

Determination of Cup-Burner Extinguishing Concentration Using the Perfectly Stirred Reactor Model

Shiling Liu^a, Marios C. Soteriou^a, Meredith B. Colket^a, Joseph A. Senecal^b and Rob Lade^c

- a. United Technologies Research Center, East Hartford, CT 06108 USA
- b. United Technologies Fire and Security, Ashland, MA 01721 USA
- c. United Technologies Fire and Security, Colnbrook, Berkshire SL3 0HB UK

Emails: Shiling Liu, lius@utrc.utc.com
Marios C. Soteriou, soterimc@utrc.utc.com
Meredith B. Colket, colketmb@utrc.utc.com
Joseph A. Senecal, joseph.senecal@kidde-fenwal.com
Rob Lade, rob.lade@fs.utc.com

Abstract

A Perfectly Stirred Reactor model (PSR) is introduced to determine the Minimum Extinguishing Concentration (MEC) of gaseous fire suppression agents. Both physical and chemical mechanisms of fire suppression are considered in PSR modeling. Results are contrasted to experimental data and to a semi-analytical approach based on assumption that heat absorption by the agent is the primary extinguishing mechanism; good agreement is achieved. Results verified that agent heat capacity has the first order effect in the determination of the MEC, whereas the direct chemical effect of the oxygen concentration reduction appears less significant. The PSR model is also used in assessments of the impact on the MEC of inert agents at various conditions including the cooling due to the rapid gas expansion during discharge, high altitude and various relative humidity levels.

Keywords: Minimum extinguishing concentration, Inert gas agent, Cup-burner modeling, Perfectly stirred reactor

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 [1-13]. Effective modeling of the cup-burner is important in the development of an in-depth understanding of the dominant mechanisms by which different agents suppress the combustion process and in exploiting this understanding towards the design of more effective fire-fighting agents. Researchers have determined the MEC of gaseous agents using various approaches and configurations. Phenomenological models [3, 6-8] assumed the adiabatic flame temperature of the cup-burner flames at the extinction condition to be almost constant for all agents. This approach generated a relationship of inert gas MEC in terms of integrated heat capacity and fuel properties in which the change of reactant (oxygen) concentration due to inert gas addition is neglected. The cup-burner test was also interpreted using one-step, activation-energy asymptotic theories and the results were used to provide a rough indication of the thermal and chemical influence of reacting agents on the flame structure [9]. Other modeling approaches employed nonpremixed and premixed flames experimentally and numerically to predict the agent MEC. In co-flow jet diffusion flames [10-12], the extinguishing concentration is indicated by the blowoff

condition at the burner base. In counterflow diffusion flames [9, 12-13], the effectiveness of the extinguishing agent is characterized by quantifying the decrease of the ratio of the flame temperature to the extinguishing temperature as a function of the global strain rate. In premixed flames [14-16], the inhibition effect of agents is described by the reduction of the laminar flame speed. Simulations using either premixed or nonpremixed flames captured the changes of flame behavior and predicted the agent MEC at relatively higher computational cost. In this study, we introduce the Perfectly Stirred Reactor (PSR) model as an effective means of establishing the cup-burner MEC and we employ this model to probe further into the extinguishing mechanisms of gaseous substances.

Description of PSR model

The perfectly stirred reactor consists of a reactor that is represented by two states: the inlet and internal/outlet states. A schematic of such a reactor is shown in Fig. 1. A steady flow of a well mixed mixture of fuel and oxidizer is introduced to the reactor. Internal mixing is assumed to be infinitely fast so that the contents of the reactor are spatially uniform. As a result, the conversion of reactants to products is only controlled by the competition between the chemical reaction rate and the reactor residence time (effectively a flow through time) i.e. mixing processes play no role. Thus, the reactor is uniquely characterized by the residence time and the inlet mixture composition and temperature. The internal state of the reactor is computed by numerically solving the integral differential form of the energy and species conservation equations. In this work, a steady state implementation of a PSR is considered [17]. Under this condition the aforementioned equations reduce to algebraic equations:

$$\dot{m}(Y_k - Y_k^*) - \dot{\omega}_k W_k V = 0 \quad (1)$$

$$\dot{m} \sum_{k=1}^K (Y_k h_k - Y_k^* h_k^*) + Q = 0 \quad (2)$$

In these equations, Y_k is the mass fraction of the k th species (total K species), W_k , $\dot{\omega}_k$, h_k are the molecular weight, the molar rate of production by chemical reaction per unit volume, and the specific enthalpy of the k th species, respectively, V is the reactor volume, \dot{m} is the mass flow rate and Q the reactor heat loss. The superscript (*) indicates the inlet conditions. In this work the reactor is assumed to be adiabatic, $Q = 0$.

The reactor residence time τ is related to the reactor volume and the mass flow rate by

$$\tau = \rho V / \dot{m} \quad (3)$$

The mass density is calculated from the ideal gas equation of state,

$$\rho = PW / RT \quad (4)$$

where P is the pressure, T the temperature, R the universal gas constant and W the mixture's mean molecular weight.

A detailed chemical kinetics mechanism for n-heptane is used to calculate reaction rate of each species together with a detailed description of the thermochemical properties [18-20]. Calculations with detailed chemical kinetics allow for the evaluation of effects of different inlet reactant composition, temperature, and pressure on the reaction rate (or chemical reaction time) and other characteristics of the reactor, such as extinction time, which is discussed next.

“Extinguishment” of a combustion reaction occurs when competition between chemical reaction time and residence time becomes unfavorable. When the residence time is shorter than a critical value, chemical reactions cannot occur; this critical value is referred to as the extinction time. Assuming the cup-burner reaction region can be represented by a PSR, the fire extinction process can then be simulated by the PSR extinction time. By benchmarking the extinction time of a known agent MEC (e.g. N_2), the MEC value of any other agent can be evaluated assuming the extinction time remains the same for the same extinguishing effectiveness. This implicitly assumes that the differences in the mixing/transport characteristics of various agents are small. Specifically, for moderate changes in density of inlet/outlet mixtures for different agents, fluid dynamics of the reaction region will be similar under similar amount of heat release near extinction. The advantage of this approach is that results can be obtained in a few minutes as opposed to hours of computation time required for premixed or non-premixed flame calculations while the same chemistry effects can still be captured. Stoichiometric conditions are assumed for all simulations as they represent the peak temperature in the reactor.

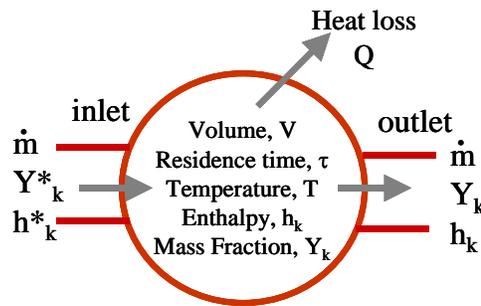


Figure 1 Schematic representation of a perfectly stirred reactor (PSR)

Results and Discussions

As mentioned earlier, to use the PSR residence time to predict the MEC of different agents, a known agent MEC needs to be provided. In this study, a MEC value of 32.4% for nitrogen in air is used as benchmarking agent (consensus mean of [21]). Specifically, a mixture of air (67.6%) and N_2 (32.4%) stoichiometrically mixes with fuel (n-heptane) at room temperature (300K) and ambient pressure (1 atm). PSR calculations were performed to obtain the reactor temperatures as a function of residence time. Chemical equilibrium can be reached for a longer residence time, whereas chemical reactions can be extinguished if residence time is below a critical value. As mentioned earlier, this critical residence time is defined as the extinction time. Figure 2 shows the reactor temperatures as a function of residence time for four air/ N_2 mixtures. It indicates that with the decrease of residence time, reactor temperature decreases gradually due to the increased mass of fluid that needs to be heated by the chemical energy release and then suddenly decreases to the original inlet mixture temperature due to extinguishment of chemical reactions. The residence time at which the sudden decrease occurs is the extinction time of the reactor, τ_{ex} . As is marked in Fig. 2, this time depends on the inlet mixture composition, e.g., $\tau_{ex} = 0.45$ ms for air/ N_2 mixtures of 67.6%/32.4%. That is, the greater the level of N_2 dilution the easier the extinguishment and, hence, the larger the extinction time – for a given reactor this implies extinction at lower flowrates, as shown in Fig. 3, the extinguishing time as a function of nitrogen concentration in air. Clearly only one of all the extinction times is relevant to the MEC – only

one would be relevant to the cup-burner experiment. At this juncture, it is not apparent how to calculate this time from first principles (using Eq.(3))– one would need to physically relate the cup-burner reaction region to the PSR volume to accomplish this. This limits the ability of the PSR model to be predictive in an absolute sense. If the MEC for a particular inert was known, however, the PSR model itself could be used to provide the extinction time. The earlier assumption that the fluid dynamic/transport features of the cup-burner experiment remain similar across different inerting mixtures would then imply that so should this extinction time. In this work we define the MEC related extinction time using the MEC for N₂ noted above, i.e. $\tau_{ex} = 0.45$ ms for the air/N₂=67.6%/32.4% mixture.

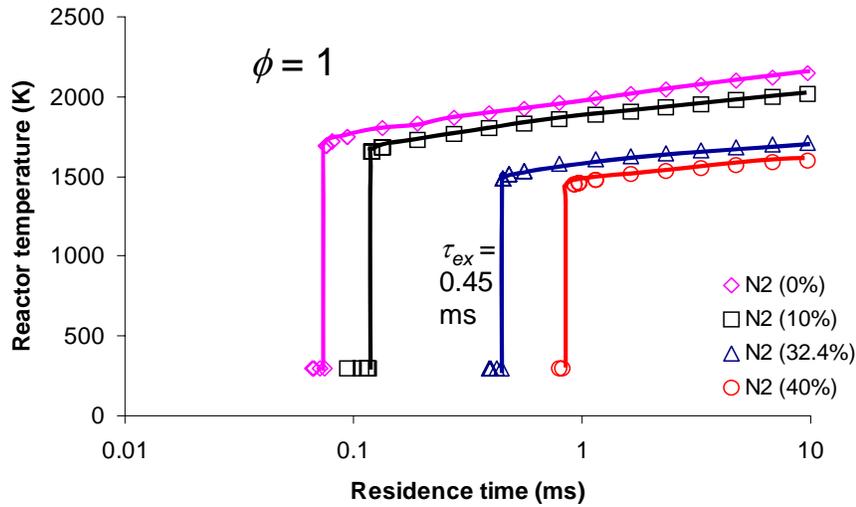


Figure 2 Reactor temperatures as a function of residence time for air and air/N₂ mixture.

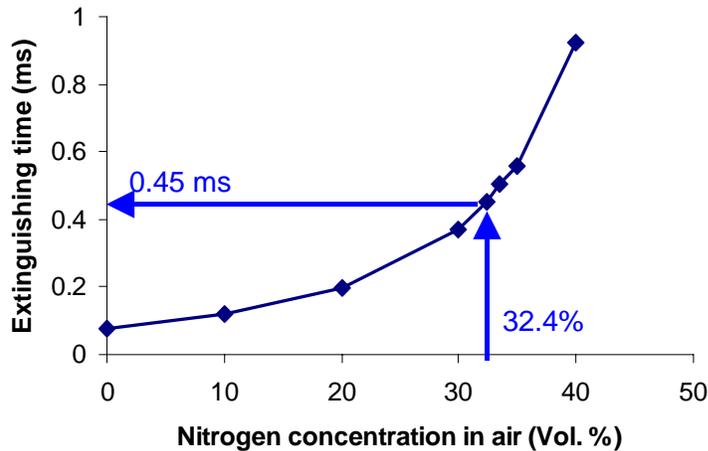


Figure 3 Extinguishing time as a function of nitrogen concentration in air.

Next, we obtain the MEC for other inerting agents such as argon, argonite, inergen, water vapor, CO₂, and etc, by varying the inlet mixture composition to the PSR until the $\tau_{ex} = 0.45$ ms was

attained. Table 1 shows MEC value for various agents calculated using the PSR model and Senecal's formula [3] along with a wide range of cup-burner data [2-7, 12]. It should be noted that chemical effects of decomposition of trifluoro-methane (CHF_3) are not accounted for in the current PSR calculation due to unavailability of trifluoro-methane kinetics mechanism. Also note that in Table 1 the integrated heat capacity for various agents are calculated using the Chemkin thermodynamic database [18-19] for temperatures from 298 to 1600K for comparison with cup-burner data, whereas the integrated heat capacity for temperatures from 298 to 1845K was used in Senecal formula [3] in which trifluoro-methane is treated as inert gas without chemical reactions.

Table 1

Inert agent	Integrated heat capacity	Senecal formula [3] (Vol %)	PSR calculated MEC(Vol %)	Cup-burner MEC values, Vol. %, fuel: n-heptane						
				Moore et al. [2]	Senecal data [3]	Hirst and Booth [4]	Dlugogorski et al. [5]	Saito et al. [6]	Sheinson et al. [7]	Katta et al. [12]
Argon (IG-01)	27.1	42.98	41.50	38.0	42.5		39.0	43.3	41.0	
Argonite (IG-55)	34.5	36.95	36.20	28.0	36.4					
Inergen (IG-541)	38.0	34.64	33.70		34.3		32.0	35.6		
Nitrogen (IG-100)	41.9	32.40	32.44	30.0	31.9	30.2	29.0	33.6	30.0	
CO_2	67.5	22.80	21.10	20.4	20.9	20.5		22.0	21.0	
CHF_3	110.9	15.17	17.00							11.7

Figure 4 shows the MECs of various agents as functions of their integrated heat capacity (298 ~ 1600K). Good agreement is obtained except for trifluoro-methane where chemical effects are neglected in both calculations. Note that both the PSR and the analytical formula suffer from this problem. However, the PSR model can potentially address this problem by incorporating in it a chemical mechanism for trifluoro-methane combustion in air. Indeed the PSR can be used to establish the MEC of any chemically reactive agent as long as the relevant kinetic mechanisms are available, whereas the integrated heat capacity approach is limited to inerts.

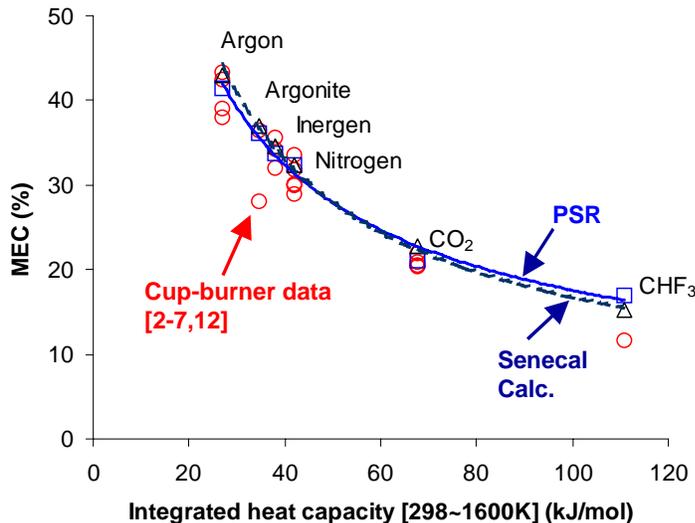


Figure 4 MEC values as functions of integrated heat capacity for various agents.

Results show that agent heat capacity has the first order effect in the determination of the MEC for inert agents, whereas the direct chemical effect of the oxygen concentration reduction in the mixture appears less significant. As mentioned earlier, PSR calculations account for the oxygen concentration reduction due to agent addition, whereas in the heat capacity approach the effect of oxygen dilution on the reaction rate is neglected. The effect of oxygen concentration can be seen in Fig. 5, in which a comparison between PSR calculations and Senecal formula is made by normalizing to the same MEC of argon. It is clearly indicated that with the increase of oxygen concentration (as agent concentration decreases), the PSR model predicts a larger value of MEC. The differences between the two approaches increase to as much as 16% for the agents investigated in this work. This difference can be more significant as agent integrated heat capacity becomes large. The increased oxygen concentration significantly increases reaction rate, making fire suppression hard and thus a higher agent concentration is needed.

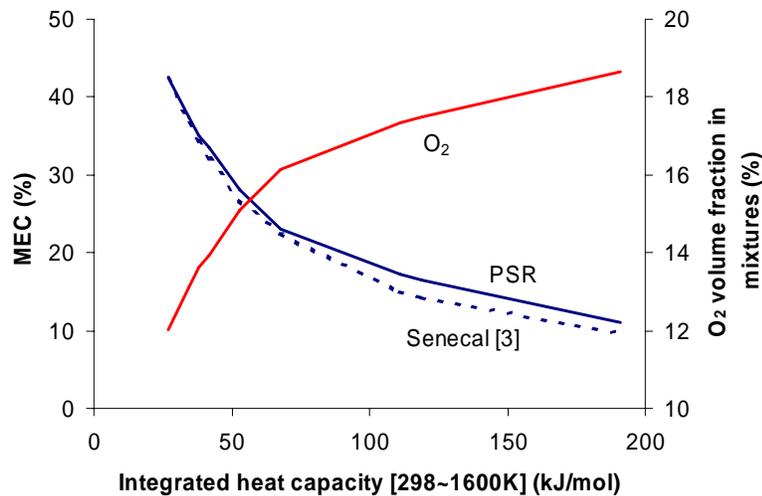


Figure 5 Comparison of MECs between PSR calculation and heat capacity approach.

Parameter studies

Once the PSR model is validated, it is a powerful tool to evaluate the effects of different parameters on fire suppression effectiveness. In addition, using the tool to predict MEC of agents eliminates the inconsistency of the cup-burner test among different laboratories, as indicated in [21]. As an example of using the tool, we now demonstrate the parametric studies on selected parameters, such as agent discharge temperature, altitude and relative humidity.

Figure 6 shows a sensitivity analysis for cooled nitrogen as the extinguishing agent with temperatures lower than the room temperature at which air and fuel are present. Results show that even for rather extreme temperature drops (e.g. from 300K to 100K) the nitrogen MEC only decreases slightly (7%). Thus, one would not expect the effect of the cooling of the Nitrogen due to the expansion during discharge to nullify estimates established using the MEC defined in a cup-burner test.

Figure 7 shows the effect of altitude on the MEC value of nitrogen in air. With the increase of altitude, ambient pressure decreases, leading to reduced chemical reactions. This results in the reduced MEC of the same agent to suppress a weaker fire. An 11% decrease in MEC of nitrogen is predicted for an altitude increase from sea level to 3000 meters.

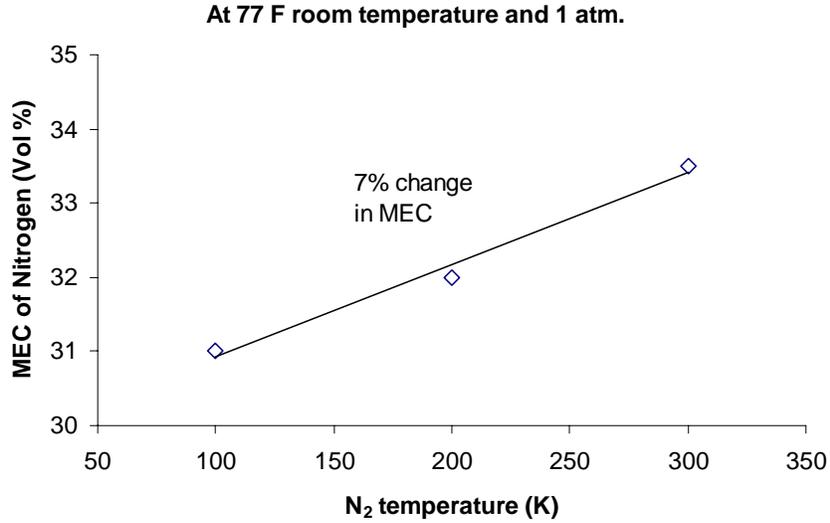


Figure 6 Sensitivity analysis of nitrogen MEC for cooled nitrogen using PSR tool.

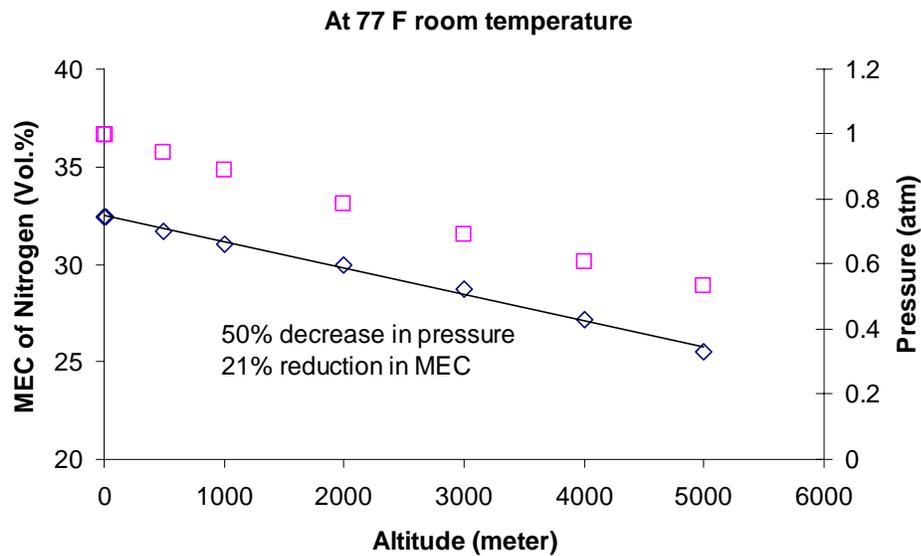


Figure 7 Sensitivity analysis of nitrogen MEC for altitude change using PSR tool.

In Fig. 8, the MEC of nitrogen in air at various relative humidity conditions is calculated. Assuming the consensus mean MEC value of nitrogen (32.4Vol. %) is obtained at 0% relative

humidity, an 8% reduction of MEC at 100% relative humidity is predicted. This indicates that water vapor in air does help to suppress a fire, since the heat capacity per mole of water vapor is higher than that of nitrogen, thus reducing the need of nitrogen.

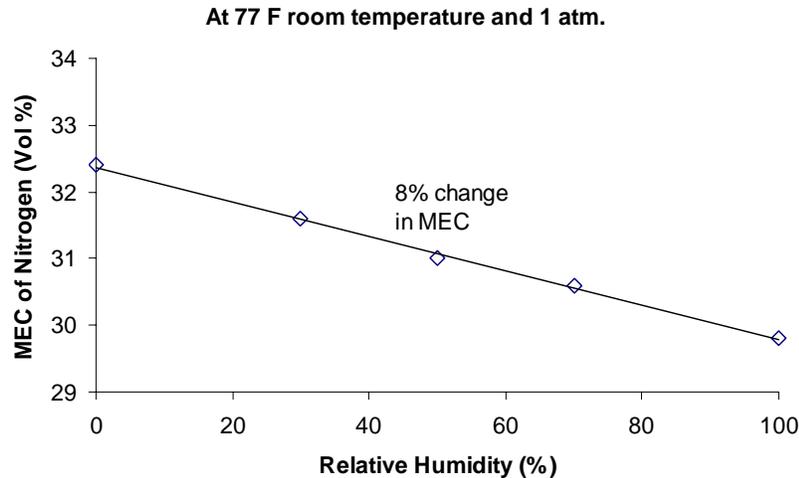


Figure 8 Sensitivity analysis of nitrogen MEC for relative humidity variation using PSR tool.

Conclusion

The PSR model has been demonstrated to be a simple and promising tool in predicting the cup-burner MEC of inert agents. Results agree with previous work and indicate a dominant effect of inert heat capacity on the MEC and only a secondary effect of oxygen depletion. It is also indicated that for the agents considered here lowering of inert inlet temperature has a secondary effect on MEC. With an increase of altitude, a reduced MEC value is predicted due to the fact that chemical reactions are reduced at low pressure conditions. Relative humidity does affect the MEC value; an 8% reduction in MEC of nitrogen is predicted from dry to saturated air conditions. Additional investigation on chemically active agents is suggested to further validate the model. This will require chemical kinetic mechanisms for the active agents.

References

1. B.T. Fisher, A.R. Awtry, R.S. Sheinson, J.W. Fleming, "Flow behavior impact on the suppression effectiveness of sub-10-um water drops in propane/air co-flow non-premixed flames", *Proceedings of the Combustion Institute* 31 (2006)
2. T.A. Moore, C.A. Weitz, R.E. Tapscott, "An update on NMERI cup-burner test results", *Halon Options Technical Working Conference*, 1996
3. J.A. Senecal, "Flame extinguishing in the cup-burner by inert gases", *Fire Safety Journal*, 40 (2005) 579-591
4. R. Hirst, K. Booth, "Measurement of flame-extinguishing concentrations", *Fire Technol* 5 (1977) 296-315
5. B.Z. Dlugogorski, E.M. Kennedy, K.A. Morris, "Thermal behaviors of cup burners", *Interflam 96* (1996) 445-457

6. N. Saito, Y. Ogawa, Y. Saso, C. Liao, R. Sakei, "Flame-extinguishing concentration and peak concentrations of N₂, Ar, CO₂ and their mixtures for hydrocarbon fuels", *Fire Safety Journal* 27 (1996) 185-200
7. R.S. Sheinson, J.E. Penner-Hahn, D. Indritz, "The physical and chemical actions of fire suppressants", *Fire Safety Journal* 15, (1998) 437-350
8. N. Vahdat, Y. Zou, M. Collins, "Fire-extinguishing effectiveness of new binary agents", *Fire Safety Journal* 38 (2003) 553-567
9. A. Hamins, D. Trees, K. Seshadri, H.K. Chelliah, "Extinction of nonpremixed flames with halogenated fire suppressants", *Combust. Flame* 99 (1994) 221-230
10. V.R. Katta, F. Takahashi, G.T. Linteris, "Suppression of cup-burner flames using carbon dioxide in microgravity", *Combust. Flame* 137 (2004) 506-522
11. G.T. Linteris, V.R. Katta, F. Takahashi, "Experimental and numerical evaluation on metallic compounds for suppressing cup-burner flames", *Combust. Flame* 138 (2004) 78-96
12. V.R. Katta, F. Takahashi, G.T. Linteris, "Fire-suppression characteristics of CF₃H in a cup-burner", *Combust. Flame* 144 (2006) 645-661
13. E.J.P. Zegers, B.A. Williams, E.M. Fisher, J.W. Fleming, R.S. Sheinson, "Suppression of nonpremixed flames by fluorinated ethanes and propanes", *Combust. Flame* 121 (2000) 471-487
14. C.K. Westbrook, *Combust. Sci. Tech.* 34 (1983) 201-225
15. V. Babushok, D.F.R. Burgess, G. Linteris, W. Tsang, A. Miziolek, "Modeling of hydrogen fluoride formation from flame suppressants during combustion", *Halon Options Technical Working Conference*, Albuquerque, NM, May 9-11, 1995
16. G.T. Linteris, M.D. Rumminger, V. Babushok, W. Tsang, "Flame inhibition by ferrocene and blends of inert and catalytic agents", *Proceedings of the Combustion Institute* 28 (2000) 2965-2972
17. P. Glarborg, R.J. Kee, J.F. Grcar, J.A. Miller, "PSR: A Fortran program for modeling well-stirred reactors", Sandia Report SAND86-8209 UC-4, 1988
18. T.J. Held, A.J. Marchese, F.L. Dryer, "A semi-empirical reaction mechanism for n-heptane oxidation and pyrolysis", *Combust. Sci. Tech.* 123 (1997) 107-146
19. 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).
20. S. Zeppieri, modified [18] to treat kinetics in the negative temperature coefficient regime, personal communication, UTRC
21. J.A. Senecal, "Standardizing the measurement of minimum extinguishing concentrations of gaseous agents", SUPDET 2007, March 5-8, Orlando, Florida (2007)