Modeling Cup-burner Minimum Extinguishing Concentration of Halogenated Agents

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1. Introduction

The cup-burner test is widely used to determine the Minimum Extinguishing Concentration (MEC) of gaseous fire suppression agents against flammable liquid hazards such as n-heptane [1-8]. In [3], Senecal explored a phenomenological model for inert agents that correlated integrated heat capacities with their ability to extinguish the flame in cup-burner tests. Prior efforts by Sheinson, et al [6] and Tucker, et al [9] are consistent with this approach. Liu, et al [10] recently demonstrated that a model, based on extinction of a 'perfectly stirred reactor' (PSR) but calibrated by a single point (to define the extinction condition for nitrogen), could be used to define the limiting MEC for a range of other inerting agents. In this study, we extend Liu, et al's prior work to explore the ability to predict the MEC of chemical agents, in particular selected fluorinated and brominated species. If such a tool can be shown to be viable, then such an approach might be useful for identifying conditions for flame extinction and then tabulated versions of these limits can be accessible by CFD codes used to simulate fire suppression without adding significant complexities to the combustion model.

2. Review of Prior PSR Modeling Methodologies

A perfectly stirred reactor (PSR) consists of an idealized reactor that is represented by two states: the inlet and internal/outlet states. The reactor is uniquely characterized by the residence time and the inlet mixture composition and temperature. "Extinguishment" of a combustion reaction occurs when there is insufficient residence time to allow for chemical reaction and heat release; this critical value is referred to as the extinction time. We argue that by benchmarking the extinction time of a known agent MEC (e.g. N_2), the MEC value of any other agent can be evaluated [10] assuming the extinction time remains the same for the same extinguishing effectiveness. Stoichiometric conditions are assumed for all simulations.

Since the known MEC of N_2 is 32.4% volume in air, the 0.45 ms extinction residence time is taken as the benchmark, or calibration, for all other agents [10]. When calculating the MEC for other agents, the volume fraction of the agent is varied until the 'calibrated' extinction residence time of 0.45 ms is reached and this agent volume fraction is assigned as the computed MEC. The detailed chemical kinetics mechanism for n-heptane used to calculate reaction rate of each species together with a detailed description of the thermochemical properties were obtained from Held, et al, [11] and Kee, et al. [12] while the PSR extinction model is based on the work of Glarborg, et al [13].

3. Extension of PSR Model to Reactive Agents

To extend this methodology to reactive agents, the detailed chemical kinetics of fluoro- [14] and bromine [15] species are employed in addition to the base n-heptane combustion mechanism [11]. When applying this approach, we determined that the halogenated species needed to be considered when identifying stoichiometric conditions. Consider Trifluoromethane (CHF_3) as an example. The atoms need to be balanced between reactants and products:

$$aC_7H_{16} + b(O_2 + 3.76N_2) + dCHF_3 \Rightarrow (7a+d)CO_2 + 3dHF + \frac{16a + d - 3d}{2} H_2O + 3.76\,b\,N_2$$

Where the halogen (F) is assumed to form HF as the stoichiometric product. The constants, *a*, *b*, *d*, are the coefficients of fuel, oxidizer, and halogenated species, respectively. The balance of O_2 yields $a = (b\text{-}0.5d)/11$, where the definition of MEC determines $b = 0.21(1\text{-}d)$. The MEC of this halogenated agent is $d/(4.76b+d)$ (Vol. % is $100\,d/(4.76b+d)$)

4. Results

The fluorinated agents in this study include CH_2F_2, CHF_3, CF_4, CH_2FCF_3, CHF_2CHF_2, C_2HF_5 and CF_6. The brominated species include Br_2, CHF_2Br, CF_3Br, and CF_2Br_2. Two methods of computation were employed: in the first, "inert PSR" case only the n-heptane reaction chemistry was included and the agent acted solely as an inert with no thermal decomposition or reaction; in the second, or "reactive PSR" case, agent-related chemistry was included. It is noteworthy that for the "reactive PSR" frequently the extinction temperatures are higher than for both the N_2 agent (calibration) and for the "inert PSR" runs. This result is consistent with the boost in exothermicity provided by the fluorinated agents [8].

Results are presented in Table 1 and plotted in Fig. 1 for fluorinated agents together with inert agents and in Fig. 2 for brominated agents. Note that the line in the figures is the curve fit of MEC of inerts. These results are also contrasted against experimental data [2] also shown in Figs. 1 and 2 and Table 1. A few things can be derived from the plot. First, the computed "inert PSR" values agreed very well with the experimental MEC data for most fluorinated agents except CHF_3 and CH_2F_2. This agreement indicates the inhibition of chemical reactions by these other fluorinated agents is insignificant. Except for CF_4, the 'reactive' PSR over predicts the inhibition effects for other agents. Second, CF_4 "reactive PSR" results also agree with "inert PSR" and experimental data. This indicates that CF_4 has no chemical inhibition effect, which is verified by the sensitivity analysis (not shown) that none of fluorinated species has significant impact on H consumption rate. Also this result is consistent with prior understanding of the effect by this molecule [8]. Third, CH_2F_2 "reactive PSR" agrees reasonably well with the experimental data indicating the capability of the "reactive PSR" model to calculate the MEC of reactive agents (or at least this one). Fourth, the experimental data for CHF_3 is between the "inert PSR" and "reactive PSR", and hence our model over predicts the chemical suppression. Lastly, the reactive PSR captures the relative MEC difference of CH_2FCF_3 (predicted MEC 5.35, data 10.5) vs. its isomer CHF_2CHF_2 (predicted MEC 7.1, data 11.2) as indicated in Fig. 1 and Table 1, although the absolute values are under predicted. This is consistent with the experimental data for heptane and also for cup-burner data with other fuels (ethane and propane) [8, 16-17].

For brominated agents, the "reactive PSR" results show very good agreement with experimental data for CF_3Br. For the other two brominated compounds, CHF_2Br and CF_2Br_2, there are no kinetics mechanisms available at this time, so only data and "inert PSR" prediction are presented. No experimental data of MEC for molecular bromine in n-heptane cup-burner are available, but such data are available with methane as fuel (not shown in Fig. 2). The reactive PSR predicted a MEC 10% higher than the experimental data for bromine in methane [16]. The effectiveness of these compounds is consistent with the known strong effect of the heavier MW halogens [17-18].

5. Conclusion

The reactive PSR model has been demonstrated to be a fast and effective tool in predicting the cup-burner MEC of chemically reactive agents assuming the kinetics mechanism is reasonably well established. Due to the simplicity of this tool, analyses can identify readily whether a compound provides a chemical inhibition, only an inerting action or a complex, competitive kinetic and thermal interplay resulting in an apparent inerting effect by perturbing key rate constants (not shown). The reactive PSR reasonably predicted MECs of several fluorinated and brominated agents such as CH_2F_2, CF_4, and CF_3Br. The impact of CF_3 group on the MEC is also predicted. We conclude that the tool can be useful for identifying key reaction steps that are worth further investigation, such as the reaction series: $CF_i+H=CF_{i-1}+HF$ with i=1 to 3.

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7. References

[1] B.T. Fisher, A.R. Awtry, R.S. Sheinson, J.W. Fleming, Proc. Combust. Inst. 31 (2006) 2731-2739
[2] T.A. Moore, C.A. Weitz, R.E. Tapscott, Halon Options Technical Working Conference, Albuquerque, NM, 1996, p. 551
[3] J.A. Senecal, Fire Safety Journal, 40 (2005) 579-591
[4] R. Hirst, K. Booth, Fire Technol. 5 (1977) 296-315
[5] B.Z. Dlugogorski, E.M. Kennedy, K.A. Morris, Interflam 96 (1996) 445-457
[6] R.S. Sheinson, J.E. Penner-Hahn, D. Indritz, Fire Safety Journal 15 (1998) 437-350
[7] V.R. Katta, F. Takahashi, G.T. Linteris, Combust. Flame 144 (2006) 645-661
[8] E.J.P. Zegers, B.A. Williams, E.M. Fisher, J.W. Fleming, R.S. Sheinson, Combust. Flame 121 (2000) 471-487
[9] D.M. Tucker, D.D. Drysdale, D.J. Rasbash**,** Combust. Flame, 41 (1981) 293-300
[10] S. Liu, M. Soteriou, M. Colket, J. Senecal, Fire Safety Journal 43 (2008) 589-597
[11] T.J. Held, A.J. Marchese, F.L. Dryer, Combust. Sci. Tech. 123 (1997) 107-146
[12] R.J. Kee, F.M. Rupley, J.A. Miller, M.E. Coltrin, J.F. Grcar, E. Meeks, H.K. Moffat, A.E. Lutz, G. Dixon-Lewis, M.D. Smooke, J. Warnatz, G.H. Evans, R.S. Larson, R.E. Mitchell, L.R. Petzold, W.C. Reynolds, M.

Caracotsios, W.E. Stewart, P. Glarborg, C. Wang, and O. Adigun, The Chemkin Thermodynamic Database, CHEMKIN Collection, Release 3.0, Reaction Design, Inc., San Diego, CA (1997)
[13] P. Glarborg, R.J. Kee, J.F. Grcar, and J.A. Miller, "PSR: A Fortran Program for Modeling Well-Stirred Reactors", Sandia Report, SAND86-8209, 1988.
[14] D.R. Burgess Jr., available at <http://www.cstl.nist.gov/div836/ckmech/>
[15] V. Babushok, T. Noto, D.F.R. Burgess, A. Hamins, W. Tsang, Combust. Flame 107 (1996) 351-367
[16] F. Takahashi, G.T. Linters, V.R. Katta, Proc. Combust. Inst. 31 (2007) 2721-2729
[17] G. T. Linteris, F. Takashi, V. R. Katta, Combust. Flame 149 (2007) 91-103
[18] R.G. Gann, Editor, Advanced Technology for Fire Suppression in Aircraft, NIST Special Publication 1069, June, 2007.

Table 1. Comparison of MECs, integrated heat capacities and computed temperatures at extinction

Agent	Agent name	Integrated heat capacity (kJ/mole, 298~1840K)	Experiment MEC (%)	MEC of Reactive PSR (Vol. %)	MEC of Inert PSR (Vol. %)	Temperature at extinction (Reactive PSR) (K)
CH2F2	Difluoromethane	124.91	8.8	10.3	18.1	1866
CHF3(FE-13TM)	Trifluoromethane	135.60	12.6	7.9	17	1721
CF4	Tetrafluoromethane(R-14)	181	13.8	15.1	15.6	1492
C2H2F4(CHF2-CHF2)	1,1,2,2-Tetrafluoroethane(HFC-134)	225	11.2	7.1	11.2	1764
C2H2F4(CH2F-CF3)	1,1,1,2-Tetrafluoroethane(HFC-134a)	227	10.5	5.35	10.8	1816
C2HF5 (CHF2-CF3)	Pentafluoroethane (R125)	237	9.4	5.2	10.3	1752
C2F6(CF3-CF3)	Hexafluoroethane(R-116)	249	7.8	4.8	10.0	1659
BR2	Bromine	58.18		2.35	30.0	1934
CF3BR(Halon 1301)	Bromotrifluoromethane	151.43	2.9	3.3	15	1900
CHF2Br	Bromodifluoromethane	139.83	4.4		15.5	
CF2Br2	Dibromodifluoromethane	155	2.2		14.7	
N2	Nitrogen	50.58	32.4		32.4	1494

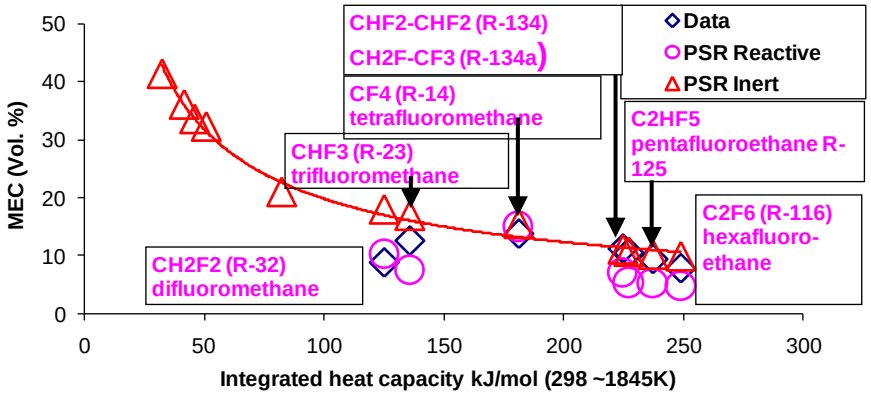

Figure 1 MECs of fluorinated agents

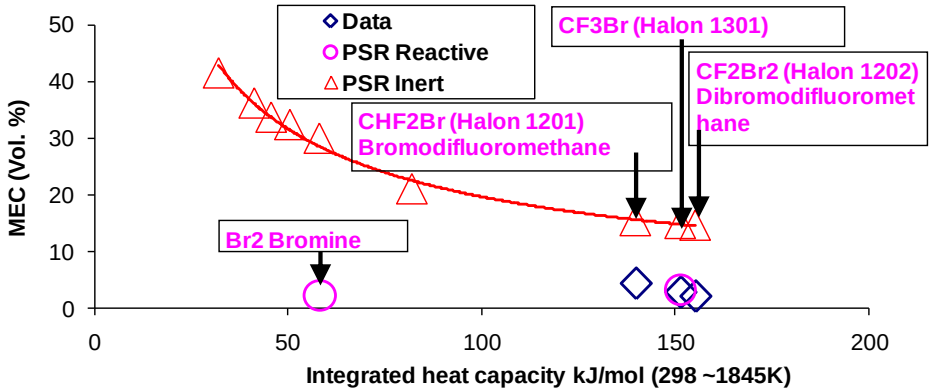

Figure 2. MECs of brominated agents