

TODOp

1. Find how garrett made charts in his manuscript
2. Make charts better or change input data
3. Do comparisons of Cl species with F species
 - (a) Garrett seems to have started doing that in lagrangian hi res mass frac.ipynb, but he doesn't include measured Cl data.

cfs2canteraPD

1. Get injected_species from netj_file
2. Get conc.cutoff from netj_file (inject conc)
3. Make it run PFRTP-Garrett and cfs_post if needed

cfs_post

1. Make trajectory selection faster
2. Make it run PFRTP-Garrett if needed

PFRTP-Garrett

1. Make interactive widget to choose run conditions
2. Fix thing with flame temperature estimate
3. Temperatures shouldn't go down then back up

Instructions

1. Run netj_generate.ipynb to generate input files from lists of run conditions
2. Run cfs_batchrun.ipynb to send the generated .netj files to CFS and run the simulations
3. Run PFRTP-Garrett.ipynb to use Cantera to perform the same simulations.
4. Run cfs_post.ipynb, and select .netj files.
5. Run cfs2canteraPD.ipynb to generate path diagrams using Cantera.

Problems

1. There are many many .ipynb files in Modeling.GPD, many of which are near duplicates of each other, scattered across folders. It is difficult to tell which ones are the most up to date and which ones are obsolete.
2. Residence Time column from cantera has no duplicate times. CFS will have 3-7 rows of identical times
3. Cantera increases time steps constantly, CFS has variable time steps
4. Concentrations of non-major species in cantera are around 1e-100, in CFS they are around 1e-15
 - (a) Produces problems for reaction path diagrams because cantera can't tell which is the major species
 - (b) Concentrations are all 0 until injection, then they all instantly increase
 - i. This is probably because the transient solution solves from the injection point and then tries to work backwards to the flame. Injecting at the flame may fix this.
5. CF3O_r has 15 reactions, CF2s has 74, CF4 15, C2F6 6. C2F6 behavior in path diagrams may be caused by incomplete reactions
 - (a) C2F6 may just not have that many reactions because it is a larger molecule, and the C-C bond is the most likely to break
6. Several reactions are "ambiguous" and cantera will use the designated default reaction
 - (a) Default reaction may not be conducive for simulating C2F6
7. Some reactions are not parsed (they may just not be relevant)

Notes

1. CF4 will never be destroyed at temps below 1200K, 100% DE for temps >1600 C
2. Higher values of MAXIT seem to produce more residence time steps

Table 1: Files, Folders, and Descriptions

File	Folder	Description
flow_convert.ipynb	PFAS_Modeling/	Converts liters per minute to kilograms per second for air and for CH4 using cantera
netj_generate.ipynb	PFAS_Modeling/	Takes a set of varying run conditions and produces netj files to do all iterations
cfs_batchrun.ipynb	PFAS_Modeling/	Uses CFS batch method to run generated netj files, prompts user for inputs to determine simulation duration
PF RTP-Garrett.ipynb	PFAS_Modeling/Pseudo_PFR	Uses a PFR simulation in Cantera to make similar results as CFS
cfs_post.ipynb	PFAS_Modeling/	Runs CFS in GUI mode to automate post-processing of vtk files to include species concentration
cfs2canteraPD.ipynb	PFAS_Modeling/	Converts vtk to csv data, then produces a path diagram using Cantera for a specified trajectory, residence time, and threshold.
pfr.ipynb	PFAS_Modeling/	Example PFR that came with Cantera
pfr2.ipynb	PFAS_Modeling/	Example Cantera PFR that includes heat loss
vtk2csv.py	PFAS_Modeling/	Stand alone script for converting a specific vtk to a csv
lagrangian hi res mass frac.ipynb	L:/Lab/AMCD-PFAS_Incineration/Modeling_GPD/Cantera/PFR DE S Curves/	Makes plots of multiple species DE% vs Temperature
eulerian <injectant>.ipynb	L:/Lab/AMCD-PFAS_Incineration/Modeling_GPD/Cantera/influent concentration/	Make multidimensional color plots for conc. vs Temperature vs DE%. Also absolute and relative yield vs conc.
paths <SR>.ipynb	L:/Lab/AMCD-PFAS_Incineration/Modeling_GPD/Cantera/paths/	Makes path diagrams for several species at specified SR
T99.ipynb	L:/Lab/AMCD-PFAS_Incineration/Modeling_GPD/Cantera/T99/	Makes T99 plots of multiple species
lagrangian.ipynb	L:/Lab/AMCD-PFAS_Incineration/Modeling_GPD/Cantera/PFR DE S Curves/archive/	Makes plots of species DE vs Temperature. Plots from this script don't look the same as plots in the doc, so it is probably outdated.

Table 6: C1, C2, and C3 Chlorinated and Fluorinated Species

Formula	Species Name	Incinerability Index	Formula	Species Name	Incinerability Index
CNCl	Cyanogen Chloride	17-18	C ₃ H ₄ ClN	3-Chloropropionitrile	143-144
CH ₃ Cl	Chloromethane	29-30	C ₃ H ₆ Cl ₂ O	1,3-Dichloropropan-2-ol	145-146
COCl ₂	Phosgene	39-40	CHClF ₂	Chlorodifluoromethane	151-153
C ₂ H ₃ ClO ₂	Methyl Chloroformate	46-50	CHCl ₂ F	Dichlorofluoromethane	154-157
C ₂ H ₂ Cl ₂	Dichloroethene	54	C ₂ HCl ₅	Pentachloroethane	154-157
C ₂ H ₄ FNO	Fluoroacetamide	55-56	C ₂ H ₃ Cl ₃	Trichloroethane	158-161
C ₂ H ₃ Cl	Vinyl Chloride	60-64	CHCl ₃	Chloroform	158-161
CH ₂ Cl ₂	Dichloromethane	65-66	C ₃ H ₆ Cl ₂	1,3-Dichloropropane	165
CClF ₂ CCl ₂ F	1,2,2-Trichloro-1,1,2-Trifluoroethane	81-84	C ₃ H ₅ Cl ₃	1,2,3-Trichloropropane	168-173
CCl ₂ F ₂	Dichlorodifluoromethane	85-88	C ₂ H ₄ Cl ₂	1,1-Dichloroethane	175-178
CCl ₃ F	Trichlorofluoromethane	85-88	C ₃ H ₅ ClO	1-Chloro-2,3-epoxypropane	183-186
C ₃ H ₄ Cl ₂	1,2-Dichloropropene	89-91	CHCl ₃ S	Trichloromethanethiol	189-192
CH ₃ COCl	Acetyl Chloride	92-97	C ₂ Cl ₆	Hexachloroethane	202-203
C ₂ H ₂ Cl ₄	Tetrachloroethane	121-125	C ₂ H ₅ ClO	Chloromethyl Methyl Ether	218-220
C ₂ H ₅ Cl	Chloroethane	126	C ₂ H ₄ Cl ₂ O	bis(Chloromethyl) Ether	222-223
C ₂ H ₄ Cl ₂	Dichloroethane	131	C ₃ Cl ₆	Hexachloropropene	234
CCl ₄	Carbon Tetrachloride	136-140			

Table 2: Validated Path Diagrams - CFS

	CF4				CHF3				C2F6			
	Ports				Ports				Ports			
	1	4	6	8	1	4	6	8	1	4	6	8
27.5 kW									×			×
45 kW	×	✓							×	×		×

Table 3: Validated Path Diagrams - Cantera

	CF4				CHF3				C2F6			
	Ports				Ports				Ports			
	1	4	6	8	1	4	6	8	1	4	6	8
27.5 kW	×	×	×	×					✓	✓	✓	✓
45 kW	✓	✓	✓	✓					✓	✓	✓	✓

Table 4: CFS Executed Simulations

	CF4				CHF3				C2F6			
	Ports				Ports				Ports			
	1	4	6	8	1	4	6	8	1	4	6	8
27.5 kW		✓							✓	✓	✓	✓
45 kW	✓	✓			✓	✓	✓		✓	✓	✓	✓

Table 5: Cantera Executed Simulations

	CF4				CHF3				C2F6			
	Ports				Ports				Ports			
	1	4	6	8	1	4	6	8	1	4	6	8
27.5 kW	✓	✓	✓	✓					✓	✓	✓	✓
45 kW	✓	✓	✓	✓					✓	✓	✓	✓

Emails with Bill

1. go through these lists and identify any C1, C2, and possibly C3 F and Cl species and their ranking
2. (CCl4 (✓, 136-140), CHCl3(✓, 195-196), C2Cl6(✓, 202-203), CF4(×), CHF3(×), C2F6(×)) listed?
3. other C1, C2, and C3 chloro or fluorocarbons
4. mixed Cl-F species?

• mainly CFCs
5. analyze the fraction of chlorinated species, and number of fluorinated species included

• Does this mean *all* chlorinated species, or only those with 1-3 C?

• There are 320 total species in the list.

• Chlorinated species account for 113 species. Chlorinated C1-C3 species account for 40 of them.
- 3

- Fluorinated species account for 8 species. Only two do not contain 1 to 3 carbons (Sulfur Hexafluoride and Fluoroacetic Acid)

6. anything you think notable.

- It's interesting how the only fluorinated species on the list that aren't CFCs are SF₆ and C₂H₃FO₂

7. Find incinerability index for species

I'd like to begin the introduction of our Cl/F paper with a discussion of the Incinerability Index, and why we chose to study these 6 compounds. The main reasons are their combinations of different molecular structures, bond types, and their available/published kinetics.

Talk about why the incinerability index is used instead of other measures.

Talk about properties of these compounds.

Heat of combustion was used for a while, but it wasn't accurate because:

Why, specifically, is the thermal stability used instead of other measures?

Why are these compounds chosen? What makes them good candidates for this study?

What is it about the molecular structures that makes these representative compounds?

CCl₄ has tetrahedral, single covalent bonds. CHCl₃ is tetrahedral, like methane but with 3 Hs replaced with Cls. C₂Cl₆ is two carbons connected linearly, with each carbon bonded to three chlorine atoms in a trigonal planar arrangement. CF₄ is tetrahedral, like methane but with all Hs replaced with Fs. CHF₃ is tetrahedral, like methane but with 2 Hs replaced with Fs. C₂F₆ is two carbons connected linearly, with each carbon bonded to three fluorine atoms in a trigonal planar arrangement. The fluorine compounds all have higher bond energies than the chlorinated compounds.

What is it about the bond types that makes these representative compounds?

Not sure if he means that having the fluorinated and chlorinated compounds allows for comparing the behavior of the bond energies of the C-F and C-Cl bonds, or if he means that the bond types of the compounds themselves are important.

Having the chlorinated analogues of the fluorinated compounds could allow for establishing a routine to compare the two?

What is it about the kinetics that makes these representative compounds?

I think it's because the mechanisms of destruction of these compounds are expected to be used in more complex compounds. Basically, larger PFAS probably break apart into these compounds.

Make comparisons of fluorinated and chlorinated compounds

All the fluorinated compounds have higher bond energies, and usually slightly denser molecules.

As you will see many of the Class 1 species are PAHs with ring structures.

- Most of the PAHs have many carbons, so I'm not sure if they're relevant for the discussion of C1-C3 species

I'm thinking a discussion of these species and bond energies might be a good place to start.

Email with Bill about Incinerability Index

Thank you! This is a great summary. I do not know how species were selected for incinerability ranking, but I had thought that all were evaluated experimentally. Did you learn otherwise?

I was able to find that not all species in the index were evaluated experimentally. I found this paragraph in D.2, page 106 of the document:

"Currently, sixty-one compounds have been experimentally evaluated by UDRI These compounds, for which experimental data has been generated. . . are designated experimentally evaluated and are listed in boldface. Compounds which have not been experimentally studied . . . but for which experimental data exist within the open literature, are listed in italics. The remaining compounds were ranked based on limited experimental data on the actual compound, data on similar compounds, and/or reaction kinetic theory. For this latter group, which includes the majority of the ranking, sufficient data were not available to designate the compounds as experimentally evaluated. Thus, their ranking should be considered tentative and subject to change following experimental study."

I think the ones that have more than just reaction kinetic theory are printed in bold or italicized, because the tables have this footnote at the bottom:

FOOTNOTES:

1. UNITS OF TEMPERATURE ARE DEGREES CELSIUS.
2. **BOLDFACE** INDICATES COMPOUND THERMAL STABILITY IS "EXPERIMENTALLY EVALUATED" (RANKING BASED ON UDRI EXPERIMENTAL DATA COUPLED WITH REACTION KINETIC THEORY).
3. *NON-APPENDIX VIII* COMPOUND.
4. *N.O.S. LISTING*; RANKING IS PRESENTED BASED ON EITHER UDRI OR LITERATURE EXPERIMENTAL DATA COUPLED WITH REACTION KINETIC THEORY.
5. *ITALICS* INDICATE COMPOUND THERMAL STABILITY IS RANKED BASED ON LITERATURE EXPERIMENTAL DATA COUPLED WITH REACTION KINETIC THEORY.

I think that the species that are printed in plain formatting are not experimentally evaluated, and only come from reaction kinetics. So, in the below screen clip, I think Chloropropene and Tetrachloroethane are

the only species that Taylor and Bellinger experimented evaluated. The Chloroethane and Hydrazine have some experimental data that was gathered from the literature, but Taylor and Bellinger didn't get the data themselves. The remaining species I think only have reaction kinetics to support their position.

CLASS 4	
CHLOROPROPENE 3-{ALLYL CHLORIDE} [2]	120
DICHLOROPROPENE (cis-1,3-)	121-125
DICHLOROPROPENE (trans-1,3-)	121-125
TETRACHLOROETHANE (1,1,2,2-) [2]	121-125
TRICHLOROPHENOL (2,4,5-)	121-125
TRICHLOROPHENOL (2,4,6-)	121-125
CHLOROETHANE (ETHYL CHLORIDE) [4] [5]	126
DICHLOROPROPENE (2,3-)	127-130
HYDRAZINE (DIAMINE) [5]	127-130

Also, I can see multiple parts of this document that say something like "this list is tentative and will be updated annually," but I have not been able to find another index produced by the EPA.

Did you learn why specific species were selected back in the 1980s? I think they used the list of compounds from Appendix VIII to Part 261 (eCFR :: 40 CFR Chapter I Subchapter I – Solid Wastes) because they say on page 106, "The ranking includes all individually-listed organic compounds included on the current Appendix VIII list. . . . Trace metal-containing compounds were not included in this ranking since the metal itself is a toxic moiety and is not destroyed in the incineration process."

You mention 11 fluorinated species on the list. On Table 6, I see: C₂H₄FNO, CHClF₂, CHCl₂F What are the others? Are they all mixed F-Cl species? I assume they are either γ C₃ or not organic? I believe that you indicate that none of our F species (CF₄, CHF₃, C₂F₆) are on the list but all our Cl species (CCl₄ 136-140, CHCl₃ 158-161, C₂Cl₆ 202-203). I don't see CCl₄ in Table 6. The fluorinated species in the index are sulfur hexafluoride, fluoroacetic acid, fluoroacetamide, 1,2,2-Trichloro-1,1,2-Trifluoroethane, dichlorodifluoromethane, trichlorofluoromethane, chlorodifluoromethane, and dichlorofluoromethane, for a total of 8 fluorinated species. The original count of 11 is a mistake, because I was originally counting species with "fluorene" as fluorine, but the table has been updated to include the proper species. So, the final count is 8 fluorinated species with 6 organic species. I don't think the list includes any γ C₃ fluorine species. I have also included CCl₄ in the table.

I would like to understand why the Incinerability Index was designed the way it was. It predated me, but the idea was to either calculate or measure the ability to destroy a species in a specific reactor at a specific temp for a specific residence time. PICs were not yet on the horizon. This was done at the U of Dayton by a professor, Barry Dellinger, and his postdoc, Phil Taylor. They would literally vaporize and introduce these chemicals into a hot tube furnace at a specific temp and measure the amount in the exhaust 1 or 2 sec later using an online GC/MS. **Can you learn how this was done specifically?** They obviously didn't care about F unless it was associated with Cl. Remember, the concern back then was very Cl centric. These were the days of Love Canal and the Valley of the Drums. A lot of new Superfund sites were being discovered. Most of the problem were associated with discarded chlorinated solvents.

I was able to find this paper (Thermal degradation characteristics of chloromethane mixtures — Environmental Science and Technology (acs.org)) that is referenced in the manual in section D.2, where they say "Currently, sixty-one compounds have been experimentally evaluated by UDRI under a consistent set of experimental conditions which was devised based on the previous discussion [Dellinger and Taylor (1987), Taylor and Dellinger (1987)]."

After looking at that article, in the "Experimental Approach" section, it says, "Decomposition of chloromethanes and PIC formation as a function of temperature was measured by the combined analytical capability of the thermal decomposition unit-gas chromatographic system and the thermal decomposition analytical system. . . .Details of these systems have been discussed at length elsewhere (26-28)" The articles it sources here are:

- (26) Rubey, W. A.; Carnes, R. A. *Rev. Sci. Instrum.* **1985**, *56*(9), 1795-1798.
- (27) Rubey, W. A.; Fiscus, I. B.; Torres, J. L. "Description and Operation of a Thermal Decomposition Unit-Gas Chromatographic System"; EPA Report under Cooperative Agreement CR-807815-01-0; U.S. Government Printing Office: Washington, DC, Dec 1982.
- (28) Rubey, W. A. *Design Considerations Associated with the Development of a Thermal Decomposition Analytical System*; U.S. Environmental Protection Agency: Cincinnati, OH, 1980, EPA-600/2-80-098.

However, I am having some difficulty finding and accessing these articles because they are quite old. The article does have a description of how the system works in the Experimental Approach section, though I'm not sure if it's detailed enough to really explain everything.

In the 1990s, during the atmospheric ozone crisis, NIST began studying small fluorocarbons that were being tested as replacement flame suppressants and later refrigerants. This led to

the F kinetic set we are now using.

Email with Bill about Tsang et al

Yes, the NIST mechanism initially only included C1 and C2 fluorocarbons. Since then, it now includes some C3 species. Even limited to C1-C3 fluorocarbons, I think it includes ~ 1000 reactions. Of course, if a species and reaction pathway is not included, the model cannot predict its formation, so larger species are not possible.

First order reactions refer to those involving only 1 reactant. Unimolecular decomposition like CHF_3 to $\text{CF}_3(\text{rad}) + \text{H}(\text{rad})$ is an example. Second order reactions involve 2 reactants like $\text{CHF}_3 + \text{OH}(\text{rad})$ to $\text{CF}_3(\text{rad}) + \text{H}_2\text{O}$. Both result in a $\text{CF}_3(\text{rad})$ but one is dependent on concentrations of two species and reaction rates of these two reactions may be very different. Second order reactions do not need to result in molecular growth. Second order reactions can happen even for C1 species. Free radical reactions in flames are second order. Some happen extremely fast. They happen because concentrations of flame radicals are extremely high in flames.

Unimolecular decomposition (first order rxns) can happen anywhere if sufficient energies are available. Second order reactions occur only in areas with both reactants in high concentrations. Most kinetic studies focus on unimolecular reactions, most ignore the free radical chemistry that happen in flames. You'll notice that the NCSU mechanism includes many second order reactions.