Incineration 101 and issues related to PFAS destruction

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The research described in this presentation has been funded in part by the U.S. Environmental Protection Agency (EPA). It has been subjected to review by the Office of Research and Development and approved for presentation. Approval does not signify that the contents reflect the views of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Definitions

- Combustion high-temperature exothermic redox chemical reaction of a fuel (reductant) and an oxidant (usually atmospheric oxygen in excess).
 - Complex progression of physical processes
 - Complex set of elementary reactions governed by high temperature kinetics
 - Interaction of these two results in a highly reactive flow with fast heat and mass transfer
 - Depending on fuel, reaction front often sufficiently hot to produce incandescent radiation (flame)
 - These temperatures sustain hundreds or thousands of elementary free radical (intermediate) reactions (initiation, propagation/branching, termination)
 - Thermodynamically, chemical equilibrium overwhelmingly favors reaction products
 - For hydrocarbon fuels these are CO₂ and H₂O



Definitions (cont.)

- Unfortunately, complete combustion is almost impossible to achieve due to kinetic (temperature) and transport (mixing) limitations
 - Related to three T's (time, temperature, turbulence)
 - Incomplete oxidation leads to pollutants (CO, organic HAPs, soot)
 - Oxidation of atmospheric $\rm N_2$ and fuel components and impurities leads to $\rm NO_x$ and $\rm SO_2,$ $\rm SO_3,$ HCl, HF, etc.
 - Conditions affect the behavior of inorganic ash species
- Mixing of fuels and oxidant (and resulting flames) can be premixed or diffusion, laminar or turbulent
 - Premixed fuel/oxidant are premixed before reacting (cooler flames, Bunsen burner, sometimes "flameless")
 - Diffusion fuel/oxidant introduced separately, diffuse to react at a stoichiometric flame front with very high local temperatures (inherently safer, Burke-Shumann burner)
 - Most industrial-relevant burners are diffusion flames





Definitions (cont.)

- Gasification Process of converting carbonaceous materials into H₂, CO, and CO₂ (synthesis gas, syngas, producer gas)
 - Feed materials may be highly variable, and may include fossil fuels, biomass, and wastes
 - Achieved by reacting the materials with controlled amounts of oxygen or steam at high temperatures (>700 °C)
 - Overall exothermic, sub-stoichiometic combustion (debatable)
 - Syngas is a fuel and can be burned directly in boilers, gas engines, or turbines it can also be used as a chemical feedstock
 - CO₂ may be removed prior to combustion (Kemper Co IGCC)
 - Steam addition (water-gas shift) converts CO to additional H₂ and CO products (CO + H₂O => H₂ +CO₂)
 - H₂ may be used as a feedstock or used in fuel cells or H₂ turbines (Mitsubishi-Hitachi)
 - Fischer-Tropsch process converts CO and H₂ over metal catalysts at 150-300 °C and high pressures into liquid hydrocarbons
 - $(2n+1)H_2 + CO => C_nH_{(2n+2)} + nH_2O$





Kemper Co IGCC power plant

Definitions (cont.)

Pyrolysis –Thermal decomposition (endothermic) and rearrangement of (most commonly organic) materials at elevated temperatures in an **inert atmosphere (N₂, Ar, etc.)**, breaking and reforming weak chemical bonds by thermal decomposition without oxidation

Low temperature (<500 °C) used to produce solid chars,

liquid tars, organic gases, and CO

High temperatures (~900 °C) used to produce coke from coal and activated carbons

PFAS precursors (such as $CHCIF_2$, R-22) are produced via the pyrolysis of chloroform ($CHCI_3$) and HF

<u>Combustion, Gasification, and Pyrolysis</u> are not mutually exclusive Pyrolysis precedes both gasification and combustion



Elementary reactions – consider $H_2 + O_2$

The overall (global) reaction $[2H_2 + O_2 => 2H_2O]$ does not describe the elementary reaction mechanisms that are actually occurring $\frac{1}{NO_2 - Reaction} = \frac{1}{R^2 + C_2} => 2H_2O$

,	P80.	Reservor	A .	. C.	- C
Some important elementary reactions:	1	$H + O_2 = O + OH$	3.548-1015	-0.406	16.599
some important clementary reactions.	2	$O + H_2 = OH + H$	5.080-10 ⁰⁴	2.670	6290
1 H2 + O2 => H + HO2	3	$OH + H_2 = H_2O + H$	$2.160 \cdot 10^{66}$	1.510	3430
1.112 + 02 -> 11 + 1102	4	$O + H_2O = OH + OH$	2.970-100	2.020	13,400
2. H + O2 => OH + O	5	$H_2 + M = 2H + M$	$4.581 \cdot 10^{19}$	-1.400	104,380
	6	$O + O + M = O_2 + M$	6.166-1015	-0.500	0
3. U + H2 => UH + H	7	O + H + M = OH + M	4.710-10**	-1.000	0
$1 \cap H + H = H + H = H$	8	$H + OH + M = H_2O + M$	3.802-10**	-2.000	0
4.011 + 112 -> 11 + 1120	91. 25	$H + O_2 + = HO_2(k_{cc})$	1.475(10**	0.60	0
5. H + O2 + M => HO2 + M	90	$H + O_2 + M = HO_2 + M (k_0)$	6.366-10	-1.72	3023
	10	$HO_2 + H = H_2 + O_2$	7,000-1012	0.0	8.23
6. H, O, OH => wall (loss)	11	$HO_2 + H = OH + OH$ $HO_3 + O = OH + O$	3/0/9/1017	0.000	220
$7 H\Omega^{2} + H\Omega^{2} = > H^{2}\Omega^{2} + \Omega^{2}$	13	$HO_1 + OH = H_1O + O_2$	2.891/10 ¹³	0.0	-497
7.1102 + 1102 => 11202 + 02	146	$HO_{2} + HO_{2} = H_{2}O_{2} + O_{2}$	$4.198 \cdot 10^{14}$	0.0	11.982
8. H2O2 + M => OH + OH + M	140	$HO_{2} + HO_{3} = H_{2}O_{3} + O_{3}$	$1.300 \cdot 10^{11}$	0.0	-1629
	15a	$H_1O_1 = OH + OH(k_n)$	$2.951 \cdot 10^{14}$	0	48,430
9. UH + H2U2 => HU2 + H2U	15b	$H_2O_2 + M = OH + OH + M (k_0)$	$1.202 \cdot 10^{12}$	0	45,500
$10 \text{ O} + \text{H}^2\text{O}^2 => \text{OH} + \text{H}^2\text{O}^2$	16	$H_2O_2 + H = H_2O + OH$	$2.410 \cdot 10^{13}$	0.0	3970
	17	$H_2O_3 + H = HO_2 + H_3$	$4.819 \cdot 10^{13}$	0.0	79.50
Best current models for H_2/O_2 include about	18	$H_2O_3 + O = HO_3 + OH$	9.550-1000	2.000	3970
Dest current models for hig/ og meldde doodt	19p	$H_2O_2 + OH = H_2O + HO_2$	1.000-1010	0.0	0
20 elementary reactions and 10 species	19q	$H_2O_2 + OH = H_2O + HO_2$	5,794-1014	0.0	9557
zo cicilitary reactions and to species					

Some of these species are stable (H_2 , O_2 , H_2O) and some are free radicals (unpaired valence electrons such as H, OH-hydroxyl, O, HO_2 -hydroperoxyl)

Highly chemically reactive Often very short lived (high temperatures necessary)

Free radical reactions



With respect to PFAS, C-F higly polarized (nearly ionic) bonds are particularly strong (485 kJ/mol)

CF₄ very difficult to destroy

Once formed, F reacts readily with any avialable radical

+ H => HF (565 kJ/mol) very stable ionic species, extremely corrosive acid
 Halons effective fire extinguishers because of chain termination

Elementary reactions – hydrocarbon fuels

Now consider methane combustion (CH_4)

213 elementary reactions and 48 species (Boukhalfa, 2016)

325 elementary reactions and 53 species (GRIMech 3.0)

N-butanol combustion (C_4H_9OH)

3381 elementary reactions and 263 species (Harper et al., 2011)

Add in elementary reactions and species describing additional elements N, Cl, (and now F)

N – 788 elementary reactions and 45 species (Glarborg et al. 2019)

Cl – 222 elementary reactions and 19 species (Pitz & Westbrook, 1990)



Adding fluorine elementary reactions

- Comprehensive fluorine kinetic review for C1 and C2 hydrocarbons performed by Burgess et al. (1996)
 - 689 cited publications
- C1 and C2 fluorine chemistry adds 654 elementary reactions



Prog. Energy Combust. Sci. Vol. 21, pp. 453-529, 1996 Published by Elsevier Science Ltd Printed in Great Britain.

0360-1285(95)00009--7

THERMOCHEMICAL AND CHEMICAL KINETIC DATA FOR FLUORINATED HYDROCARBONS

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Abstract—A comprehensive, detailed chemical kinetic mechanism was developed and is presented for C_1 and C_2 fluorinated hydrocarbon destruction and flame suppression. Existing fluorinated hydrocarbon thermochemistry and kinetics were compiled from the literature and evaluated. For species where no or incomplete thermochemistry was available, these data were calculated through application of *ab initio* molecular orbital theory. Group additivity values were determined consistent with experimental and *ab initio* data. For reactions where no or limited kinetics were available, these data were estimated by analogy to hydrocarbon reactions, by using empirical relationships from other fluorinated hydrocarbon reactions, by *ab initio* transition state calculations, and by application of RRKM and QRRK methods. The chemistry was modeled considering different transport conditions (plug flow, premixed flame, opposed flow diffusion flame) and using different transport conditions (plug flow, agents, agents (fluoromethanes, fluoroethanes) and agent concentrations. This report provides a compilation and analysis of the thermochemical and chemical kinetic data used in this work.





Fig. 1. Fluorinated hydrocarbon reaction pathways.

Modeling combustion kinetics

The rate of each elementary reaction is dependent on reactant concentrations and rate coefficient (k) k depends on temperature (and sometimes pressure) and is expressed in Arrhenius form as k = A exp[-Ea/RT] or k = A Tⁿ exp [-Ea/RT] pre-exponential A, activation energy Ea, temperature T, temperature exponent n, gas constant R Identifying elementary reactions and determining values for these parameters are objectives of many experimental and theoretical studies

Next, the proposed chemcical mechanism is combined with the associated rate coefficients, and the coupled rate equations are defined for each species as

d[X]/dt = total rate of forming species X – total rate of removing species X

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d[H]/dt = k1[H2][O_2] - k2[H][O_2] + k3[O][H_2] + k4[OH][H_2] - k5[H][O_2][M] - k6[H]

d[O]/dt = k2[H][O_2] - k3[O][H_2] - k6[O]

d[HO2]/dt = ......

d[H2]/dt = ......

etc.
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Modeling combustion kinetics (cont.)

Solve the set of coupled differential equations (numerically) subject to kinetic boundary conditions Large differences in timescales (stiff problem)

- Major species O_2 , H_2 , H_2O might change over seconds
- Reactive free radical intermediates OH, H have lifetimes of miliseconds, nanoseconds, or picoseconds
- Specialized numerical methods needed to solve for species concentrations
- Kinetics alone are computationally intensive
- Solution yields species concentrations at a specific temperature

Linking kinetics to fluid dynamics

However, the kinetics must be solved in conjunction with a computational fluid dynamic (CFD) model that describes the mass, momentum, and energy balances of the turbulent reacting flowfield

Navier-Stokes equations describe the (mass, momentum, energy) balances

Process is to discretize the flow field (thousands of fixed volumes with convecting flow and reacting

species passing between volumes

Reactions affect heat release and temperature

Identify initial and boundary conditions

Effectively solving the kinetic model within every discrete convective volume

Solutions provide temperatures and species concentrations within every volume





Incineration

- Incineration is combustion with the primary purpose of oxidizing waste species
 - Energy utilization is secondary
 - Maximize temperatures and oxidative environments
 - Oxidation of waste species proceeds in a highly reactive flow with fast heat and mass transfer greatly facilitates their destruction
- Hazardous waste incinerators (HWIs)— designed to combust/destroy a large variety of liquid and solid wastes with highly variable compositions, heating values, and properties
 - Designed to effectively destroy the most difficult heterogeneous waste streams
 - Destruction and removal efficiencies >99.99% desired
 - Commercial and industrial units
 - Often rotary kilns with secondary combustion chambers (SCC), acid gas, and PM control
 - Cofiring wastes in cement kilns is very effective
 - Typical requirements of >1800 °F gas temperature for >2 sec residence time



Incineration (cont.)

• Municipal solid waste incinerators & combustors (MSWIs)

- Large mass burn units (~40 tons/hr)
 - Often moving or reciprocating grate designs with under fire and overfire air and SCC, acid gas, activated carbon injection, and PM control
 - Typically achieving >1500 °F gas temperature for >2 sec residence time
 - Waste-to-energy with heat recovered for electrical generation, process steam, district heating









Incineration (cont.)

• Sewage sludge incinerators (SSIs)

- Combination of multiple hearth furnaces (variable designs) and fluidized bed incinerators
 - Sometimes only remove water, temperatures vary widely







Thermal oxidizers

Direct-fired thermal oxidizer

- Similar to a HWI afterburner refractory-lined chamber with auxiliary fuel-fired burner and standing flame
- **Process gases** introduced through or very near the swirling flame
 - Designed for process gases with known properties and compositions
 - Best for high concentration, high heating value VOCs or when high temperatures are needed to insure destruction
 - Optimize mixing and exposure to high temperatures and flame radicals
 - Often 99.99% destructions guaranteed
 - Often need large amounts of auxiliary fuel to support standing flame



Linde/T-thermal oxidizer

- Regenerative thermal oxidizer (RTO)
 - Alternate flow through multiple ceramic beds to preheat and partially oxidize process gases (VOCs) before entering combustion chamber with burner and auxiliary fuel fired flame
 - Hot combustion gases then exit through, and transfer heat to, a second ceramic bed
 - Valving alternates flow so that one bed is being heated while the other is preheating incoming gases
 - Two and three bed designs are available
 - Three bed designs minimize the possibility of small quantities of VOCs bypassing the combustion chamber during valve cycling
 - RTOs are extremely energy efficient
 - Effective for low and high concentration VOC applications
 - VOCs may not have direct flame contact and this may limit destructions to >99.5%





Recuperative thermal oxidizer

- In efforts to improve thermal efficiency of direct-fired thermal oxidizers, heat exchangers are added to recover heat from exhaust gases
- May be used to preheat waste process gases or another fluid for a separate process
- Simply indicates incorporation of a heat exchanger to recover waste heat for some useful purpose





• Flameless thermal oxidizer (FTO)

- FTOs premix VOCs, auxiliary fuel, and air before directing the mixture through a large preheated ceramic bed
- The ceramic bed heats the fuel lean mixture (kept below flammability limit) to oxidation temperatures
- Oxidation of fuel and VOCs proceeds without a flame which also release heat to the ceramic bed maintaining high temperatures
- Ceramic bed acts to control temperatures, moderate heat transfer, and provide large residence times for oxidation reactions
- Without a flame, average temperatures within the bed are relatively low minimizing thermal NO_x formation
- Destruction of fluorinated VOCs is not recommended by the vendor over concerns of corrosion of the ceramic bed caused by HF



Catalytic oxidizer

- Catalysts are materials that lower activation energies associate with chemical reactions
- Oxidation catalysts (often ceramics impregnated with metals such as Pt, Fe, V, Co, Mn) allow oxidation reactions to proceed at lower temperatures
 - Reactant diffusion to catalyst
 - Adsorption onto active catalyst sites
 - Surface mediated chemical reaction
 - Product desorption and diffusion
- Often includes a small heat source (flame) to preheat VOC gases and maintain catalyst at optimum temperature
- Well suited for low concentration VOC gases
- Catalytic oxidizers come in regenerative and recuperative variants



Recuperative catalytic thermal oxidizer



Thermal treatment of PFAS

- Group of >4000 per- and poly-fluorinated organic compounds
 - PFAS often composed of non-polar fluorinated alkyl chain and polar functional group
 - Used by the military and industry and present in a large variety of consumer products
 - Valued for their hydrophobic and lipophobic properties, thermal and chemical stability
 - Present in many industrial and municipal waste streams including air, water, and land discharges
 - Subjected to disposal by incineration using equipment with a range of operating conditions and temperatures

Highly electronegative fluorine makes C-F bonds particularly

strong, require high temperatures for destruction

Unimolecular thermal destruction calculations suggest that CF_4 requires 1,440 °C for >1 second to achieve 99.99% destruction (Tsang et al., 1998)

Sufficient temperatures, times, and turbulence are required

Functional group relatively easy to remove/oxidize

Low temperature decarboxylation as an example Information regarding potential products of incomplete combustion (PICs) is lacking



Products of incomplete combustion (PICs)

- When formed in flames, F radicals quickly terminate chain branching reactions to act as an extremely efficient flame retardant, inhibiting flame propagation
- PICs are more likely formed with F radicals than other halogens such as Cl
- PICs may be larger or smaller than the original fluorinated POHC of concern
 - CF₂ radicals preferred and relatively stable, suggesting the possibility of reforming fluorinated alkyl chains
 - Remaining C-F fragments may recombine to produce a wide variety of fluorinated PICs with no analytical method or calibration standards
 - May result in adequate PFAS destruction but unmeasured and unquantified PICs
 - Principal organic hazardous constituent (POHC)
- Very little information is published on PFAS destruction
 - Fluorine chemistry sufficiently different than Cl that we cannot extrapolate
 - Analytical methods and PFAS standards are lacking
 - Measurements focusing on POHC destruction may miss the formation of PICs
- HWIs and cement kilns may well be effective, but what about MWCs and SSIs (lower temperatures)?

Incinerability & mitigation research

- Explore minimum conditions (temperature, time, fuel H₂) for adequate PFAS destruction
 - PFAS surrogates
- Investigate relative difficulties in removing PFAS functional groups (POHC destruction) vs. full defluorination (PIC destruction)
- Effects of incineration conditions (temperature, time, and H₂) on PIC emissions
- Examine relative differences in the incinerability of fluorinated and corresponding chlorinated alkyl species
- Collaborative projects with DoD, universities, and industry partners to explore fundamental science questions and evaluate existing technologies
 - Investigate and add PFAS to incinerability index
 - Compare experimental and modeling results for incineration of C1 and C2 fluorinated species
 - Thermal treatment system for PFAS contaminated soils in Alaska
 - Fate of PFAS during GAC reactivation from treatment systems

Small pilot-scale incineration experiments

65 kW refractory lined furnace Rainbow furnace Peak temperatures ~1400 °C, and >1000 °C for ~3

sec

Combustor connected to facility APCD Afterburner, baghouse, NaOH scrubber

Introduce C1 and C2 fluorinated compounds with fuel, air, post flame measure POHC destruction and PIC formation FTIR and other real-time and extractive methods

Add modeling component using REI's CFS Configured Fireside Simulator CFD/kinetic model include C1 & C2 F chemistry from literature Burgess et al. (1996)



Bench-scale direct and indirect-fired thermal oxidation experiment

Repurpose existing equipment

- Formerly used for oxy-coal

Small scale (L/min & g/min)

Full control of post-flame temperature & time (2-3 sec)

Able to add either gas or liquid PFAS through or bypassing flame

Premixed or diffusion flames possible

Platform for measurement methods development

- SUMA, sorbent, total F, GC/ECD,
- real-time instruments





Incineration research status

- Pilot-scale experiment
 - Rainbow furnace is up and running
 - Integrated with afterburner, baghouse, NaOH scrubber
 - Verifying flows and temperatures
 - First experiments will focus on CF₄ (R14), CHF₃ (R23), and C₂F₆ (R116)
 - Quantify destruction and characterize PICs
 - Add PFAS with fuel, air, downstream
 - Real-time FTIR measurements
 - Instrument delivery scheduled for March
 - Designing sample extraction & conditioning system
- Modeling efforts progressing
 - C1 and C2 fluorine chemistry being added to REI's CFS program
- Bench-scale experiment
 - Conceptual design completed
- Other concurrent thermal research
 - Catalytic PFAS mitigation with Ca and AI (500-1000 °C)
 - Thermal degradation products from fabric application processes

History of REI's CFS Software

Reaction Engineering International

- The Configured Fireside Simulator (CFS)
 - Originally developed for the Department of Defense to evaluate operations of the chemical demilitarization incinerators processing the US chemical warfare agent stockpile
- Destruction kinetics developed for US warfare agent stockpile
 - GB, VX, HD, H, HT



CFS Software for EPA

- Adapted to provide for the ability to run "what if" scenarios of waste streams contaminated with CB agents
 - EPA's pilot-scale Rotary Kiln Incinerator Simulator (RKIS)
 - Three commercial incinerators based on design criteria for actual operating facilities
 - Medical/Pathological Waste Incinerator
 - Hazardous Waste Burning Rotary Kiln
 - Waste-to-Energy Stoker type combustor.
- CFS uses chemical kinetic data for destruction of chemical warfare agents
- Added biological agent destruction kinetic data derived from bench- and pilot-scale experiments performed at EPA's Research Triangle Park, NC facility
 - Also a generic agent Arrhenius destruction input has been added

Incinerators in the CFS

Commercial Kiln



RKIS Gas Temperature Distribution







Questions?

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