

Kinetic Routes of PFAS Destruction in Supercritical Water Oxidation

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Background/Objectives. Since the 1950s, PFAS were used for the production of aqueous film-forming foams (AFFF), water-repellent coatings for textiles, and food packaging products. The chemical stability of PFAS has resulted in the increasing contamination of surface water, groundwater, and soil. The bioaccumulation of PFAS is harmful to reproductive and immune system health, causing liver and kidney damage, thyroid disease, high cholesterol, and cancer. Incineration and landfill deposition of PFAS are not sustainable options; thus, alternative end-of-life technologies are needed. Hydrothermal processes, including supercritical water oxidation (SCWO), were shown effective in destroying recalcitrant organic molecules including PFAS. [1]

In its supercritical phase ($P_c > 22.1$ MPa, $T_c > 374^\circ\text{C}$), water becomes a non-polar fluid, with gasses and organics becoming fully miscible. The ion product of supercritical water is orders of magnitude lower than water under ambient conditions, facilitating free radical reactions. High concentration of free radicals enables rapid oxidation of organic compounds into CO_2 , H_2O , and the heteroatoms into their corresponding acid or salt. The high density of the SCWO environments and abundance of free radicals encourages free radical reactions to occur quickly, avoiding issues with the production of intermediate reaction products in the destruction of many hazardous wastes. Recent work reported SCWO treatment of PFAS, especially at temperatures sufficient to achieve high destruction and removal efficiencies and defluorination efficiencies.

Approach/Activities. We report PFAS treatment in the continuous flow lab-scale SCWO reactor as a function of operating temperature. The autogenic SCWO operation and temperature control were achieved by injection of co-fuel. The authors characterized the destruction and mineralization of multiple PFSA and PFCA in the broad temperature range ($T = 410 - 650^\circ\text{C}$). We collected liquid effluent and gaseous samples that were analyzed for the presence of intermediates. These data were used to gain insights into chemical kinetic routes of PFAS destruction in the SCWO environment. In addition, we investigated the environmental matrix effects on the PFAS destruction, e.g., landfill leachates and AFFF.

Results/Lessons Learned. At $T = 650^\circ\text{C}$, DRE $> 99.999\%$ and complete defluorination were achieved after 30 seconds of exposure. The PFASs are significantly more resistant to oxidization than PFCAs; thus, the presence of PFASs in the mixture would limit the destruction and defluorination efficiencies. All PFCAs introduced into the SCWO reactor were below the detection limit at $T = 510^\circ\text{C}$, while PFASs required $T > 610^\circ\text{C}$ to oxidize. PFASs destruction proceeds via two parallel routes, e.g., the lower temperature PFOS experiments ($T = 420 - 600^\circ\text{C}$) yielded a pool of PFCAs (PFOA, PFHxA, PFPeA, PFBA, PFPrA, TFA) in the liquid effluents as well as the emissions of VOF such as 1H-perfluoroalkane in the gas stream.[2] These routes are discussed in the context of the available free radicals participating in the PFAS degradation.

1. Li, J., et al., *Review: Hydrothermal treatment of per- and polyfluoroalkyl substances (PFAS)*. Chemosphere, 2022. **307**: p. 135888.
2. Li, J., et al., *PFOS destruction in a continuous supercritical water oxidation reactor*. Chemical Engineering Journal, 2023. **451**: p. 139063.