

# Reactive and pH-Modified Hydrothermal Decomposition of F-Refrigerant Gases in a Pressurised Aqueous Parr Reactor

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Climate change is driven largely by greenhouse gas (GHG) emissions, resulting in rising global temperatures, ice mass loss, sea-level rise, and extreme climate events. Since the 1900s, surface temperature has increased by approximately 1.4 °C. Fluorinated greenhouse gases (FGGs) are potent climate pollutants due to their very high global warming potential (Hansen et al., 2010). Chlorofluorocarbons (CFCs), once widely used as refrigerants and propellants, contributed to ozone depletion and were phased out under the Montreal Protocol. Hydrofluorocarbons (HFCs), introduced as substitutes, eliminated ozone depletion but still exhibit high GWP (Sheraz et al., 2021). Furthermore, fluorinated refrigerant gases (F-refrigerants) are highly stable because of the strong C–F bond (485–530 kJ mol<sup>-1</sup>), making their destruction energy-intensive using conventional thermal technologies. In this study, we investigate reactive and pH-modified hydrothermal decomposition of selected F-refrigerants in a pressurized aqueous environment. Experiments were conducted in a Parr 4577A high-pressure batch reactor (1 L) filled with distilled water, where the target gases were introduced via calibrated burettes. The reactor atmosphere was modified using controlled H<sub>2</sub>/N<sub>2</sub> gas mixtures, enabling reductive and inert conditions under subcritical water regimes (Liakos et al., 2026). The influence of acidic (HCl) and alkaline (NaOH) pH adjustment on C–F bond activation and fluorine mineralization was systematically evaluated. Three representative F-refrigerants were studied: Difluoromethane (R-32), Pentafluoroethane (R-125), and 1,1,1,2-Tetrafluoroethane (R-134a). Gas-phase degradation products were quantified using a Shimadzu Nexis GC-2030 equipped with Barrier Ionization Detector (GC-BID) and an Rt-Alumina BOND/CFC column, optimized for halogenated compounds (Altiparmaki et al., 2026). The partitioning and mineralization of fluorine into the aqueous phase were determined spectrophotometrically using a Hach DR1900 with LCK323 fluoride test kits. The study evaluates the temperature dependence of hydrothermal decomposition, the effect of hydrogen partial pressure, the influence of alkaline vs acidic conditions on defluorination efficiency, and the fluorine mass balance between gas and liquid phases. The results provide mechanistic insight into C–F bond activation under hydrothermal conditions and demonstrate that controlled pH and reactive gas environments can enhance mineralization pathways compared to dry thermal destruction. This approach offers a potentially lower-temperature, contained alternative for the treatment of residual F-refrigerants in compliance with global F-gas phase-down policies.

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