step synthesis of low-molecular-weight PFPE acyl fluorides by employing a reduced HFP feedstock concentration and a quartz tube reactor that had been pre-conditioned to a semi-translucent state through corrosion by the PFPE acyl fluoride product[1]. Furthermore, these reactions pose a potential explosion risk, necessitating precise control over reactant concentrations and temperature.

This paper employs hexafluoropropylene oxide (HFPO) as the raw material for the synthesis of low-molecular-weight PFPE via catalysed ring-opening polymerization[13]. This synthetic route to K-type PFPE was initially established by Selman and Skehan and later commercially scaled up by DuPont. The resulting polymer is converted into a PFPE oil through complete fluorination and marketed under the brand name Krytox® (**Figure 1**). Products with a degree of polymerisation below six are classified as low molecular weight PFPE, while those with a degree of polymerisation between 6 and 100 are designated as PFPE--K[8, 14].

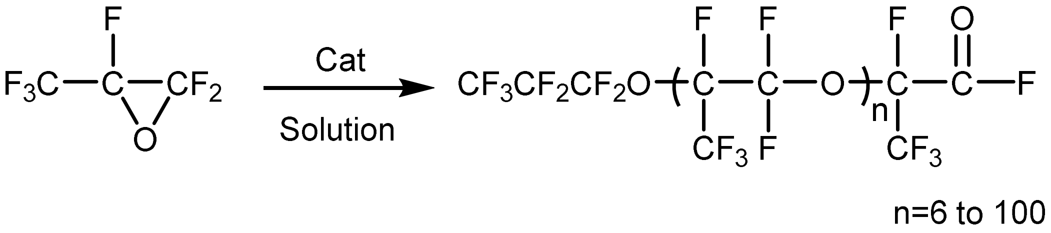

Figure 1. Krytox® PFPE synthesis process

The HFPO anion polymerisation must be conducted at low temperatures (typically below -20 °C) due to its highly exothermic nature and rapid reaction kinetics[15]. Conventional batch reactors exhibit inefficient heat and mass transfer, causing thermal inhomogeneity and promoting side reactions[16]. Consequently, the product exhibits a broad polymerization degree distribution, which directly compromises PFPE performance. In contrast, microchannel reactors provide high specific surface area[17], superior heat and mass transfer efficiency[18], and effective mixing capability[19], collectively enabling suppression of side reactions and production of narrowly distributed polymerization degrees. Moreover, their scalability through "numbering-up" rather than conventional scale-up prevents mass transfer deterioration during process amplification, thereby facilitating intelligent control and industrial implementation[20]. While HFPO anionic polymerization typically employs metal fluorides (e.g., RbF, CsF, KF) to produce medium molecular weight PFPEs[13], this study successfully synthesized low-molecular-weight perfluoropolyether acyl fluoride using tetramethylethylenediamine (TMEDA) as catalyst. The product was stabilized by methyl esterification prior to molecular weight determination.

2. Experiment

2.1 Section Headings

2.1.1 Sub-section Headings

Nitrogen gas (99%) was purchased from Zigong Jinhaiyang Gas Industry Co., Ltd., Hexafluoropropylene oxide (99%) was obtained from Shandong Dongyue Shenzhou New Materials Co., Ltd. and used as received. Diethylene glycol dimethyl ether and tetramethylethylenediamine (both 99%, Shanghai Titan Technology Co., Ltd.) were dried by storing over molecular sieves that had been activated at 800 °C for 6 hours, for a period of 24 hours prior to use.

2.2 Experimental Procedure

2.2.1 Synthesis of Perfluoropolyether Acyl Fluoride in a Microchannel Reactor

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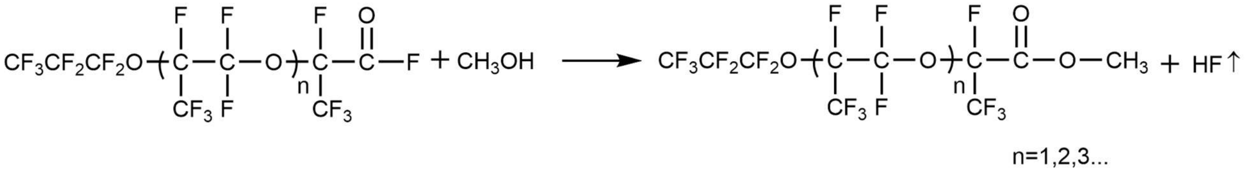
Figure 2. Schematic diagram of the synthesis of PFPE acyl fluoride in a microchannel reactor.

2.2.2 End-Capping of PFPE Acyl Fluoride via Methyl Esterification.

PFPE acyl fluoride (5 mL) was charged into a 50 mL round-bottom flask. Methanol (10 mL) was added dropwise at 0 °C, and the reaction was allowed to proceed at room temperature for 3 h under stirring (Figure 3). After completion, the mixture was transferred to a 25 mL separatory funnel and washed with deionized water (30 mL). The lower layer was collected to afford perfluoropolyether methyl ester. The reaction scheme for the methyl esterification is shown in Figure3.



$$CF_3CF_2CF_2O\left[-CF(CF_3)-CF_2-O-\right]_n-CF(CF_3)-C(=O)-F + CH_3OH \longrightarrow CF_3CF_2CF_2O\left[-CF(CF_3)-CF_2-O-\right]_n-CF(CF_3)-C(=O)-O-CH_3 + HF\uparrow$$

n=1,2,3...

Figure 3. End-Capping of PFPE Acyl Fluoride via Methyl Esterification.

3. Results and Discussion

This study examines the influence of critical process parameters on the yield and molecular weight of perfluoropolyether methyl ester. The effects of microchannel length, gas flow rate, and reaction temperature were elucidated to optimize the synthesis.

3.1 Influence of Microchannel Length, Flow Rate and Temperature on Product Molecular Weight

3.1.1 Influence of Microchannel Length and Flow Rate on Product Characteristics

(1) Reaction conditions: gas flow rate 10 mL min-1; Temperature -50 °C.

As shown in Figure 4, the molecular weight, yield, and polydispersity Index (PDI) were measured across different microchannel lengths at a gas flow rate of 10 mL min-1. Data analysis reveals that the product yield increases progressively with microchannel length. The polydispersity index (PDI) exhibits a non-monotonic trend, characterized by an initial rapid increase followed by stabilization and a subsequent decline. Meanwhile, the values of number-average molecular weight (Mn), weight-average molecular weight (Mw), and z-average molecular weight (Mz) remain relatively stable, whereas the peak molecular weight (Mp) shows significant and irregular fluctuations without a discernible pattern. Based on a comprehensive analysis, a microchannel length of 50 m has been identified as the optimum.

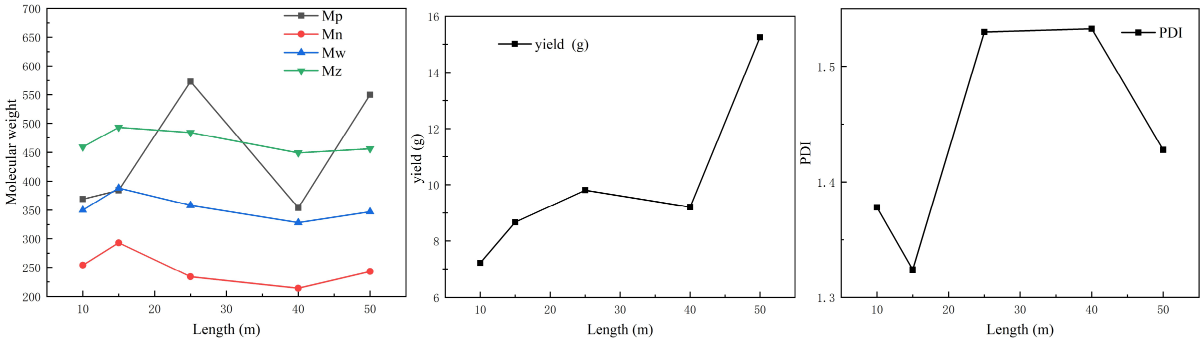


Figure 4. Influence of Microchannel Length on Product Characteristics at a Gas Flow Rate of 10 mL min^{-1}

(2) Reaction conditions: gas flow rate 15 mL min^{-1}, Temperature -50 °C.

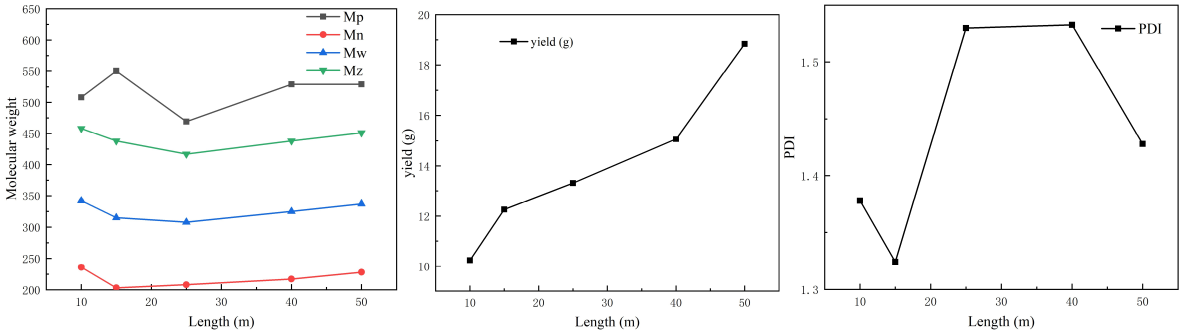


Figure 5. Influence of Microchannel Length on Product Characteristics at a Gas Flow Rate of 15 mL min^{-1}

As shown in Figure 5, the molecular weight, yield, and polydispersity Index (PDI) were measured across different microchannel lengths at a gas flow rate of 15 mL min^{-1}. Data analysis reveals a progressive increase in product yield with microchannel length. The PDI displays a non-monotonic trend, characterised by an initial rapid rise followed by a decline and subsequent stabilisation. Meanwhile, the values of Mn, Mw, and Mz plateau, whereas Mp exhibits pronounced fluctuations without a discernible pattern. Based on a comprehensive analysis, a microchannel length of 50 m has been identified as the optimal configuration.

3.1.2 Influence of Temperature and Flow Rate on Product Molecular Weight

(1) Reaction conditions: gas flow rate 10 mL min^{-1}, microchannel Length 50 m

As shown in Figure 6, the molecular weight, yield, and polydispersity Index (PDI) were measured at different temperatures under a gas flow rate of 10 mL min^{-1}. Data analysis indicates that Mn, Mw, and Mz undergo a moderate initial increase before gradually decreasing. In contrast, Mp exhibits a pronounced drop specifically at -40 °C, followed by a gradual increase at other temperatures. The PDI shows a distinct V-shaped profile, characterized by an initial decline and a subsequent rise. The highest product yield is achieved at -30 °C, under which Mp, Mn, Mw, and Mz are maintained at moderate levels and the PDI remains relatively low. An integrated evaluation of these results confirms that -30 °C represents the optimum reaction temperature.

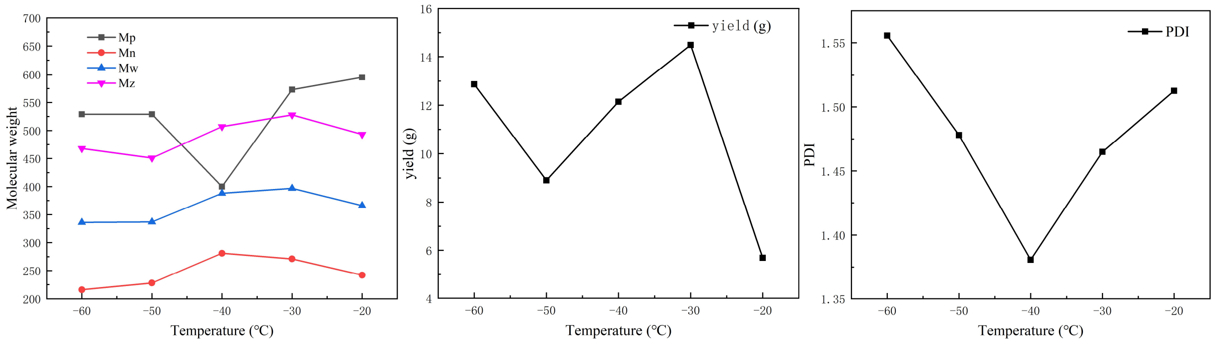


Figure 6. Influence of Temperature on Product Characteristics at a Gas Flow Rate of 10 mL min^{-1}

(2) Reaction conditions: gas flow rate: 15 mL min^{-1}; Microchannel Length: 50 m

As shown in Figure 7, the molecular weight, yield, and polydispersity Index (PDI) were measured at different temperatures under a gas flow rate of 15 mL min^{-1}. Data analysis shows that Mp, Mn, Mw, and Mz all exhibit a non-monotonic trend, characterized by an initial increase, followed by a decline, and a subsequent recovery. The PDI initially decreases sharply before increasing with fluctuations. The yield reaches its maximum at -30 °C, where the PDI remains relatively low and Mp, Mn, Mw, and Mz maintain moderate values. Taken together, these results identify -30°C as the optimal reaction temperature.

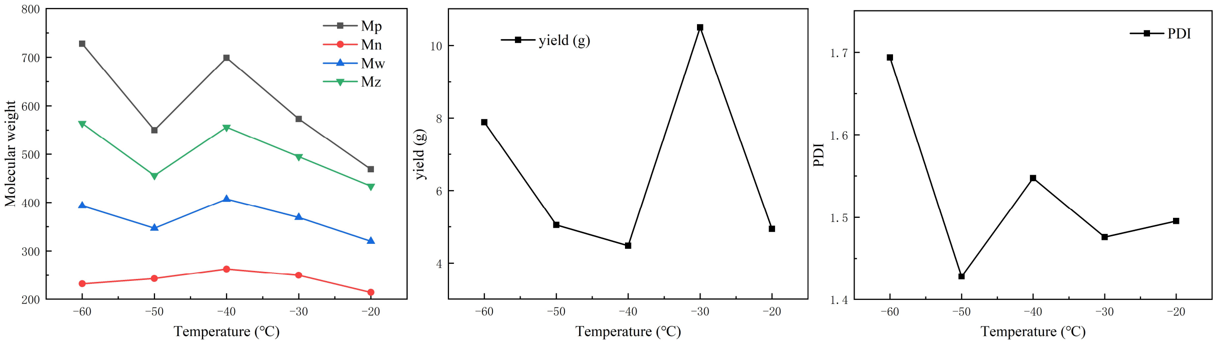
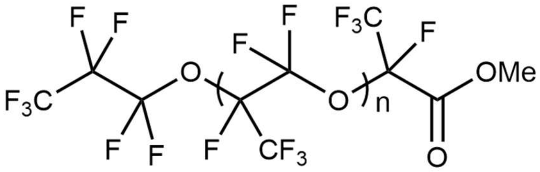
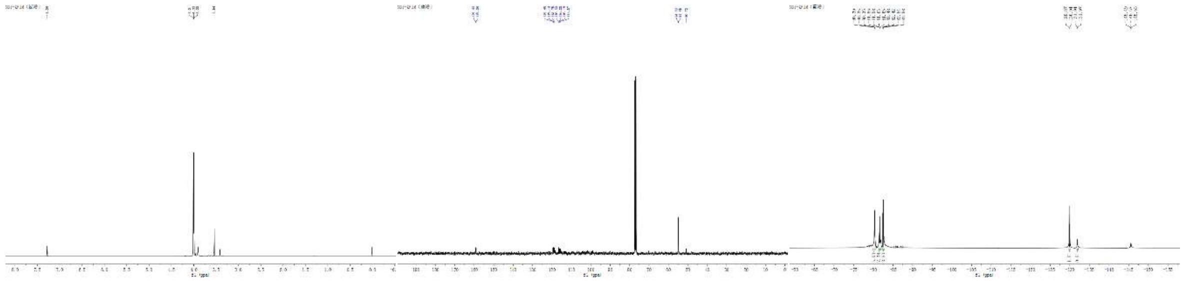


Figure 7. Influence of Temperature on Product Characteristics at a Gas Flow Rate of 15 mL min^{-1}

3.2 NMR Characterization of PFPE Methyl Ester





(a)^{1}H NMR (b)^{13}C NMR (c)^{19}F NMR

Figure 8. Nuclear Magnetic Resonance Spectrum of PFPE Methyl Ester

The structural characterization of the synthesized product was conducted using NMR spectroscopy, as shown in Figure 3-5. In the ^{1}H NMR spectrum (Figure 8a), the signals observed between 3.3–4.1 ppm are characteristic of methyl ester groups, suggesting the presence of a mixture of perfluoropolyether methyl esters. The ^{13}C NMR spectrum (Figure 8b) displays a peak at 158 ppm corresponding to the carbonyl carbon of the ester moiety, along with a signal at 54.8 ppm assigned to the methyl group ($–OCH_3$). Additional resonances in the range of 115–120 ppm are attributed to fluorine-bearing carbon environments, such as CF, CF_2, and CF_3. The ^{19}F NMR spectrum (Figure 8c) further confirms the molecular structure: the signal between –145 and –148 ppm is ascribed to the –CF group adjacent to the ester, the resonance from –128 to –133 ppm corresponds to the $–CF_2$ group adjacent to oxygen, and the multiple signals between –75 and –90 ppm originate from the remaining $–CF_2$ and $–CF_3$ groups in the perfluorinated chain. Collectively, these NMR results verify the product as perfluoropolyether methyl ester.

4. Conclusion

Based on the data analysis and structural characterization presented above, the following conclusions can be drawn:

With TMEDA as a catalyst, the anionic polymerization of hexafluoropropylene oxide in a microchannel reactor predominantly yields low molecular weight perfluoropolyether acyl fluorides.

With constant tube length, higher flow rates lead to increased product yield but lower molecular weight. At a fixed flow rate, longer tube lengths result in higher product mass and molecular weight, while the PDI initially increases and then decreases. At lower temperatures, product mass is generally higher, but molecular weight shows irregular variation with broader dispersity.

In summary, this study successfully synthesized low molecular weight perfluoropolyether acyl fluorides using a microchannel reactor, overcoming challenges such as broad molecular weight distribution and high risks associated with conventional methods. This approach provides a green and efficient alternative for the preparation of related products.

Acknowledgments

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References

[1] S. Saxena, P. Malik, G. Seshadri, A.K. Tyagi, U.K. Mandal. One step synthesis of low molecular weight perfluoropolyethers (PFPEs) by photo-oxidation of hexafluoropropylene (HFP), Radiat. Phys. Chem, vol. 165 (2019), 108417-108417.

[2] K. Dušek, D. Bušek, M. Plaček, A. Géczy, O. Krammer, B. Illés. Influence of vapor phase soldering fluid Galden on wetting forces (tombstone effect), J. Mater. Process. Technol, vol. 251 (2017), 20-25.

[3] B. Illés. Modeling Galden layer formation on PCB surface during Vapour Phase Soldering, Proc. 2013 IEEE 19th Int. Symp. Design Technol. Electron. Packag., 2013, pp. 69-74.

[4] X. Hao, A. Yoshida, N. Hoshi. ChemInform Abstract: Recyclable Hafnium(IV) Bis(perfluorooctanesulfonyl)amide Complex for Catalytic Friedel-Crafts Acylation and Prins Reaction in Fluorous Biphase System, ChemInform, vol. 39 (2008), 0-0.

[5] P. Saravanan, S. Jayaraman, D.H. Minh, S.K. Sinha. The Role of Functional End Groups of Perfluoropolyether (Z-dol and Z-03) Lubricants in Augmenting the Tribology of SU-8 Composites, Tribol. Lett, vol. 56 (2014), 423-434.

[6] F. L. Xing. Studies on Hexafluoropropylene Oligomerization, Organo-Fluorine Ind., 2016, 22-25. (In Chinese)

[7] X. Y. He, X. Hu. Preparation of Perfluoropolyether Carboxylate Surfactant from Hexafluoropropylene Oxide (HFPO), Chem. Prod. Technol, 2005, 5-7+51. (In Chinese)

[8] S.H. Korzeniowski, R.C. Buck, R.M. Newkold, et al. A critical review of the application of polymer of low concern regulatory criteria to fluoropolymers II: Fluoroplastics and fluoroelastomers, Integr. Environ. Assess. Manag, vol. 19 (2022), 326-354.

[9] W. J. Yang, C. Fang, J. C. Zhou, et al. Catalytic synthesis of perfluorolyethers, J. Cent. South Univ, vol. 20 (2013), 629-633.

[10] M.Y. Keating, J.L. Howell. Decomposition of perfluoropolyether lubricants: A study using TG–MS in the presence of alumina powder, J. Therm. Anal. Calorim., vol. 106 (2011), 213-220.

[11] Q. F. Liu, X.-Y. Wu. Study on Decomposition of Z-type Perfluoropolyether, Organo-Fluorine Ind, 2025, 1-5+10. (In Chinese)

[12] X. T. Chen, L. L. Zhang, L. Zhou, et al. Mechanism and kinetics study of the chemically initiated oxidative polymerization of hexafluoropropylene, AIChE J, vol. 70 (2024), 0-0.

[13] W. Zhang, B. Liu, M. Zhang, et al. Research Progress in Anionic Ring-opening Polymerization of Hexafluoropropylene Oxide, Organo-Fluorine Ind, 2024, 34-39. (In Chinese)

[14] M. Koyama, M. Akiyama, K. Kashiwagi, et al. Synthesis of Crystalline CF3-Rich Perfluoropolyethers from Hexafluoropropylene Oxide and (Trifluoromethyl)Trimethylsilane, Macromol. Rapid Commun, vol. 43 (2022), 0-0.

[15] M. Gleirscher, A. Wolfberger, S. Schlögl, et al. Accelerated Thermo-Catalytic Degradation of Perfluoropolyether (PFPE) Lubricants for Space Applications, Lubricants, vol. 11 (2023), 81-81.

[16] S. Jiang, Z. Yang, J. Zhang, et al. Development of a Mini-Channel Heat Exchanger Reactor with Arborescent Structures for Fast Exothermic Reactions, Ind. Eng. Chem. Res, vol. 61 (2022), 14121-14131.

[17] G. Dong, B. Chen, B. Liu, et al. Advanced oxidation processes in microreactors for water and wastewater treatment: Development, challenges, and opportunities, Water Res, vol. 211 (2022), 118047-118047.

[18] K. Subramaniam, K.Y. Wong, K.H. Wong, et al. Enhancing Biodiesel Production: A Review of Microchannel Reactor Technologies, Energies, vol. 17 (2024), 1652-1652.

[19] B. Kamenická. Critical review on enhanced production of methane in microchannel reactors as carbon dioxide utilization approach, Chem. Eng. Process. Process Intensif, vol. 217 (2025), 110532-110532.

[20] H. Liu, N. Yang, J. Jiang, et al. Seamless scale-up of tube-in-tube millireactors by annular structure and feed method design: Micromixing, residence time distribution and heat transfer, AIChE J, vol. 71 (2024), 0-0.