

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

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1. Introduction and Research Gap

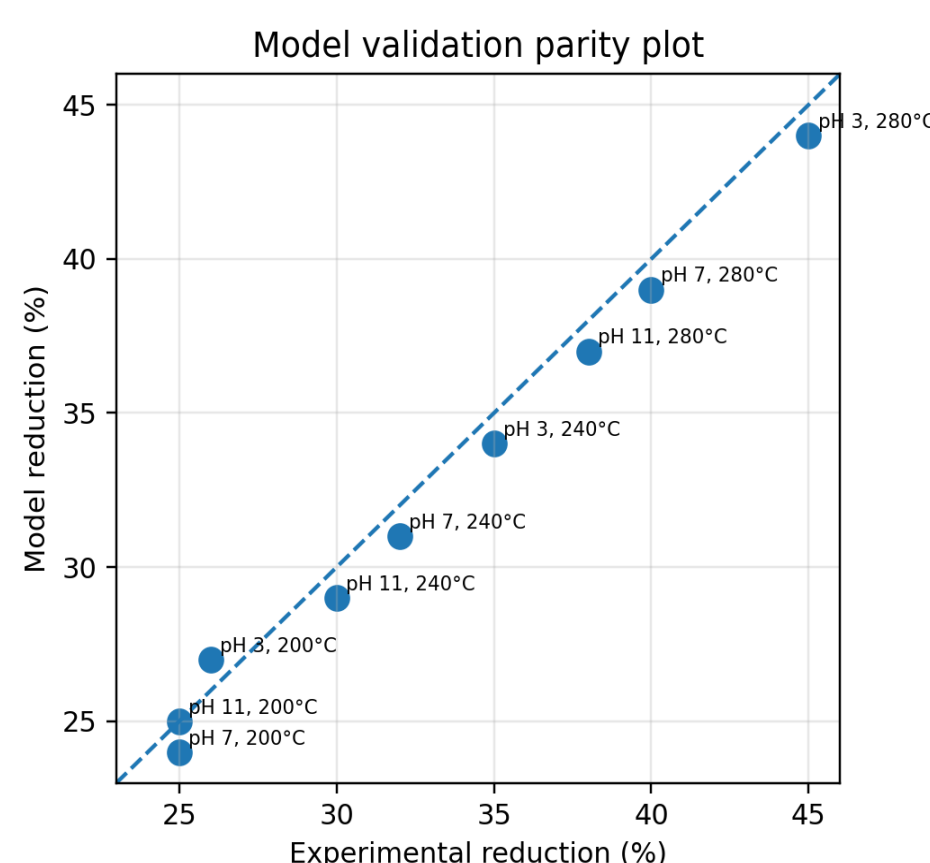
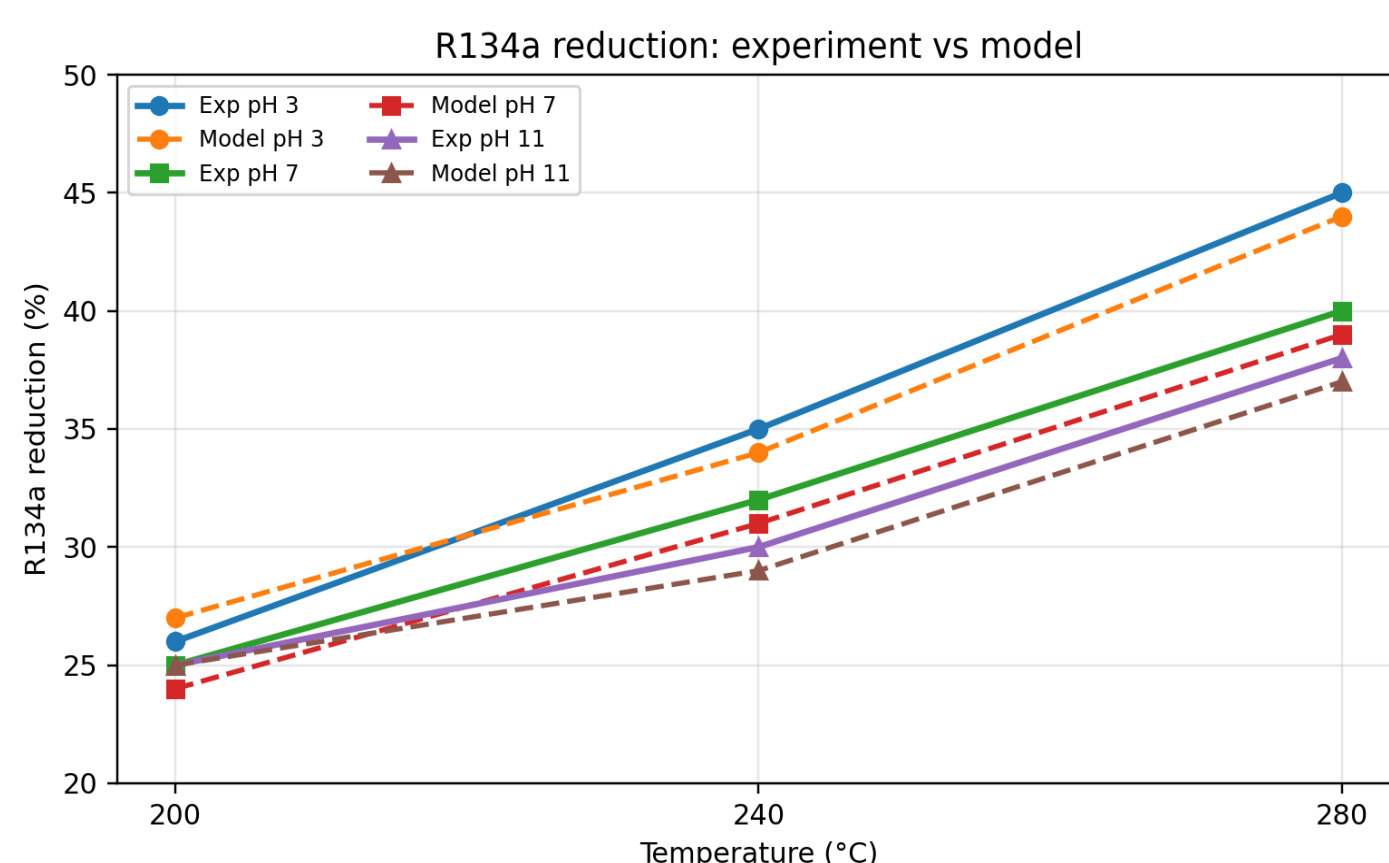
R134a is a widely used hydrofluorocarbon with high global-warming potential and exceptional chemical stability arising from strong C–F bonds. Conventional destruction methods generally require high temperatures, catalysts, or energy-intensive treatment, whereas hydrothermal processing could offer a contained, lower-temperature alternative. However, published studies mainly address dry thermal decomposition, catalytic conversion, or supercritical-water conditions, while quantitative data for subcritical water at 200–280 °C remain scarce. In particular, the combined effects of pH, gas–liquid partitioning, pressure, and reactor surfaces on short-time R134a degradation are poorly understood. This study addresses that gap by coupling a thermodynamic–empirical model with controlled autoclave experiments and aqueous fluoride measurements to evaluate degradation and defluorination pathways.

2. Methodology

- Batch experiments were performed in a 500 mL TGYF-C 500 stainless-steel autoclave, rated @ 22 MPa and 350 °C (Figure, left).
- The reactor contained pH-adjusted water (pH 3, 7, 11) and an atmosphere of N₂ containing 1 vol.% R134a
- Tests were conducted at 200, 240 and 280 °C and autogenous pressure.
- A thermodynamic–empirical model was used to predict water/R134a phase behaviour, gas–liquid partitioning, temperature- and pH-dependent degradation, and aqueous fluorine release.
- Residual R134a was quantified by GC–TCD using a GBC Nebula and Carbopack B column, while aqueous fluoride was measured with a Hach DR1900 and LCK323 test kit.
- Quality and safety controls included gas calibration, blank experiments, sample dilution within the fluoride method range, F mass-balance checks, and controlled neutralization of HF/F⁻-containing liquids.



3. Results: R134a reduction and pH response



R134a reduction (%), Experiment / Model validation matrix.

| pH | 200 °C | 240 °C | 280 °C |
|----|--------|--------|--------|
| 3 | 26/27 | 35/34 | 45/44 |
| 7 | 25/24 | 32/31 | 40/39 |
| 11 | 25/25 | 30/29 | 38/37 |

Validation metrics

- MAE = 0.9 percentage point.
- Max deviation = 1 percentage point.
- Model captures T and pH trend.

$$k_{\text{effective}} = k_{\text{Adams}}(T) \times f_{\text{phase}} \times f_{\text{pH}} \times f_{\text{wall/catalyst}} \times f_{\text{partition}}$$

- Water phase-state and R134a partitioning.
- pH-driven acceleration fitted from experiments.
- Global product pathways for gas/liquid mass balance.
- Outputs: gas R134a, gas composition and aqueous F⁻.

R134a reduction (%), Experimental

| pH / T | 200 °C | 240 °C | 280 °C |
|--------|--------|--------|--------|
| pH 3 | 26% | 35% | 45% |
| pH 7 | 25% | 32% | 40% |
| pH 11 | 25% | 30% | 38% |

Main outcomes

- Reduction range : 25–45%.
- Maximum: pH 3 and 280 °C.
- Temperature enhances degradation at all pH values.
- Aqueous fluoride confirms defluorination
- Mineralization should be considered

4. Discussion and Conclusions

- R134a reduction reached 25–45%, peaking at pH 3 and 280 °C—well above the neutral literature baseline for short residence times.
- Degradation increased consistently with temperature, while the stronger acidic response indicates that pH-dependent reaction and phase-partitioning effects are important for C–F bond activation.
- The model reproduced the experimental trends closely, with a mean absolute error of 0.9 percentage point and a maximum deviation of only 1 percentage point.
- Fluoride detected in the aqueous phase confirms C–F bond cleavage and fluorine transfer to water. However, complete mineralization must be verified through a closed fluorine mass balance.
- The validated modelling–experimental workflow provides a strong platform for residence-time studies, identification of partially fluorinated intermediates, comparison of N₂ and H₂/N₂ atmospheres, and extension to R32 and R125.