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Fluoroform (CHF_3) production from CF_3CHO photolysis and implications for the decomposition of hydrofluoroolefins and hydrochlorofluoroolefins in the atmosphere

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Abstract: Hydrofluoroolefins (HFOs) and hydrochlorofluoroolefins (HCFOs) are the leading synthetic replacements for compounds successively banned by the Montreal Protocol and amendments. HFOs and HCFOs readily decompose in the atmosphere to form fluorinated carbonyls, including CF_3CHO in yields up to 100%, which are then photolyzed. A longstanding issue, critical for the transition to safe industrial gases, is whether atmospheric decomposition of CF_3CHO yields any quantity of CHF_3 (HFC-23), which is one of the most environmentally hazardous greenhouse gases. This comprehensive experimental investigation employs purpose-built photoionization mass spectrometry, Fourier-transform infrared and microwave spectroscopy techniques and confirms production of CHF_3 following excitation at a tropospherically-relevant wavelength ($\lambda = 308$ nm) and under atmospheric pressure conditions. Pressure-dependent CHF_3 quantum (Φ) and molar (Y) yields are reported from $\Phi = Y = 0.16 \pm 0.03$ under collision-free conditions to $\Phi = (2.3 \pm 0.3) \times 10^{-4}$, $Y = (1.17 \pm 0.27) \times 10^{-3}$ at 1 bar N_2 .

Hydrofluoroolefins (HFOs) are emerging as the next generation of synthetic refrigerants, foam-blowing agents, fire retardants, propellants, *etc.*, following the global phase-out of chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) due to their ozone depletion potential (ODP), and the phase-down of hydrofluorocarbons (HFCs) due to their potent global warming potential (GWP). HFOs are HFC derivatives that incorporate a carbon-carbon double bond and rapid tropospheric oxidation prevents them becoming long-lived greenhouse gases (GHGs). The reported ODPs and GWPs of HFOs are typically near zero.¹ The environmental risk of CFCs was recognized too late, after the damage to the ozone layer had occurred. HFC phase-down began in 2016, yet they will still contribute significantly to global surface heating throughout this century.² It is critical that the long-term consequences of large-scale emission of HFOs are determined now.

(*E*)-1,3,3,3-tetrafluoropropene (HFO-1234ze(*E*)) is one of the most important HFOs. Its structure and abridged atmospheric chemistry is shown in the scheme in Fig. 1. It is reported to yield trifluoroacetaldehyde (CF_3CHO) in 100% molar yield following oxidation by OH radicals, which is the dominant atmospheric removal pathway.³ Indeed, CF_3CHO

is a decomposition product of other hydrofluoroolefins⁴ and hydrochlorofluoroolefins,⁵ and is formed in high yield from the decomposition of some hydrofluorocarbons.⁶ This aldehyde, like most carbonyls, is photolyzed predominantly by a Norrish reaction producing radical products CF_3 and HCO (**(R1)** in Fig. 1) that are expected to ultimately form CO_2 and HF in the atmosphere.³ The CF_3CHO photolysis quantum yield at 308 nm and 700 torr, $\Phi_{\text{total}}(308 \text{ nm}) = 0.17 \pm 0.03$, is well-characterized⁷ and presently attributed fully to this Norrish type reaction. Unlike C-F bonds, H-F bonds participate in environmental chemistry and are expected to be buffered by the planet and the fluorine eventually returned to its natural state as fluoride minerals, presenting a low environmental risk.

Several studies dating back to the 1950s have identified a possible second photolysis pathway for CF_3CHO producing CHF_3 (fluoroform, HFC-23) following photolysis with atmospherically relevant wavelengths (**(R2)** in Fig. 1).^{8–10} CHF_3 is one of the most potent HFC GHGs with a 100-year global warming potential of $\text{GWP}_{100} = 14\,600$.¹ The magnitude of this GWP means that minor branching into this pathway could produce a non-negligible indirect GWP for the parent HFO. Recent studies at 0.13 to 1 bar total pressure of O_2 and N_2 at various mixing ratios have failed to detect CHF_3 .^{7,11,12} A recent study at shorter wavelength (254 nm) concludes that this photodissociation pathway may be important in the stratosphere.¹³ However, this is a difficult reaction to characterize under tropospherically-relevant wavelengths due to the low yields of this pathway and the overlapping infrared spectral features of the parent (CF_3CHO), the major reaction product (CF_3 as CF_3NO , *vide infra*) and the minor reaction product (CHF_3). An even more recent study demonstrates that atmospheric ozonolysis of (*E*)-1,3,3,3-tetrafluoropropene may produce CHF_3 with an overall yield of 9.2×10^{-4} .¹⁴

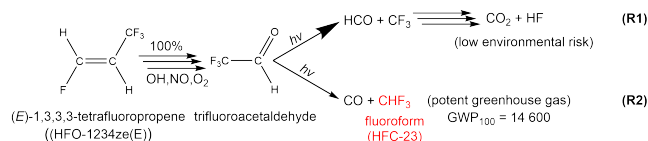


Figure 1. Abridged scheme for the atmospheric decomposition of (*E*)-1,3,3,3-tetrafluoropropene highlighting the importance of trifluoroacetaldehyde photolysis in determining the indirect GWP.

We have used three different experimental techniques to determine the absolute yield of CHF_3 from the $\lambda = 308$ nm photolysis of CF_3CHO in three distinctly different environments: collision-free (zero pressure) and low temperature (5 K); low pressure of helium (0.005 bar) and room temperature (295 K), and atmospheric pressure (0.1 - 1.0 bar) and room temperature (295 K). The first two experiments detect CO from reaction R2 using ionization techniques. The third experiment measures the production of CHF_3 from R2, using microwave spectroscopy.

The first set of experiments were performed in a molecular beam, presenting a collision-free (zero-pressure) environment at low internal temperature (~ 5 K). This method minimizes the internal energy of the reactant, clarifying whether (**R2**) is a thermodynamically allowed unimolecular pathway. We confirmed **R2** is active following excitation at 308 nm by recording 2-dimensional resonance enhanced multiphoton ionization (2D REMPI) spectra of the CO product. The 2D REMPI spectrum (Fig. S5) is presented and described in the Supporting Information (Section S2.1) where it is strikingly similar to that published previously for CH_3CHO .¹⁵ The dissociation of CH_3CHO via its equivalent (**R2**) has been reported to occur via up to three different dynamical channels. Although the interpretation of each channel is still not agreed upon in the literature,^{15–17} the key factor for this work is that all hypothesized channels yield CH_4 and CO as photoproducts following dynamics on S_0 after initial photoexcitation to S_1 . The two different CO dynamical signatures from CF_3CHO dissociation in Fig. S5 are consistent with the multiple dynamical processes in CH_3CHO .

The POPTARTS (Proportionation of Photoproducts by Tetralaser-measurement and Analysis of REMPI and Translational Spectra) method was purpose-built for this study. It quantifies the relative branching into photolysis channels producing HCO and CO by exploiting the photolytic conversion of HCO into CO. The technique has been described in detail previously, where it was benchmarked to the well-established photolysis of formaldehyde.¹⁸ The specifics of the present experiment can be found in the Supporting Information (Section S1.2). In brief, four lasers intersect a molecular beam of $\approx 1\%$ CF_3CHO in He. Laser 1 photolyzes CF_3CHO at 308 nm. Lasers 2 and 3 ionize HCO from R1 and CO from R2 respectively, after which they are accelerated through a time-of-flight mass spectrometer then detected on a multichannel plate and phosphor screen (Fig. S1A). The 4th laser converts HCO to CO by photolysis. By converting the products of one reaction into the products of another, POPTARTS measures true zero pressure molar yields in cases where there are only two chemical pathways. Under collision-free conditions, the molar yield equals the photolysis quantum yield, provided radiative quantum yields (*e.g.* fluorescence) are small, as is the case for CF_3CHO at 308 nm excitation.¹⁹

The key data from the POPTARTS experiments are shown in Fig. 2. Panel A shows the CO rotational population distribution following 308 nm photolysis of CF_3CHO with the HCO photolysis laser off (red triangles). When the HCO photolysis laser is turned on the CO signal increases by 113% (blue circles). Fig. 2B shows the difference between the two datasets in Panel A, which is equivalent to the CO rotational population distribution from only the photolysis of the HCO photoproduct. This compares well to a literature population distribution for the photolysis of HCO at the same wavelength (black line).²⁰ Representative uncer-

tainties (1σ) are shown as error bars on the $J_{\text{CO}}=21$ data-point. Lastly, Fig. 2C presents representative HCO signal recorded as the HCO photolysis laser is turned on and off every 200 seconds. Average HCO depletion from photolysis is 20%.

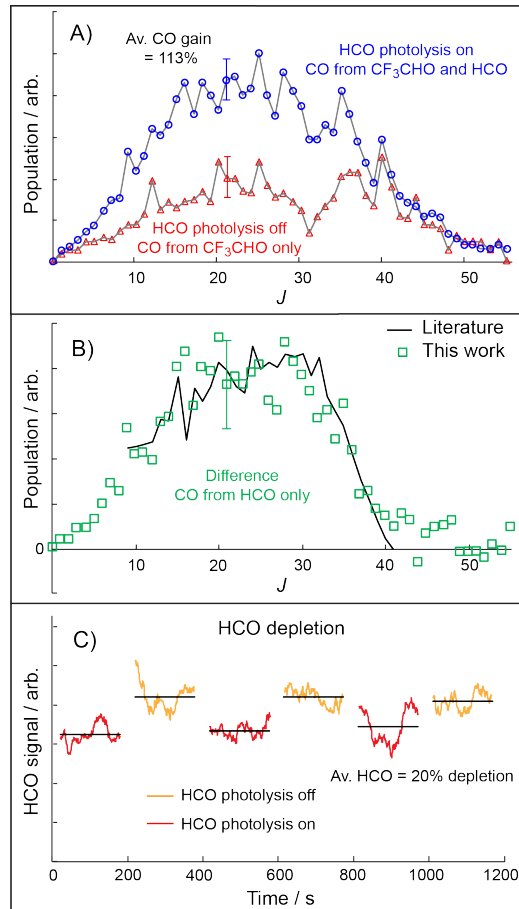


Figure 2. POPTARTS data following $\lambda = 308$ nm photolysis of CF_3CHO . (A) Photoproduct CO product rotational state distribution with HCO photolysis laser off (red) and on (blue), (B) difference between CO product state distributions with HCO photolysis laser on and off compared to a literature distribution for following HCO photolysis,²⁰ (C) time series of photoproduct HCO signal as the HCO photolysis laser is toggled on and off.

The HCO and CO quantum yields are calculated from the HCO-depletion and CO-increase in Fig. 2 as shown in Equation 1:

$$F(\text{HCO}_{\text{depletion}}) \times \Phi_{\text{HCO}} = F(\text{CO}_{\text{production}}) \times \Phi_{\text{CO}} \quad (1)$$

where F represents the fractional increase or decrease in CO/HCO signal upon photolyzing the HCO population, and the Φ are the CF_3CHO quantum yields for HCO and CO. The fractional increase in CO and decrease in HCO signal is scaled by the fraction of each pathway that yields $\nu(\text{CO}) = 0$. From analysis of these data, we conclude that the quantum yield for the production of CHF_3 following 308 nm photolysis of CF_3CHO , under collision-free conditions, *i.e.* at zero pressure, is $\Phi_{\text{CHF}_3} = 0.16 \pm 0.03$. The analysis is described in detail in the Supporting Information (Section S2.2).

The second set of experiments bring the temperature to 295 K, but retain low pressure of Helium in a flow cell. This ensures that the effects of collisions are minimised, but that the internal energy of the reactant is relevant to atmospheric conditions. The multiplexed photoionization

mass spectrometry (MPIMS) experiment²¹ at the Advanced Light Source (ALS) synchrotron measures the time dependence of the mixing ratio of chemical species sampled from a flow tube reactor relative to excitation with a 308 nm laser pulse. A constant flow of 1% (*p/p*) CF₃CHO in 4 torr of helium was irradiated with the laser. A pinhole admits a small sample into a vacuum chamber where reactant and product molecules are irradiated with vacuum ultraviolet radiation from the synchrotron. Resulting ions are accelerated in a time-of-flight mass spectrometer. A three-dimensional cube of data, spanning ionization energy, mass and kinetic time is obtained and analyzed.

Fig. 3 plots the time evolution of CO produced following photolysis of CF₃CHO. The CO concentration increases from $t = 0$. The data cannot be reproduced using a single, bimolecular kinetic model due to the instrument-limited, fast rise at early time. The dark blue trace represents the prediction of a two-component kinetic model, describing bimolecular reactions of HCO that produce CO using published reaction rate coefficients (Table S1) and a fitted wall loss to give the cyan trace, and an instrument-limited initial photolysis rate (red trace). This model provides an excellent fit to the experimental data and is described fully in Supporting Information (Section S2.3). The presence of photolytic CO provides a verification that CHF₃ is a primary photoproduct of low pressure CF₃CHO photolysis at room temperature. The fit produced a relative yield of 0.105 ± 0.025 CO from photolysis compared to the total CO yield. Assuming the total photolysis quantum yield remains about 1, and that the secondary CO arises from primary HCO, then $\Phi_{\text{CHF}_3} \approx 0.10 \pm 0.03$ under these conditions.

Another important outcome from these experiments is the absence of any signal on the mass channel corresponding to CF₂. This is important because a CF₃CHO photolysis channel producing CO, HF and CF₂ has been located computationally and shown to be accessible with these photon energies.¹⁹ The absence of CF₂ signal in these sensitive experiments eliminates the possibility that this theoretical reaction occurs.

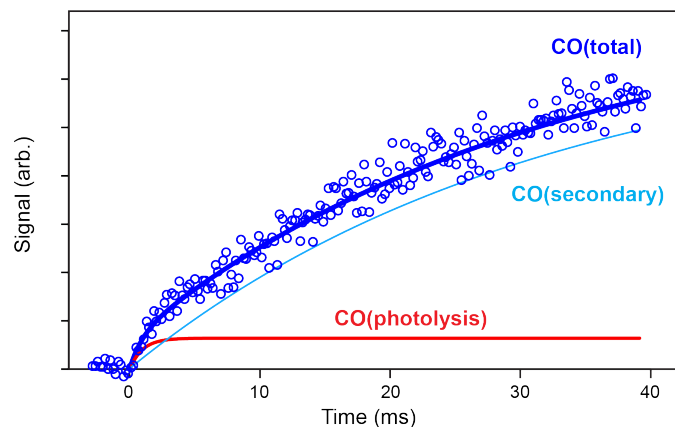


Figure 3. Time evolution of CO signal (blue circles) following $\lambda = 308$ nm photolysis of 1% CF₃CHO in helium (4 torr total pressure) overlaid with the model output for total CO (blue line), photoproduct CO (red line) and CO from secondary reactions following photolysis (cyan line)

The final experiment in this investigation was to determine pressure-dependent quantum yields of CHF₃ from CF₃CHO photolysis in a room temperature bulb with N₂ buffer gas at pressures from 0.1 to 1.0 bar. Approximately 1 mbar of CF₃CHO was combined with a ~ 10 -fold excess of

NO and diluted to various total pressures of N₂. NO is a radical scavenger that is used in many contemporary studies and reliably arrests any secondary chemistry that may generate CHF₃ *e.g.* CF₃ + CF₃CHO $\rightarrow$ CHF₃ + CF₃CO. The gas mixture was irradiated with a 308 nm pulsed laser (1 - 2 mJ/pulse) for 20 - 60 minutes. Fourier-Transform Infrared (FTIR) spectra were recorded every 30 s, starting 5 minutes before photolysis, throughout the photolysis period and then another 5 minutes after photolysis.

The FTIR spectra quantify the disappearance of CF₃CHO parent and the appearance of CF₃ photoproduct (**R1**), which manifests as CF₃NO in the presence of the NO radical scavenger. As found in previous experiments, the sensitivity is insufficient to detect low yields of CHF₃ (**R2**) due to spectral overlap of other species with the CF₃ chromophore, for example the intact parent (CF₃CHO) and major photolysis product (CF₃NO).

The yield of CHF₃ in these experiments was instead measured using Chirped-Pulse, Fourier-Transform MicroWave (CPFTMW) spectrometry. This is a new experiment and is described in detail in Supplementary Information (Section S2.4). In brief, the photolysed gas mix from the photolysis cell was expanded into a stainless steel bulb of known volume ratio, which was subsequently filled with helium to 6 bar total pressure. The gas in the bulb was regulated to 3 bar and expanded into a vacuum chamber as a free jet expansion using a pulsed nozzle operating at ~ 7 Hz. The free jet expansion was crossed with microwave radiation of frequencies spanning 16-26 GHz.

The intensity of the MW absorption at 20.698 GHz, corresponding to the $^4R_0(0)$ transition of CHF₃ was recorded and averaged for ~ 5000 -20000 pulses. The mixing ratio of CHF₃ in the photolysed sample was determined by reference to a calibration curve made from a series of standard mixtures of CHF₃ in He under the same conditions (see Supplementary Information).

The molar yield, Y , of CHF₃ was determined from the number of moles of CHF₃ produced (MW detected) to CF₃CHO lost (FTIR detected). Quantum yields, Φ , were determined by actinometry via a factory-calibrated laser energy meter and the published CF₃CHO absorption cross section at 308 nm.¹¹ We note that CF₃NO does have a non-zero absorption cross-section at $\lambda=308$ nm, but its photolysis yields CF₃ and NO and, with NO always in large excess, does not affect the observed products of CF₃CHO photolysis. Supplementary Information also includes a discussion of evaluation of wall effects, multiphoton processes and NO radical scavenging.

Table 1 reports the molar yields and photochemical quantum yields for CHF₃ production following 308 nm excitation. The reported $\Phi_{\text{tot}}(1 \text{ bar}) = 0.19 \pm 0.05$ is consistent with 0.17 ± 0.03 reported by Chiappero *et al.* from the disappearance of the CF₃CHO parent compound.⁷

Fig. 4 is a Stern-Volmer plot that graphs $\Phi_{\text{CHF}_3}^{-1}$ against the total pressure of the photolyzed CF₃CHO mixture. The zero pressure quantum yield determined using POPTARTS is also included. The linear relationship between $\Phi_{\text{CHF}_3}^{-1}$ and pressure indicates there is a single photolysis mechanism producing CHF₃ and that it is *efficiently* quenched through collisions with N₂. Indeed, the data in Table 1 reveals that total photolysis (Φ_{total}) is also quenched with (**R2**) being quenched $\sim 140\times$ more than (**R1**).

Table 1 shows the quantum yield for the production of CHF₃ following 308 nm photolysis of CF₃CHO, in 1 bar of

Table 1. Molar yields, Y , and quantum yields, Φ , for CHF_3 production following $\lambda = 308$ nm photolysis of CF_3CHO with N_2 buffer gas at several pressures, P . Also reported are the ratios of Y to Φ (discussed in the text) and the total photolysis quantum yield determined from the HFC-23 molar and quantum yields. Uncertainties reported to 1σ .

P / bar	T / K	Y_{CHF_3}	Φ_{CHF_3}	$Y_{\text{CHF}_3}/\Phi_{\text{CHF}_3}$	Φ_{total}
0	5	0.16 ± 0.03	0.16 ± 0.03	1.0 ± 0.2	1.00 ± 0.2
0.005*	295	0.10 ± 0.03	0.10 ± 0.03	1.0 ± 0.3	$\sim 1.00 \pm 0.3$
0.102 ± 0.001	295	$(5.4 \pm 0.9) \times 10^{-3}$	$(3.6 \pm 0.9) \times 10^{-3}$	1.5 ± 0.5	0.67 ± 0.20
0.306 ± 0.002	295	$(2.2 \pm 0.4) \times 10^{-3}$	$(7.8 \pm 1.9) \times 10^{-4}$	3.0 ± 0.9	0.34 ± 0.10
0.412 ± 0.006	295	$(2.7 \pm 0.6) \times 10^{-3}$	$(5.5 \pm 1.9) \times 10^{-4}$	5.0 ± 2.0	0.20 ± 0.08
1.016 ± 0.006	295	$(1.2 \pm 0.3) \times 10^{-3}$	$(2.3 \pm 0.4) \times 10^{-4}$	5.4 ± 1.5	0.19 ± 0.05

* He buffer gas

N_2 , is $\Phi_{\text{CHF}_3} = (2.3 \pm 0.4) \times 10^{-4}$, with a corresponding molar yield of $(1.2 \pm 0.3) \times 10^{-3}$. Oxygen (O_2) comprises 21% of the atmosphere, however, we expect O_2 to quench this reaction with a similar quenching efficiency as N_2 , as has been shown for 254 nm photolysis of CF_3CHO previously.¹²

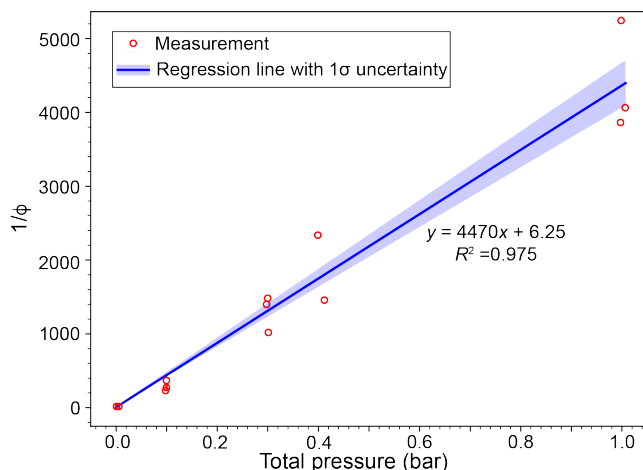


Figure 4. Pressure dependence of the reciprocal photolysis quantum yield of the CHF_3 -producing photolysis channel of CF_3CHO (Stern-Volmer) plot.

Table 1 also reports the ratio of molar yield to quantum yield (Y/Φ) at each pressure. We refer to this ratio as the turnover number - the average number of times CF_3CHO absorbs a photon before fragmenting. At 1 bar, each CF_3CHO molecule has to absorb an average of 5.4 photons before photodissociating. $Y/\Phi > 1$ reflects that quenching returns a fraction of the excited molecules to their ground state without reacting, where they become available to absorb another photon and repeat the cycle. As the pressure is lowered, the turnover number becomes smaller because quenching is reduced, reaching the limiting case at zero pressure where $Y = \Phi$.

In the simplified environment of a laboratory cell and 1 bar of N_2 buffer gas, where we assume no other significant loss mechanisms for CF_3CHO , the photolysis turnover number is simply $1/\Phi_{\text{total}}$. However, in the environment of the authentic atmosphere, other processes can remove CF_3CHO , thereby reducing the molar yield, for the same quantum yield. Recent atmospheric box model simulations incorporating observations from the 2012 London ClearFlo campaign and two of the most important competing removal pathways, OH reaction and deposition, predicted a photolysis turnover number ranging from 2.8 to 4.4.²² This value is similar to, but ~ 20 –50% less than, that determined under our laboratory conditions where these competing processes are excluded. Note that the turnover number in the

atmosphere will depend on local environmental conditions, including humidity, OH, NO and O_3 mixing ratios and pressure. The turnover number is expected to be larger (higher molar yield for fixed quantum yield) in pristine/rural environments where the mixing fractions of OH and O_3 are lower, or higher altitude where quenching is reduced. But the turnover number should be smaller (smaller molar yield) at high humidity because of increased deposition.

Notwithstanding the differences that will be present in an authentic atmosphere, discussed above, we can use our laboratory atmospheric-pressure molar yield, $Y_{\text{CHF}_3} = (1.2 \pm 0.3) \times 10^{-3}$, to estimate a crude upper limit 100-year GWP for CF_3CHO , and hence indirect GWP_{100} for (*E*)-1,3,3,3-tetrafluoropropene due to CF_3CHO photolysis, of $\text{GWP}_{100} \leq 10$. This would bring it into line with “natural refrigerants” such as propane, which has recently been shown to exhibit an indirect GWP_{100} of 10 due to its secondary atmospheric chemistry.²³ To determine the true environmental impact, rigorous atmospheric modelling is needed and this study provides the quantum yield data that are required to do so.

In summary, this paper demonstrates that CHF_3 is produced following the photolysis of CF_3CHO under atmospherically relevant pressures and wavelengths, and reports quantum yields for this reaction following 308 nm photolysis at a range of pressures from collision-free to 1 bar. These data will enable the inclusion of this CHF_3 formation pathway in atmospheric models, which are necessary to quantitatively assess the long-term impact of large scale emission of (*E*)-1,3,3,3-tetrafluoropropene.

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results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the USDOE or the US Government.

Supporting Information Available

Detailed description of materials and methods, and supplementary results supporting those presented in this manuscript.

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TOC Graphic

