Technical Note 1871

Workshop on the Research Needs Concerning the Exothermic Reaction of Halogenated Hydrocarbons

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Workshop on the Research Needs Concerning the Exothermic Reaction of Halogenated Hydrocarbons

WORKSHOP PROCEEDINGS

February 9, 2015

National Institute of Standards and Technology
Gaithersburg, MD
October 27-28, 2014

Gregory T. Linteris, and Jeffrey A. Manion, Editors

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1. ABSTRACT

A workshop was held at NIST Gaithersburg on October 27 and 28, 2014 to discuss the exothermic reaction of halogenated hydrocarbons. The industries that gathered to discuss the topic were the fire suppression industry with both ground-based and aircraft applications, and the Heating, Ventilating, Air Conditioning, and Refrigeration industries. In the former, the compounds of interest are used as fire suppressants, and in the latter, as working fluids for vapor compression heating/cooling equipment. The purpose of the workshop was to identify the important parameters controlling the flammability of the compounds, and identify research needs for overcoming the obstacles to their safe and effective use.

2. ACKNOWLEDGEMENTS

The workshop was highly successful, which was a direct result of the eagerness of attendees to attend and actively participate. In particular, the clear, high-quality, and appropriate talks by the presenters provided excellent background both to understand the challenges, and formulate the discussion as to what next is required. Of course, the willingness of the companies represented to permit their researchers and engineers to share their results was the essential first step in this process, from which the open discourse and clear understanding then flowed naturally. Finally, the list of participants was developed using input from individuals in the HVAC/R, aircraft fire safety, and fire suppression industries, as well as Chairs of the ASHRAE committee members, and the authors gratefully acknowledge that input, which was very helpful.

3. LIST OF ABBREVIATIONS

2-BTP – $C_3H_2F_3Br$, CH_2CBrCF_3

AHRI – Air-Conditioning, Heating, and Refrigeration Institute

ASHRAE – American Society of Heating, Refrigeration, and Air-Conditioning Engineers

FAA – Federal Aviation Administration

FAA-ACT – Federal Aviation Administration Aerosol Can Test

FLACS – Flame Acceleration Simulator

GWP – global warming potential

Halon 1301 – CF_3Br

HFC – hydrofluorocarbon

HFO – hydrofluoroolefin

HVAC/R – Heating, Ventilating, Air-Conditioning and Refrigeration

NIST – National Institute of Standards and Technology

NFPA – National Fire Protection Association

Novec 1230 – $C_6F_{12}O$, FK-5-1-12, $CF_3CF_2C(=O)CF(CF_3)_2$

ODP – ozone depletion potential

R1234yf – 2,3,3,3-Tetrafluoropropene, $C_3H_2F_4$, CH_2CFCF_3

R1234ze(E) – 1,3,3,3-Tetrafluoropropene, $C_3H_2F_4$, $CFHCHCF_3$

R125 – CHF_2CF_3, HFC-125

R32 – CH_2F_2, HFC-32

4. INTRODUCTION

This document presents the results for a workshop held at NIST in Gaithersburg, MD, on Oct. 27 to Oct. 28, 2014, dealing with the high-temperature, exothermic reaction of halogenated hydrocarbons in hydrocarbon-air combustion environments.

The high-temperature reaction of halogenated hydrocarbons is important in several areas, many of which are of high recent interest, including: civilian aircraft Halon (CF_3Br) replacement, clean agent fire suppression, suppression of electrically energized fires, and refrigerant flammability. These disparate industries are related in that the chemical compounds are often similar or the same. Interest in industry and among researchers has piqued lately for reasons described below.

In civilian aviation, some fire suppressants, considered as replacements for CF_3Br in aircraft cargo bays, unexpectedly failed an FAA-mandated test (exacerbating the explosion rather than suppressing it). Moreover, recent analysis by NIST has estimated that at the conditions of the enhanced combustion, the expected burning velocities of the mixtures were in the range of only a few cm/s (significantly below the usual rule-of thumb flammability limit value of around 5 cm/s). For example, in the FAA test, mixtures with a very low overall reaction rate (characterized by the burning velocity) can react and have an overpressure up to 5 bar higher than with no agent. For the civilian airline industry, the problem is pressing because the European Union deadline for halon replacement is now approaching.

In the HVAC/R industry, the high-ODP (ozone-depletion potential) refrigerant working fluids (typically also high-GWP, global-warming potential) have been largely phased-out (as a result of the Montreal Protocol); however, the replacements typically still have relatively high-GWP. The refrigerant working fluids have been estimated to be a major contributor to the expected increase in global warming caused by human activities.[1] Low-GWP replacements have been (and are being) developed; however, they tend to be mildly flammable. While use of the low-GWP, mildly-flammable refrigerants would have great environmental benefits, their adoption has been hindered because there do not exist codes and standards for their safe use.

Finally, given that these suppressants can react exothermically and add heat to the fire/explosion, it would be helpful for the system designer if rules for safe and effective applications can be developed.

In order to overcome the challenges in these fields, a workshop was held at NIST in Gaithersburg, MD on Oct. 27-28, 2014 to bring together a small number of select researchers from industry, government, and academia who have relevant expertise. This manuscript describes the results of the workshop and its recommendations.

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[1] A recent *Science* article estimated that of the total increase (between 2012 and 2050) in the atmosphere's radiative forcing from <u>all</u> sources, about 20 ± 5% will be due to refrigerant working fluids.

5. WORKSHOP ORGANIZATION AND OBJECTIVES

The workshop participants (listed in the next section) consisted of researchers, engineers, and managers from industry, academia, government, and codes and standards organizations. There were approximately fifty registered attendees (and several more informal participants), representing world experts in their respective areas. Two major industries were represented at the workshop: aircraft manufactures (and their associated fire suppression suppliers), and residential and commercial Heating, Ventilating, and Air Conditioning/Refrigeration (HVAC/R) industries (and their suppliers). While these industries are somewhat disparate, they share an interest in the flammability of the relevant compounds—which are often the same compounds, or similar ones, but used for different purposes (i.e., as fire suppressants, or vapor-compression system working fluids). Nonetheless, the research of the two industries in this area has been separate, and it seemed of value to combine the communities at the workshop to facilitate the sharing their results, approaches, and background work.

There were several objectives of the workshop. The major objective was to formulate a list of research priorities for understanding the exothermic reaction of halogenated hydrocarbons, as it relates to air craft fire suppression, and refrigerant flammability, so as to allow the safe use of the relevant compounds in their desired application. The second was to bring together interested parties to open the flow of information between the individuals and industries so that mechanisms of collaboration could be explored. In an overall sense, the goal was to share information to aid each community in solving its problems related to the flammability of the halogenated hydrocarbons.

The meeting was facilitated by NIST personnel from the Fire Research Division and the Chemical Sciences Division. Fifteen presentations were given, and their titles are listed in the Agenda Section below. For some talks, the presenters were able to make the materials available to anyone, and those talks are presented in the Appendix[2]. After the presentations, two break-out groups were formed, representing the two industries. A list of research priorities was prepared by each group, and these are listed in Section 5 below. The conference ended with more informal discussion and laboratory tours of NIST facilities of relevance to the workshop.

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[2] The policy of NIST is to provide statements of uncertainty for all original measurements. In this document however, data from organizations outside NIST are shown, which may include measurements in non-metric units or measurements without uncertainty statements.

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7. AGENDA

NIST Workshop on the Exothermic Reaction of Halogenated Hydrocarbons
National Institute of Standards and Technology
Gaithersburg, MD

Monday, October 27, 2014; Bldg 101, Heritage Room

7:50 Check-in at NIST Main Gate (from 7:50 to 8:10), and proceed to Bldg. 101: Heritage Room

8:30 Welcome Remarks; *Joannie Chin, Deputy Director, Engineering Laboratory, NIST*
Workshop Agenda, Purpose of Meeting; *Greg Linteris, Flammability Reduction Group, NIST*

Introductions:

8:45 Short Introductory Remarks from Participants
Attendees

Overviews:

9:25 A Perspective on Lower GWP Refrigerant Performance Tradeoff's versus Open Flammability Knowledge Gaps for HVACR Products
Stephen Kujak / Bill Hansen, Ingersoll Rand

9:55 Fluorocarbons as Gaseous Fire Extinguishing Agents: Features, Benefits, and Challenges
Joe Senecal, UTC Kidde

10:15 Coffee Break

Problem Definition

10:30 Barriers to Accepting Flammable Refrigerants
Robert Richard, Honeywell

11:00 Clean Agents in Explosion Inerting
Adam Chattaway, UTC/Kidde

11:30 Flammability Testing in HVAC Configurations using Low GWP, Alternative Refrigerants
Paul Papas, UTRC

12:15 Lunch NIST Cafeteria

13:15 Testing of Aqueous Solutions of Inhibitors for Mitigation of Vapour Cloud Explosions
Dirk Roosendans, TOTAL Refining and Chemicals

Metrics

13:45 Burning Velocity and Flame Quenching Issues for Mildly Flammable Compounds
Kenji Takizawa, AIST

14:15 Coffee Break

14:30 Ignition of R-32 and R-410A Refrigerant Mixtures with Lubricating Oil

Peter Sunderland, Univ. of Maryland

15:00 Laminar Flame Speed Measurements and Calculations
Med Colket, Consultant/UTRC

15:30 Experimental and Numerical Approaches for Understanding Explosive Behavior of Mildly Flammable Combustible Gases
Scott Davis, Gexcon

16:00 Discussion

18:00 Dinner

AGENDA (continued)

Tuesday, Oct. 28, 2014 - Building 101; Heritage Room

(Please go to the NIST Main Gate at around 8am; you can use the same badge and ID as on Monday, and don't have to stop in the Visitors' Center)

Tools and Approaches for Solutions

8:30 Review of Standard and Code Changes to Reduce GWP Gas Emissions and to Support the Use of new 2L Semi-Flammable Refrigerants
Dick Lord, Carrier

9:00 The Use of Thermodynamic and Chemical Kinetic Models to Understand Explosive Behavior of Mildly Flammable Combustible Gases
Greg Linteris, NIST

9:30 Reduced-Scale Experiments for Screening, Model Validation and Understanding Full-Scale Results of Marginally-Flammable Mixtures
John Pagliaro, Univ. of Maryland

10:00 Coffee Break

10:15 Measurements & Data for Fundamental Kinetic Modeling of Halocarbon Flammability
Jeff Manion, NIST

10:40 Assorted Properties of Mildly Flammable Systems
Greg Linteris, NIST

Workshop Participants' Recommendations

11:00 Break-out Groups:

Research Needs (in Support of Codes and Standards) in Fire Suppression by Halogenated Compounds. (Facilitator: Greg Linteris, NIST)

Research Needs (in Support of Codes and Standards) for the Safe Use of Mildly Flammable Refrigerants. (Facilitator: Jeff Manion, NIST)

11:45 Presentation of Break-out Group Recommendations.

12:00 Lunch NIST Cafeteria

13:00 Discussion

14:00 Tour of Fire Research Division Labs
Gas-phase Flame Inhibition, *Greg Linteris, NIST*

Tour of Chemical Sciences Division
Gas-Phase Chemical Kinetics Laboratory, *Jeff Manion, NIST*

15:30 Adjourn

8. WORKSHOP ATTENDEE RECOMMENDATIONS

Two break-out sessions were conducted (in parallel) at the end of the second day. The first included participants whose primary interest was in aircraft fire suppression, and the second, refrigerant flammability. The sessions were moderated by Greg Linteris (NIST), and Jeff Manion (NIST), respectively. Using hand-written notes from, and audio recordings of the sessions, the following research recommendations have been assembled based on the suggestions of the participants.

8.1 Aircraft Fire Suppression Research Recommendations (related to the use of halogenated hydrocarbons)

1. Issue

Effects of temperature, pressure, and humidity need to be understood for various active flame-inhibiting moieties and hydrocarbon components of the agents.

Need

Improve the understanding of the parameters (e.g., humidity, temperature, pressure, active chemical moiety) affecting agent chemical inhibition and enhancement, to provide guidance on the necessary properties of new compounds or blends for effective suppression of the FAA-ACT.

Background

Aircraft operate over a range of temperature, pressure, and humidity. For a given agent, there is competition between the fuel effect and the inhibition effect. There appears to be an overall reaction rate (or alternatively, flame speed) for mixtures below which the FAA-ACT explosion will not occur. Temperature and humidity will likely have a large influence on this limiting overall reaction rate for a given agent, determining whether suppression or enhancement occurs. Both simulations and reduced-scale screening experiments can be performed to find the values of each variable necessary for inhibition rather than explosion. The focus of this work is to understand the effects of temperature, pressure, and humidity on the behavior of a range of representative compounds (e.g., hydrofluorocarbons HFCs, hydrofluoroolefins HFOs, inerts, etc.).

Comments

Even in the absence of a new, effective agent, surrogates can be used to assess the potential of a new agent to work in the FAA-ACT. For example, blends of C_2H_2, CF_3Br, and N_2 were found to be good surrogates for 2-BTP. By performing screening tests and numerical simulations using surrogates, the parameters of chemical activity, inert activity, and fuel activity can be varied. For example, by starting with 2-BTP, an agent with added chemical activity can be simulated by adding Br_2 (which has nearly a pure chemical effect in the flame), N_2 (inert), or C_3H_8 (fuel). One can then answer whether an agent, with various amounts of Cl, F, Br, I or other element, combined with various amounts of hydrocarbon, HFC, or HFO, can likely work.

2. Issue

2-BTP has varying effectiveness in different flame types and experimental configurations.

Need

Develop a better understanding of why 2-BTP behaves so differently in different flame types.

Background

Good understanding of the behavior of 2-BTP in premixed methane-air flames of various stoichiometries has been obtained through modeling and reduced-scale experiments. The reasons for the enhancement have been postulated, and it would be good to test them for other fuels and flame types. For example, the relative importance of combustion enhancement needs to be assessed for more typical flames (e.g., diffusion flames), different fuels, elevated temperatures and with water vapor.

Comments

This need addresses whether the properties of 2-BTP observed in the FAA-ACT are generally relevant, or specific to the FAA-ACT.

3. Issue

Existing agents have all failed the FAA Aerosol Can Test for their use in aircraft cargo bay fire protection. Is a new agent possible?

Need

Perform a comprehensive exploration of all the possible molecules which might meet the system requirements (vapor pressure, toxicity, over pressure, flame suppression, etc.) in the FAA-ACT.

Background

Developing a new fire suppressant molecule is challenging because of the multiple requirements for the agent, including fire suppression effectiveness (in a variety of tests), low toxicity, low ODP, low GWP, acceptable cost and weight, material compatibility, high vapor pressure, and low residue. There was active research in the 1990s to find a halon replacement, and that work resulted in the use of the current agents. However, with potential GWP restrictions, and failure of the agents in the FAA-ACT, new agents with additional features are now required. There was work to explore new agents and approaches, supported by the Next Generation Project; however, that program was discontinued due to a change in funding priorities.

Comments

It would be of value to review the recommendation of the NGP project to assess the potential of any chemicals or classes of chemicals suggested. Further, there has recently been work done at NIST Boulder to explore the entire range of possible chemicals for use as refrigerant working fluids. A similar approach to explore the range of possible options for chemically acting fire suppressants would be of value.

4. Issue

All agents tested, except CF_3Br, have failed the FAA-ACT, so a new agent (or approach) is necessary.

Need

Determine if blends of agents can work in the FAA-ACT.

Background

The halogen-based halon replacement agents work by lowering the reactivity of the reacting mixture through the interaction of the halogen-containing species with the normal fuel chemistry. The halogen-containing species reduce radical concentrations either through gas-phase catalytic cycles (Br, I, and to some extent Cl), or by trapping H atoms to form HF). Unfortunately, the halogen atoms are typically attached to hydrocarbon molecules, which have a fuel-like character, increasing the flame temperature (in fuel-lean mixtures) and increasing reaction rates. Hence, there is competition between these two effects, and which predominates depends upon the fire scenario. It is possible that mixtures of inert agents with the halon replacement might overcome the higher temperature caused by the agent, and hence be effective in the FAA-ACT.

Comments

The effectiveness of the blends can be explored either through reduced-scale tests or kinetic calculations. These would likely give good indication as to the potential of the blends in full-scale tests in the FAA-ACT. The FAA tested mixtures of CF_3Br and N_2 in the FAA-ACT, and found conditions (concentration of each component, CF_3Br or N_2) for which the explosion was suppressed. Using stirred-reactor simulations, this boundary was subsequently predicted via numerical simulations. This procedure can be repeated for the halon replacements with inert compounds: the locus of conditions bounding flammable vs. non-flammable can be found for the concentration of each component (agent and inert; e.g., 2-BTP and N_2) for the compounds of interest. The effect of the inert is likely to vary from agent to agent, since the mechanism of inhibition is different. These predictions can then be tested using the reduced-scale screening methods recently developed. If the results are promising, tests can then be conducted in the FAA-ACT.

The approach described above for adding inert compounds can also be repeated for chemically active compounds. For example, if the 2-BTP molecule had a little more chemical inhibition character, it might suppress the FAA-ACT at a concentration low enough such that the fuel effect (and ensuing pressure rise) of the 2-BTP was not relevant. The boundaries of the desired behavior can be explored by added a nearly purely-acting chemical additive (e.g., Br_2) to mixtures of 2-BTP and the FAA-ACT fuel, thereby simulating a 2-BTP molecule with higher chemical activity. Exploring the range of behavior of such mixtures will allow one to understand the ultimate potential of new compounds, which still have a hydrocarbon backbone, but have a higher chemical activity than does 2-BTP. The work would answer a question such as: How much chemical inhibition character is required for a given amount of hydrocarbon character? Such information would be very helpful for understanding the potential of new compounds which might be developed.

5. Issue

Flammability behavior of halogenated hydrocarbon fire suppressants in non-premixed flames.

Need

Understand the flammability behavior of halogenated hydrocarbon fire suppressants in non-premixed flames representative of fire threats (i.e., diffusion flames).

Background

Most practical fires to suppress are diffusion flames, but most of the work to understand the agents has been done in premixed systems. In the premixed systems, the combustion enhancement by the alternative agents depends strongly upon the proportions of fuel and air in the mixture. For explosion suppression, premixed flames represent a worst-case scenario. Nonetheless, the importance of the enhancement effect for many practical applications (e.g., nacelle fires) depends upon the particular configuration of the fire to be suppressed. Since many fires to be suppressed are diffusion flames (fuel and oxidizer initially separate), more work needs to be done to understand any potential combustion enhancement for those situations.

Comments

This work can be done using either calculations or experiments, or both. Useful flame types are cup-burner flames and counterflow diffusion flames, both of which are experimentally and computationally tractable. An approach would be to add agent to either the fuel or air stream, at varying concentrations, and assess its effect on flame extinction and the rate of total heat release.

6. Issue:

Fluid mechanics of agent dispersion.

Need:

Improve the understanding of the fluid mechanics of agent dispersion and distribution.

Background:

With Halon 1301, the agent was so effective that system design did not have to be optimized as well. Since use of the alternatives requires more agent, agent distribution efficiency has a larger effect on weight and performance. This is especially true for agents with lower vapor pressure (i.e., higher boiling points). Finally, poor distribution and mixing of the agent can lead to sub-inerting concentrations, in which exothermic reaction of the agent can occur.

Comments:

Many of the issues with overpressure at sub-inerting concentrations might be overcome with good system design (nozzle design, placement, discharge location, effects of obstructions, etc.). Temperatures in protected spaces can vary from -40°F to 110°F, and pressure is lower at altitude. For effective system design, better understanding of the effects of temperature, pressure, and geometry on agent dispersion would be useful, particularly for low vapor pressure agents. An understanding of how venting requirements change with concentration non-uniformities would be useful.

8.2 Refrigerant Flammability Research Recommendations

1. Issue

Roadmap for the safe implementation of marginally flammable refrigerants.

Need

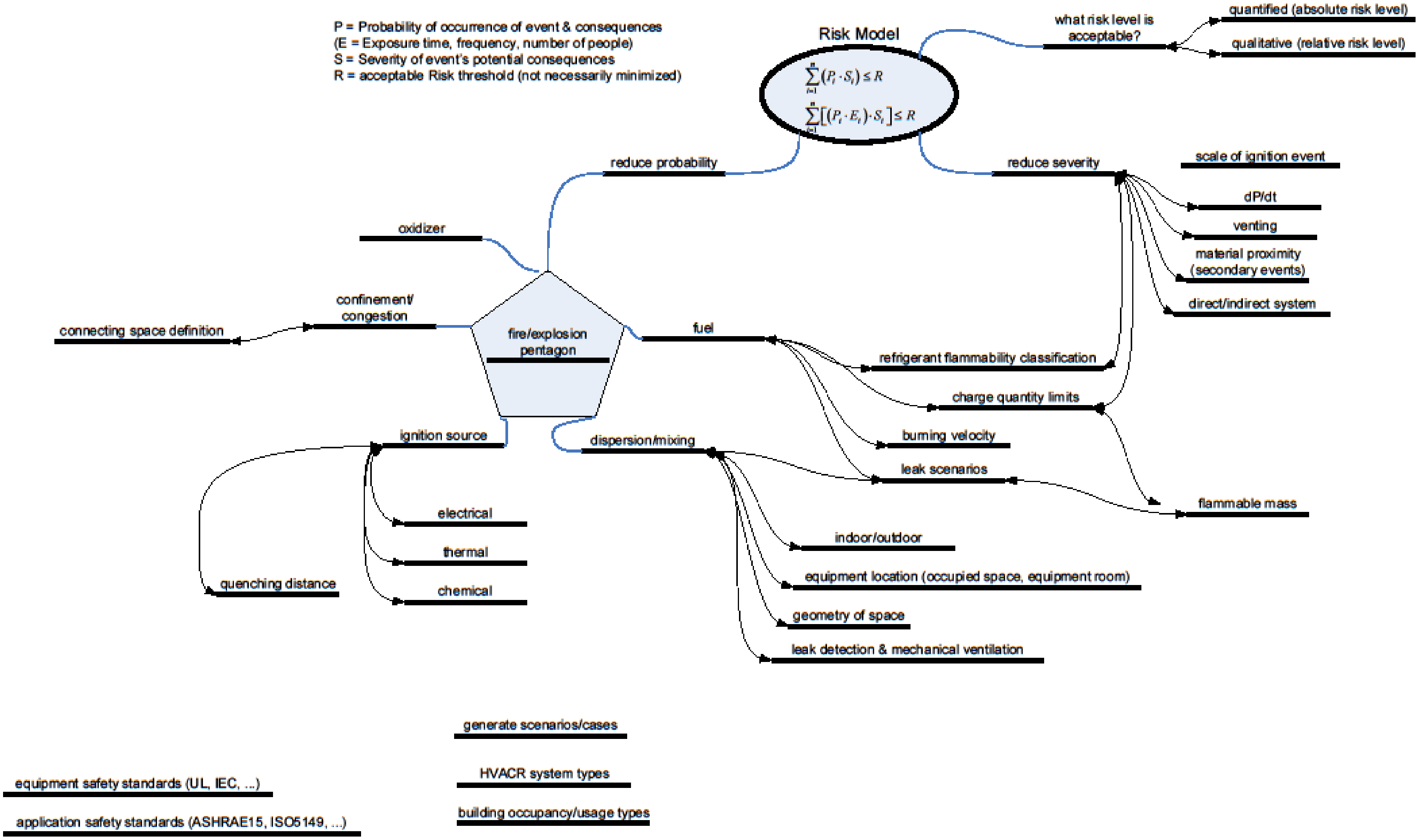
Develop a roadmap outlining the information and steps required for the safe implementation of marginally flammable refrigerants. This would include an understanding of all of the components of a risk assessment for the use of the compounds.

Background

The fire and explosion risk from marginally flammable refrigerants depends upon many factors, including: the refrigerant reactivity, temperature, and concentration; the volume of the equipment space, ventilation rates, and humidity; the ignition sources; and the presence of other flammable materials, among others. A risk model attempts to quantify the probability of an event and its severity, and make some determination of acceptable overall risk. This is a multifaceted problem, and accurate specification of the various elements is very helpful. It was suggested that a roadmap for the risk model would be a useful starting point to solve the engineering problems posed, to focus activity, and start the necessary communication required for the industry to move forward.

Comments

Phil Johnson provided a roadmap (attached below) to serve as a starting point for discussion, or perhaps formation of a working group.


P = Probability of occurrence of event & consequences
(E = Exposure time, frequency, number of people)
S = Severity of event's potential consequences
R = acceptable Risk threshold (not necessarily minimized)
Risk Model
$\sum_{i=1}^{n}(P_i \cdot S_i) \le R$
$\sum_{i=1}^{n}[(P_i \cdot E_i) \cdot S_i] \le R$
what risk level is acceptable?
quantified (absolute risk level)
qualitative (relative risk level)
reduce probability
reduce severity
scale of ignition event
dP/dt
venting
material proximity (secondary events)
direct/indirect system
oxidizer
confinement/ congestion
connecting space definition
fire/explosion pentagon
fuel
refrigerant flammability classification
charge quantity limits
burning velocity
leak scenarios
flammable mass
ignition source
electrical
thermal
chemical
quenching distance
dispersion/mixing
indoor/outdoor
equipment location (occupied space, equipment room)
geometry of space
leak detection & mechanical ventilation
generate scenarios/cases
HVACR system types
building occupancy/usage types
equipment safety standards (UL, IEC, ...)
application safety standards (ASHRAE15, ISO5149, ...)

2. Issue

Scenario definition .

Need

Develop a list of possible, plausible, and most common scenarios in which a refrigerant-air mixture might be ignited, so that the risk and consequences can be determined.

Background

There was concern among the participants that the possible scenarios for refrigerant leakage and ignition in residential settings was almost infinite, making it difficult to quantify the risks and develop methods to ameliorate them. Hence, they saw value in trying to develop a list of plausible scenarios, and then choose some as base-case examples, representing the entire range of those that might be encountered in practice. To do this, it would probably be necessary to use numerical modeling to understand the controlling parameters of the full-scale experiments, so that the examples are both representative, and conservative.

Comments

Typically, refrigerant charges are released as jets, and for marginally-flammable compounds, the jets can be ignited, but then produce weak flames that are very unstable. On the other hand, most of the risk is from the explosion potential of premixed refrigerant-air mixtures. Any degree of stratification will produce non-premixed conditions, and the flame propagation rates will be lower. Hence, while it certainly is necessary to understand the explosive behavior of premixed gases, this condition may be a special case, rather than a typical one. Nonetheless, the presence of turbulence greatly increases the propagation rate of the deflagration and the rate of pressure build up, but the generation of turbulence is very configuration dependent. Hence, the difficult but important task represented here is to come up with possible, representative, and conservative scenarios that represent the range of risks in different room configurations with different equipment types. By exploring both typical and worst-case scenarios, performing full-scale experiments, and then analyzing the results with numerical modeling, the important parameters can be determined. From these, it is believed that the large range of potential scenarios can be reduced to some model cases, from which the relevant codes and standards can be written.

3. Issue

Behavior of halogenated hydrocarbon refrigerants in non-premixed flames.

Need

Perform experiments and analyses to understand how the flame type (e.g., premixed vs. diffusion) influences the safe use of marginally flammable materials.

Background

As a refrigerant leak occurs, the potential fuel (the refrigerant) and oxidizer (air) are separate, and any flame would be a non-premixed (i.e., diffusion) flame. For jet release of the agent, and with time, however, the air and fuel mix such that the flame (if stable) might eventually be a premixed flame. Hence, it is important to understand both premixed and diffusion flame behavior of the compounds. Also, turbulence is important since it has a large effect on ignition, mixing of the fuel and oxidizer, and the subsequent propagation of the premixed flame.

Comments

There is experimental evidence for combustion of these mildly flammable refrigerants, particularly in premixed systems. Very limited data exist, however, on their behavior in non-premixed (i.e., diffusion flame) systems. Future rules, guidelines, and standards need to be based on representative scenarios. Hence, there is a need for more data on the behavior of these compounds in non-premixed systems, with and without turbulence.

4. Issue

Refrigerant leakage rates.

Need

Develop a database of refrigerant leakage rates in the field.

Background

In order to design equipment spaces in which the flammability risk has been mitigated, it is necessary to know the leakage rate of the working fluid. This is important for understanding the subsequent dispersion of the agent, as well as the ventilation requirements to keep the space below the lean flammability limit.

Comments

The industry does not collect data on leakage rates, so while this information would be useful, actual field data might be hard to come by.

5. Issue

Ignition properties of marginally flammable refrigerants with air

Need

Determine the ignition properties of marginally flammable refrigerants with air (i.e., the ability of different ignition sources to initiate a flame of marginally flammable refrigerants with air).

Background

One approach to limit the risk from marginally flammable refrigerants is to control the ignition sources. Flames of these compounds generally have much higher minimum ignition energy than those of hydrocarbons. Hence, certain types of ignition sources which are important for hydrocarbons may not be of concern for the refrigerants. Thus, there is a need to characterize the ability of different types of ignition sources to create flames.

Comments

The need appears to be an understanding of the ability of practical ignition sources, such as hot surfaces, contactors, flames, etc., to ignite these compounds, and a determination of which of the myriad ignition sources are of concern.

6. Issue

Venting requirements to reduce overpressure from refrigerant-air deflagration.

Need

Develop accurate, validated correlations and modeling capabilities for specifying venting requirements to prevent overpressure from flames of marginally-flammable refrigerants.

Background

If a deflagration occurs in an enclosure, venting can be used to limit the overpressure to safe values. For combustion of typical hydrocarbons with air, which have high laminar burning velocities, there exist correlations (for example, those used in NFPA-68) and modelling tools (e.g. FLACS) which are accurate for design purposes. However, these correlations are known to be poor for low burning velocity fuels, or near the end of the propagation, when quenching (i.e., heat loss) becomes important. Accurate, validated correlations and modeling capabilities are needed for specifying venting requirements to prevent overpressure of marginally-flammable compounds.

Comments

Tests need to be conducted to see if the existing correlations are accurate for low-burning velocity compounds. If not, new correlations need to be developed. The whole question of quenching, and how is may be more important for low burning velocity compounds needs to be addressed.

7. Issue

Accuracy of overpressure correlations/calculations for marginally-flammable compounds in air.

Need

Improve the accuracy of overpressure correlations/calculations for marginally-flammable compounds in air.

Background

There are design tools and numerical codes for predicting venting requirements for hydrocarbon explosions. These are empirically-based, and require experimental validation (or benchmarking). Their applicability to low flame speed fuels is unknown.

Comments

This is an extension of the previous issue: the need for guidelines for venting requirements. What system manufacturers ultimately need, however, is a way to predict the flammability behavior of a given chemical in a given configuration. One might envision this, for example, as using the NIST Fire Dynamics Simulator (FDS) program to predict the growth of a fire ball, and the resulting overpressure, for a particular room in a building, with given dilution, suppression, and venting systems. For a given leak rate and type, it would include the provision for describing the mixing of the agent with the air, dilution and settling, leak detection, system response, dilution/ventilation, ignition, flame growth, turbulence generation, turbulent flame propagation, overpressure, and vent activation. This is undoubtedly, a longer-term project, but one which is possible within the near future, and which would be of great value. While it may seem daunting, it is not unlike the needs in industry, where useful codes have been developed based on a combination of empirical rules, full-scale calibration, and first principles. That approach is not unlike what is done in FDS (for example, with radiation from soot, among many other examples). The goal here is to improve our understanding of the various phenomena participating in the overall process.

8. *Issue*

Existence of critical burning velocity for explosion risk

Need

Determine if there exists a critical burning velocity, below which heat losses will prevent turbulent enhancement of the laminar flame speed and large increase in the flame propagation rate.

Background

Turbulence, caused by inherent flame instabilities and by clutter in the flow field, greatly increases the propagation rate of a deflagration. Under certain conditions, however, the overall reaction rate (which can be measured by the laminar burning velocity), is too low to support any flame propagation. This is caused by the combination of the low reaction rate and radiant or conductive heat loss from the flame. It would be of value to determine if there is a fundamental burning velocity below which, there is no risk of explosion. (Analysis of the FAA Aerosol Can Test result with added fire suppressants implies that this is true.)

Comments

Understanding the existence of such a limit, and how it varies with fuel, stoichiometry, lubricant, temperature, and pressure, as well as configuration, will provide insight useful for designing new refrigerant mixtures which do not have an explosion risk.

9. Issue

Flammability of Mixtures of R32, R290, CO_2, and 1234yf, 1234ze(E)

Need

Develop the capability to predict the flammability of mixtures of R32, R290, CO2, 1234yf, and 1234ze(E).

Background

The Alternative Refrigerant Evaluation Program (AREP) considers about forty fluids, which are mostly mixtures of R32, R290, CO_2, 1234yf, and 1234ze(E). The NIST database RefProp and RefLeak describe the thermodynamic and physical properties of the mixtures, and their behavior in leaks. It would be of great value to have a similar program, perhaps RefFlam, which would describe the flammability properties of arbitrary mixtures of these compounds. Parameters to include would be the adiabatic flame temperature, maximum pressure rise, laminar burning velocity, and minimum ignition energy for arbitrary mixtures of these compounds, as functions of temperature, pressure, and humidity, for their most reactive mixture.

Comments

The database would be experimentally based, with numerical simulations used to develop correlations for mixtures and their P, T, and humidity dependence, so that a tractable number of tests could be performed. In order to perform the numerical simulations, detailed kinetic models would be used, or developed as necessary. These would describe the elementary rates of chemical reactions occurring in the chemical system of interest.

10. Issue

Standard Test(s) for Refrigerant Flammability

Need

Determine the most appropriate standard test(s) for ranking the flammability of alternative refrigerants, to be used in specifying the safety requirements for their use.

Background

Current flammability rankings of refrigerants are based on the heat of combustion, lower flammability limit, and laminar burning velocity. While these are clearly important parameters, there may be others that would be useful to properly evaluate the explosion risk. These include the minimum ignition energy, the maximum explosion pressure, and the turbulent explosion index.

Comments

It was noted that while additional indices would be useful, they (for example, the explosion pressure) are often dependent upon the ignition source. The work here would be to determine which of the available (or possible) tests would be most useful for specifying safe use of the materials.

11. Issue

HF formation from refrigerant flame reactions

Need

Develop and understanding of how to deal with HF formation (which will occur if there is a flame of air and a fluorine-containing marginally flammable refrigerant).

Background

Flame reactions of hydrofluorocarbon agents produce large quantities of HF (for example, there is about 30% HF in the product gases of a stoichiometric R32-air flame). HF is toxic and corrosive, and there need to be approaches developed for dealing with its adverse properties.

Comments

HF gives a citrus smell, which is easily detected. Nonetheless, it is a new, potentially dangerous byproduct for which safe responses and codes need to be developed.

12. Issue:

Better detection of refrigerant gases or their decomposition byproducts

Need:

Improve sensors for detection of refrigerants or their decomposition byproducts. This would increase safety by allowing automated venting upon their detection, reducing the hazard from their presence.

Background

An explosion of a flammable mixture has a lower likelihood but a larger consequence. Explosion can be prevented with rapid venting and dilution of the refrigerant-air mixture, bringing the space into the non-flammable regime. Present detectors are somewhat expensive and not very sensitive. Increased sensitivity and lower cost would facilitate prevention of the explosive mixtures. Similarly, HF is a toxic byproduct of combustion of the refrigerants; more sensitive and rapid detectors would facilitate venting of the space, increasing safety.

Comments

Detectors exist for both, but improvements are needed to achieve the rapid, economical, removal of the compounds from the occupied space.

9. SUMMARY/CONCLUSIONS / FOLLOW-UP

The research needs in the above section are the core outcome of the workshop. There was a general consensus that the problems in both industries (related to the exothermic reaction of halogenated hydrocarbons) are complex and more research would help to delineate the problem and aid in designing around any adverse properties of the materials (when that is possible). The results of two the breakout groups are summarized separately below.

9.1 Aircraft Fire Suppression Summary

The research recommendations developed in the Aircraft Fire Suppression breakout group (described in the previous section) are listed in Table 1 below. As the table (and the previous section) describes, most of the recommended work involves improving the understanding of the behavior of potential new compounds and blends of existing compounds. For the FAA Aerosol Can Test, the needed information involves understanding how the molecular structure (or combination of compounds) affects the tradeoff between inhibition and enhancement of the explosion, and how this is affected by other parameters. For other aircraft fire suppression applications, this same information would be useful, as well as an understanding of how the different flame environments affect the overpressure/inhibition tradeoff. In particular, it would be useful to understand if the overpressure caused by some agents in the FAA-ACT can possibly occur in other configurations (e.g., diffusion flames).

Table 1 - List of research needs developed in the Aircraft Fire Suppression breakout group.

1. Improve the understanding of the parameters (e.g., humidity, temperature, pressure, active chemical moiety) affecting agent chemical inhibition and enhancement, to provide guidance on the necessary properties of new compounds, or blends, for effective suppression of the FAA-ACT.
2. Develop a better understanding of why 2-BTP behaves so differently in different flame types.
3. Perform a comprehensive exploration of all the possible molecules which might meet the system requirements (vapor pressure, toxicity, over pressure, flame suppression, etc.) in the FAA-ACT.
4. Determine if blends of agents can work in the FAA-ACT.
5. Understand the flammability behavior of halogenated hydrocarbon fire suppressants in non-premixed flames representative of fire threats (i.e., diffusion flames).
6. Improve the understanding of the fluid mechanics of agent dispersion and distribution.

9.2 Marginally Flammable Refrigerants Summary

The research recommendations developed in the Marginally Flammable Refrigerants breakout group (described in the previous section) are listed in Table 2. It was generally agreed that the problem is likely to be solvable, but that it is complex because it involves many different components and possible scenarios. Hence, the group embraced the value of a roadmap to delineate the different parts of the problem that need to be addressed. The research needs emphasized at the workshop highlight some of the elements of the roadmap, including scenario definition, flammability properties of the compounds, pressure rise, as well as HF formation and detector improvements. The flammability properties (e.g., response to different ignition sources, flammability limits, minimum ignition energy, burning velocity, turbulent flame acceleration, overpressure, and critical burning velocity for inertion) are related to the reactivity of the mixture. The participants affirmed the value of flame measurements and simulations that improve the understanding of the various parameters influencing the chemical reaction rate, which ultimately affects flammability. These parameters include the effects of different chemical moieties, humidity, temperature, and flow-field on the overall reaction rate; in particular, the importance of understanding the reaction rate (i.e., burning velocity) of blends of compounds was noted. The need for improved theoretical and computational tools for predicting pressure rise was endorsed, particularly for low burning velocity systems, for which current capabilities are known to be limited. Finally, the need for understanding HF formation and its fate was described, as was better and less expensive sensors for HF (and for the refrigerants themselves).

It is important to keep in mind that the scope of the workshop was limited to research questions related to the exothermic reaction of halogenated hydrocarbons when used for aircraft fire suppression, or as refrigerant working fluids. Thus, research recommendations related to the larger questions (e.g., such as developing or using other, non-reacting working fluids, or fire suppressants) were not specifically addressed, but would supply additional areas needing investigation.

Participants in both industries felt that follow-up meetings on a regular basis would be helpful, and that we should move forward to identify the resources and expertise required to solve the problems discussed.

Table 2 - List of research needs developed in the Marginally Flammable Refrigerants breakout group.

1. Develop a roadmap outlining the information and steps required for safe implementation of marginally flammable refrigerants.
2. Develop a list of possible, plausible, and most common scenarios in which a refrigerant-air mixture might be ignited, so that the risk and consequences can be determined.
3. Perform experiments and analyses to understand how the flame type (e.g., premixed vs. diffusion) influences the safe use of marginally flammable materials.
4. Develop a database of refrigerant leakage rates in the field.
5. Determine the ignition properties of marginally flammable refrigerants with air.
6. Develop accurate, validated correlations and modeling capabilities for specifying venting requirements to prevent overpressure from flames of marginally-flammable refrigerants.
7. Improve the accuracy of overpressure correlations/calculations for marginally-flammable compounds in air.
8. Determine the existence of critical burning velocity for explosion risk.
9. Develop the capability to predict the flammability of mixtures of R32, R290, CO_2, 1234yf, and 1234ze(E).

10. Determine the best standard test(s) for refrigerant flammability.
11. Understand the formation of HF from refrigerant / flame reactions.
12. Improve sensors for detection of refrigerant gases or their decomposition byproducts.

10. APPENDIX: PRESENTATIONS CLEARED FOR GENERAL RELEASE

The presentations (as pdfs) are presented below. When the talk was cleared or general release, the entire talk is given, otherwise, only the title page is given. Many of the talks had embedded videos, and they are not reproduced here.

Fluorocarbons as Gaseous Fire Extinguishing Agents

by

Joe Senecal

Senior Fellow, UTCFS

Kidde-Fenwal, Inc.

NIST Workshop on the Exothermic Reaction
of Halogenated Hydrocarbons
October 27, 2014

United Technologies
Climate | Controls | Security

Barriers to using flammable refrigerants

NIST workshop

October 27, 2014

Robert Richard

Problem

- Nearly Everybody Knows
  - Flammable hydrocarbons explode.
  - Flammable liquids make for big fires that spreads rapidly.
  - The flame triangle.
- Professional Knowledge
  - Fire marshals – fire fighters
  - Chemical process safety
  - Academia
- Unknowns
  - Fear of not knowing what you don’t know
  - The border between small controlled fires and large catastrophic events

What's new about halogenated material and what difference does it make?

Questions/Outline

- What is the risk of using flammable refrigerants?
- What have experimenters observed?
- What is needed to mitigate the risk?
- What should be the safety factors employed?
- What is the importance of confinement-congestion-unrestricted on vapor cloud ignitions? Leaked/spilled refrigerant.
- What is the role of flame stability in ignition, flame propagation and extinguishment?
- What can be and to what extent can it be relaxed for ASHRAE/ISO flammable class 2L (Su< 10cm/s)?

Observations

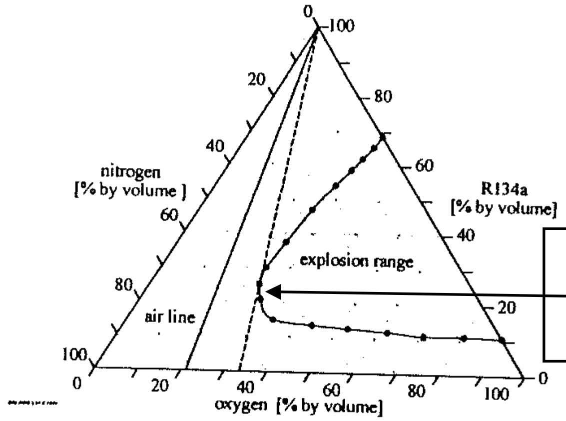
- We need environmentally friendly refrigerant.
- Blends have been employed to meet the required properties and still be nonflammable.
- Experience and experimental investigation show that not all flammables materials/mixtures have the same hazard.
  - The general trend is well described using burning velocity.
- This parameter (burning velocity) is used for classification but is not used in designing mitigation for HVAC&R systems.

Why is burning velocity important and how can/should it be used?

Borderline-Fire suppressant?

R134a can become flammable at higher pressures or temperatures if sufficient oxygen and an ignition source is present

R-134a Flammability as f $(P)_T$	
Temp (^{o}C)	Pressure (Bars)
280	1
25	8



Lower and upper Flame Limit

Figure 1. Explosion range of R134a/nitrogen/oxygen-mixtures at room temperature and atmospheric pressure

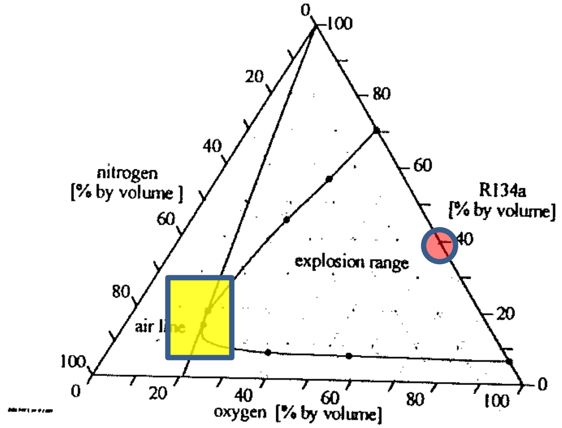


Figure 2. Explosion range of R134a/nitrogen/oxygen-mixtures at 280 °C and atmospheric pressure

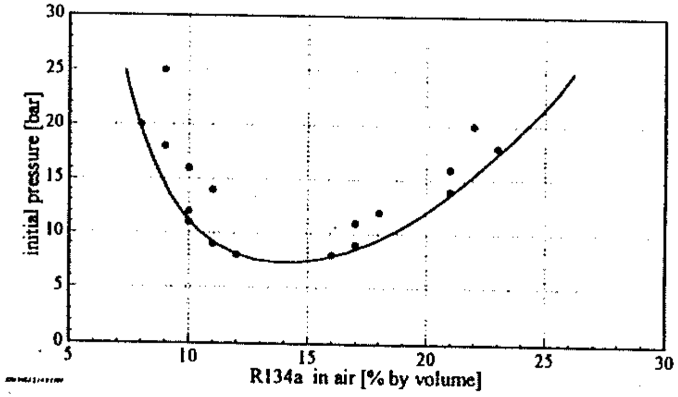


Figure 3. Pressure dependence of the explosion limits of R134a in mixture with air at a temperature of 25 °C measured in a 2.2 litres autoclave.

The risk of using flammable refrigerants.

- Light
- Sound
- Consumption of oxygen
- Stabilized flame and secondary fires
- Blast damage – projectiles, structural failure

What is needed to mitigate the blast risk or risk of a stable flame.

- Avoid flammable concentrations (but a leak is at a concentration of 100%, flammable zone ATEX)
- Eliminate Ignition source (but open flames are common)
- Reduce quantity that leaks
  - Reduce total amount, limit charge.
  - Mix to uniformly distribute. Allowing larger quantities of flammable to be release before exceeding the LFL.
- Use the fact that the minimum ignition energy is high
- Use the fact that flames are buoyant and are unstable.

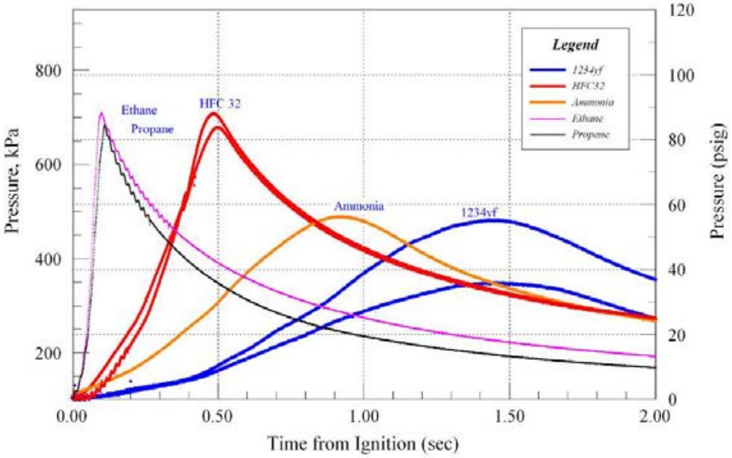
What should be the safety factor employed.

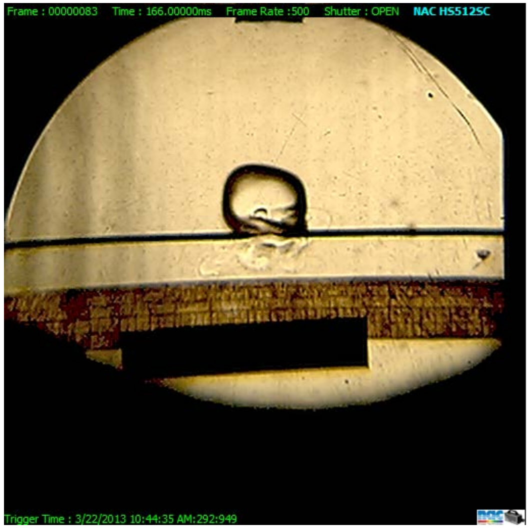
- The greater the hazard of event the greater the effort to avoid it should be. The greater the probability of a severe event the larger the safety factor.
  - Currently 20% or 25% of LFL if total charge is released and uniformly mixed. To account for pooling or unknowns.
  - Accidental release an concentration that peak ; 75% of LFL for short periods of time.
  - Design for pooling and concentrations up to the LFL.

What is the relationship between hazardous event and safety factor?

The importance of Confinement

- The energy of combustion is nearly the same for all material of interest.
- The difference is in the rate of release and efficiency of the release of this energy, i.e., burning velocity and completeness of propagation.





What is the role of flame stability in ignition, flame propagation and extinguishment.

- How can this be used in safety standards, equipment standard, and codes etc.?
- Does this allow for relaxation of safety rules?

Proper consideration of flame stability

Research Needs

- Blast models assume rapid kinetics; we need models that properly model and are validated for slower reacting materials and pneumonia.
- Relationship between reaction rate (burning velocity) and severity - probability leading to safety factors
- Flame stability has important influence on ignition, propagation, extinction, efficiency of energy release.

UTC Aerospace Systems

Clean Agents in Explosion Inerting

Behaviour of fluorinated compounds at sub-inert concentrations in explosion suppression

NIST Workshop on the Exothermic Reaction of Halogenated Hydrocarbons
Gaithersburg, MD Oct 27-28, 2014

Work Carried out by Josephine Gatsonides; Presented by Adam Chattaway

United Technologies
Research Center

Flammability Testing in HVAC Configurations using Low GWP, Alternative Refrigerants

Presented by Paul Papas

NIST Workshop on the Exothermic Reaction of Halogenated Hydrocarbons
October 27-28, 2014

TOTAL
COMMITTED TO BETTER ENERGY

Inhibition of Vapor Cloud Explosions

Workshop on Exothermic Reaction of Halogenated Hydrocarbons
27-28 October 2014
NIST, Gaithersburg

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Quenching distance measurement of highly to mildly flammable compounds

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ABSTRACT

Quenching distance measurements were carried out for 11 highly to only mildly flammable gases (which include alkanes, fluorinated alkanes and alkenes, and ammonia) to elucidate the ignition and quenching characteristics of low-GWP (global warming potential) alternative materials. For buoyant flames of mildly flammable compounds, conventional 25 mm diameter parallel plates in the vertical position provided significantly smaller quenching distance (d_q) than 100 mm diameter plates in the horizontal position. A good correlation was obtained between the quenching distance ($d_{q,h}$ in mm) measured by the latter test apparatus and the maximum burning velocity ($S_{u0,max}$ in cm s^{-1}) for these compounds: $d_{q,h} = 58.12\left(\rho_u S_{u0,\,max}\right)^{-0.926}$, where ρ_u is the unburned gas density. The mildly flammable compounds that have $S_{u0,max}$ below 10 cm s^{-1} have a d_q more than three times larger than that of propane. Initial development of the schlieren flame radius was observed for mildly flammable CH_2F_2/air mixture using thin electrodes and a variety of spark energies. It was confirmed that the parallel plate quenching distance was essentially equal to the minimum flame diameter in a free space. By applying the measured $d_{q,h}$ and $S_{u0,max}$ in the simplified heat loss theory, the minimum ignition energy (E_{min} in mJ) was expressed by $E_{min}=0.0712 d_{q,h}^{2.97}$. The results showed that the mildly flammable compounds have E_{min} that is more than an order of magnitude greater than that of propane.

1. Introduction

In order to reduce environmental impacts, phase-out of high global warming potential (GWP) materials is currently a very important issue for the industries related to refrigerants, insulating foaming agents, and blowing agents. Regulations for the phase-out of R-134a (CH_2FCF_3) as a refrigerant of automotive air conditioning system has already come into effect in the EU and are anticipated to spread to other regions and applications. Because high-GWP compounds are stable in the atmosphere, the less stable compounds are now taken into consideration as lower-GWP alternatives. The properties that make the new compounds have higher reactivity in the atmosphere also make them more flammable. Considering this risk tradeoff, low-GWP compounds with mild flammability appear to be alternatives that provide the optimum balance of acceptable safety properties and environmental performance. Thus, risk assessments of mildly flammable compounds will need to be made before they are used in practical applications. (Hereafter, a compound whose maximum burning velocity ($S_{u0,\ max}$) is not higher than 10 cm s^{-1} is called “mildly flammable compound”).

Considering the probability of fire hazard due to flammable gases, minimum ignition energy and quenching distance are some of the most important indices. Experimentally, minimum ignition energy (E_{min}) is the lowest spark discharge energy that can ignite a flammable gas mixture at the most ignitable concentration. Parallel plate quenching distance (d_q) is the minimum distance between two surfaces above which self-sustained propagation of a flame is achieved. A standard test method for determining E_{min} and d_q is specified in ASTM E582 [1]. These parameters, if obtained appropriately, are useful for designing the electrical equipment that may be deployed in areas with a potentially flammable gas atmosphere. Table 1 summarizes the published data of E_{min} and d_q for compounds relevant to this study [2–17]. For propane, the reported E_{min} range from 0.247 mJ [3] to 0.48 mJ [9]. For mildly flammable compounds, the reported E_{min} vary widely from < 10 mJ to > 10 J. This makes assessing the fire risk based on E_{min} very difficult. The difficulty in determining the reliable E_{min} is that it is very dependent on the electrode size, the gap between the electrodes, and the ignition spark density and duration [3,5,18–20].

Compared to measuring E_{min}, measuring d_q seems to be much easier, and provides reliable data on mildly flammable compounds. As listed in Table 1, the reported d_q of propane range from 1.7 to 1.9 mm; i.e., they are in good agreement. For mildly

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Ignition of R-32 and R-410A Refrigerant Mixtures with Lubricating Oil

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ABSTRACT

This study examines the flammability risk of refrigerant and oil mixtures. The flammability risk associated with refrigerants is an important property to consider prior to their use in residential and commercial HVAC systems. This research was conducted to compare the ignition characteristics of R-32 with R-410A, and the effects of lubricating oil. Unpiloted hot-plate ignition tests and computational fluid dynamics (CFD) were used to determine the autoignition temperature and ignition probability data. The results indicate that the ignition temperature of R-32 impinging a hot plate is 764 °C. This is 116 °C higher than the reported autoignition temperature of R-32, but it is very close to the reported open top autoignition temperature. R-410A was found to ignite at a slightly higher temperature than R-32: 790 °C. Tests with polyolester (POE) oil indicate that the R-32 ignition temperature is reduced to nearly that of the ignition of oil alone. CFD predictions for a jet of R-32 impacting a hot plate at a temperature close to autoignition temperature of R-32 show that ignition should happen only away from the jet point of impact and in rich regions.

1. INTRODUCTION

Two important risks associated with refrigerants are their environmental impact and their flammability. Difluoromethane, or R-32 (CH_2F_2) is a non-ozone depleting refrigerant with a global warming potential (GWP) of 675. R-32 is slightly flammable, with flammability limits of 13.3 – 29.3% by volume in air, has a laminar flame speed of 6.7 cm/s (Jabbour, 2004), and has a heat of combustion of 9.4 kJ/g. It is classified as a 2L refrigerant (Hihara, 2012). R-410A is a mixture of R-32 (CH_2F_2) and R-125 (pentafluoroethane, formula $CH_2F_2CF_3$); it is a non-ozone depleting working fluid with a GWP of 2088, which is more than three time that of R-32. R-32 has entered service in Japan and is being considered for service in the US. However, its adoption is being hindered by its slight flammability in air.

This work is motivated by the possibility of an accidental release of working fluid within a refrigeration system. Under certain conditions, this release may produce mixtures with localized flammable concentrations of refrigerant vapors in the surrounding air. This scenario may lead to a subsequent fire if this flammable gas comes into contact with an ignition source. Because the vapors are heavier than air, higher concentrations may develop near the floor or near the bottom of a refrigerant unit, and this region may remain flammable for an extended period of time.

The autoignition temperature of a fuel, or AIT, is the lowest temperature at which quiescent isothermal fuel/air mixture will spontaneously ignite unaided by an external ignition source. Ignition occurs when the rate of heat produced exceeds the rate at which heat is dissipated.

This study was conducted to better understand ignition risks due to an accidental refrigerant leak within a system using R-32 or R-410A. Past research has examined the flammability of pure refrigerants without considering the effects of the presence of lubricating oil. The concentration of oil released in a refrigerant leak can vary depending on the location of the leak and the operating state of the equipment. In this study, mixtures of R-32 and R-410A with lubricating oil are impinged onto a hot horizontal metal surface to examine ignition behavior. The ignition temperatures of R-32 and R-410A were determined using hot surface ignition test methods. Additionally, computational fluid dynamics (CFD) simulations were performed to provide physical insight associated with hot-plate ignition, to validate ignition chemistry, and to aid a systematic risk assessment in various configurations.

2. METHODS

The most widely used method to measure the autoignition temperature of liquid fuels is ASTM E659, the Standard Test Method for Autoignition Temperature of Liquid Chemicals. This standard provides the conditions for sustained combustion of a quiescent, isothermal, homogeneous mixture (simulating a perfectly stirred reactor). In such conditions, the reported AIT for R-32 is 648 °C (Goetzler, 1998). However, the original source of this measurement is a personal communication with no documentation. In terms of risk analysis, these conditions are unlikely to occur in practice and therefore can be considered as conservative.

The present tests aim to characterize the ignition temperature (IT) of refrigerants through contact with an isothermal, hot metallic surface. Figure 1 illustrates the design and components of the isothermal hot plate. The apparatus consisted of two 20 × 20 cm square copper plates. The top cover plate, used as the testing surface, was 6.35 mm thick; the bottom plate was 3.175 mm thick. Copper was chosen due to its good thermal conductivity and its resistance to oxidation. The test plate was heated using four cylindrical electrical heaters with a diameter of 9.5 mm. Each heating element operated at a maximum power density of 11 W/cm^2. The maximum operating temperature of the heating elements indicated by the manufacturer is 1150 °C. The four heating elements were powered by two variable autotransformers, delivering 120 V and up to 33 A. Exposed sections of the apparatus were insulated with kaowool insulating panels (on the sides) and a thick mineral wool insulator minimized the heat losses from the sides and from the bottom plate. Additionally, insulation was placed on top of the hot plate surface, providing a 3 cm tall draft shield along the outer perimeter of the hot plate. With these precautions, the test plate was kept isothermal, and elevated temperatures (up to 900 °C) was reached. The temperature of the hot plate could then be controlled by varying the power delivered by the autotransformers.

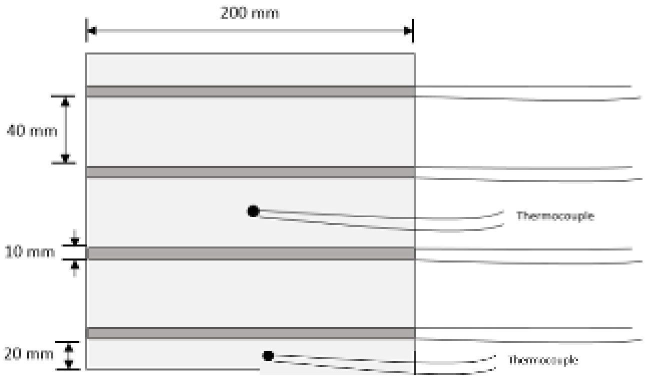


Figure 1: Hot plate schematic.

The temperature of the hot plate was monitored using two type-K thermocouples. Two small bead thermocouples were used, one peened into the center of the plate and the other fixed to the plate edge. The center thermocouple was directly under the discharge nozzle and the second thermocouple was used to verify temperature uniformity away from the center. The temperatures were recorded with a data acquisition software at a frequency of 10 Hz. The experimental uncertainty of the measured temperatures was ± 10 ºC. At elevated temperatures (above 500 °C), measurable temperature fluctuations were observed. This is attributed to the increased turbulent motion caused by natural convection.

R-32 and R-410A were delivered in the gas phase at ambient temperature through an aluminum circular nozzle, with an inner diameter of 1.58 cm. The delivery assembly consisted of refrigerant hose tubing, a solenoid valve, a single-shot timer relay, a needle valve, soft silicone rubber tubing, and an aluminum discharge tube. Prior to each discharge, the programmable timer relay was set to the desired discharge time, between 1 – 2 s, and the needle valve was set to the desired flow rate. For each discharge, the release of refrigerant was initiated with a switch, opening the solenoid valve. The vertical discharge nozzle was 5 cm above the hot plate. Figure 2 illustrates the experimental apparatus.

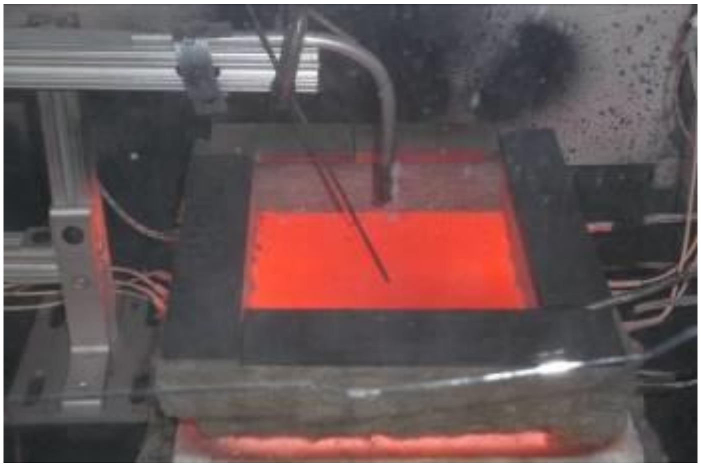


Figure 2: Color image of hot plate.

Four different cases were tested: pure R-32, pure R-410A, POE oil, and R-32 mixed with oil. Flow rate tests showed a negligible influence of the gas flow rate on the observed ignition temperatures. To reduce excessive refrigerant release, all subsequent tests were conducted with a constant refrigerant mass flow rate discharge of 1.1 g/s. Pure refrigerant was delivered in the gas phase. While the refrigerant supply tank was kept at ambient temperature, some frost was noted at the end of each refrigerant injection. For each test, the hot plate was first covered and heated to 800-900 ºC and maintained for approximately 30 minutes to ensure an even temperature distribution. Once steady state was reached, the plate temperature was slowly reduced by either removing the cover insulation or by reducing the power supplied to the heating elements. The occurrence of refrigerant mixtures ignition was determined by visual inspection and the tests were recorded by video for later analyses. For tests involving a mixture of refrigerant/oil, POE oil was introduced manually using a tube and syringe assembly discharging roughly 0.02 mL of oil. This corresponds to an oil-to-gas ratio of approximately 1% by volume. For each refrigerant mixture tested, the test was repeated at least three times. In total, approximately 150 tests were conducted.

3. RESULTS

Figures 3a, 3b, and 3c show photographs of R-410A, R-32, and POE oil ignition, respectively. They were captured at temperatures slightly above their critical ignition temperatures. Several differences in the burning characteristics of the fuels were observed: the refrigerants ignited more rapidly than oil, but combustion did not sustain burning after injection, whereas oil ignited with a slight delay but combustion lasted longer. A similar relationship was observed when oil and refrigerant are introduced simultaneously. For hot plate temperatures above the pure refrigerant critical IT, the refrigerant vapor and POE oil mixture ignited simultaneously. For hot plate temperatures below the refrigerant IT, oil ignited before the refrigerant.

(a) (b) (c)

Figure 3: (a) R-410A ignition at 820 ºC, (b) R-32 ignition at 789 ºC, and (c) POE oil ignition at 654 ºC.

For both R-410A and R-32, orange flames were observed close to the plate surface and blue flames were observed at the periphery of the burning region. A similar phenomenon was documented in the hot plate ignition report done by Bannister *et al.* (2005), where they described the blue flame regions of fuel/air mixtures as being lean, or oxygen rich, but lacked the heat to sustain ignition. This phenomenon is evident in R-32 and R-410A combustion tests. When unburned fuel vapors escape the heated plate area, the heat flux provided by the combustion reaction alone was insufficient to propagate to unburned vapors and thus the flame self-extinguished.

Table 1 reports the critical ignition temperatures recorded and compares them with published values. The lowest R-32 IT observed was 764 ºC, which is 116 ºC higher than the published, albeit in a different setup. Richard (2012) reported that the autoignition temperature was above 700 ºC in an open top measurement. This measurement is closer to ours.

The lowest R-410A IT was observed at 790 ºC. POE lubricating oil ignited at 645 ºC. Differences between the observed IT values and those in the literature arise from the differences in the test conditions or methods used, as explained by Affens (1974). Smyth and Bryner (1997) further discussed this, and highlighted the IT dependence on the fuel structure, surface material properties, surface temperature, fuel/air stoichiometry, surface size, surface orientation, and ambient pressure conditions.

Table 1: Present work observed ignition temperature along with values reported in literature.

Fuel	Ignition Temperature, in °C	
	Present work	Literature
R-32	764 (+/- 10)	648[a] to >700[b]
R-410A	790 (+/- 10)	-
POE Oil	645	371-427[c]
R-32 mixed with POE Oil	649	-

[a] Ref (Airgas, 2010)
[b] Ref (Richard, 2012)
[c] Ref (Kuchta, 1968)

Many literature sources report R-410A as a non-flammable refrigerant, but it was found here to burn. The measured critical ignition temperature of pure R-410A is 26 °C higher than pure R-32. Furthermore, the addition of 1% POE oil lowers significantly the IT of R-32 refrigerant/oil mixtures, to a value very close to the ignition temperature of the oil. In this study, we found that the ignition temperature of the POE oil is 645 °C. Tests show that when mixed with this oil, the ignition temperature of R-32 is reduced to 649 °C; a decrease of 125 °C .The oil provides sufficient energy to ignite the refrigerant vapors. Further results are depicted graphically in Figure 4.

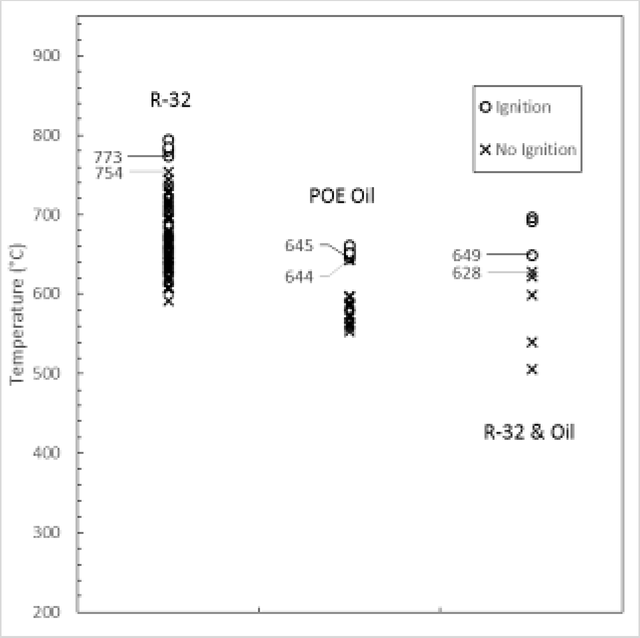


Figure 4: Hot-plate ignition temperature for pure R-32, POE oil alone, and a 1% mixture of R-32-oil.

4. CFD MODEL

To provide an improved understanding of the experiments, a LES code, the Fire Dynamics Simulator (FDS, McGrattan, 2013) was employed. This section presents results predicted for the configuration of pure R-32 injected at a mass flow rate of 1.1 g/s and impinging the hot plate set at a temperature corresponding to the measured ignition temperature of R-32, 764 °C. Note that while the code features combustion capabilities, these were not used here.

The Fire Dynamics Simulator (FDS) is an open-source Fortran program written by the National Institute of Standard and Technology (NIST) and it is widely used in the fire modeling. FDS is a Large Eddy Simulation solver that solves the Navier-Stokes equations with the Low Mach Number assumption. See McGrattan *et al.* (McGrattan, 2013a) for a complete description of the code.

The numerical configuration for this work is similar to that of the experiment. The mesh consists of 130 points in the x and y directions and 49 points in the z-direction, taken as the vertical direction. The mesh spacing is 1.75 mm in the x and y direction and 1.25 mm in the z-direction. The dimensions of the computational domain are 227.5 mm in x and y directions, and 61.25 mm in z direction. The computational description is illustrated in Figure 5. The injection nozzle outlet is modeled with 8 points across in both directions. Due to the limitation of FDS, which can only model regular Cartesian geometry, the nozzle is modeled as a rectangular parallelepiped instead of a cylinder. The dimensions of the nozzle outlet (injection zone) were adjusted to match the area of the cylindrical nozzle used in the experiment. The mass flow rate of injected R-32 is set to 1.1 g/s. This corresponds approximately to an injection velocity of 2.8 m/s. The nozzle temperature is set to 0 °C, as it was observed during the experiment that some frost was forming on the nozzle during the injection of R-32. The nozzle is located 55 mm above the hot plate. The hot plate spans 203 mm in x and y directions and it is flanked by an insulated 30 mm high draft shield. The hot plate is modeled as an isothermal surface with a surface temperature of 764 °C. The insulated draft shield is also modeled as an isothermal surface, with a surface temperature of 394 °C. This value was chosen to account for the heat addition that originates from the hot plate. Open boundary conditions are applied in $Z = Z_{max}$, and on the vertical sides. A rough wall log-law is used as a wall model to describe the interactions flow/hot plate.

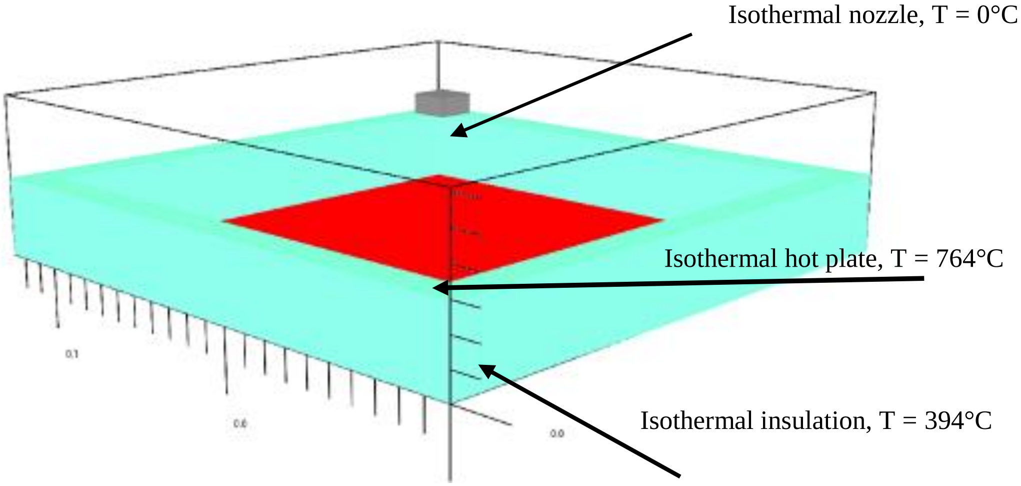


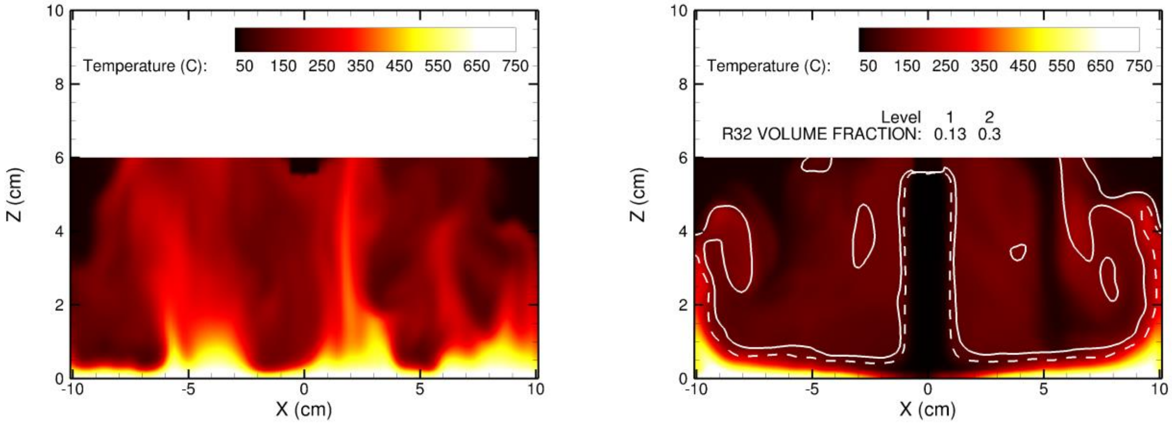
Figure 5: Geometrical description of the FDS computational domain. Open boundary conditions are used.

The simulation was initialized with still air at ambient condition (25 °C and 1.01 bar) and was run for 2.0 s prior to R-32 discharge to simulate the development of a turbulent buoyant flow generated by the presence of the hot plate. The injection of R-32 at a mass flow rate of 1.1 g/s was imposed for 1.5 seconds using a progressive linear ramp of 0.1 s. It was maintained steadily until 3.5 s, after which time it was stopped, again using a linear ramp. The simulation was stopped at 5.0 s, as it was of interest to study the presence of R-32 after the injection.

The near-wall resolution on the hot plate was verified a posteriori by checking the value of y^+ at the first grid cell above the hot-plate. Its maximum value is 6, which corresponds to a considered highly resolved simulation (McGrattan, 2013b). An additional a posteriori test was performed to measure the error associated with the mesh discretization on the velocity and scalar fields. It consists of assessing the fraction of unresolved turbulent kinetic energy over the whole turbulent kinetic energy, referred to as the measure of turbulence resolution (Pope, 2004). This dimensionless criterion takes the value of 0 for a perfect resolution and 1 for a poor resolution. A recommended practice is to keep this value lower than 0.2. It is found that this criterion is observed everywhere in the domain except in a ring located between 1 – 2 nozzle diameters away from the point of impact of the jet with the hot plate (or stagnation point, located at the origin), where the maximum value is 0.3. This is considered satisfactory for this simulation as the area of interest is located away from the stagnation point.

a) t = 1.9 s

b) t = 3.0 s



c) Averaged between 3.0 s to 3.5 s

d) t = 5.0 s

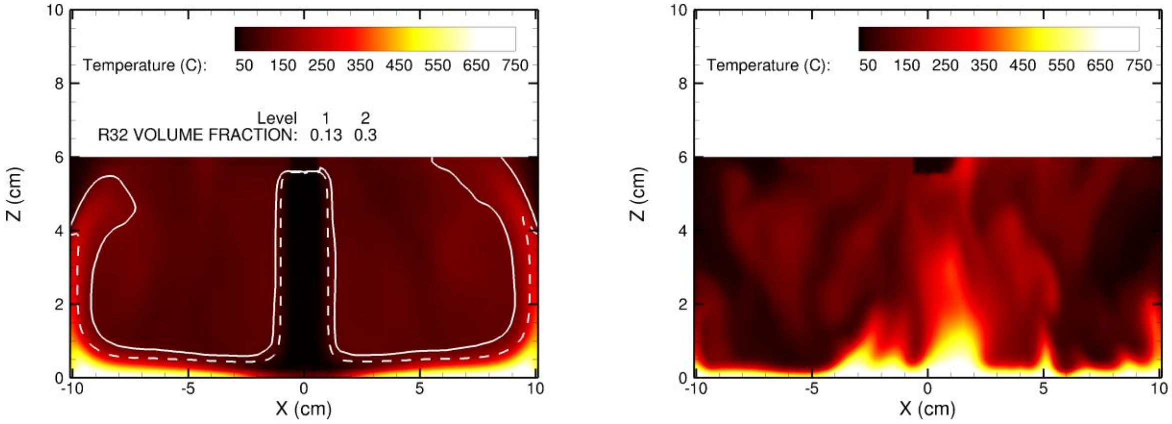


Figure 6: Cross section (at y = 0) of the temperature field and the contours of constant R-32 concentration at different times. The injection of pure R-32 from the nozzle starts at t = 2.0 s and continues for 1.5 s, until t = 3.5 s. The simulation ends at 5.0 s. Figure (a) plots the instantaneous conditions prior to R-32 injection at t = 1.9 s, (b) plots instantaneous conditions at t = 3.0 s during R-32 injection from the nozzle at x = 0 cm and z = 5.5 cm, (c) plots averaged conditions during R-32 injection between 3 and 3.5 s, and (d) plots the instantaneous conditions at the end of the simulation (t = 5 s), which is 1.5 s after the end of the R-32 injection. The solid line corresponds to where the R-32 concentration is at the lower flamability limit (13% in volume) and the dashed line corresponds to where the R-32 concentration is at the upper flamability limit (30% in volume). Neither (a) nor (d) has significant R-32 concentration levels.

Figure 6 plots the temperature fields and the contours of constant R-32 concentration corresponding to the ambient lower flammability limits (13% in volume) and the ambient upper flammability limit (30% in volume) of R-32 in air. The fields depicted correspond to the cross-section along the x and y directions at the location of y = 0 mm. Figure 6a plots the instantaneous fields prior to the R-32 injection, at 1.9 s. The turbulent nature of the buoyancy induced flow can be readily seen. As the air near the hot plate is heated, it rises and induces a turbulent motion, with a maximum vertical speed of 0.5 m/s. Some pockets of hot air are present in the domain. Figure 6b plots the instantaneous temperature field and the contours of constant R-32 concentration at t = 3.0 s. This is 0.5 after the start of injection and it corresponds to a turbulent steady state behavior. Figure 6c plots the average temperature field and contours of constant R-32 concentration over 0.5 s between 3.0 and 3.5 s. This plot illustrates the motion of the flow during the experiment. As the flow impinges the hot plate, it is conveyed toward the edge of the plate. During this process, it is heated and its temperature rises above 600 °C near the draft shield, more than 9 cm away from the point of impact. Near the draft shield, a stagnant zone exists, which is characterized by elevated temperatures and slow velocities. This implies that conditions propitious to R-32 ignition are to be expected near the draft shield and away from the jet point of impact. Figure 6d plots the temperature field at the end of the simulation. The discharge of R-32 had stopped 1.5 s earlier. Similar to Fig. 6a, buoyant turbulent structures can be readily observed. No significant concentration of R-32 remains; the concentration of R-32 falls below the lower flammability limit (13% in volume) about 0.9 seconds after the end of R-32 injection.

To gain a better understanding of the temperature variations with the distance from the jet point of impact (located at x = 0), values of temperature along the contours of constant concentration corresponding to the ambient lower flammability limit ($X_{R\text{-}32}$ = 0.13), stoichiometry ($X_{R\text{-}32}$ = 0.174) and the ambient upper flammability limit ($X_{R\text{-}32}$ = 0.30) were extracted from Fig.6c. Figure 7 plots these data along the location in the x direction. Away from the jet point of impact, the temperature increases with the concentration of R-32 (higher concentrations correspond to higher gas temperature) and, for a given concentration, the temperature increases away from the jet point of impact. Figure 7 shows that temperature at constant concentration reaches its maximum near the draft shield. Figure 7 indicates that conditions corresponding to the greatest R-32 concentration, $X_{R\text{-}32}$ = 0.30, has the highest temperature, 270 °C, at |x| = 0.09 mm. This indicates that ignition is likely at locations in refrigerant rich conditions, *i.e.*, at locations where the R-32 concentration is above the stoichiometric value and far from the center of the plate and near its edges.

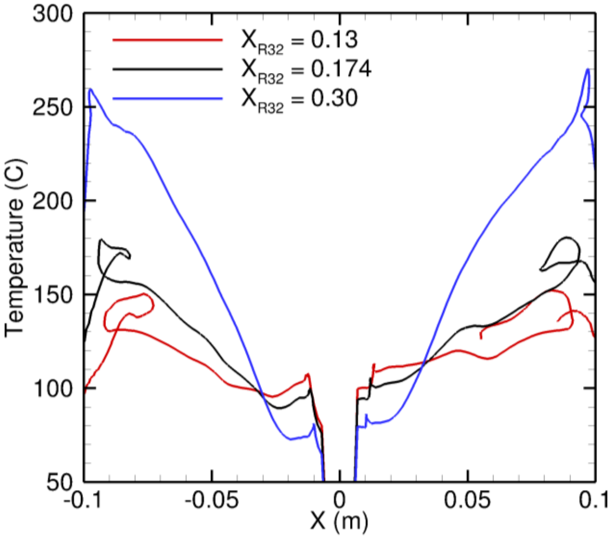


Figure 7: Temperature profiles along the x direction of different contours of constant R-32 concentration: 0.13 (which corresponds to lower flammability limit at ambient conditions) in red, 0.174 (stoichiometric) in black, and 0.3 (which corresponds to upper flammability limit at ambient conditions) in blue. Data were extracted from Figure 6c and correspond to averaged values over 0.5 s.

5. CONCLUSIONS

The experimental ignition temperatures of pure R-32 and R-410A refrigerants along with the ignition temperature of these refrigerants mixed with liquid POE oil were studied using a hot-plate configuration with a surface temperature varying from 200 – 900 °C. The hot-plate ignition temperature of R-32 was found to be 764 °C (± 10 °C), while that for R-410A was found to be at 790 °C (± 10 °C). When mixed with POE oil, the ignition temperature of the R-32 refrigerant/oil mixture was found to be very close to that of the POE oil (649 °C) employed in this study. The presence of ignited oil was found to be a driving factor of subsequent refrigerant ignition. CFD simulations using a LES code were performed to simulate the discharge of pure R-32. Simulations at 764 °C suggest that ignition begins away from the jet point of impact and for R-32 concentrations above that of stoichiometry. This work is a first step in providing an extensive fire risk assessment associated with the use of R-32 in HVAC systems as a replacement for R-410A.

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Laminar Flame Speeds of Hydrofluorocarbon-Air Mixtures

Experiments and Modeling

Paul Papas, Shiling Zhang, WonWook Kim, Steve Zeppieri,
Med Colket, Parmesh Verma

Presented by Med Colket (retired)

United Technologies Research Center
E. Hartford, CT 06108

NIST Workshop on the Exothermic Reaction
of Halogenated Hydrocarbons
Gaithersburg, MD
October 27-28, 2014

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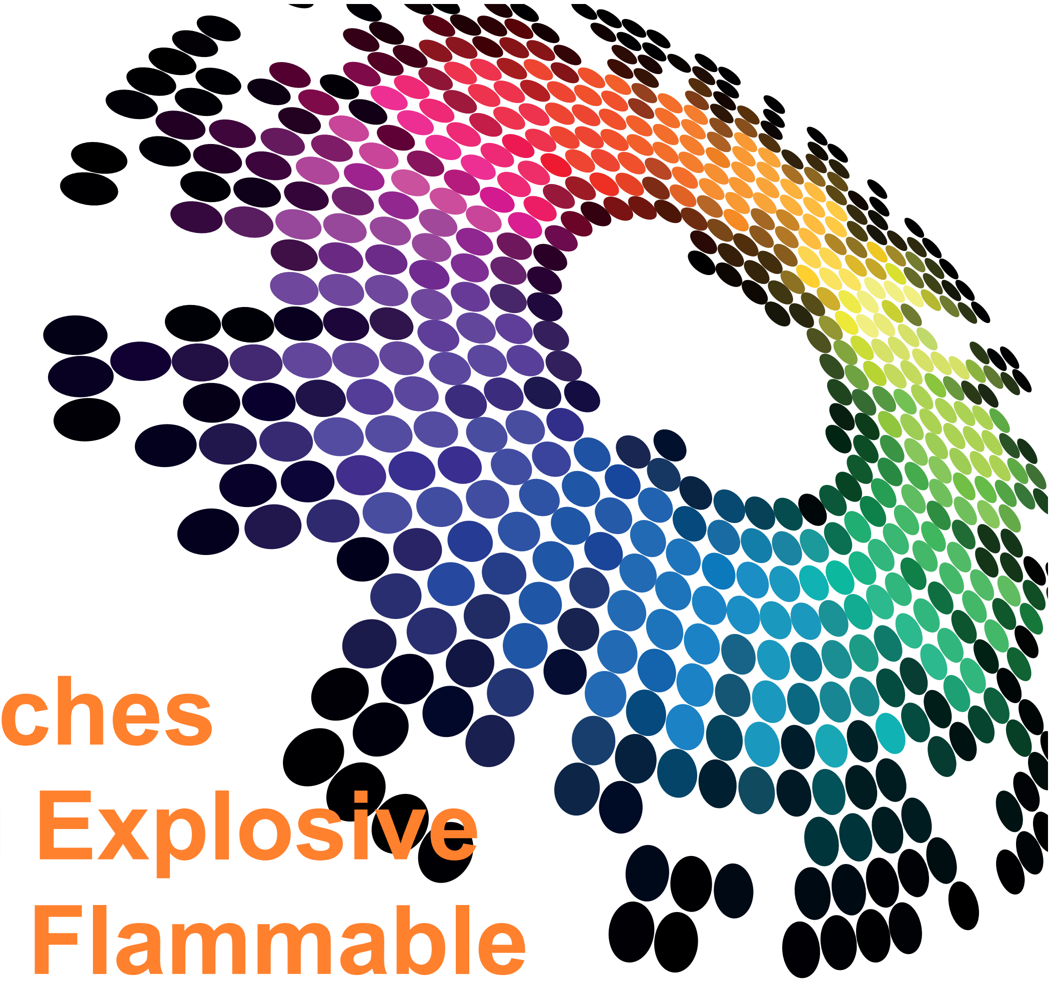


Experimental and Numerical Approaches for Understanding Explosive Behavior of Mildly Flammable Combustible Gases

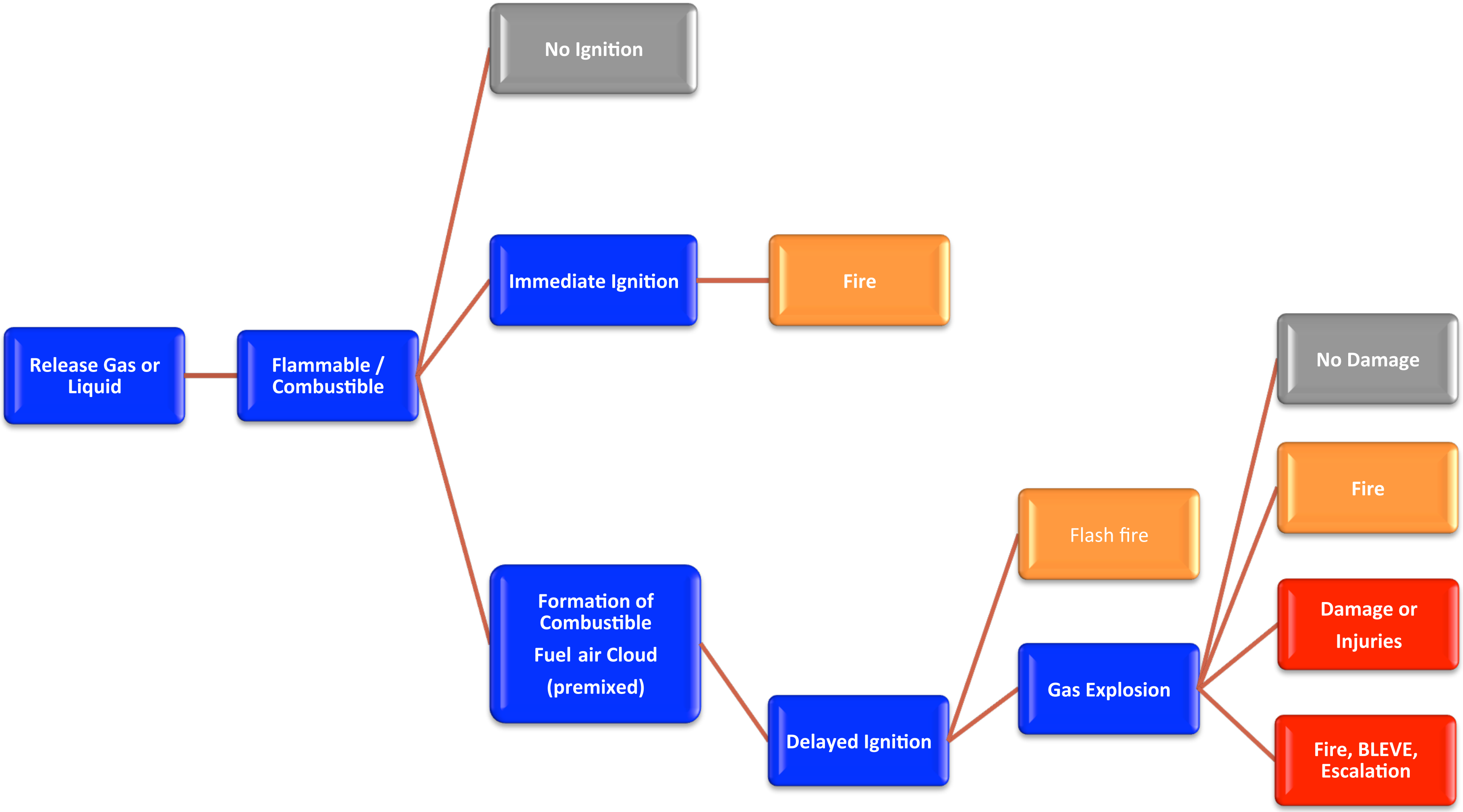
Scott Davis, PhD, PE

NIST Workshop – October 27, 2014

Outline

- Background of explosion risk and consequences
- Bench scale experimental tests
- Large scale experimental tests
- Numerical modeling of consequences

Gas explosions: chain of events


Release Gas or Liquid

Flammable / Combustible

No Ignition

Immediate Ignition

Fire

Formation of Combustible Fuel air Cloud (premixed)

Delayed Ignition

Flash fire

Gas Explosion

No Damage

Fire

Damage or Injuries

Fire, BLEVE, Escalation

Explosion Risk

Probability x Consequence

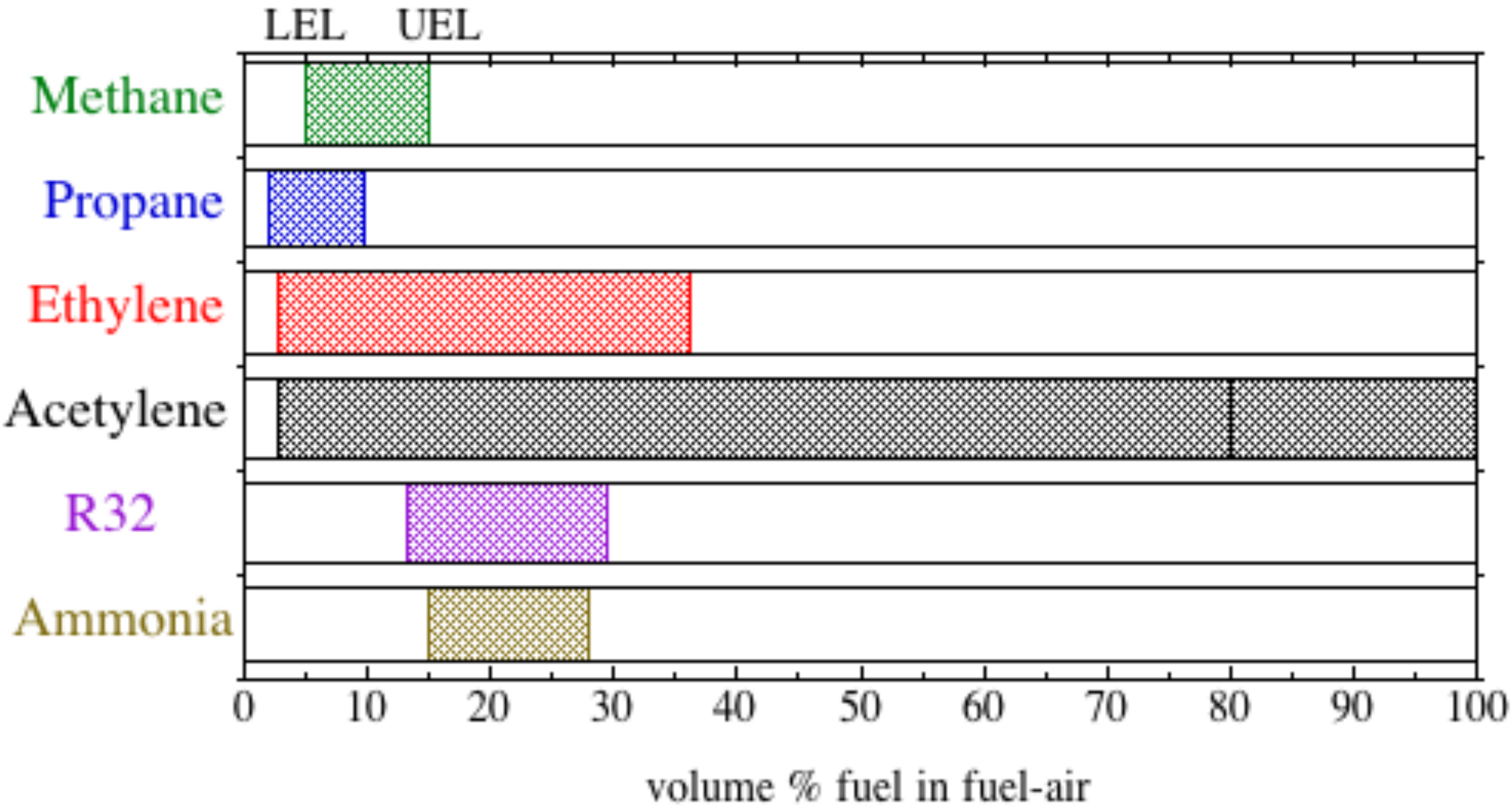
- Loss of containment
- Ignition source – probability
- Gas cloud accumulation
    - Mechanical ventilation
    - Pipe size and inventory

- Fuel type - reactivity
- Concentration of fuel
- Layout
    - Obstacle density “congestion”
- Type of gas cloud
- Venting present

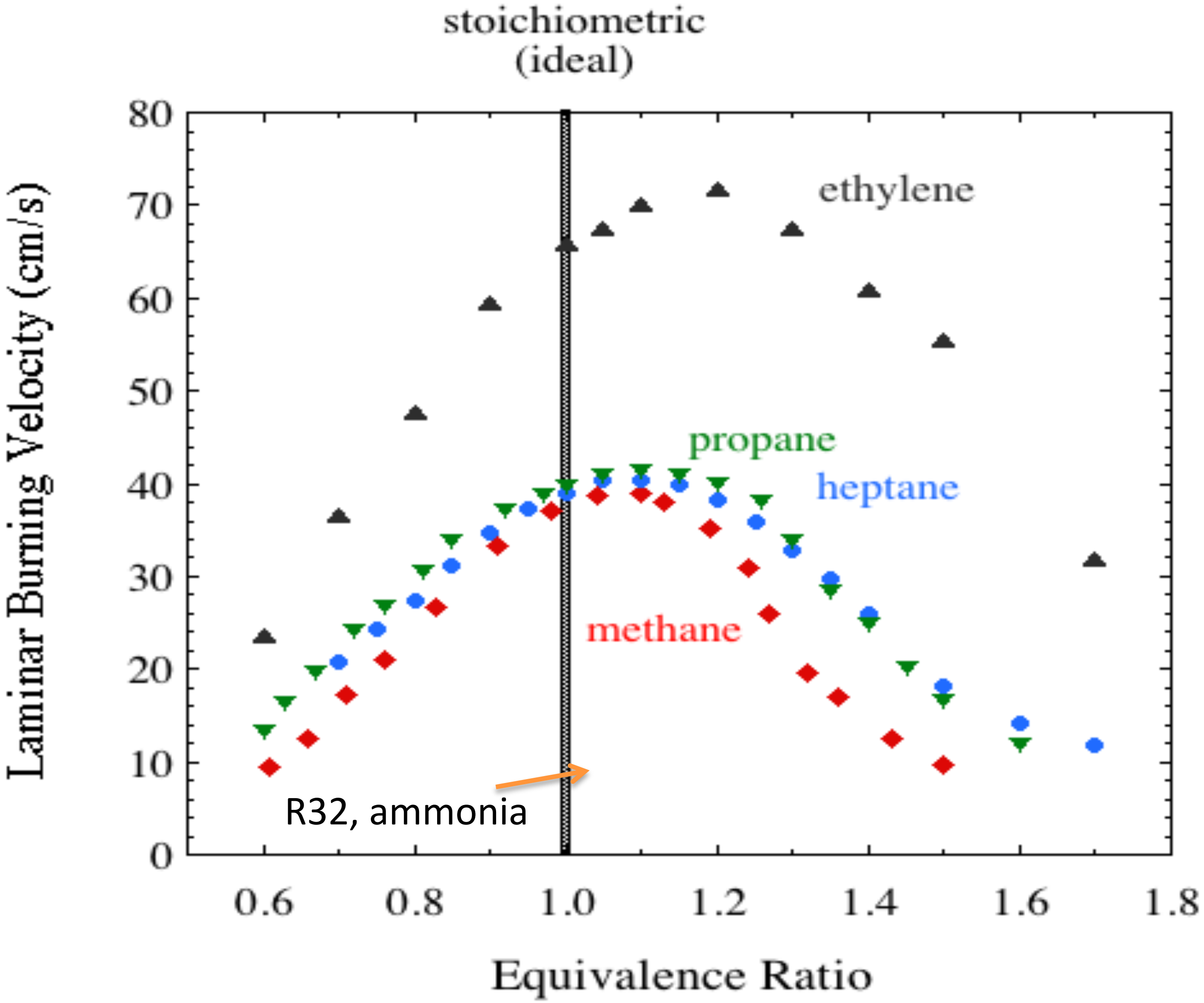
Basic Parameters – combustion properties

- Flammability limits or explosivity limits
- Laminar burning velocity – reactivity
- Ignition
  - Minimum ignition energy
  - Auto-ignition temperature

Explosive part of the cloud



Laminar burning velocity

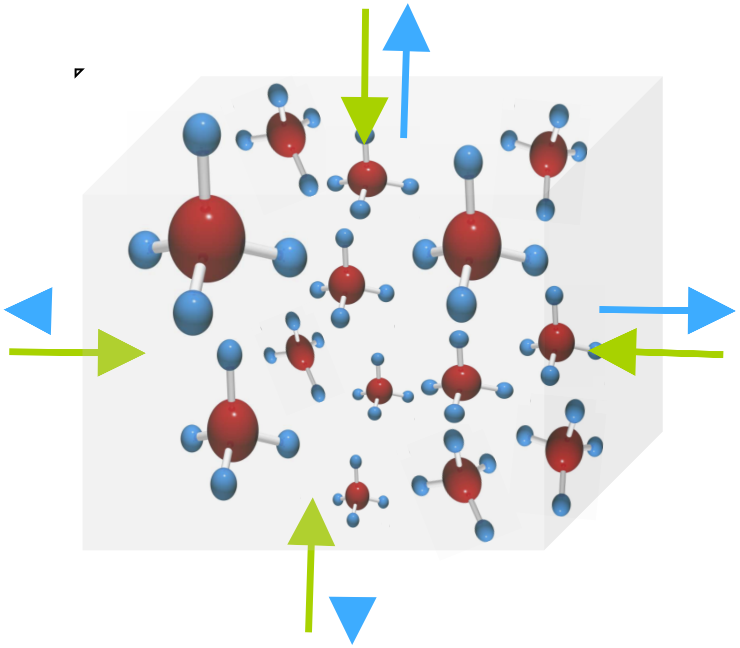


R32, ammonia

$Su \sim RR^{1/2}$

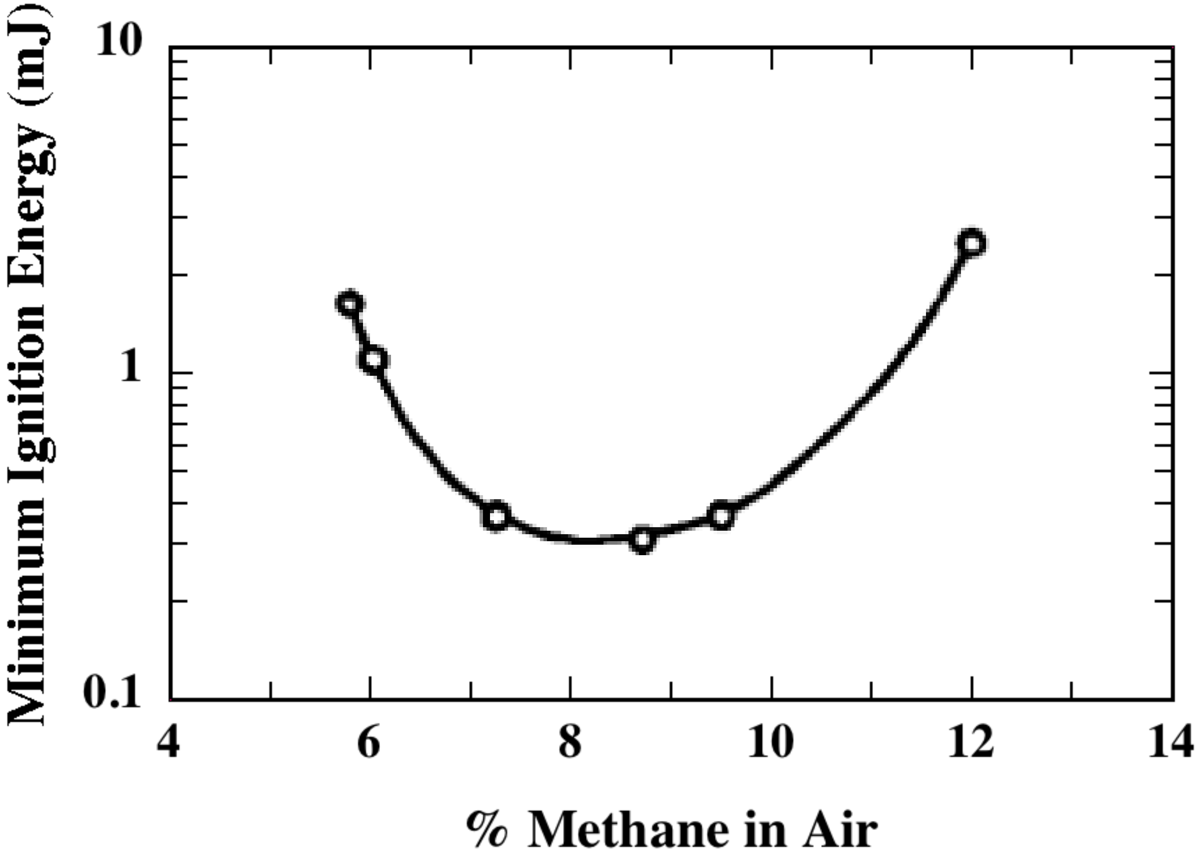
Ignition – what is it

- A process where a sufficiently amount of energy is transferred into a small volume of explosive atmosphere to initiate self sustaining flame propagation.



Heat_{in} + radical spices_{in} > Heat_{out} + radical spices_{out}

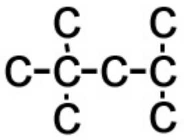
Ignition energy (electric spark)



- Hydrocarbons: MIE = 0.1 – 0.3 mJ
- R32: MIE ~ 15 mJ, Ammonia: MIE ~ 21 mJ

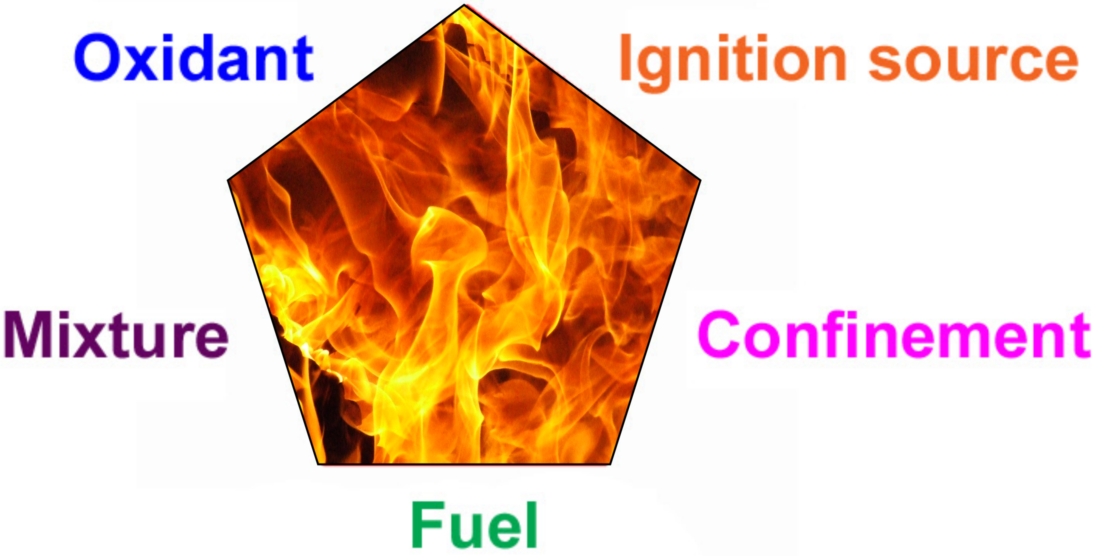
Auto-ignition temperature

- Theoretical lowest temperature of a hot surface at which a mixture of fuel and air can ignite

Methane	537°C	c
Propane	450°C	c-c-c (linear)
N-heptane	206°C	c-c-c-c-c-c-c (linear)
iso-octane	415°C	 (branched)
R32	648°C	
Ammonia	651°C	

Explosions

- Rate of pressure rise vs. rate of venting gases



Oxidant

Ignition source

Mixture

Confinement

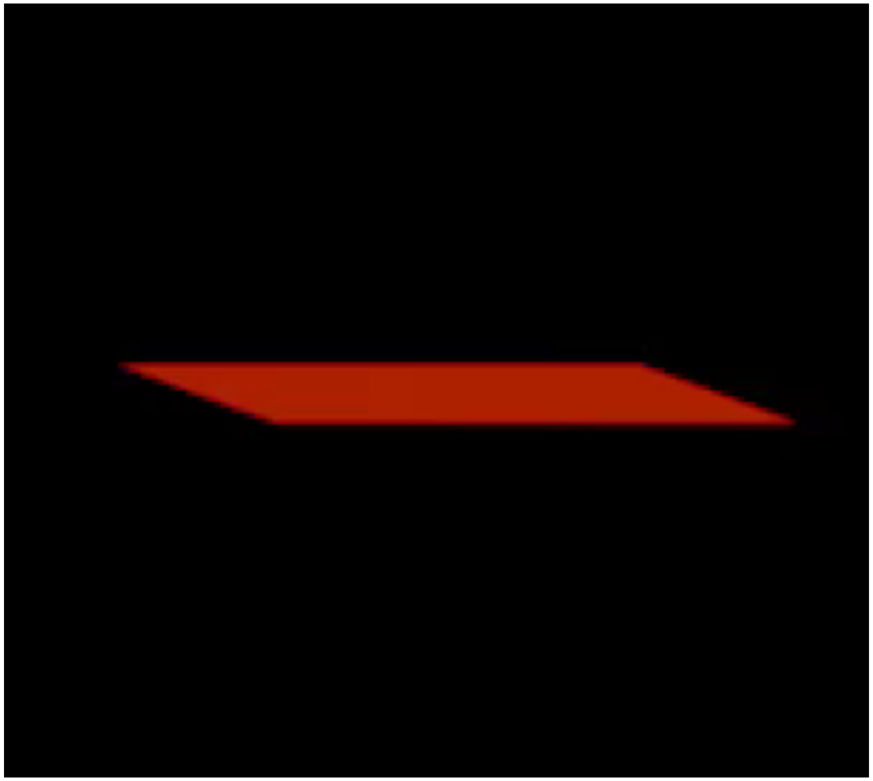
Fuel

EXPLOSION PENTAGON

Turbulent combustion

- Turbulence causes an increase of burning velocities due to an increased flame surface area

Flame speeds (expansion + combustion) can vary from 5 to more than 600 m/s



Experiments – cross flow obstructions - no confinement

Experiments – congested vs. uncongested

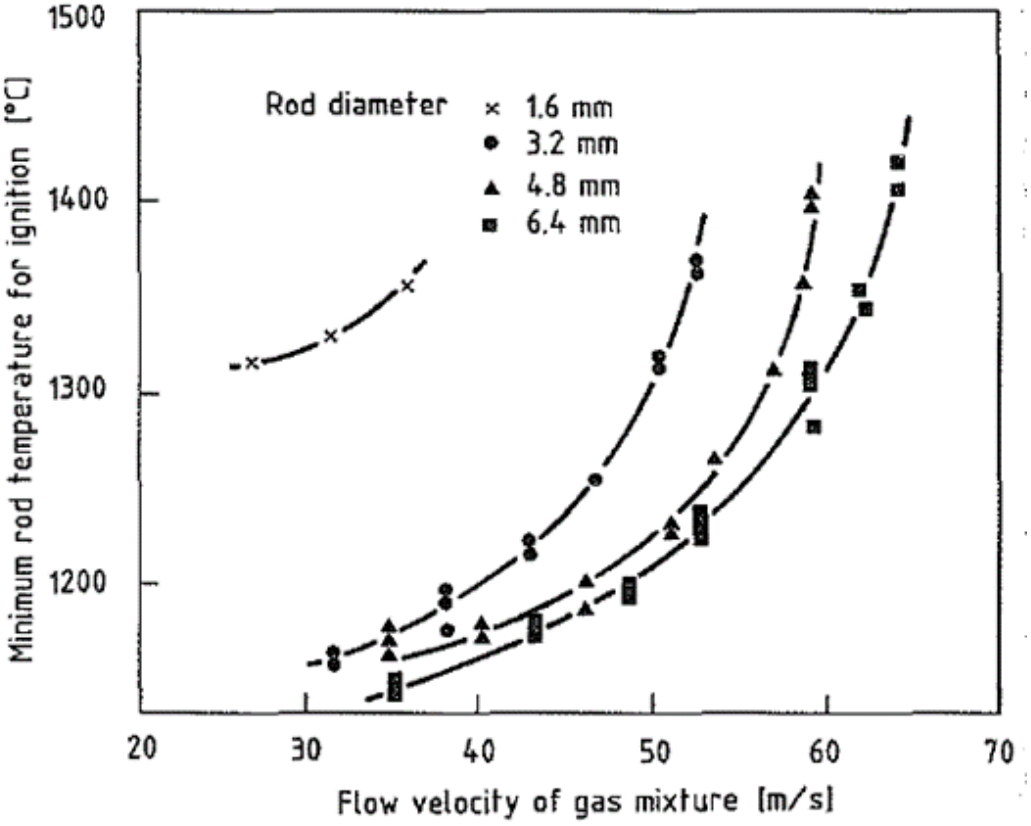
Venting

Bench scale tests

- Flammability limits (LEL – UEL)
- Ignitibility tests
  - MIE – for very low LBV may suffer from “flame quenching”
  - AIT
- Laminar burning velocity – reactivity
- Deflagration indexes: K_g (quiescent) or K_{St} (turbulent)

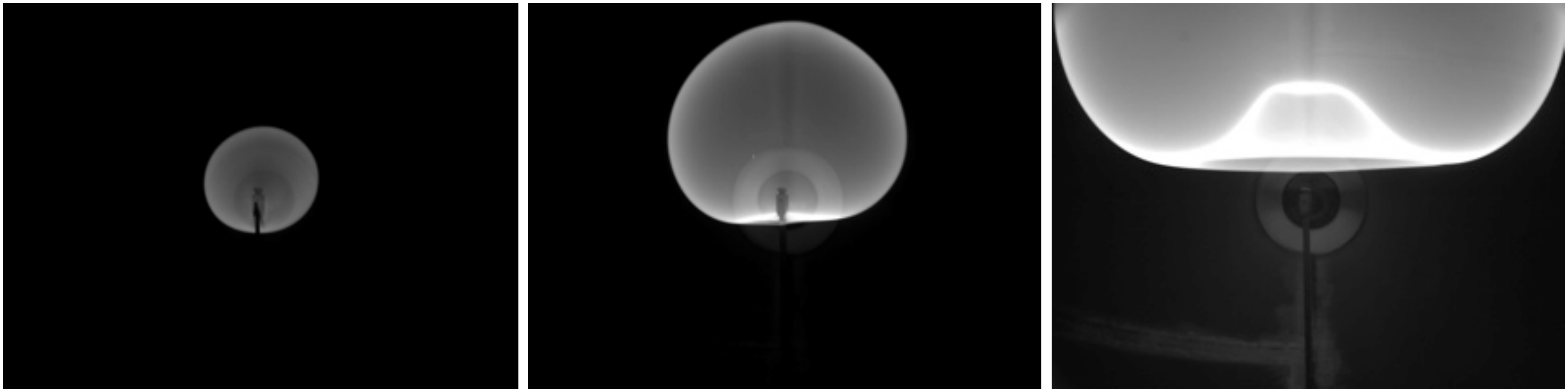
Ignition tests

- For very low LBV may suffer from "flame quenching"
- May differ from the actual release/environment

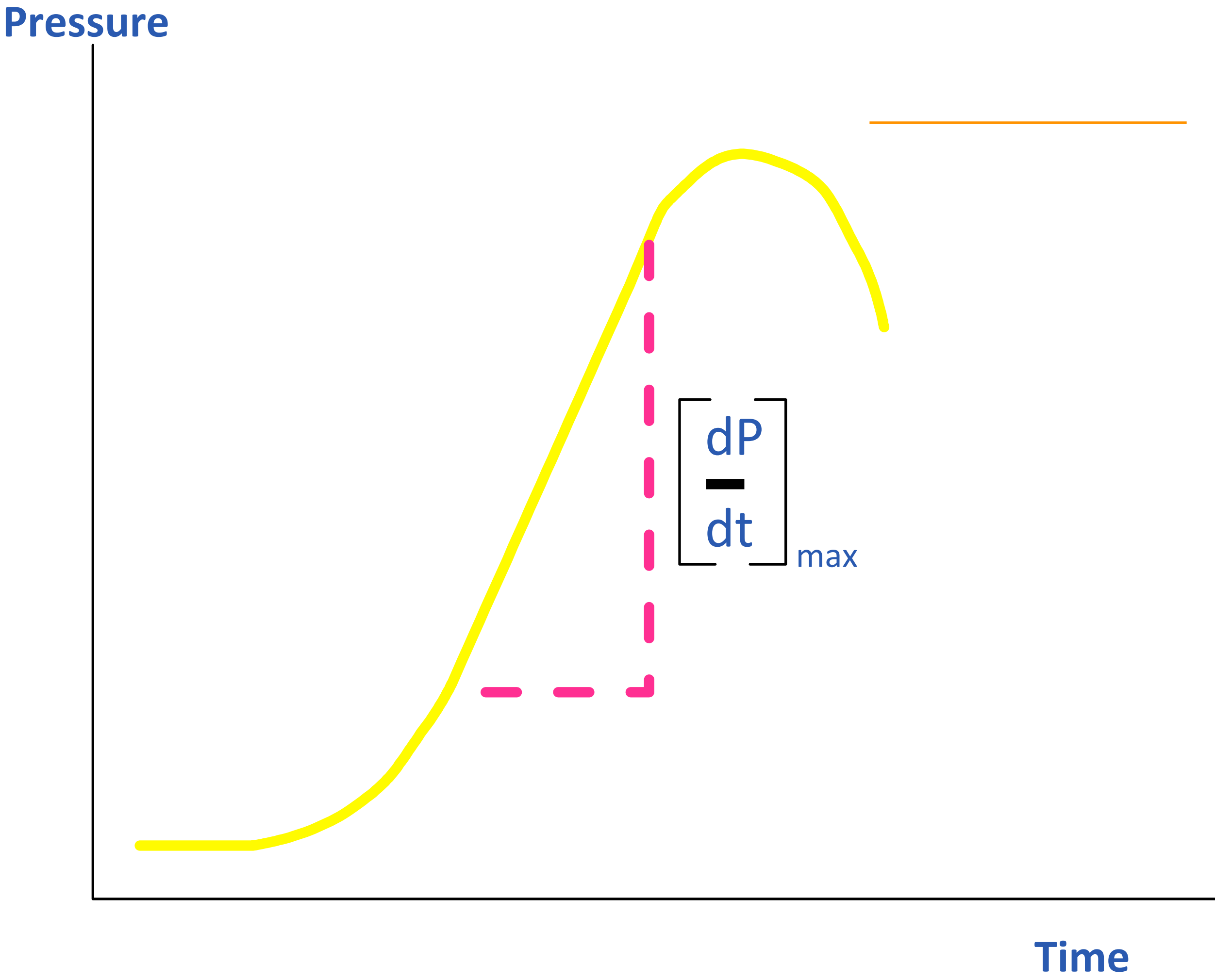


Laminar burning velocity

- Buoyancy has a great effect for mildly burning fuels
- Difficult to overcome in 1g environments



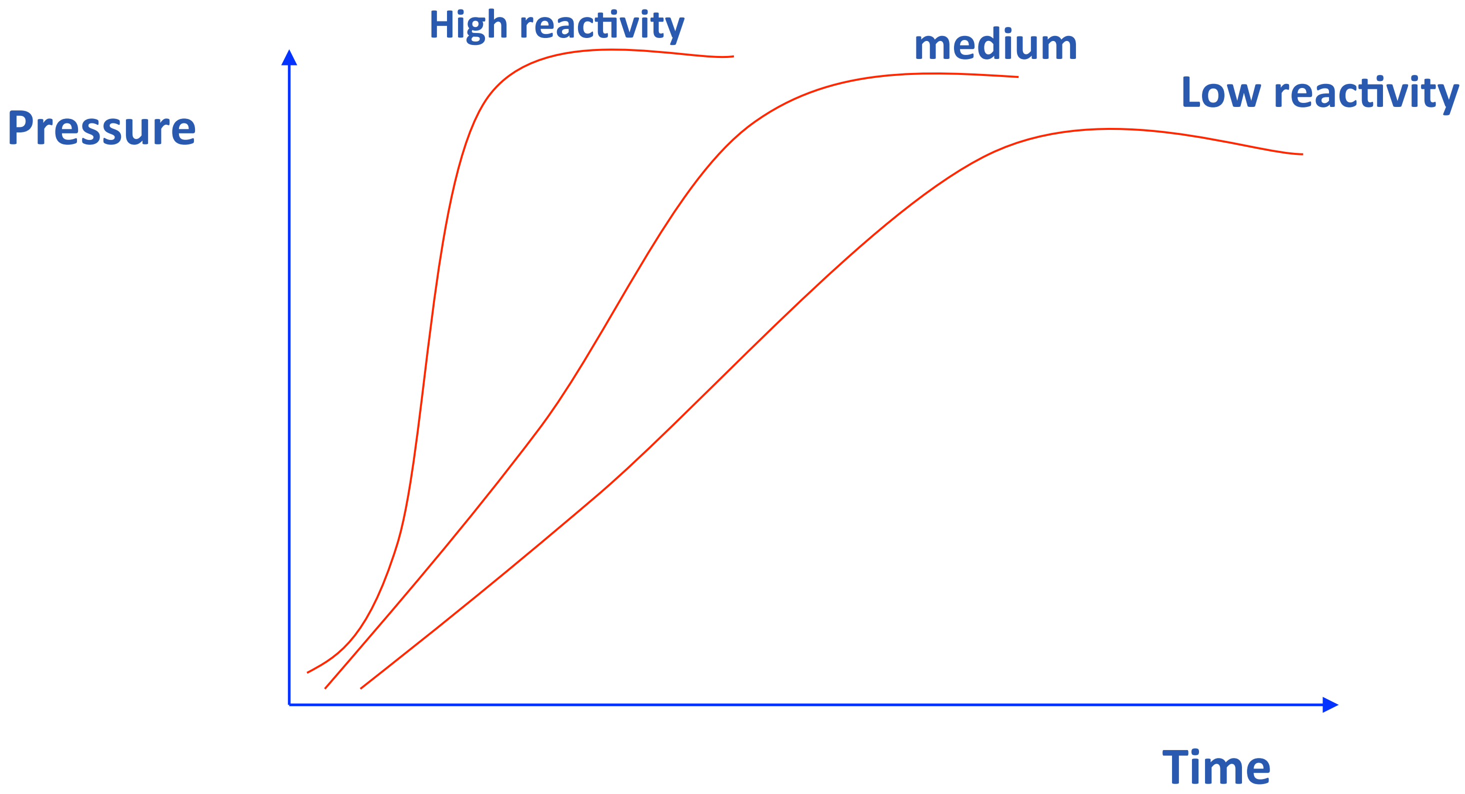
Explosivity tests – 20 liter sphere



K_g or $K_{St}=dP/dt_{[max]}\ V^{1/3}$ Optimum concentration

20 liter

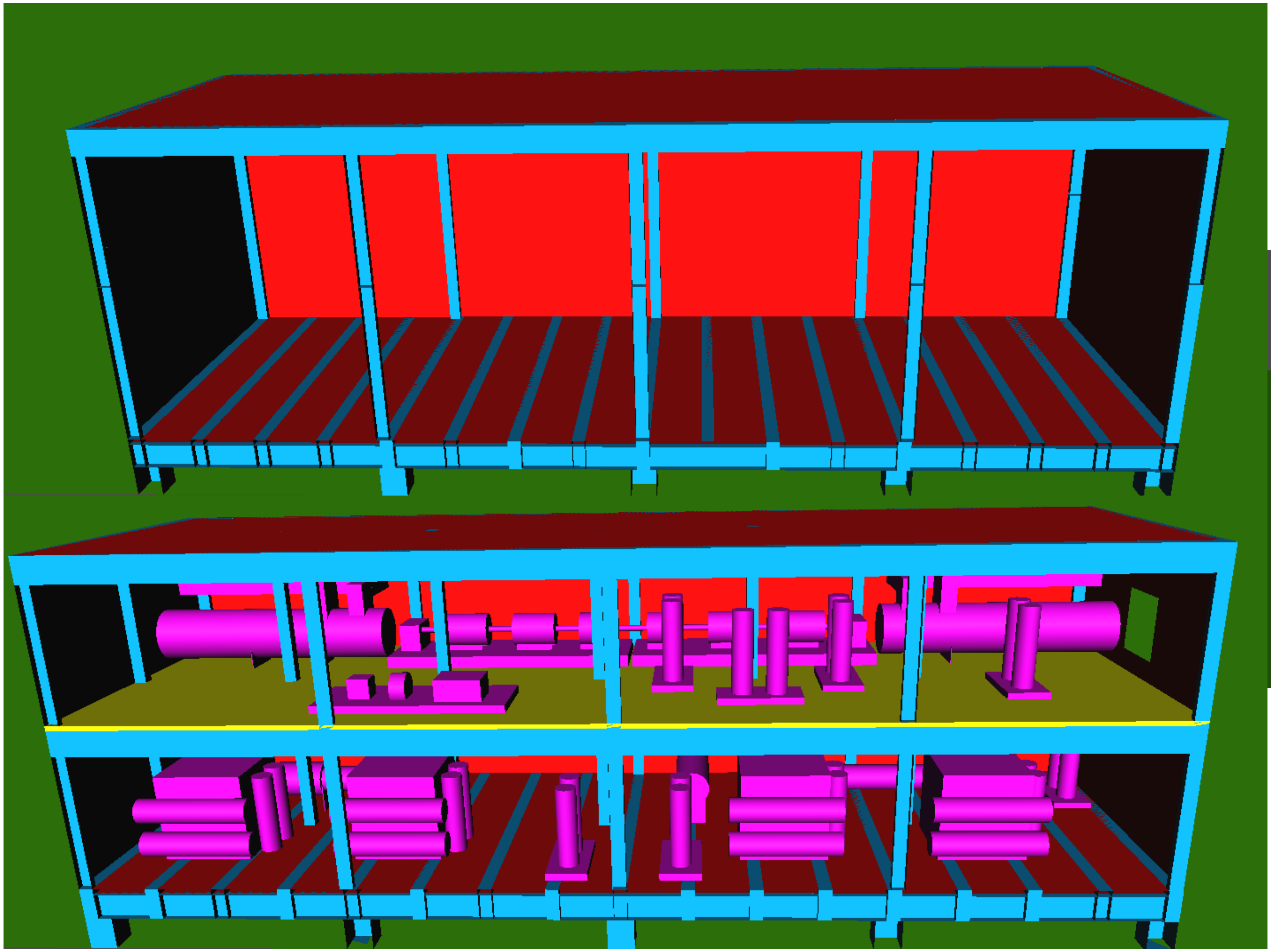
- Confined (no venting)
- Can evaluate effects of turbulence

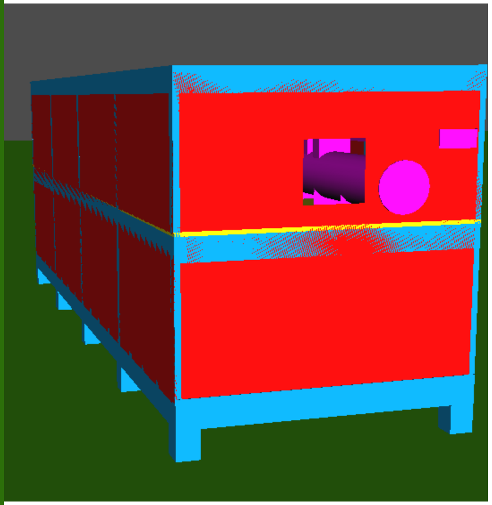


Large Scale tests - modeling

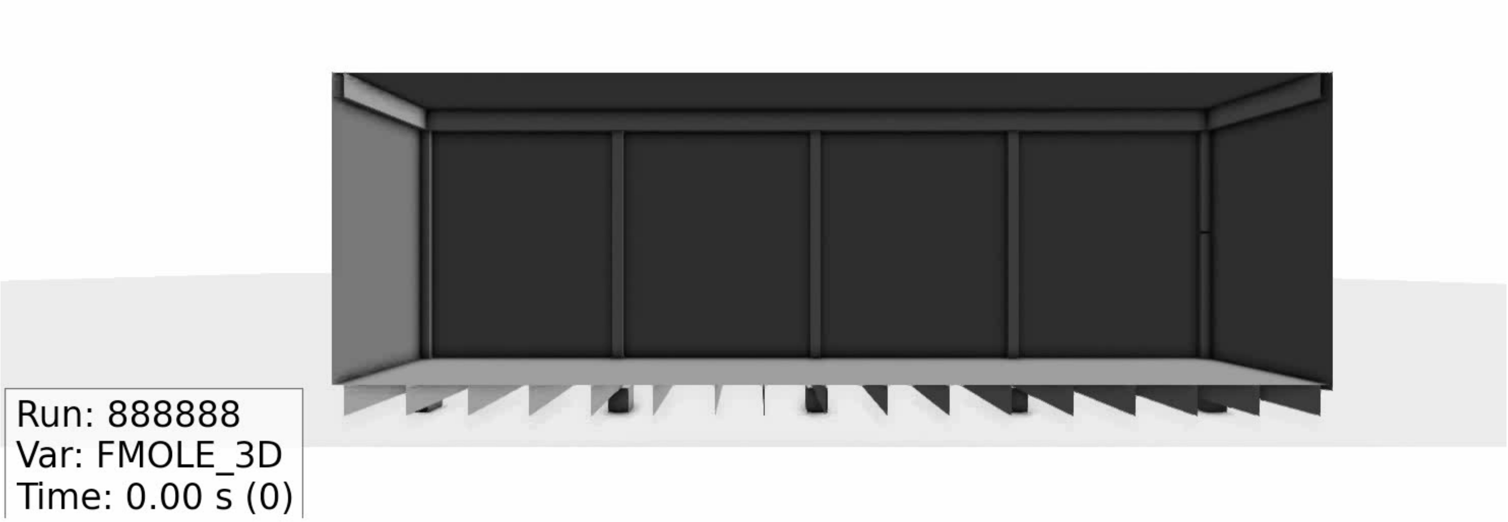
- Validate the “actual” effects at the large scale
- Evaluate rate of pressure rise versus venting
- Evaluate ignition
- Validate turbulence effects
    - Enhancing or inhibiting
- Validate CFD models

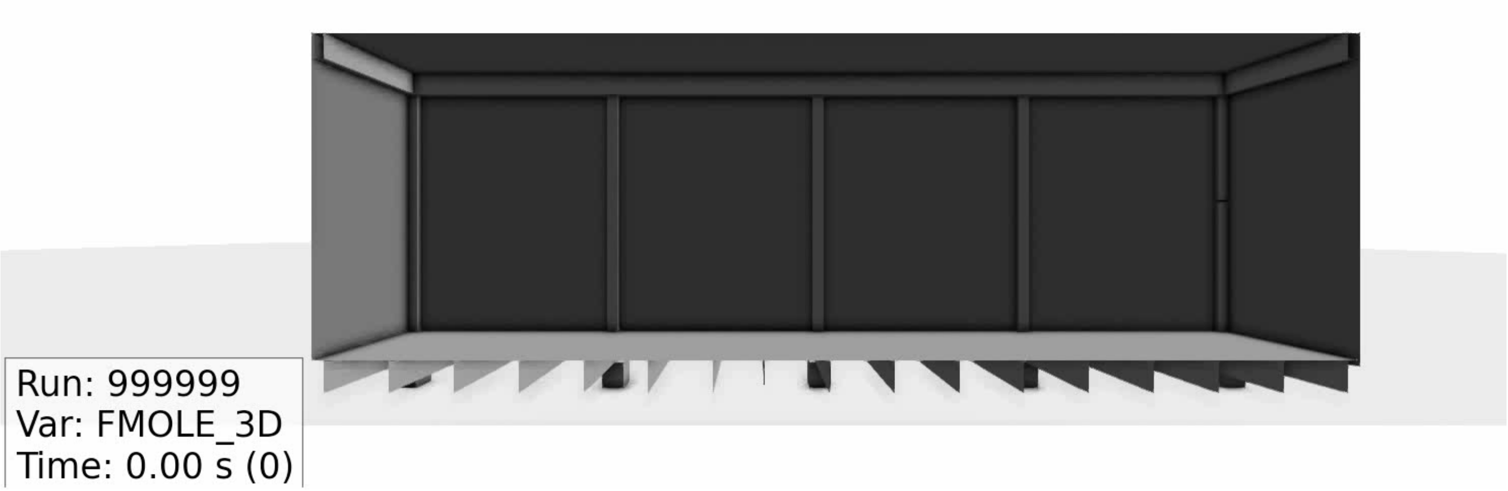
Geometry



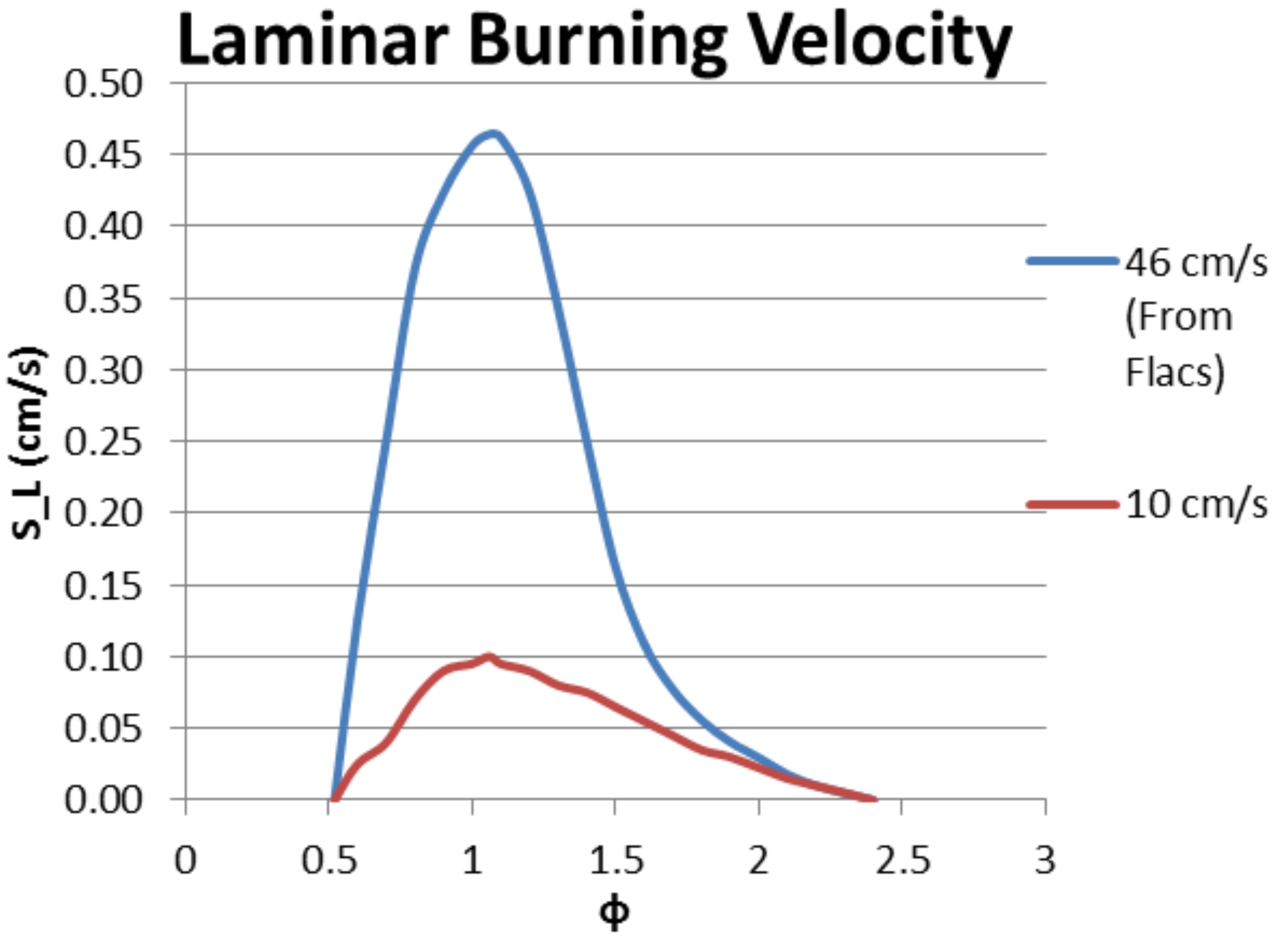


Low vs. High Momentum Release



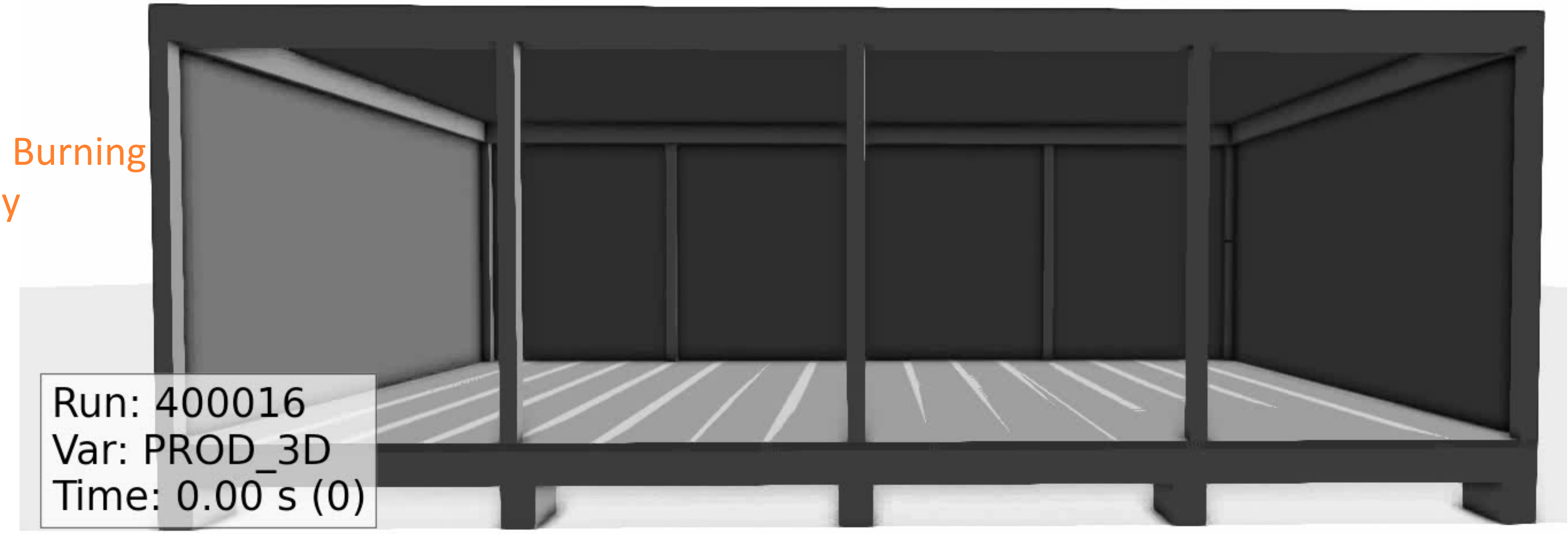


Laminar Burning Velocity

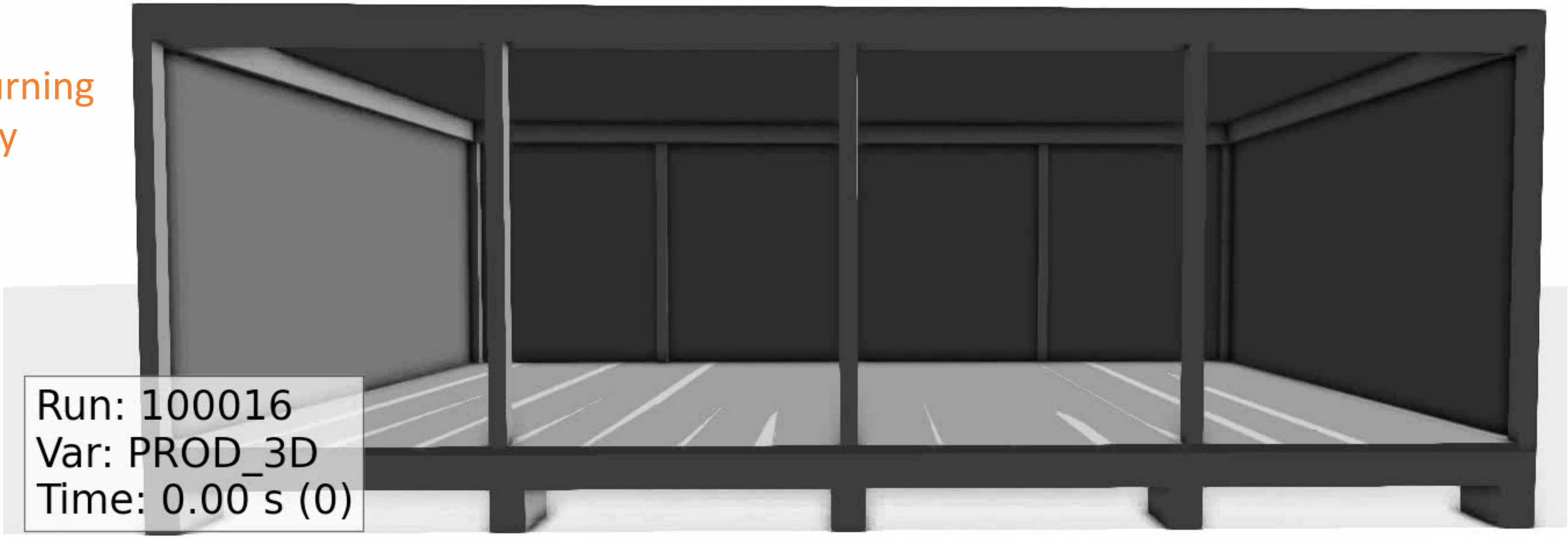


Unvented

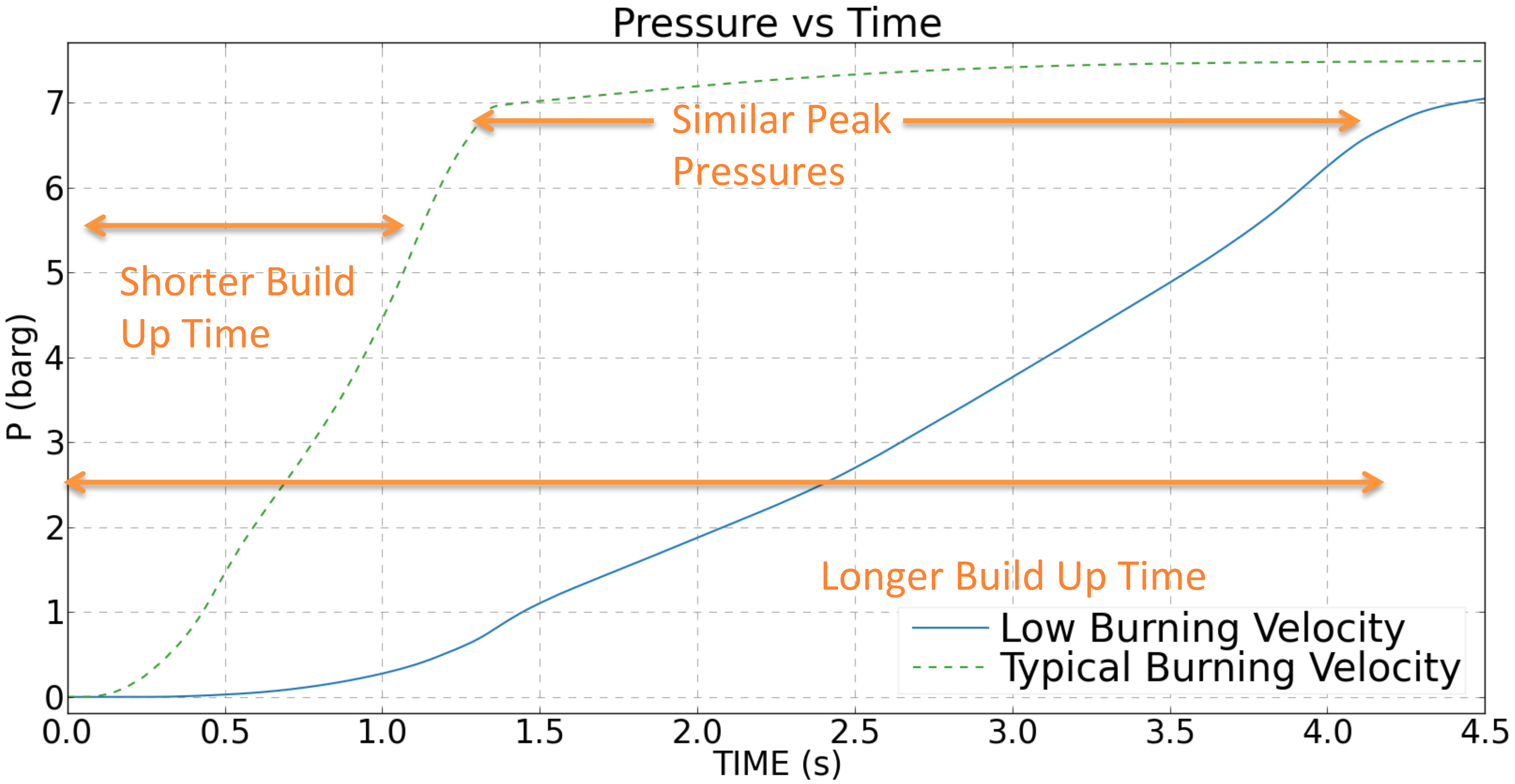
Typical Burning Velocity



Low Burning Velocity



Unvented



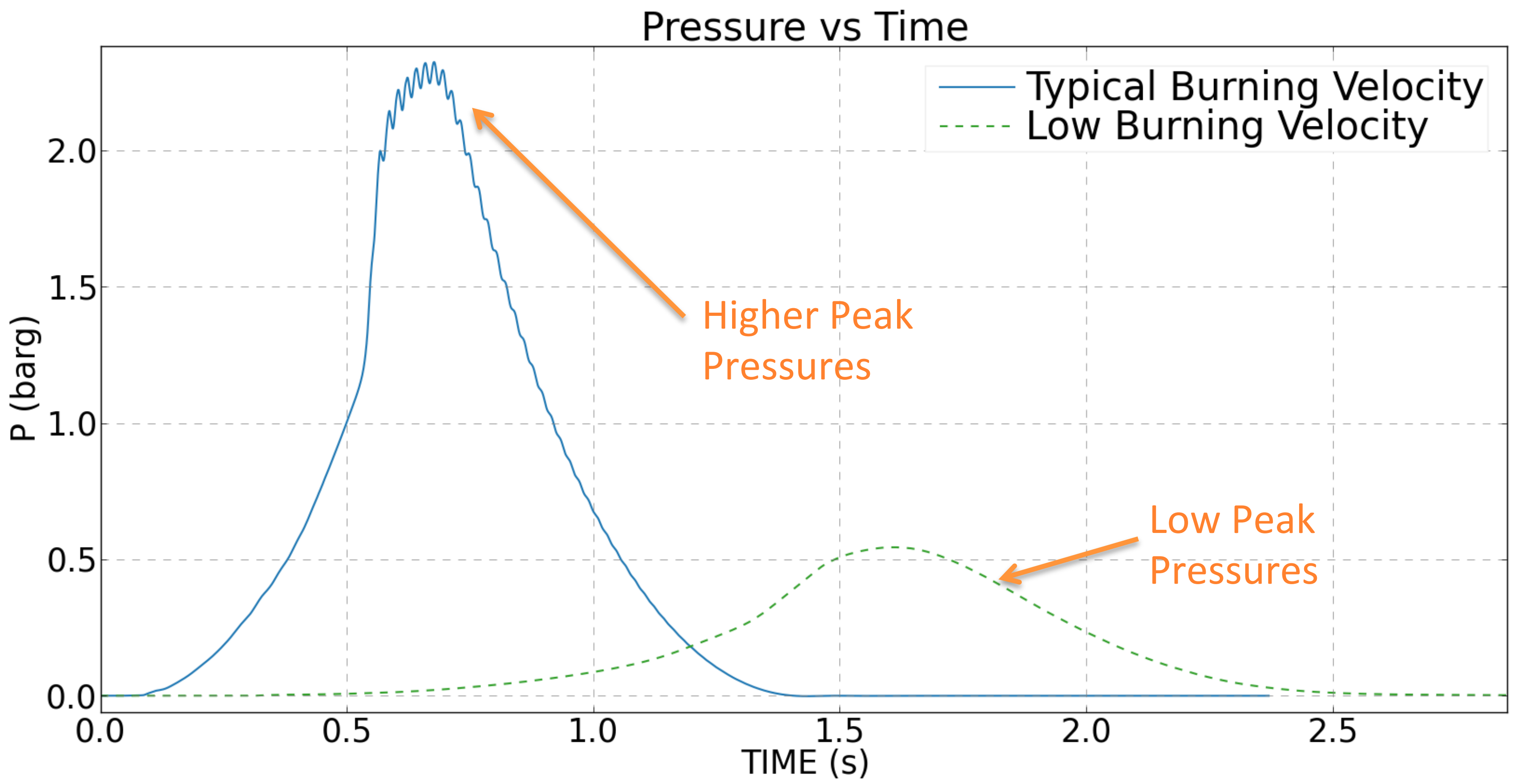
Run: 100016, 400016
Var: P

0.25 m^2 Vent

Typical Burning Velocity

Low Burning Velocity

$0.25\ m^2$ Vent

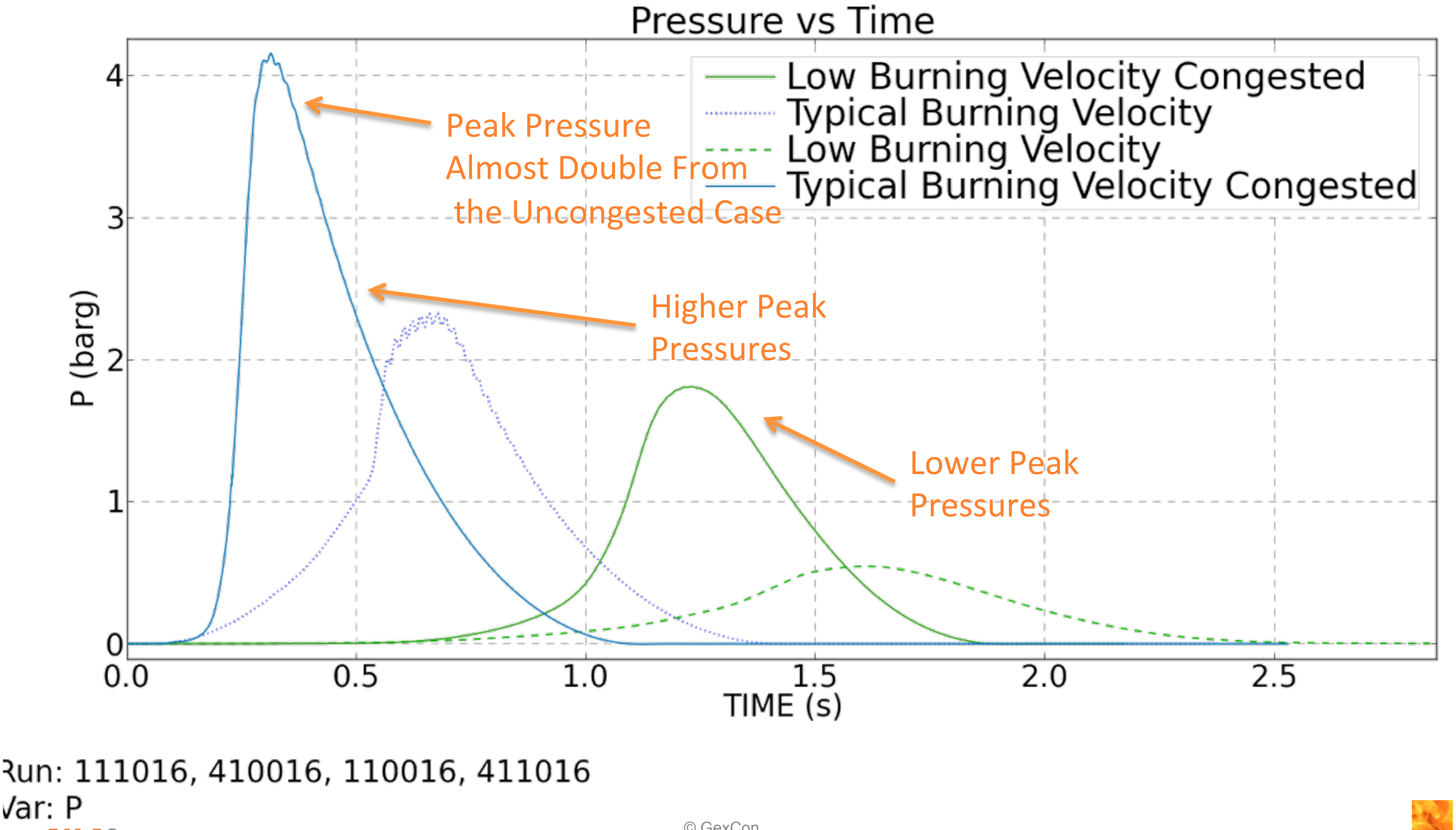


Higher Peak Pressures

Low Peak Pressures

Run: 410016, 110016
Var: P

0.25 m^2 Vent With Congestion

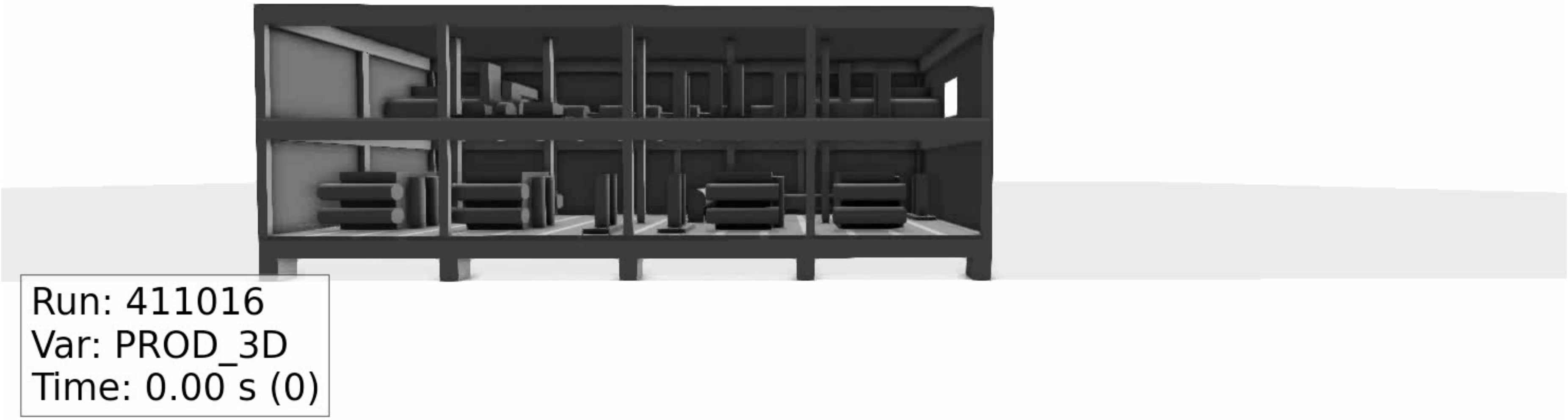


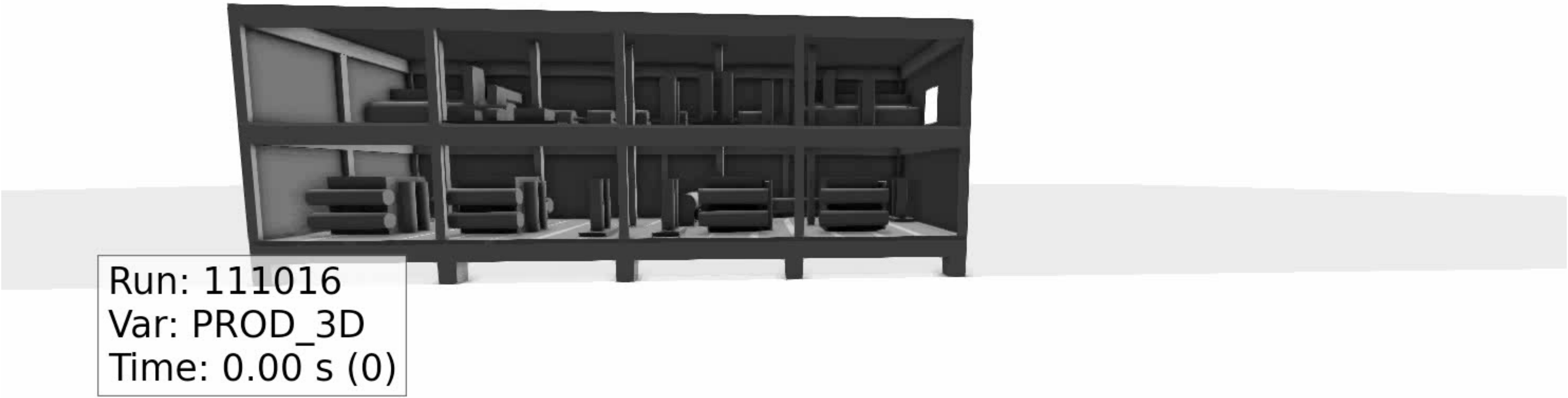
Peak Pressure Almost Double From the Uncongested Case

Higher Peak Pressures

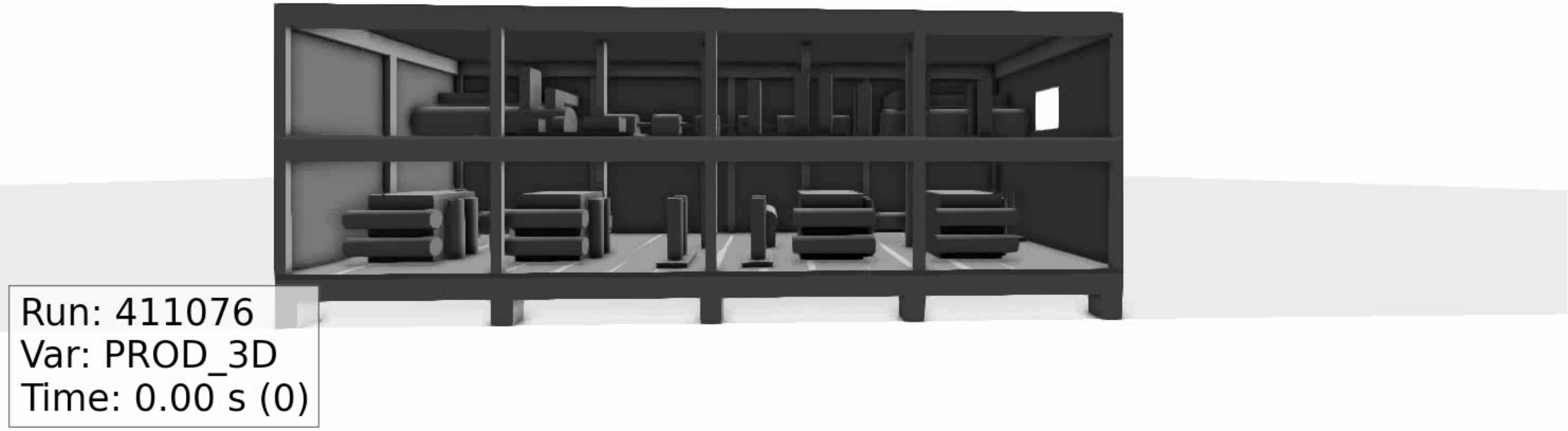
Lower Peak Pressures

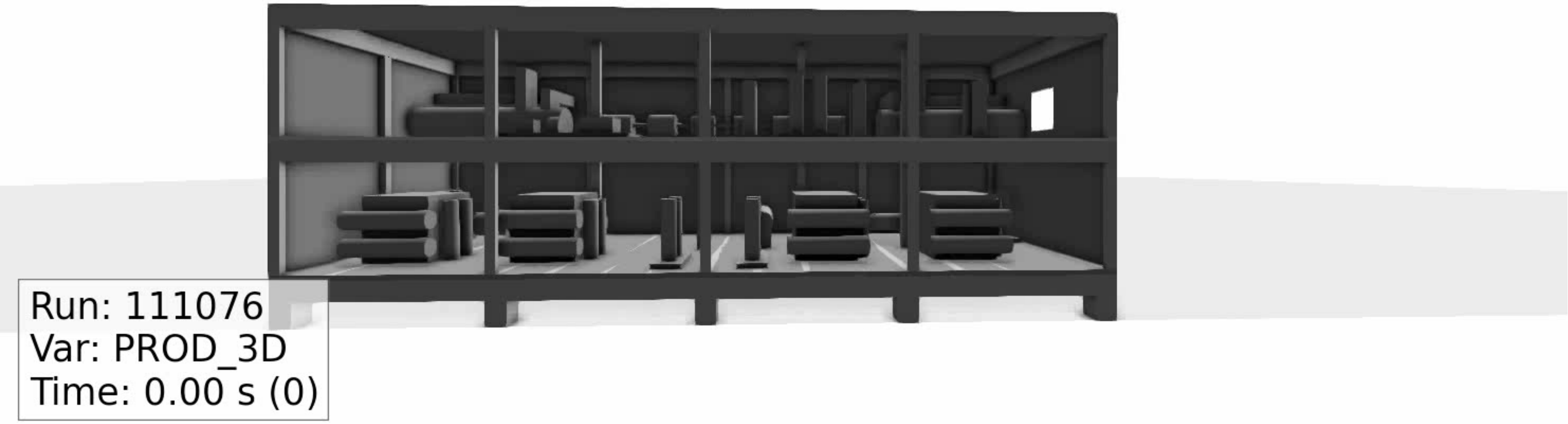
0.25 m^2 Vent With Congestion



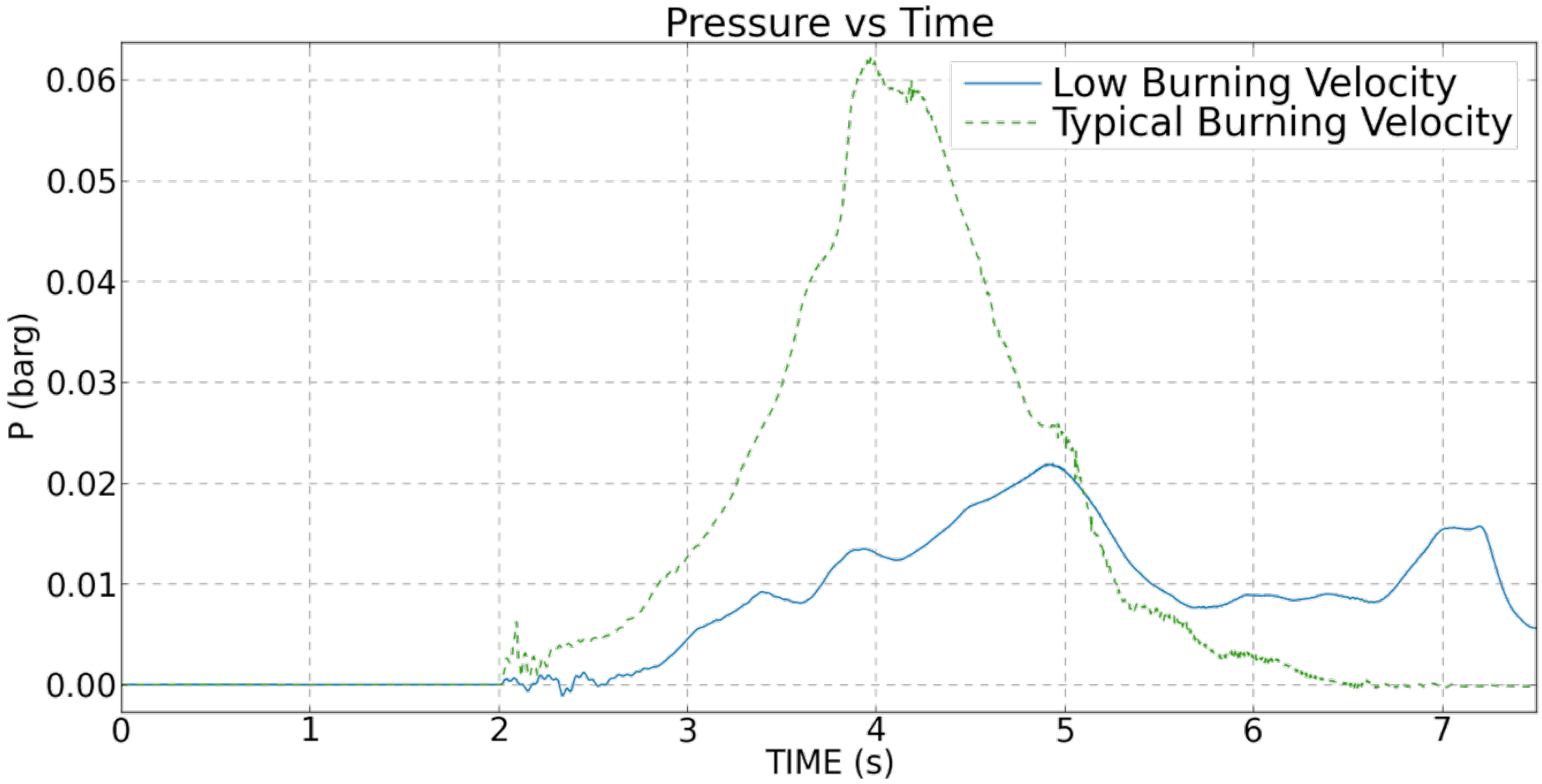


Rich Layer


Run: 411076
Var: PROD_3D
Time: 0.00 s (0)


Run: 111076
Var: PROD_3D
Time: 0.00 s (0)

Rich Layer



Run: 111076, 411076
Var: P

Summary

- Explosion risk is based on both the likelihood of having an event and its potential consequences
- Need to develop a method of evaluating the relative risk of mildly burning combustible gases
    - Based on “standard” bench scale tests
    - Validated on large scale
    - Incorporated into advanced 3D models.
- Update predictive 3D models to accurately predict the potential consequences of release events

GexCon

sgdavis@gexcon.com

United Technologies

Building & Industrial Systems

Review of Regulations, Standards, and Codes related to reductions in Global Warming Gas Emissions and to Support the Use of New Refrigerant Options

NIST Workshop- October 27-28, 2014

Richard Lord – Carrier & ASHRAE Fellow

Revision 3

The Use of Thermodynamic and Chemical Kinetic Models to Understand Explosive Behavior of Mildly Flammable Combustible Gases

NIST Workshop on the Exothermic Reaction of Halogenated Hydrocarbons

Gaithersburg, MD Nov. 27-28, 2014

	Greg Linteris*,	*NIST Fire Research*
Kinetics	Jeff Manion / Wing Tsang / Don Burgess,	*NIST Chemical Kinetics*
	Valeri Babushok,	*(NIST GR)*
Flame modeling	Vish Katta,	*Innovative Scientific Sol. Inc.*
	Fumi Takahashi,	*Case Western Reserve Univ.*
Experiments	Peter Sunderland, John Pagliaro	*Univ. of Maryland*

**Presenter*

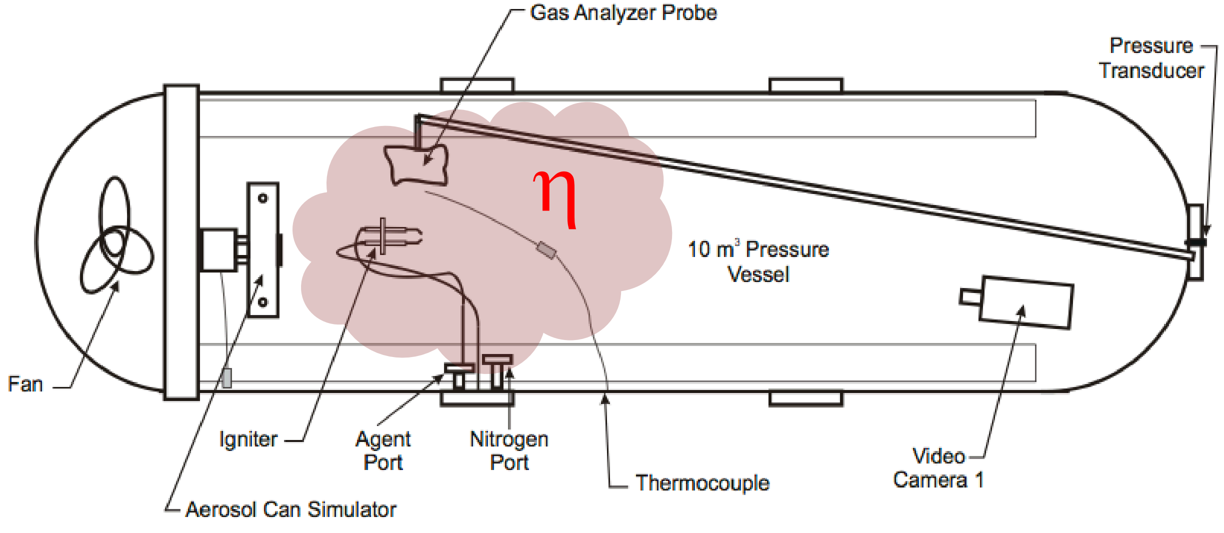
The work was supported by The Boeing Company, NIST Internal Funds, ARRA Grant.

FAA-Aerosol Can Test (FAA-ACT)

Goal: Understand the overpressure phenomena in the FAA Aerosol Can Test

1. Why is the overpressure occurring with the added suppressants—which were expected to inert the explosion?
2. Connection to refrigerants?


FAA Aerosol Can Test Chamber

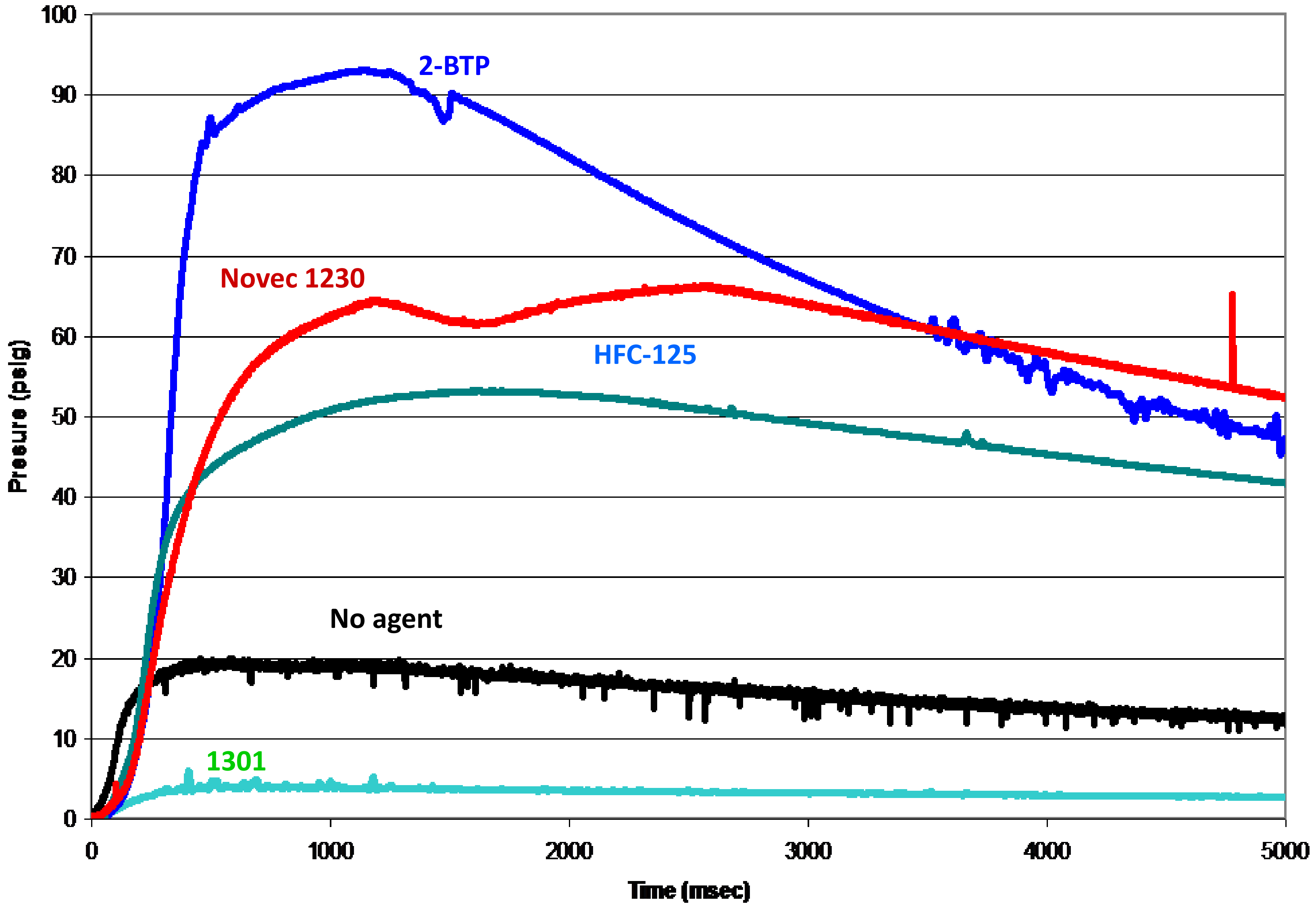


(Top View)

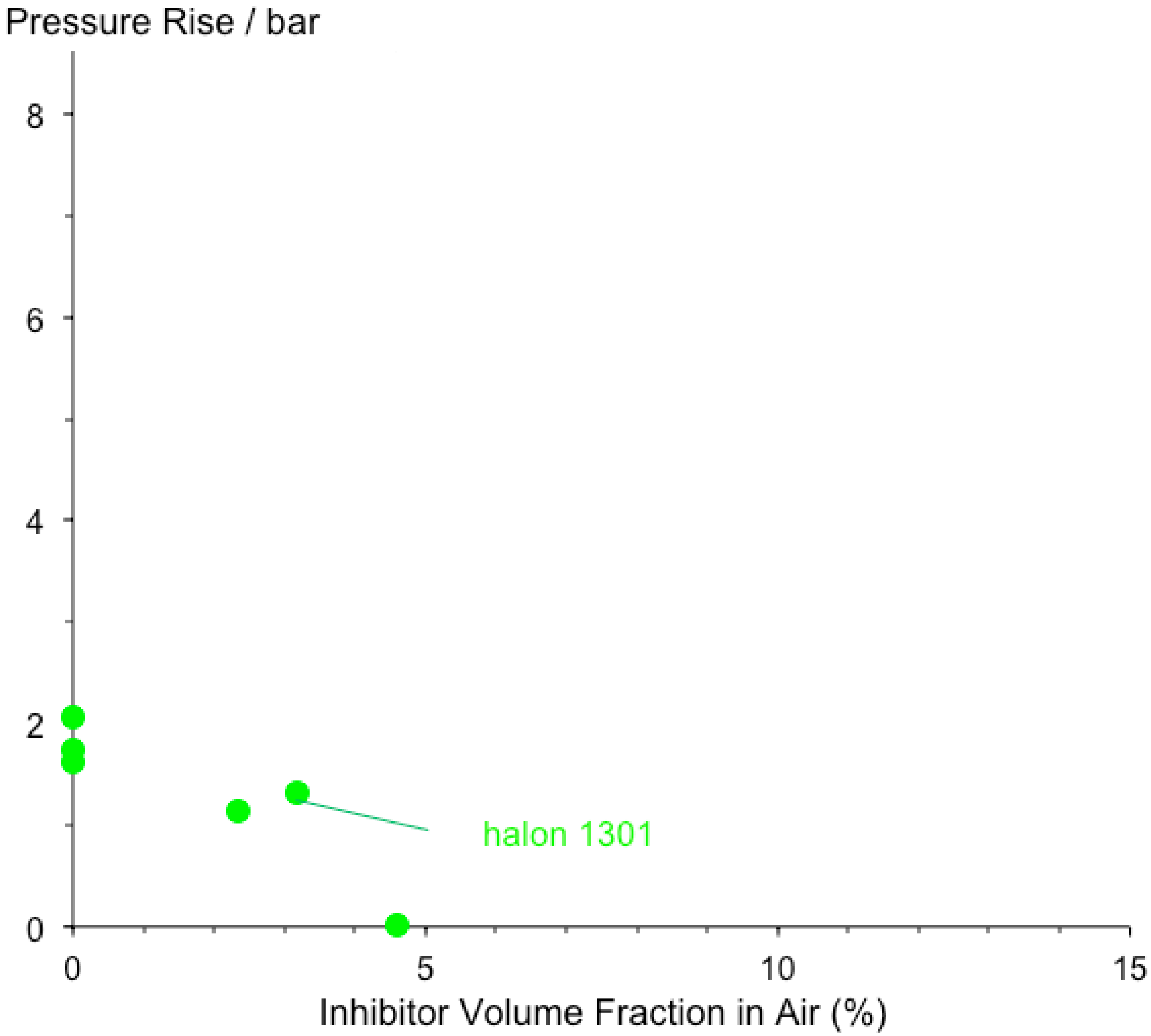
1. Pressure vessel (v= 11.4 m^3)
2. P_{init} ≈ 1.01 mPa ; T_{init} =13 ± 9 º
3. Fuel: ethanol+propane+water spray.
4. Ignition: constant high-voltage DC arc, (max 10 kV, 20 mA).

FAA-Aerosol Can Test (FAA-ACT)

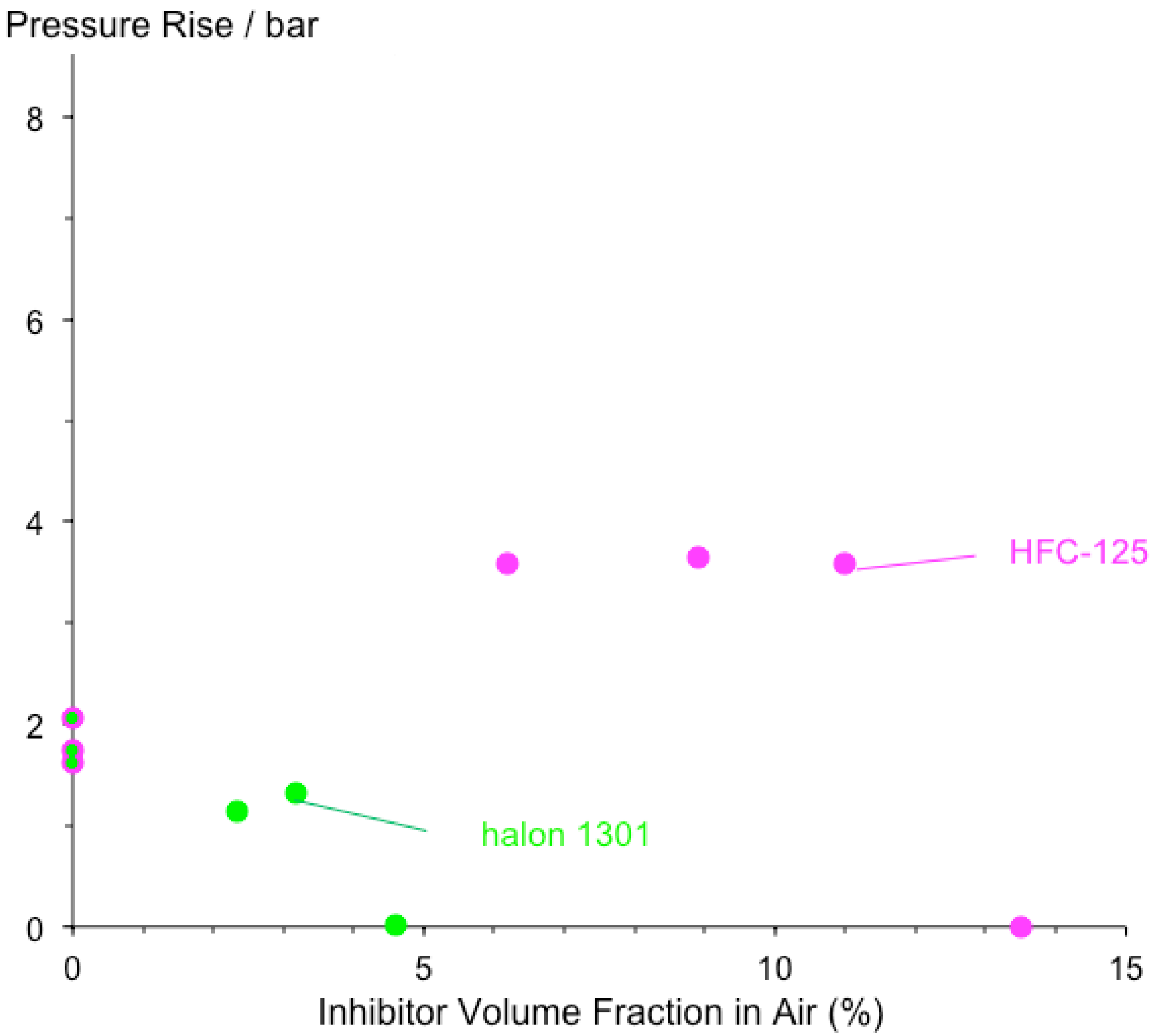
When added at sub-inerting concentrations, pressure rise is higher than with no agent.



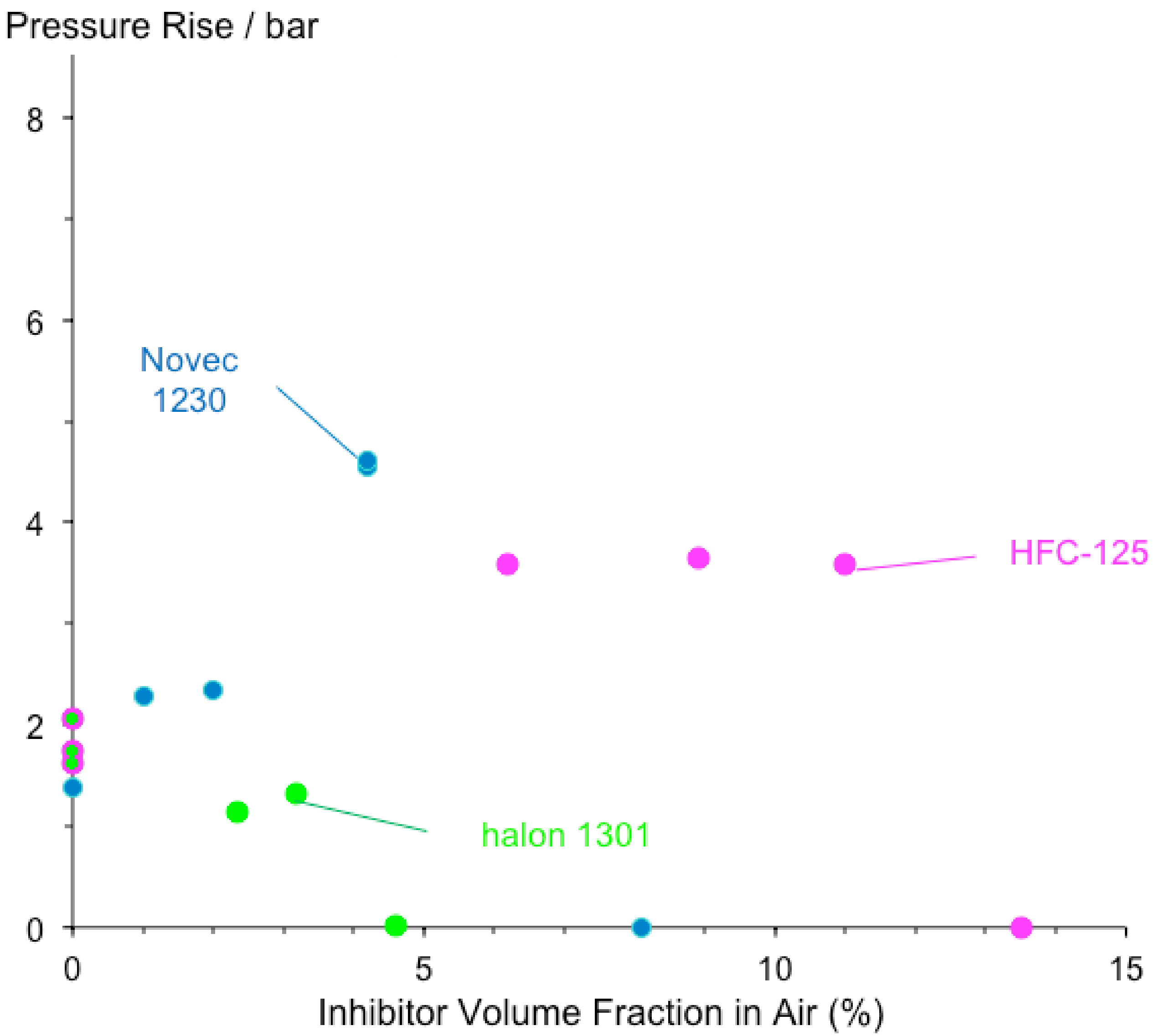
Pressure rise in FAA-ACT with added suppresants



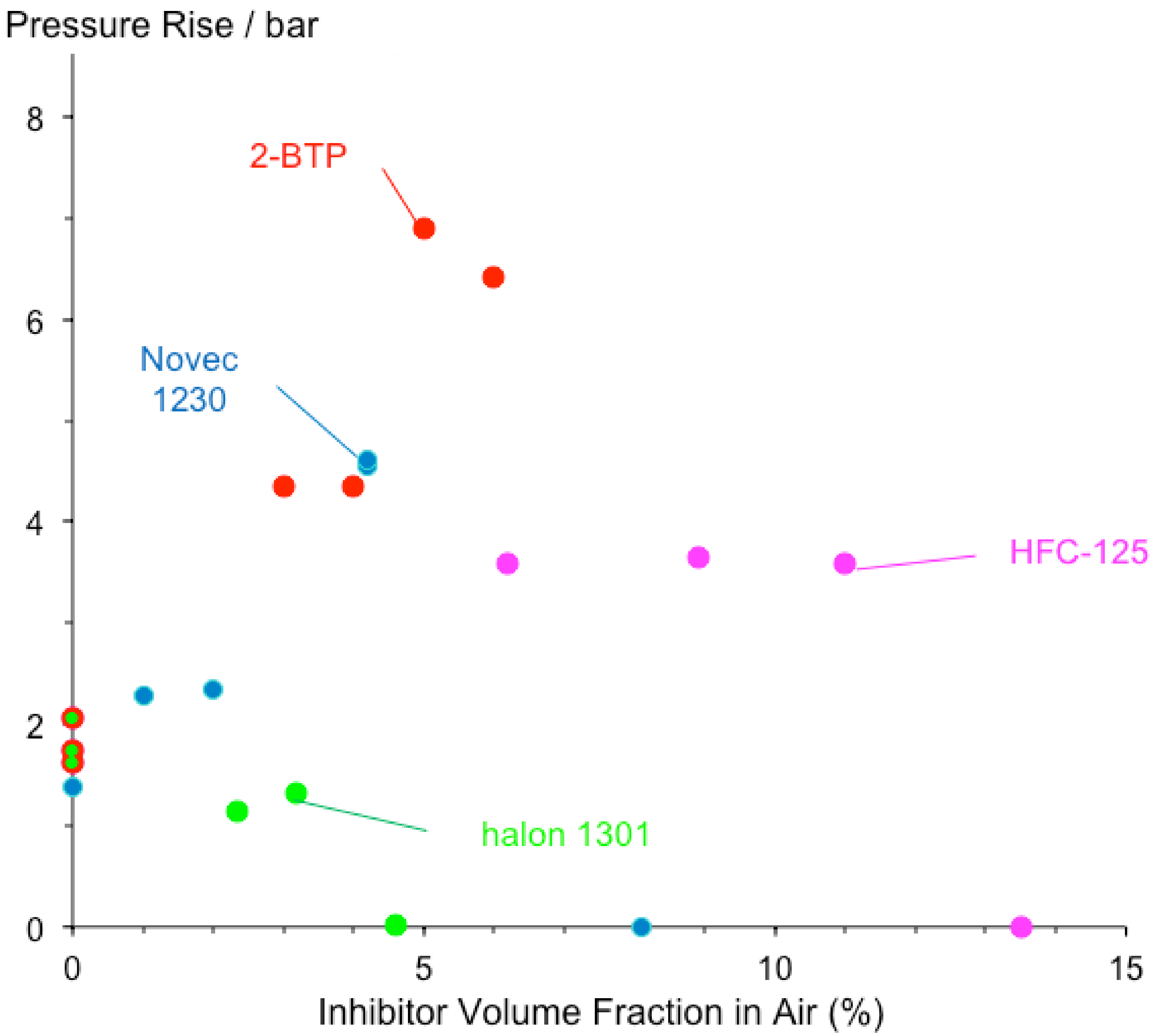
Pressure rise in FAA-ACT with added suppresants



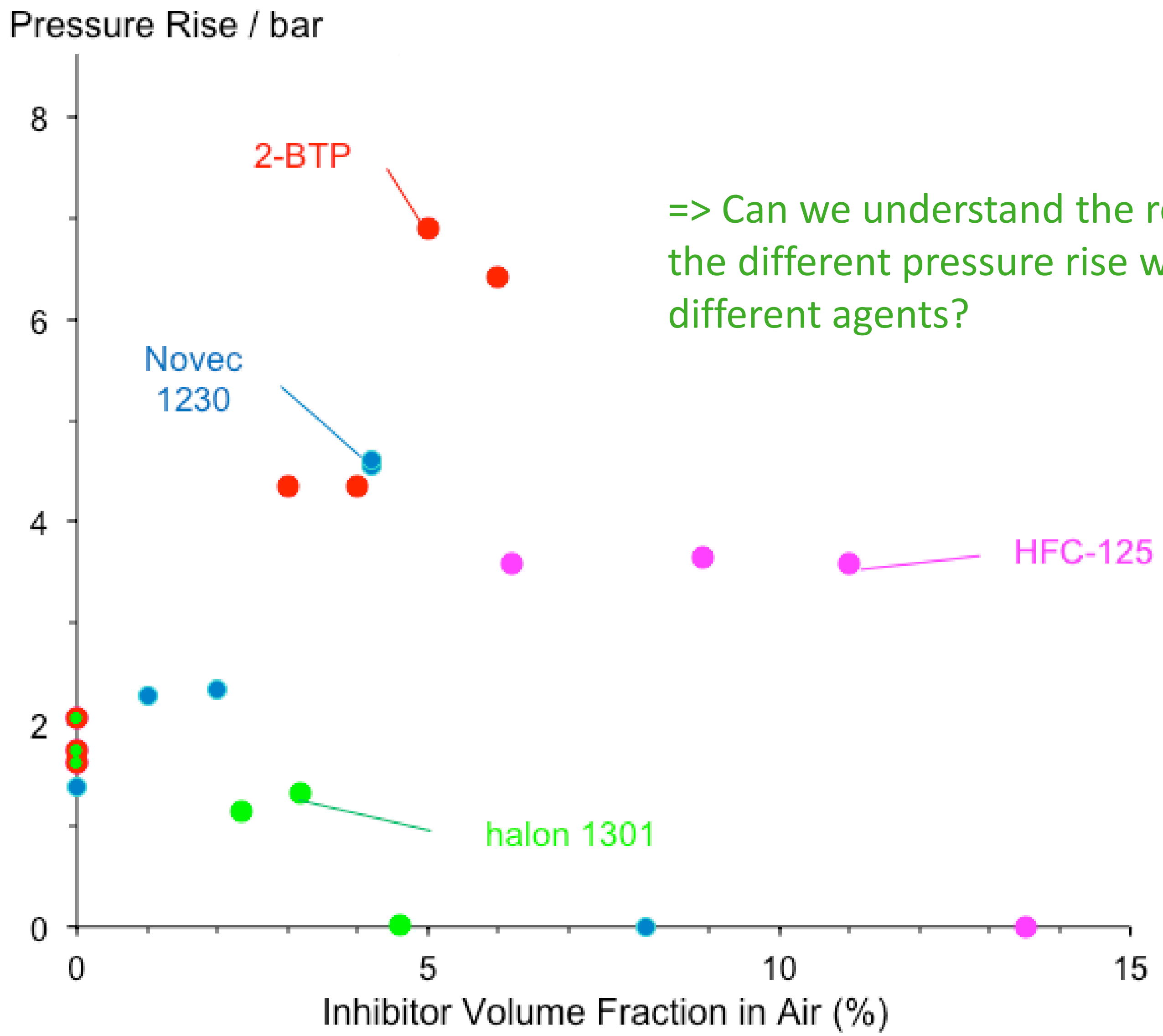
Pressure rise in FAA-ACT with added suppresants



Pressure rise in FAA-ACT with added suppresants



Pressure rise in FAA-ACT with added suppresants



=> Can we understand the reasons for the different pressure rise with the different agents?

To Estimate Pressure Rise: Use Thermodynamics

Assume fuel and oxidizer mix in ratio which gives peak temperature (like a typical diffusion flame).

η – fraction of chamber oxidizer that reacts.
$1-\eta$ – fraction of chamber oxidizer that is inert.

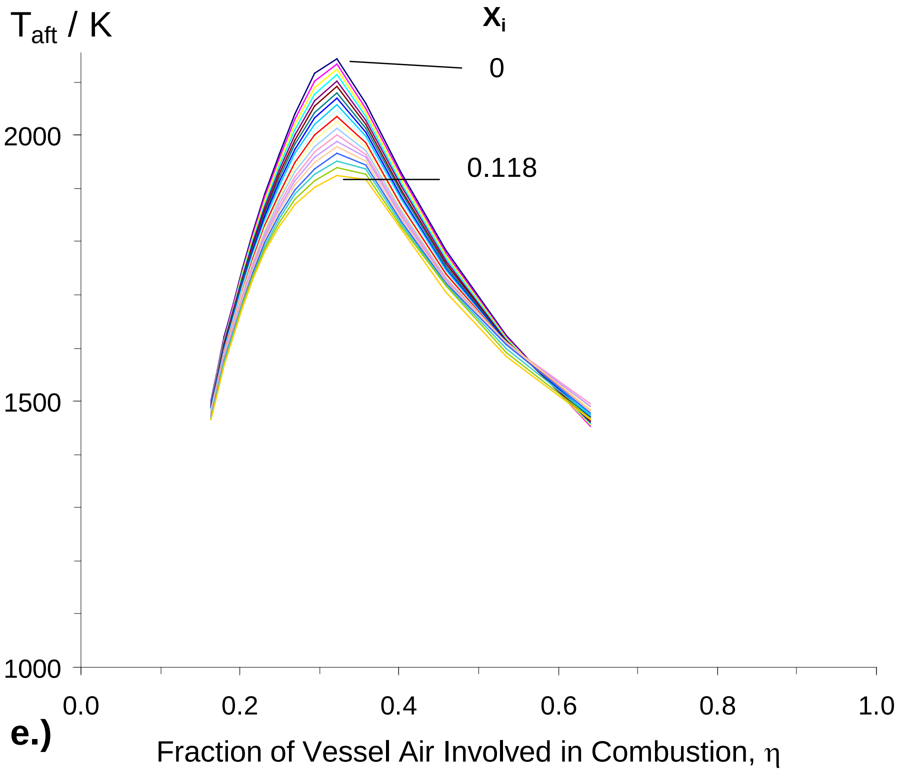
Find η as that which gives peak T_{ad}.

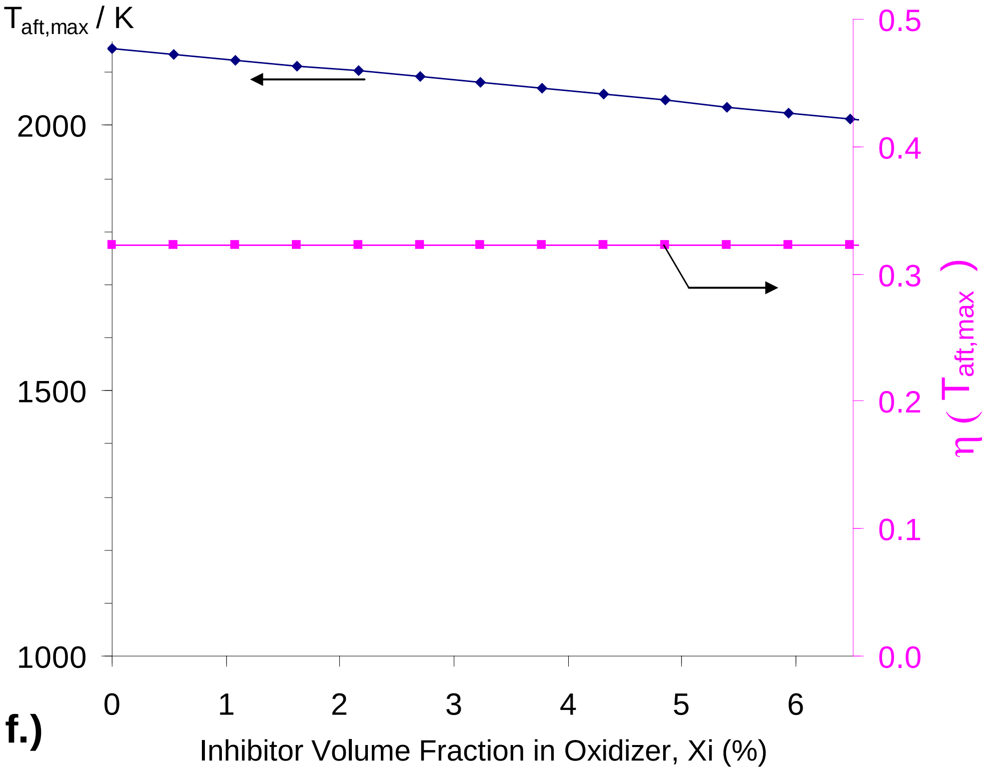
Let reacting (η)fraction go to equilibrium products.

Mix with inert ($1-\eta$) fraction.

Halon 1301: Adiabatic Flame Temperature (T_{ad})

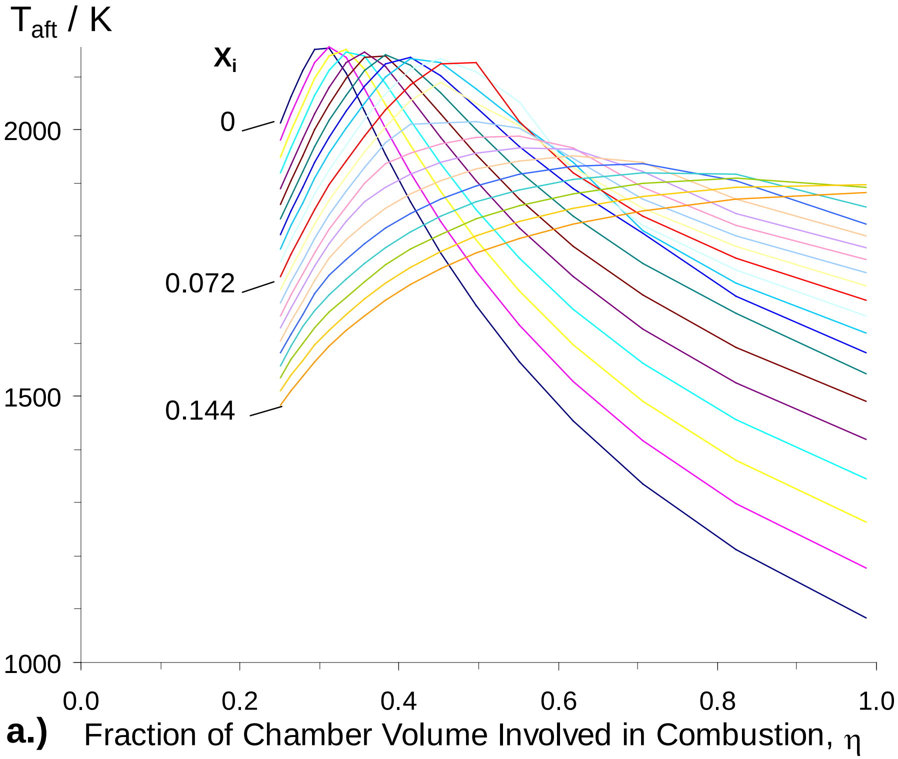
Thermodynamic Equilibrium Calculations



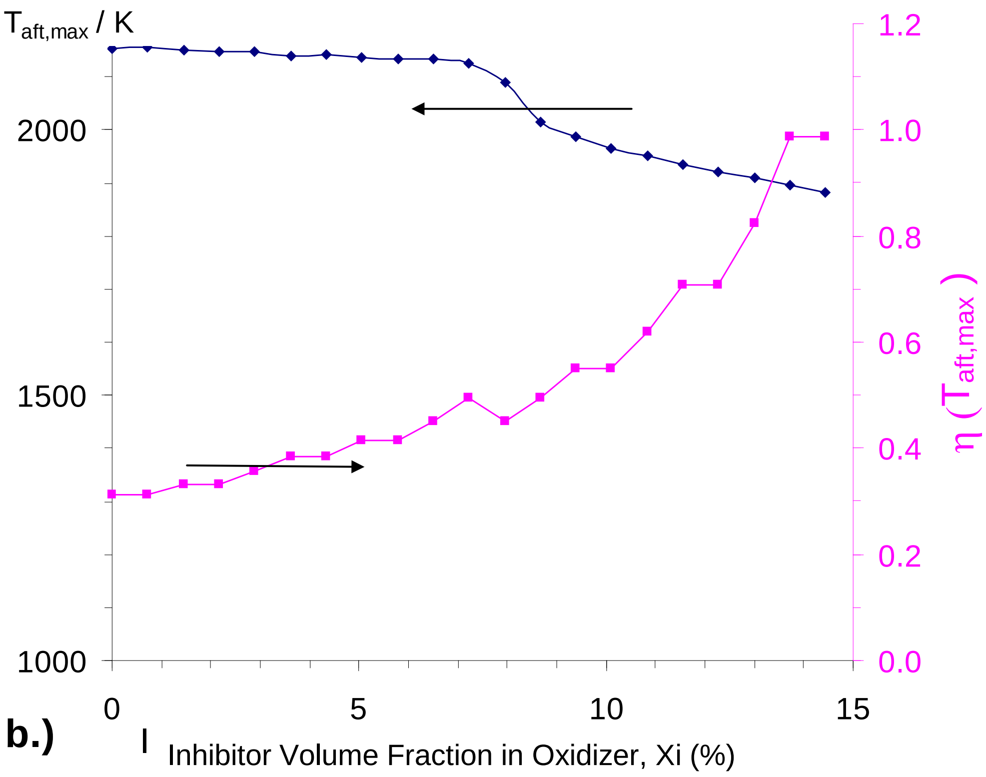


HFC-125: Adiabatic Flame Temperature (T_{ad})

Thermodynamic Equilibrium Calculations

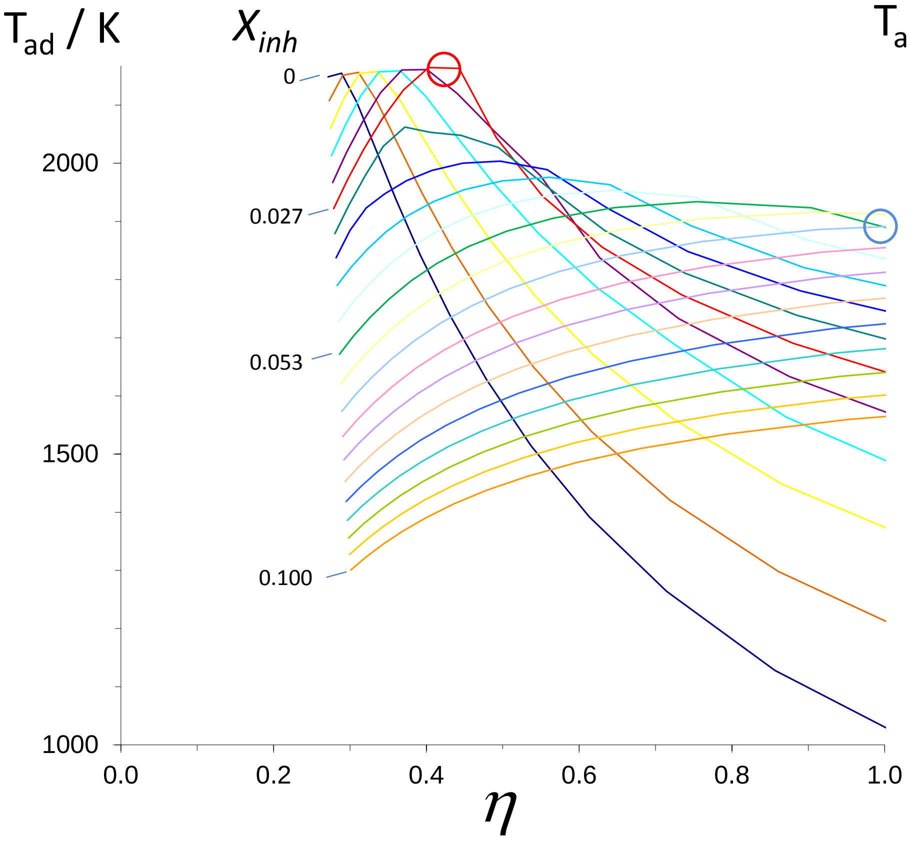


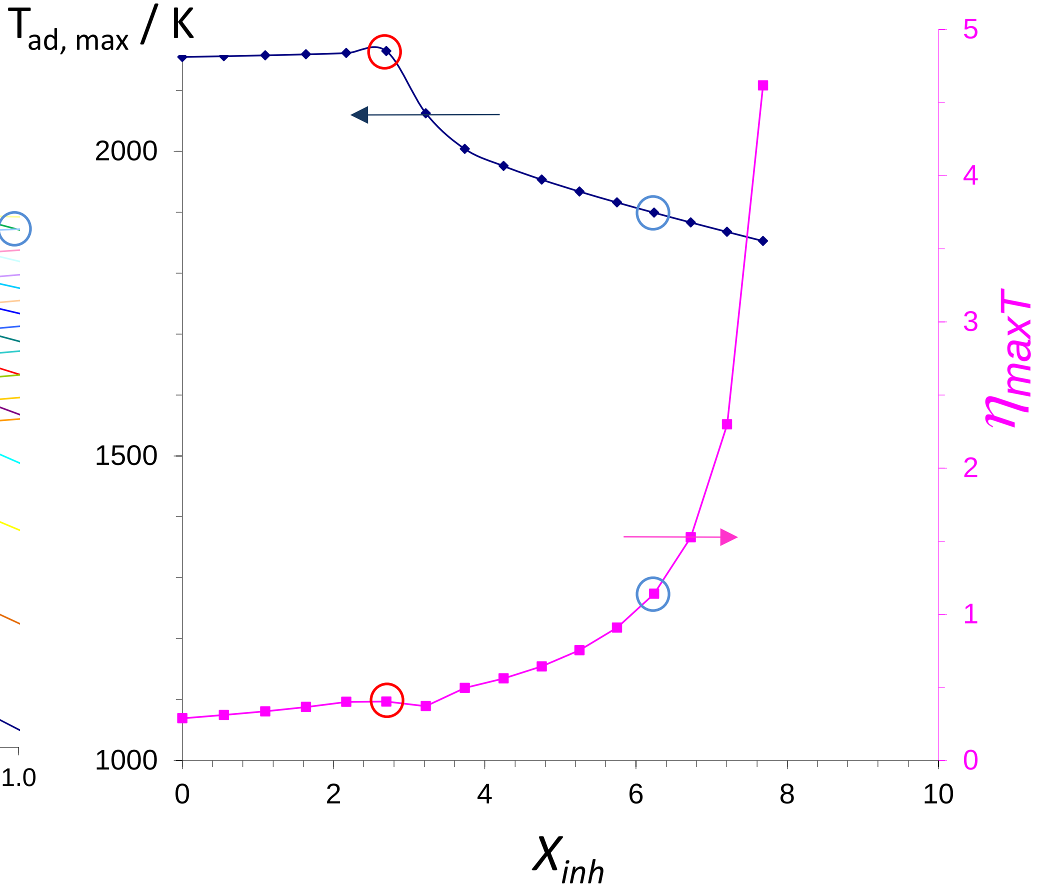
a.)



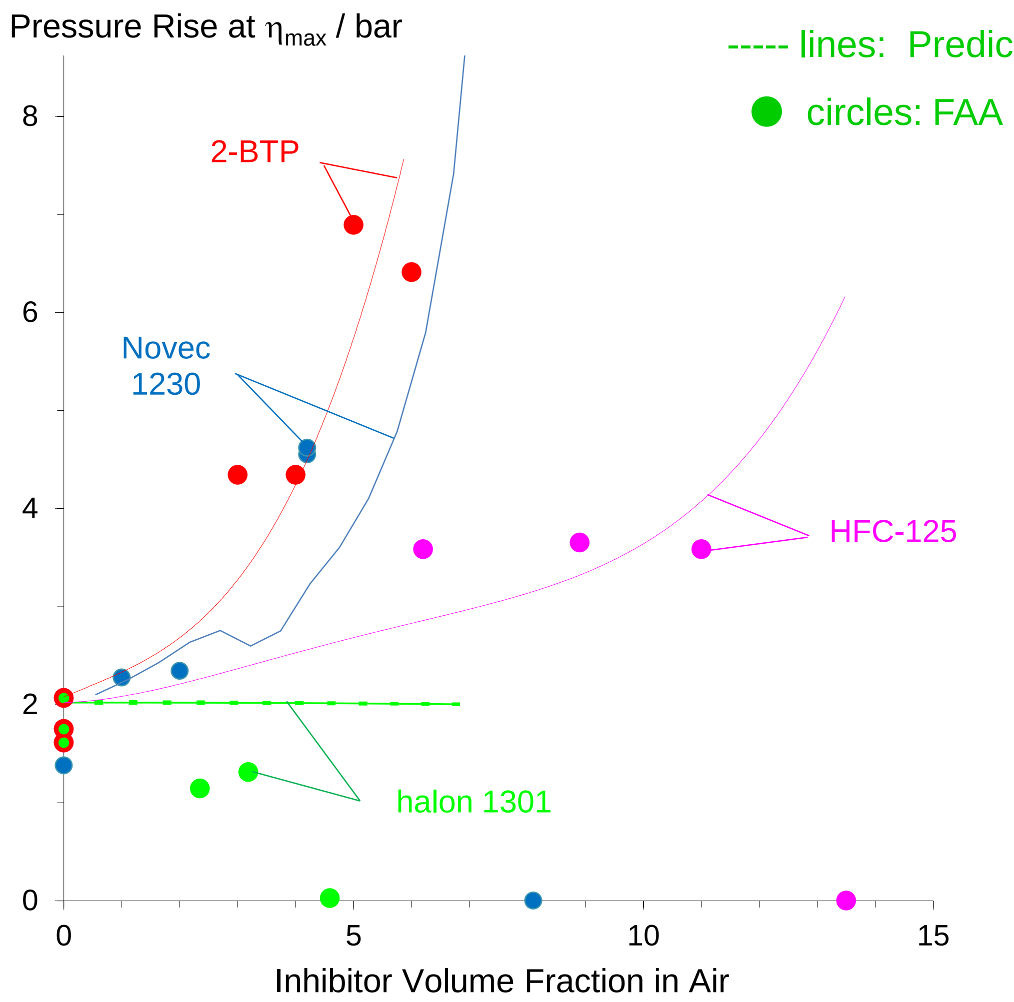
b.)

Novec 1230: Adiabatic Flame Temperature (T_{ad})





For most agents, pressure rise can be predicted based on thermodynamics.



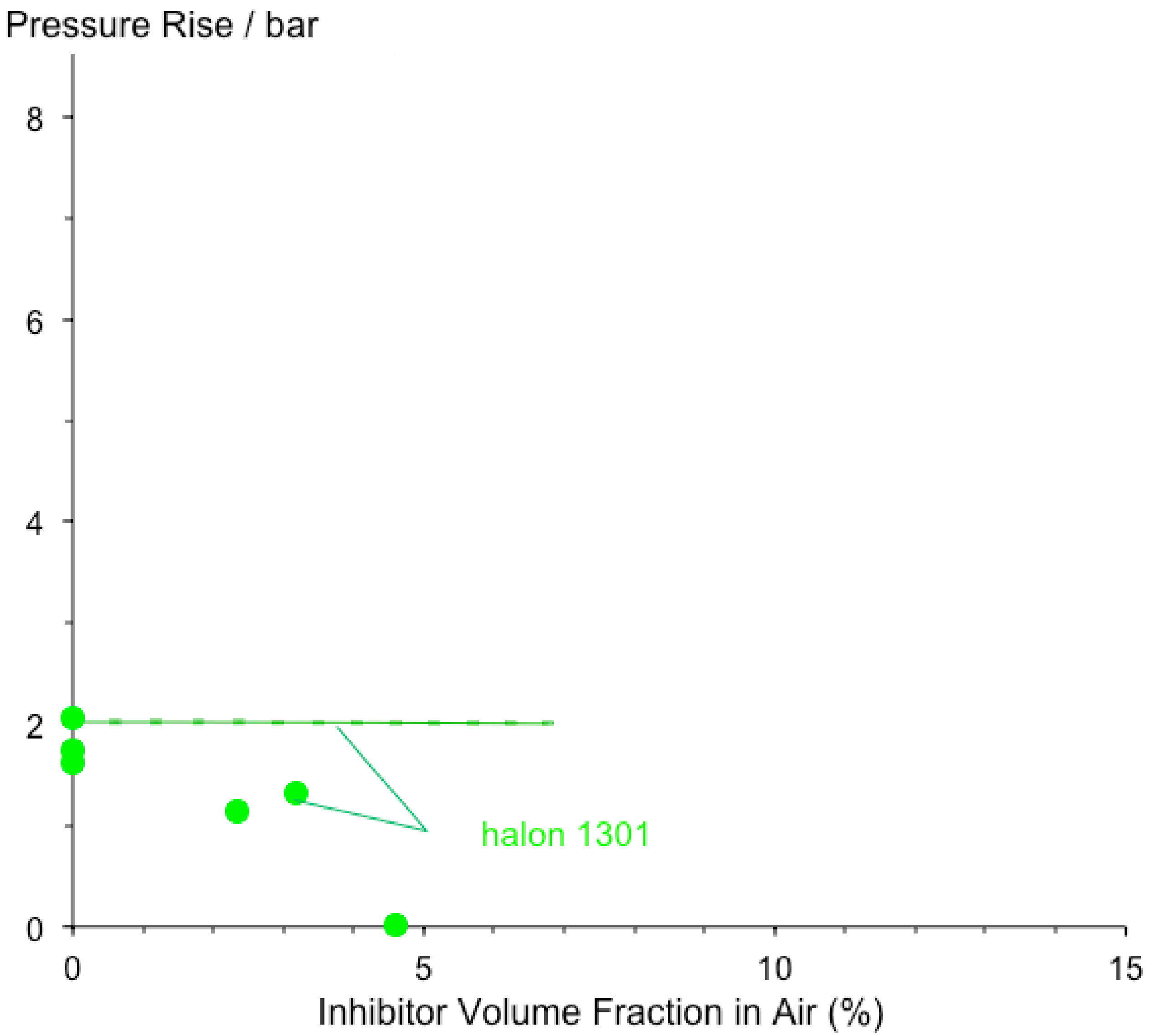
----- lines: Predictions.

● circles: FAA Experimental Results

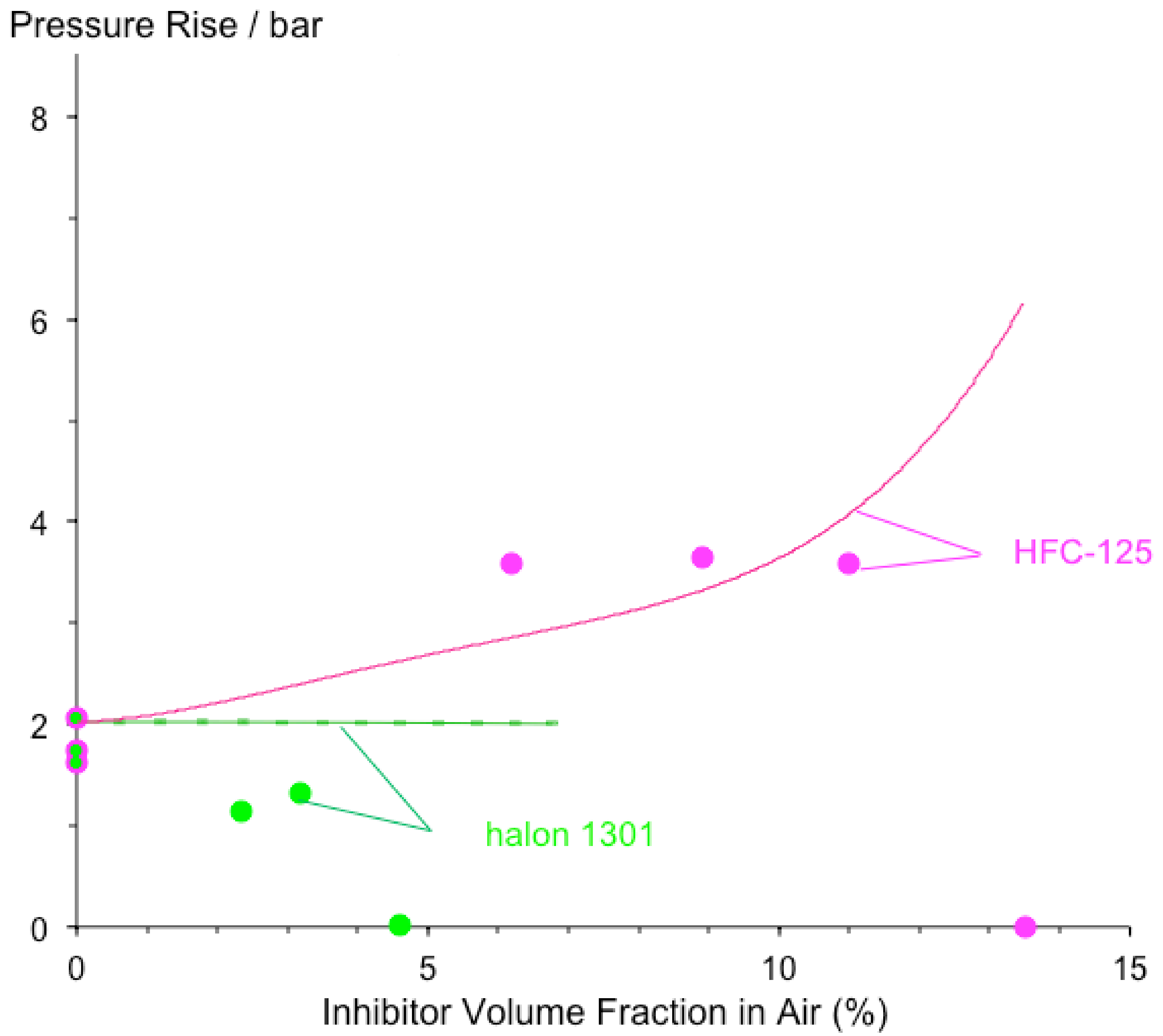
- Thermodynamics determines possible pressure rise.
- Kinetics determines fraction of pressure rise achieved.
- For the alternative agents, kinetics is generally not important except at the inertion point.

Return

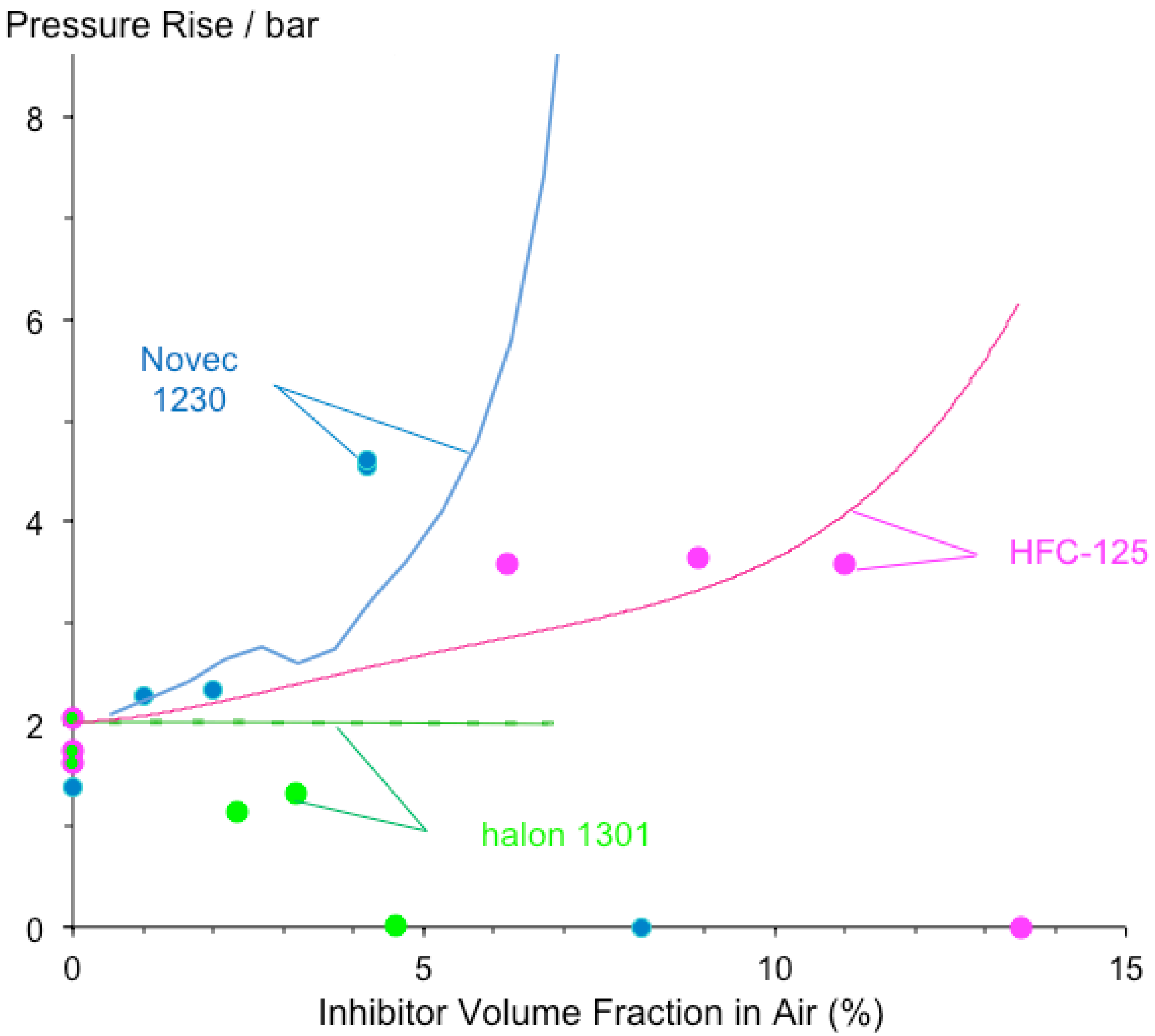
Predicted vs. measured pressure rise in FAA-ACT with added suppresants



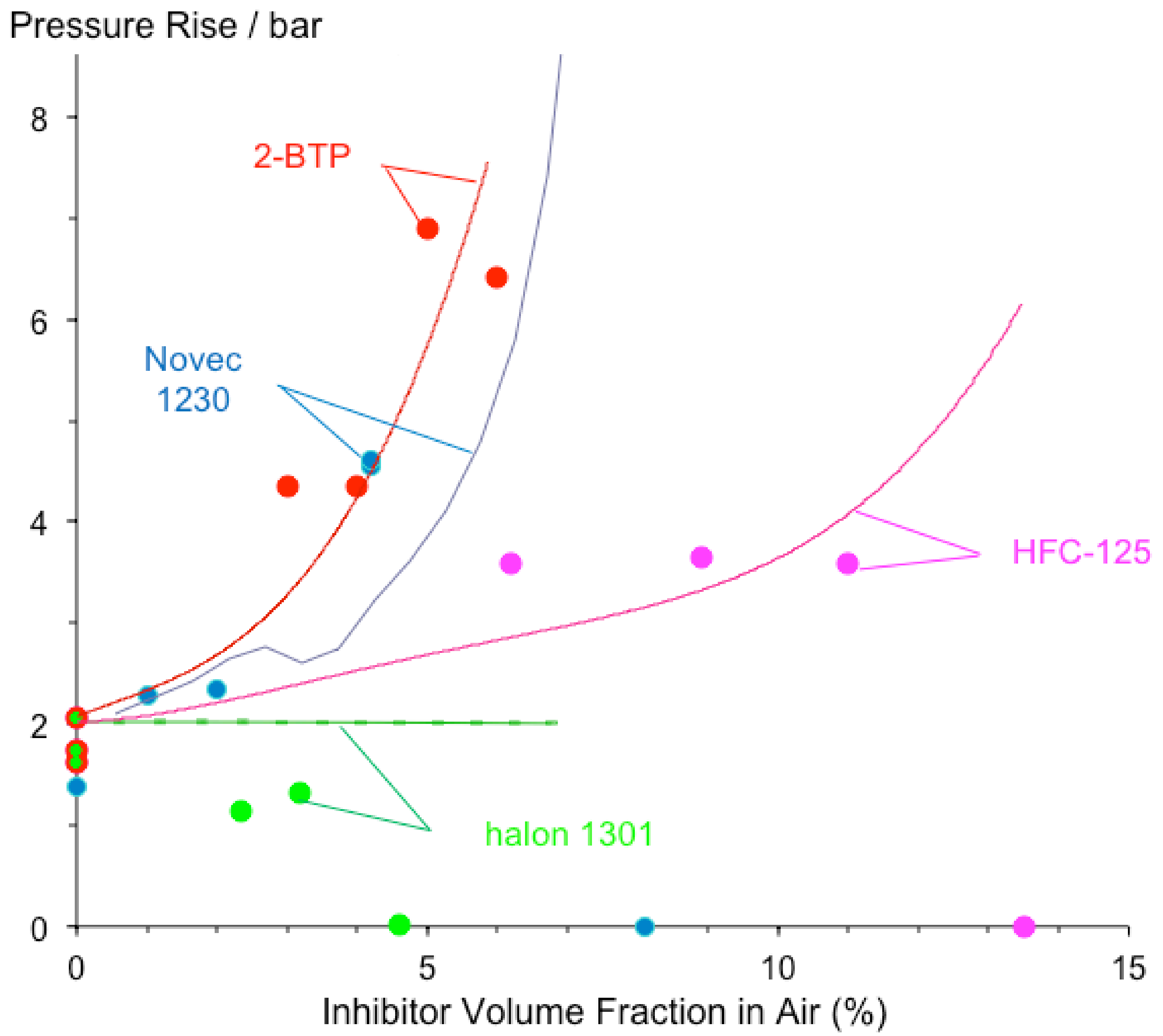
Predicted vs. measured pressure rise in FAA-ACT with added suppresants



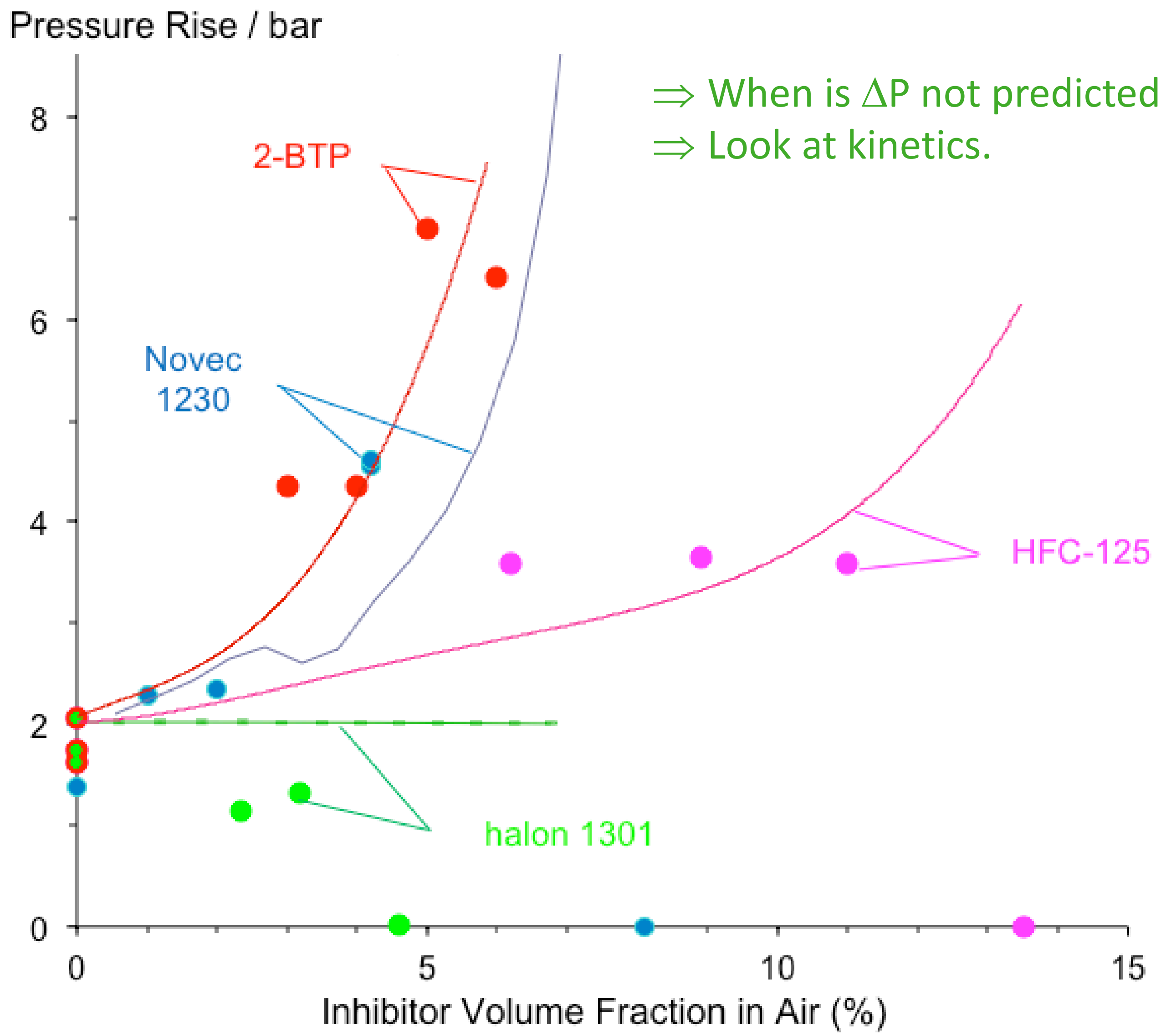
Predicted vs. measured pressure rise in FAA-ACT with added suppresants



Predicted vs. measured pressure rise in FAA-ACT with added suppresants



Predicted vs. measured pressure rise in FAA-ACT with added suppresants



⇒ When is ΔP not predicted well?

⇒ Look at kinetics.

Kinetic limitations to pressure rise in FAA-ACT

Estimate variation in overall reaction rate with:

- Agent type
- X_{inh}
- η

To do this, we need:

- A kinetic mechanism.
- A reaction rate measure.
- The reactants.

Kinetic Mechanism*

Aerosol Can Test Kinetic Model	Species	Reactions	Type
C_3-C_4 Hydrocarbon mechanism (Wang et al.) with C_2H_50H reactions (Dryer et al.)	116	820	Acquired
NIST C_1, C_2 HFC, for hydrocarbon flame inhibition + update for pure flames	171	1467	Updated, Developed
FM200	178	1504	Updated
Novec 1230	181	1513	Developed
CF_3Br	181	1568	Updated
CF_3I	181	1563	Updated
2-BTP	188	1609	Developed
HCFC-123	242	1959	Developed

* It should be emphasized that the mechanisms adopted for the present calculations should be considered only as a starting point. Numerous changes to both the rates and the reactions incorporated may be made once a variety of experimental and theoretical data are available for testing the mechanisms.

Reaction Rate Measure

Many available.

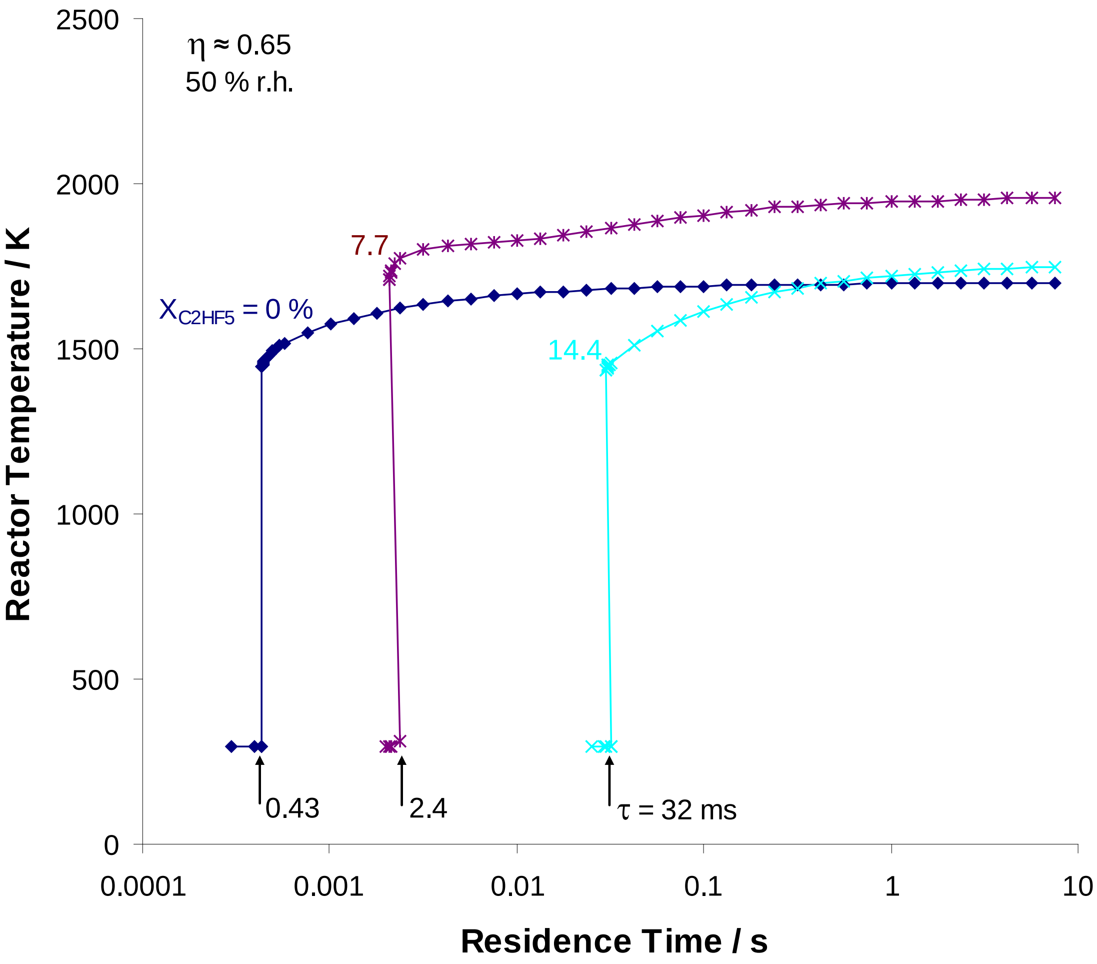
We use:
- Laminar burning velocity (S_L)
- Perfectly-stirred reactor (PSR) overall rate (ω_{psr}).

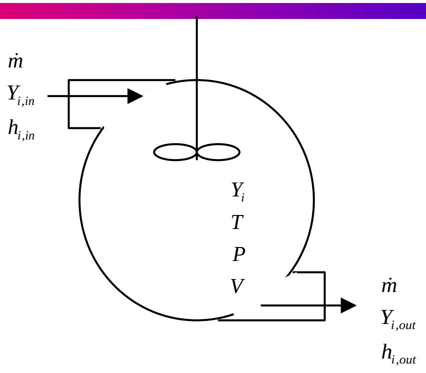
(these are related).

Both:
- measured or
- calculated

Using:
- detailed kinetic mechanisms and
- conservation equations.

Overall Chemical Rate from PSR (ω_{psr})





Just above the blowout flow rate,

$$\tau_{chem} = \tau_{res}$$

$$\omega_{psr} = 1 / \tau_{res} = 1/ \tau_{chem}$$

(estimate of overall chemical rate at T).

To find the blow-out condition:

- calculate T_{psr} at decreasing values of the residence time, τ_{res}.
- T_{psr} drops to inlet temperature at blow-out).

Reactants:

Get from:

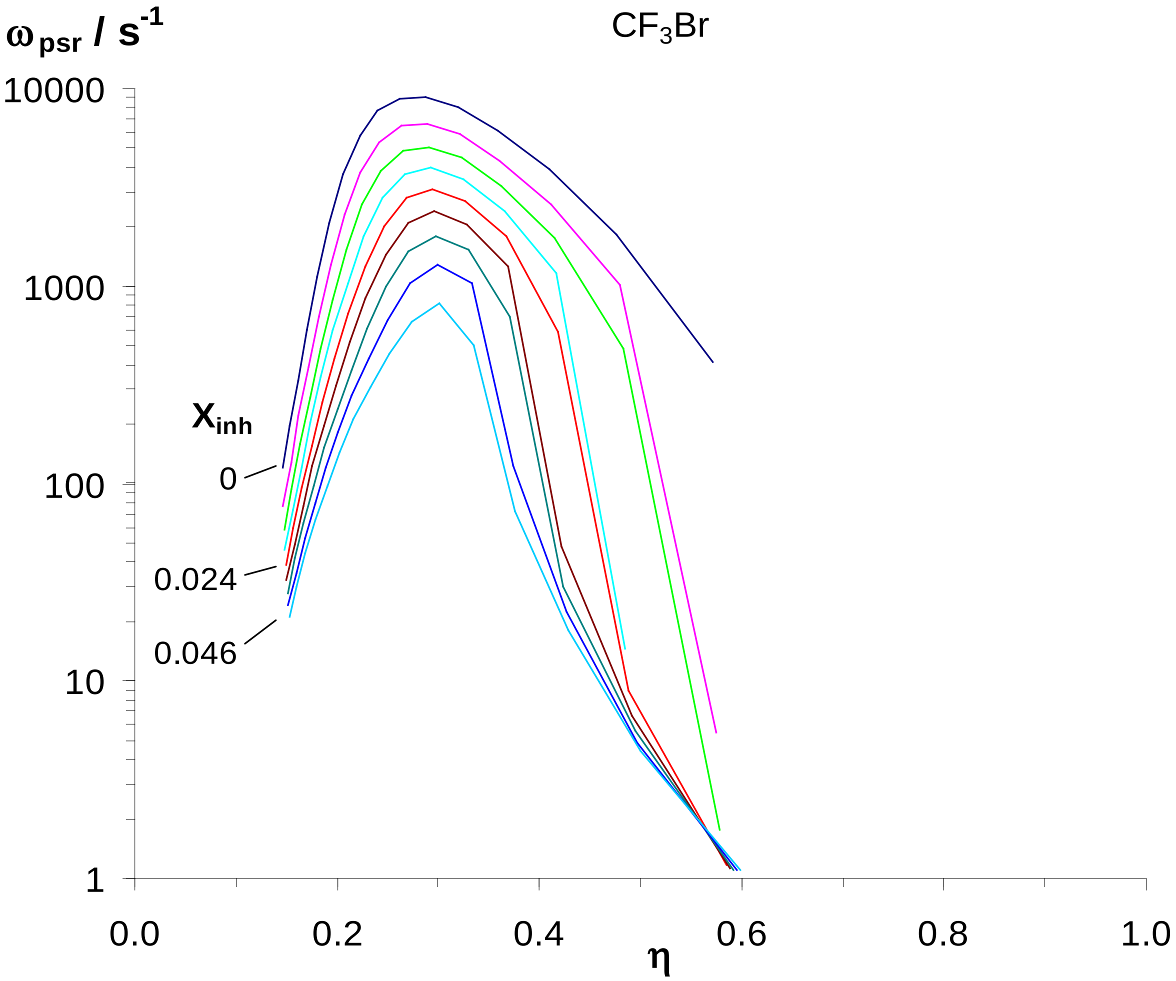
- initial loading of agent X_{inh} (specified)
- fuel-oxidizer ratio (η) (from that which gave peak T_{ad})

How does reaction rate of system vary with η and X_{inh}?

Perform PSR simulations over range of :

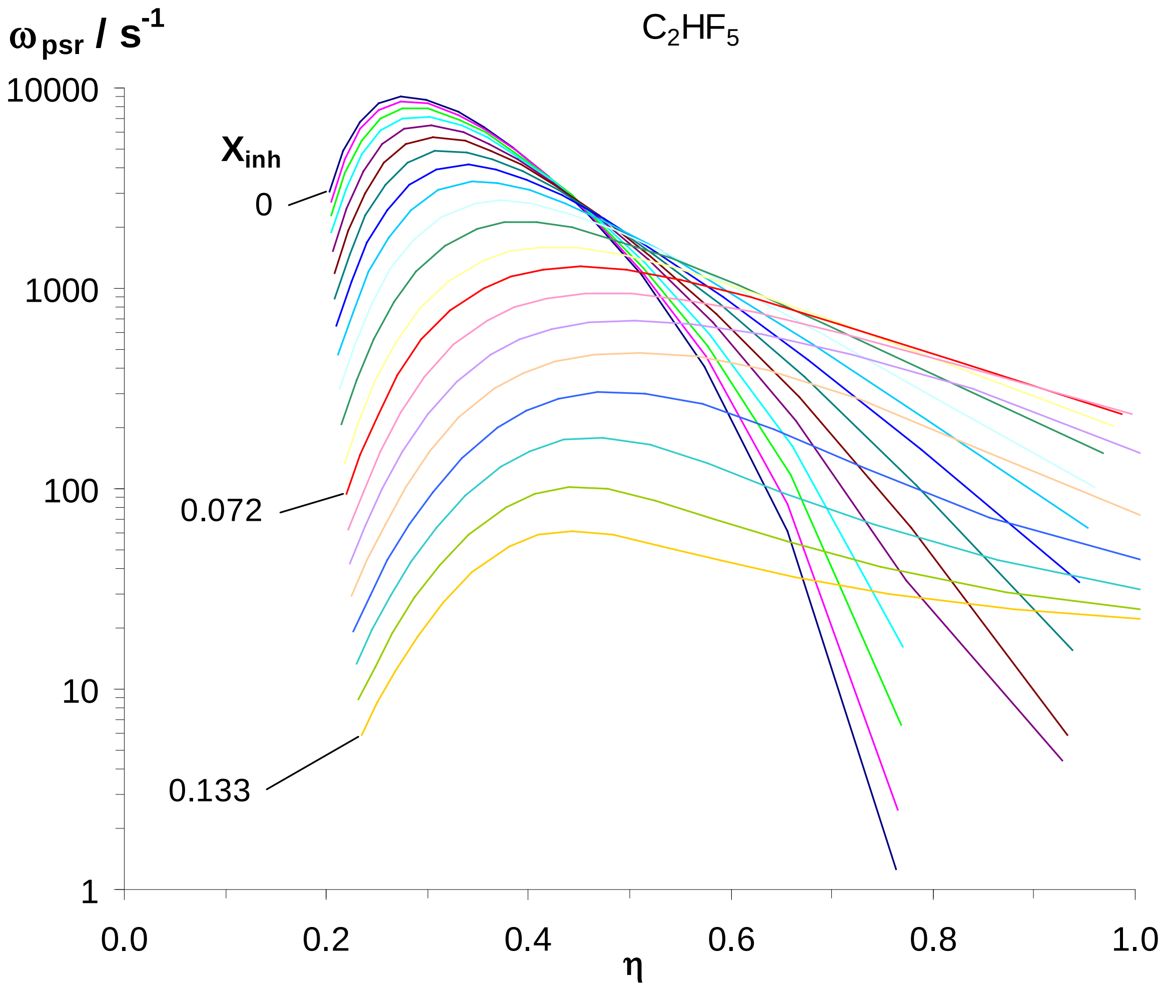
- Agent type
- X_{inh}
- η

Overall Chemical Rate with 1301



- Adding 1301 <u>always</u> lowers ω_{chem} (for all η)
- ω_{chem} falls off very steeply with η (for all X_{inh}; follows temperature results).

Overall Chemical Rate with R-125



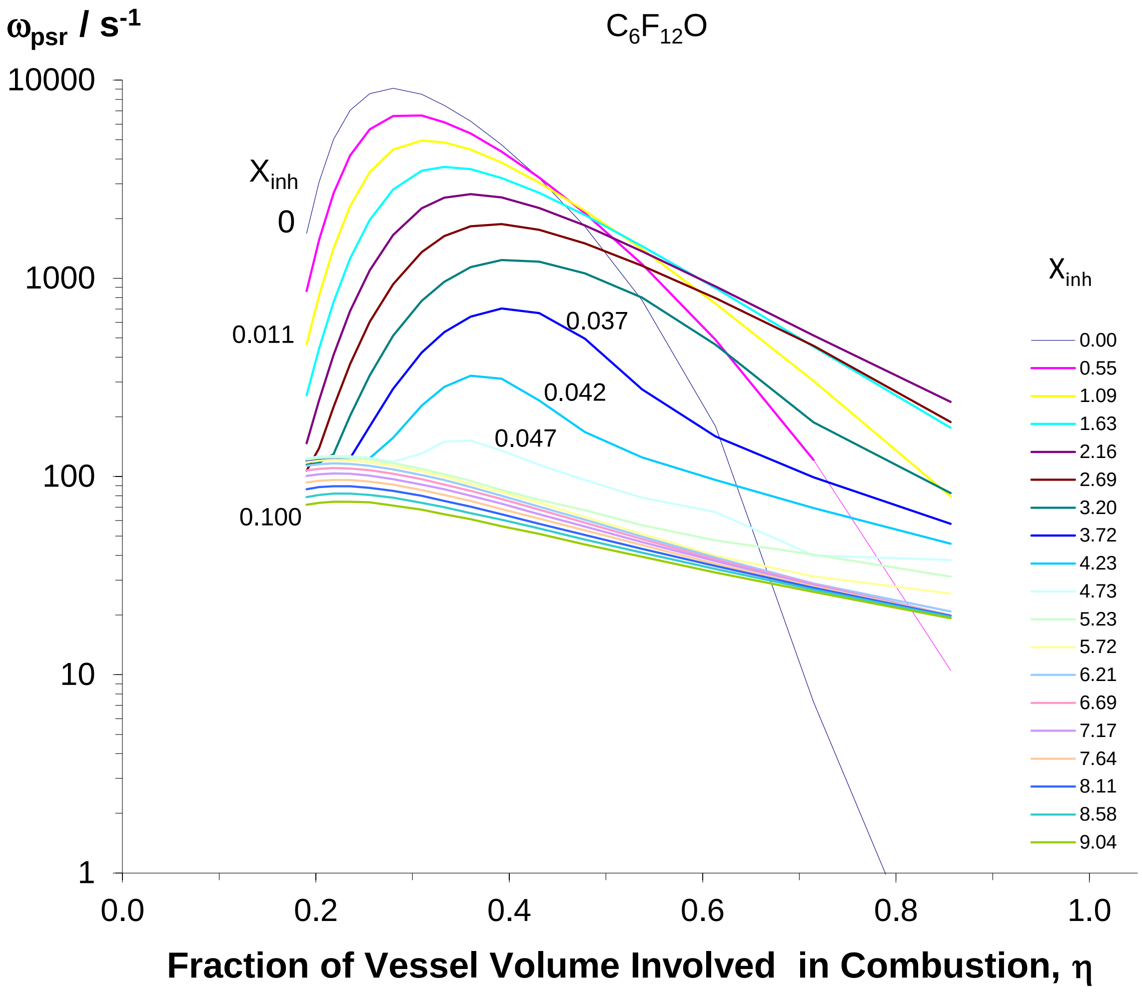
- Adding R-125 lowers ω_{chem} for rich mixtures (low η), but raises (then lowers) it for lean mixtures (high η).

–η has a big effect on overall chemical rate at low X_i, less effect at high X_i (follows temperature results).

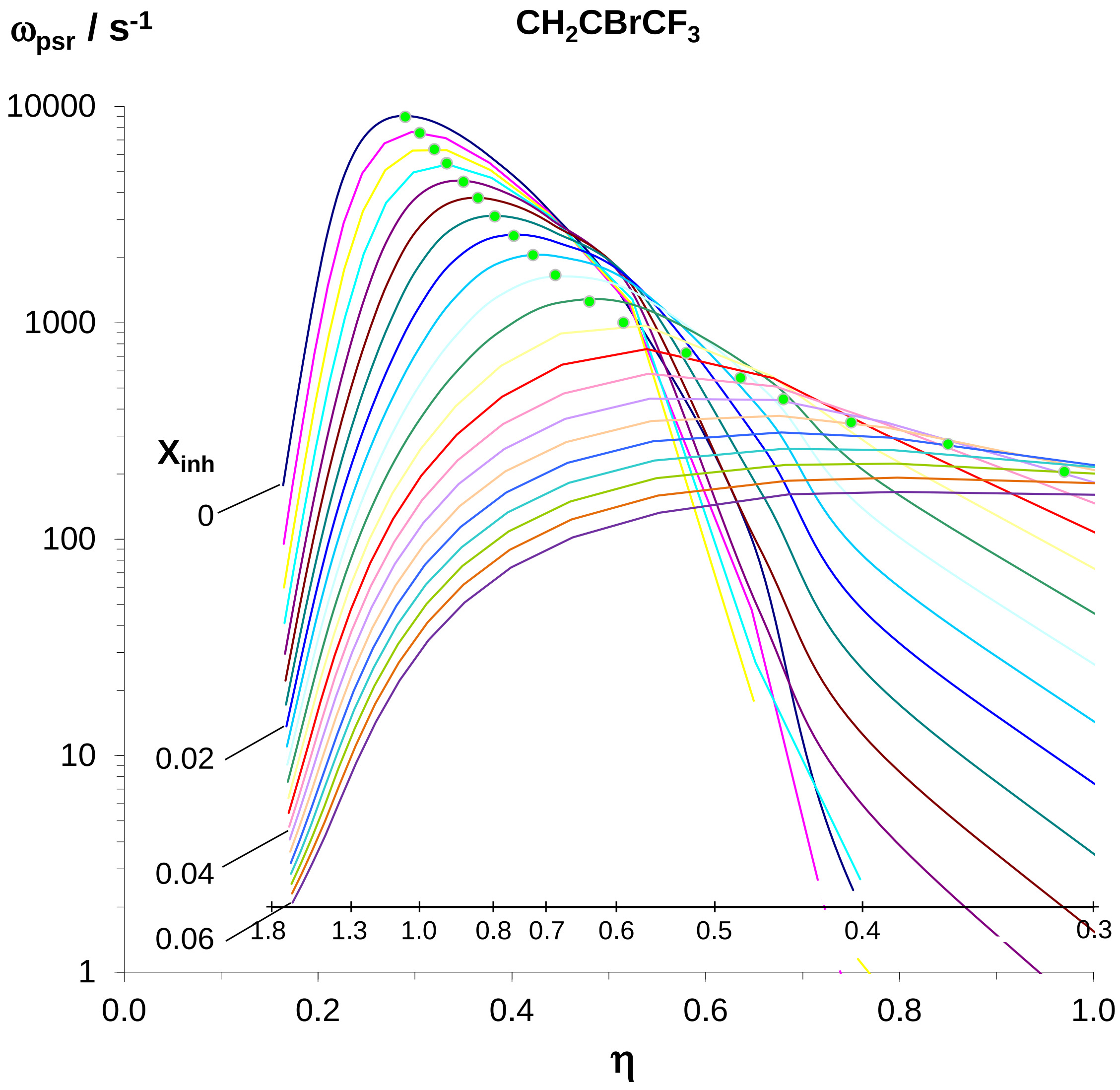
- i.e., for higher X_i, these curves flatten (ω_{chem} is insensitive to η for η > 0.4).

Perfectly-Stirred Reactor (PSR)

Overall Chemical Rate with Novec

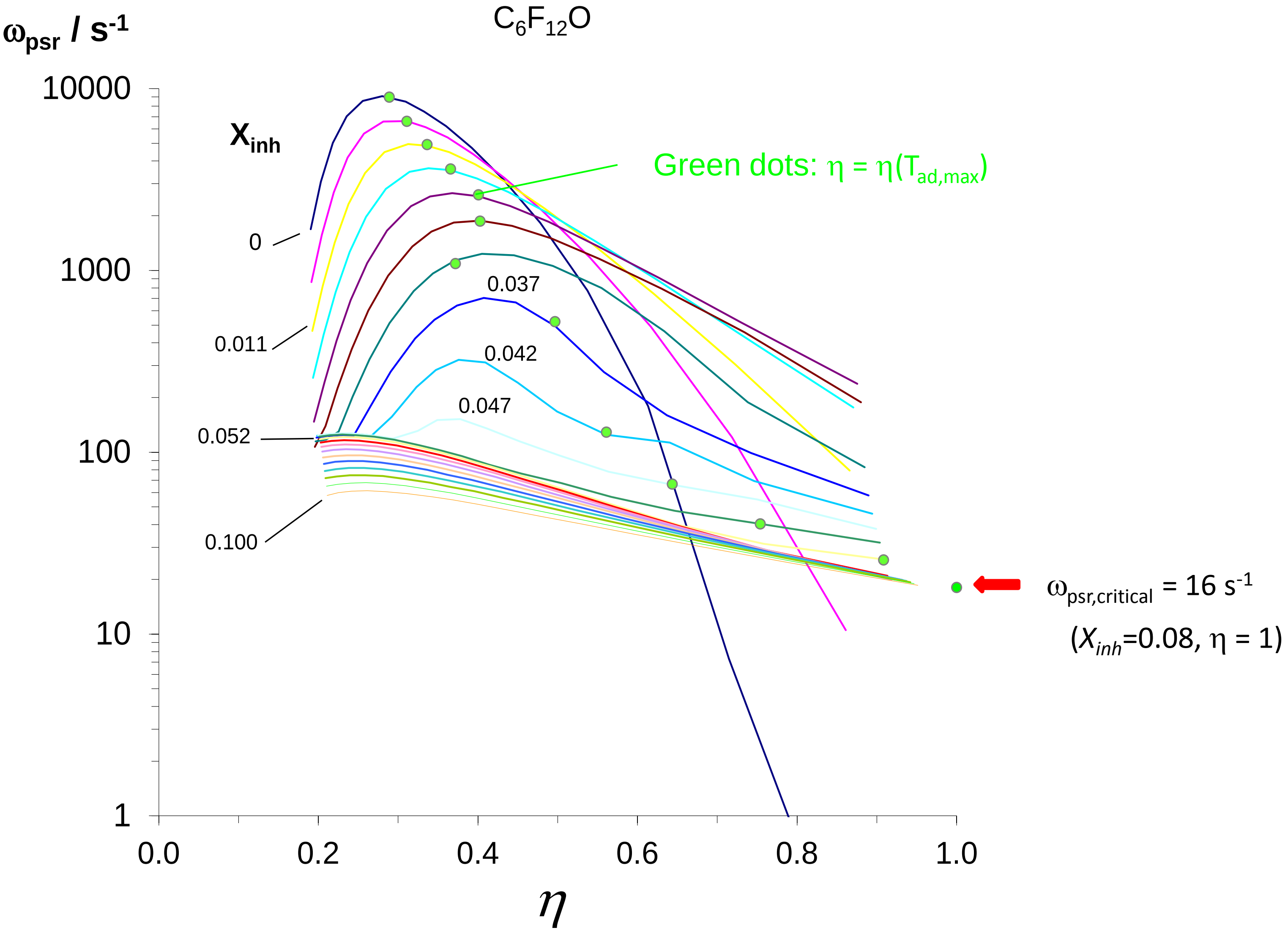


Use Pressure Rise to get η



Perfectly-Stirred Reactor (PSR) Novec 1230

Use Pressure Rise to get η

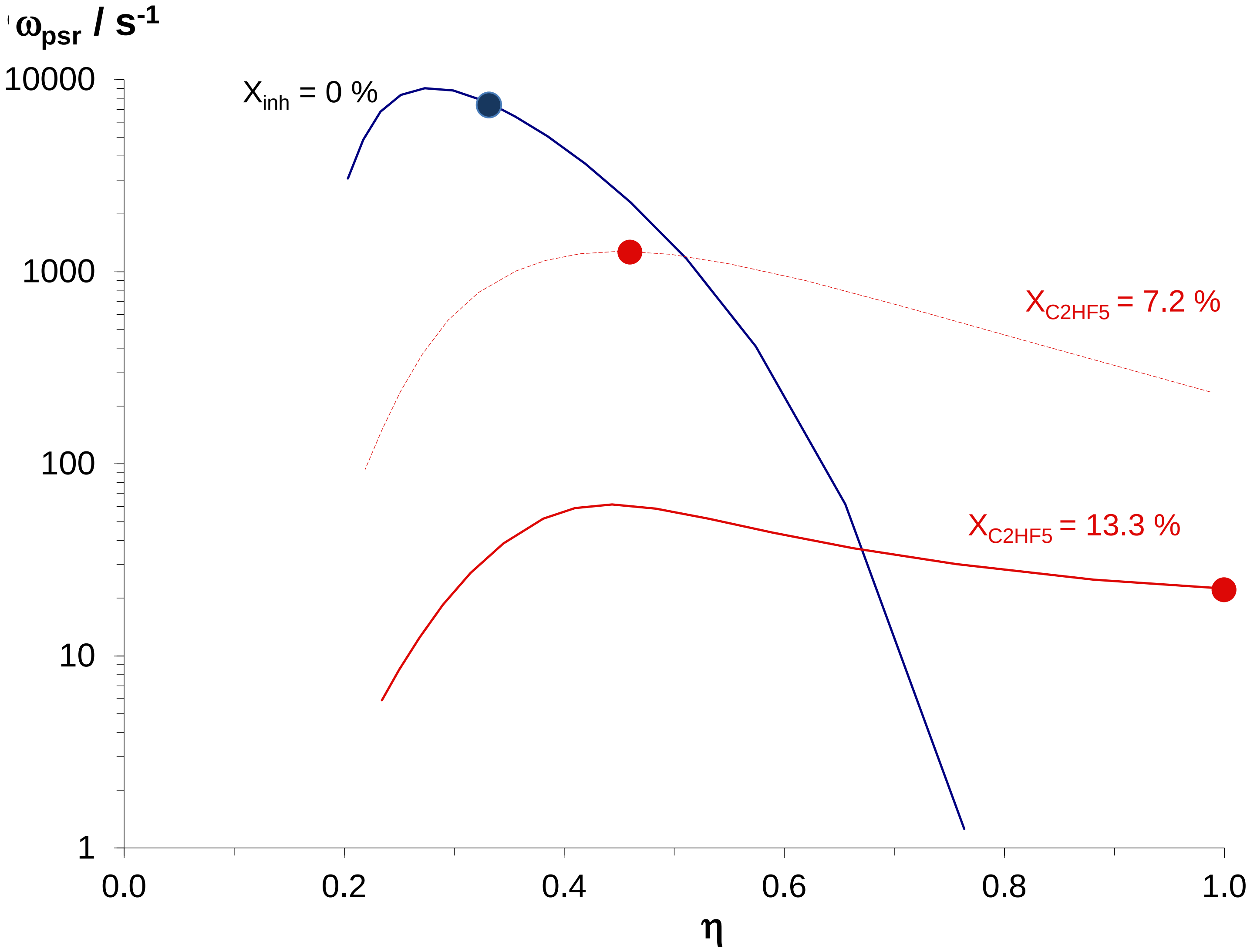


Kinetic Limitations to Pressure Rise

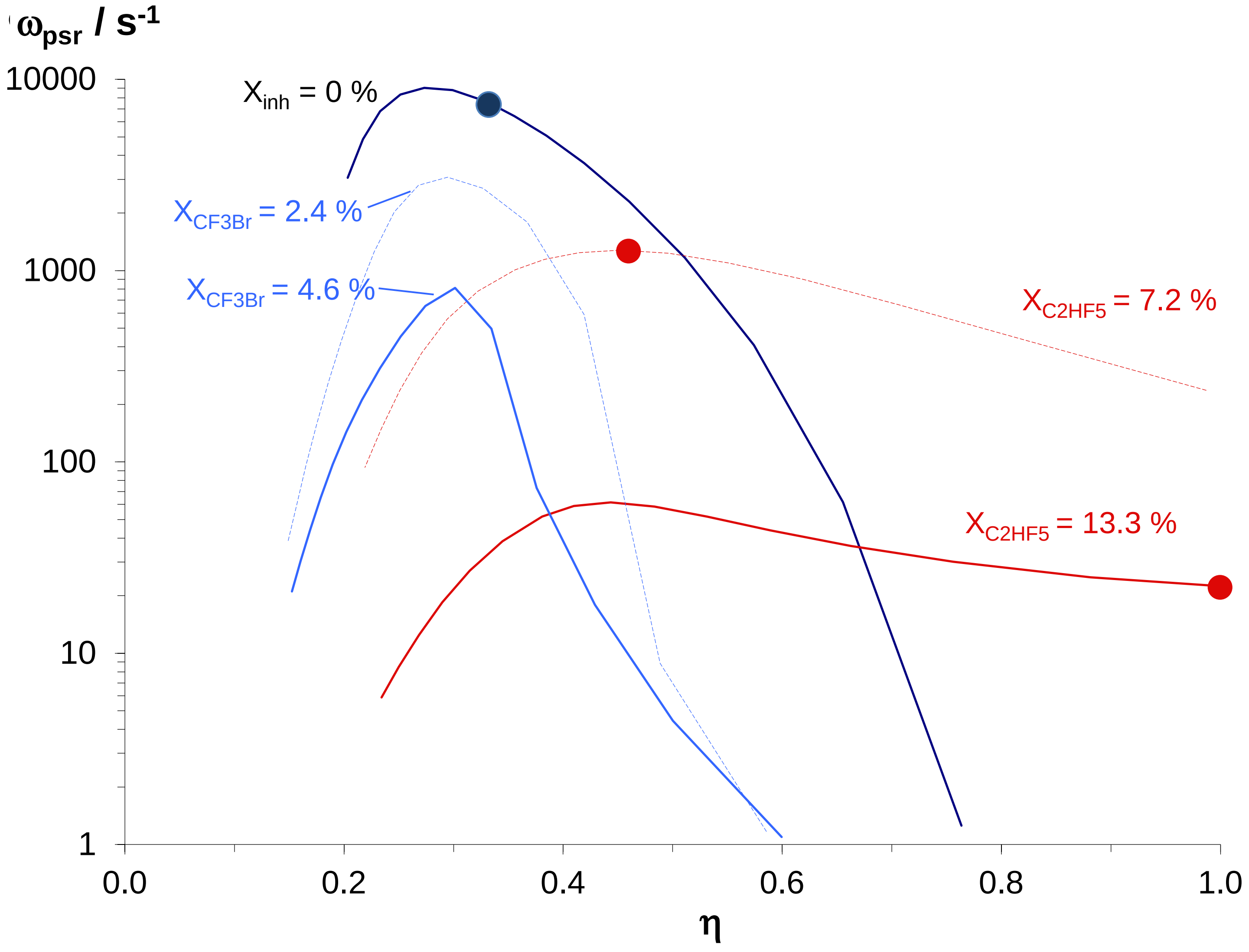
=> Want to compare ω_{psr} of alternative agents with that of CF_3Br.

But! We don't know η for CF_3Br.

Overall Reaction Rate with Added HFC-125 (η from ΔP)

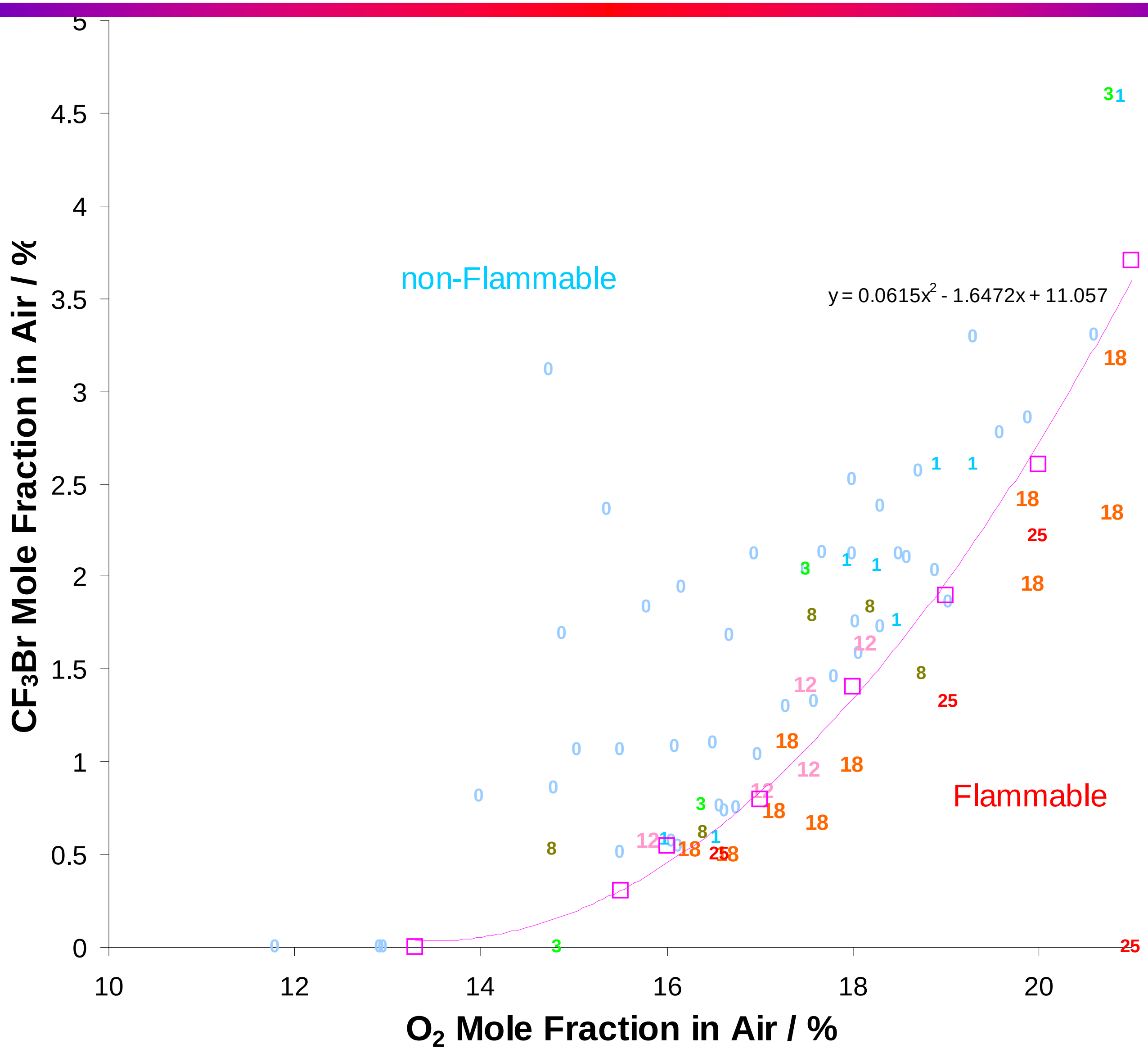


Overall Reaction Rate with Added CF_3Br (η ?)

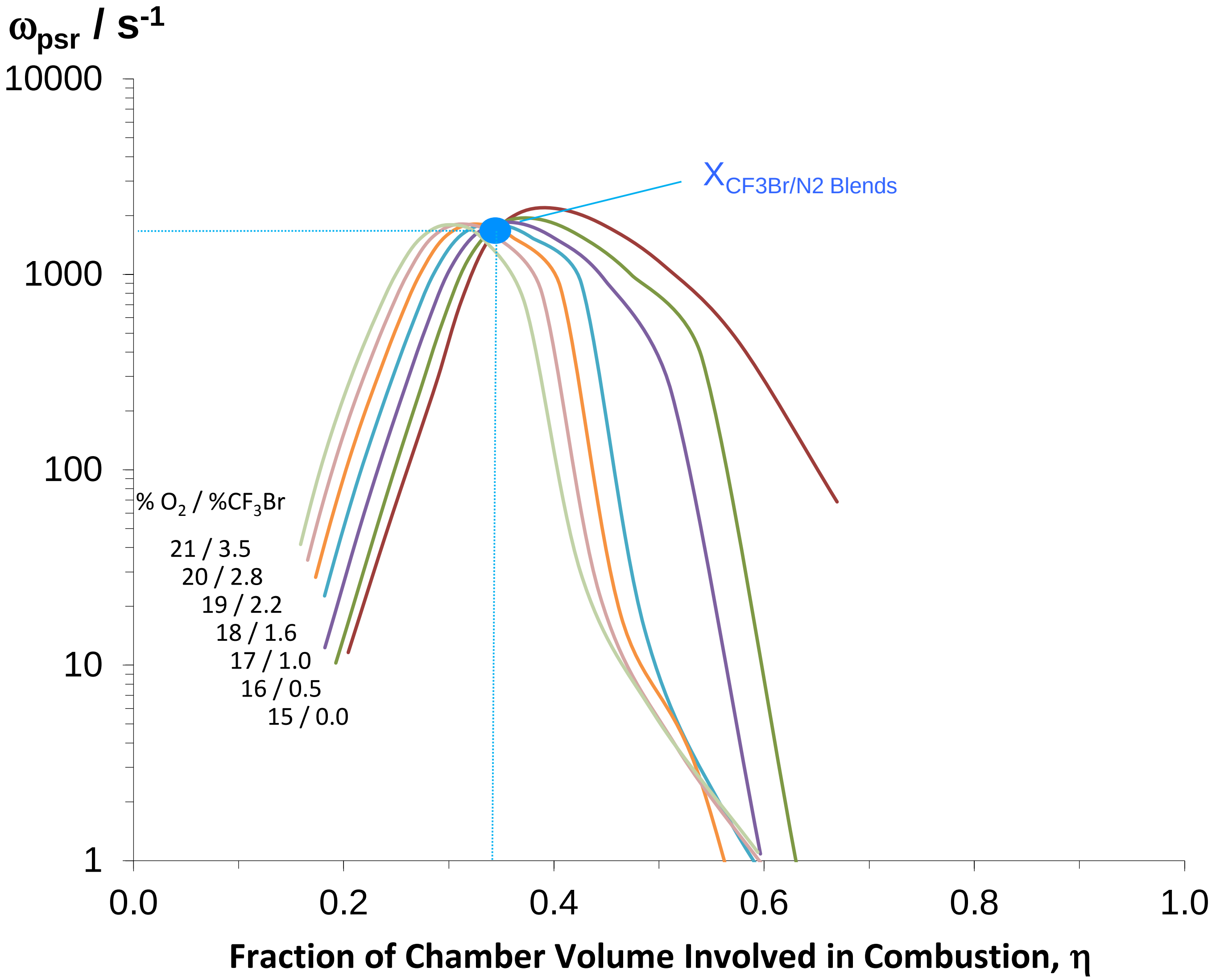


But we can get η from experiments with CF_3Br / N_2 mix in FAA-ACT.

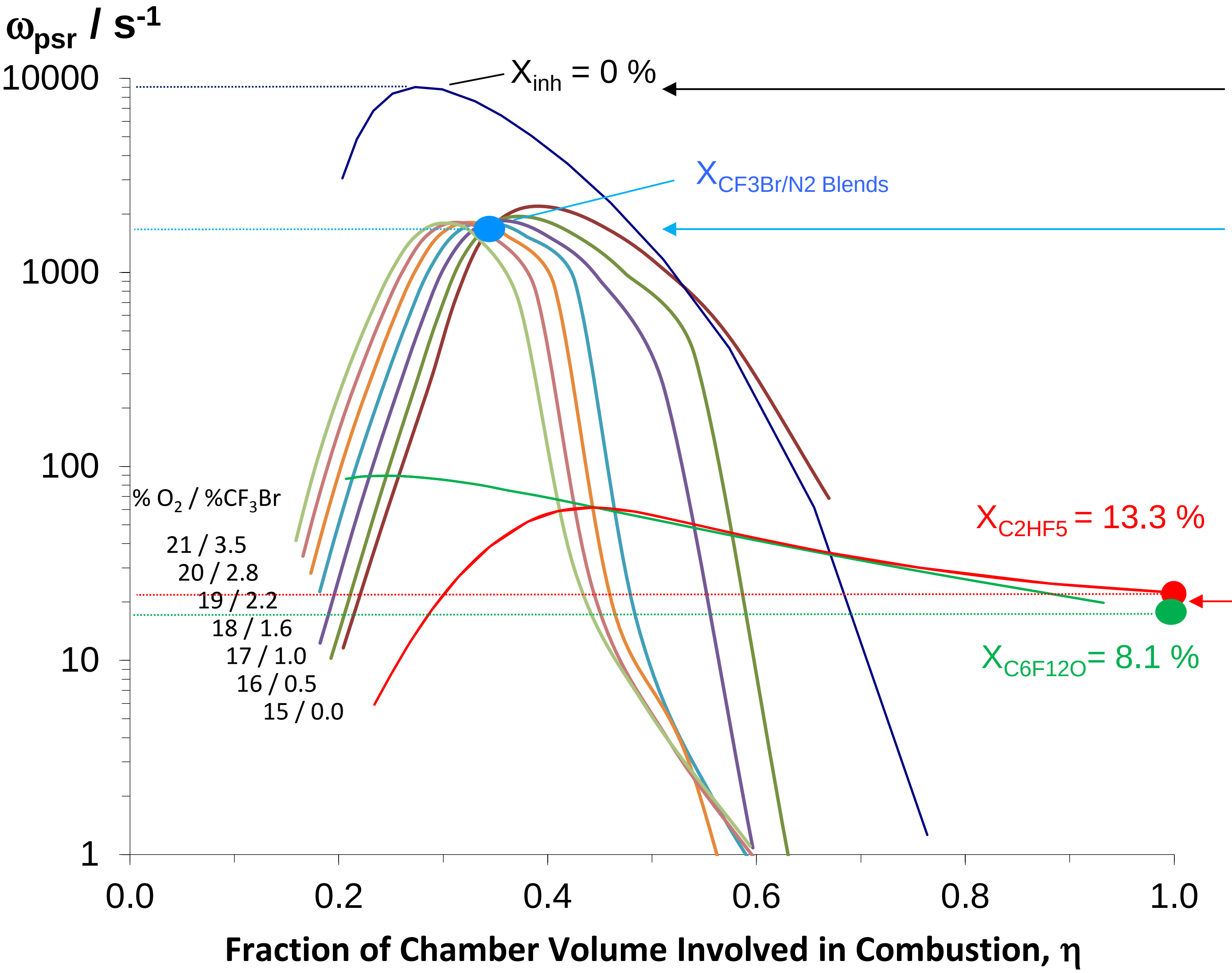
FAA-ACT with CF_3Br with Varying $X_{O2,ox}$



Inertion Cond. of Mixtures of CF_3Br and N_2 all imply ≈ same value of η and ω_{psr}



For inertion of the FAA-ACT, HFC-125, 2-BTP, or Novec 1230 must lower the reaction rate 100 x more than CF_3Br/N_2 mixtures



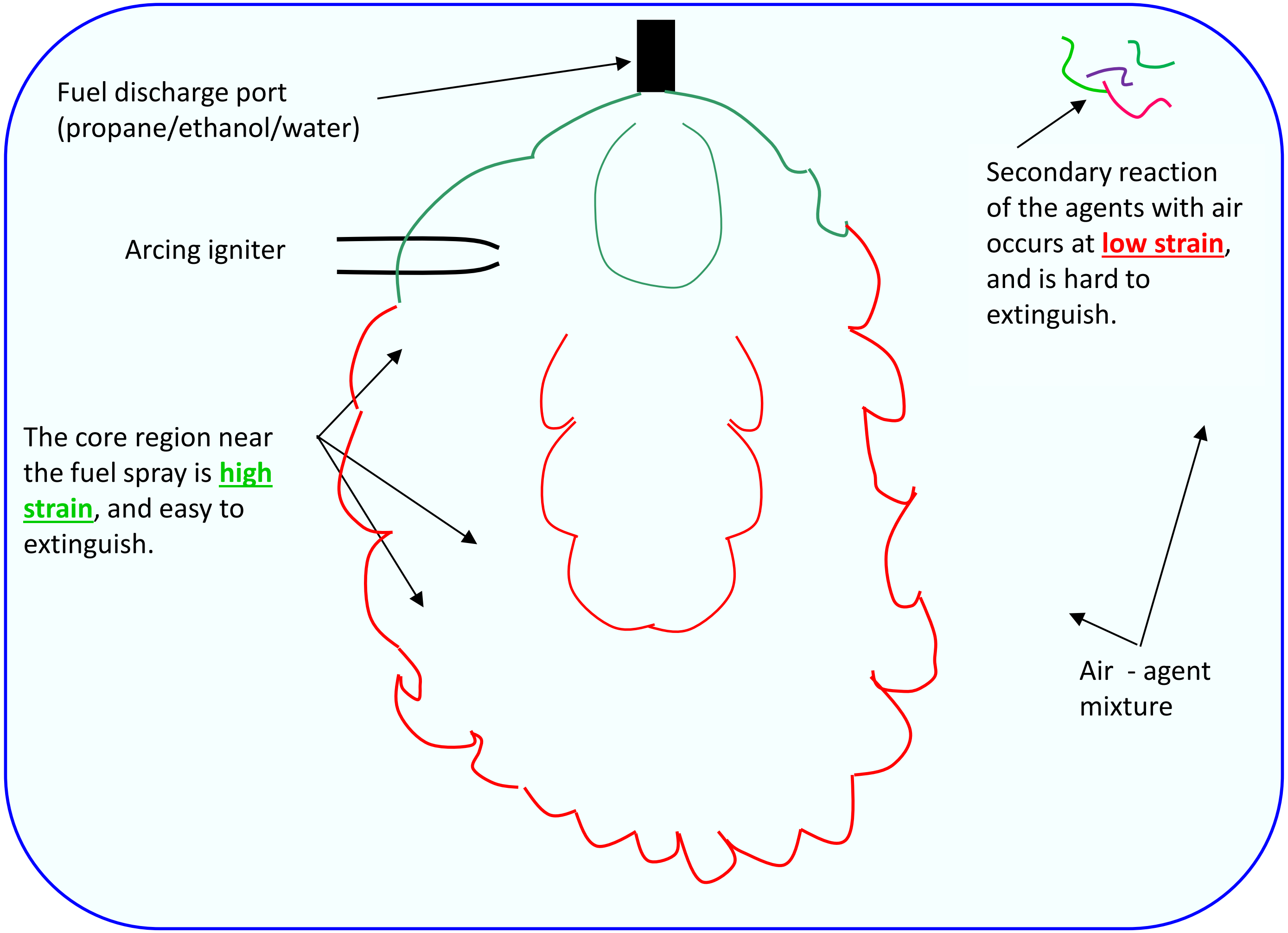
Uninhibited flames have a reaction rate of about 9000 s^{-1}.

CF_3Br / N_2 Mixtures Show that in Turbulent Zone, the overall reaction rate must be lowered below about 1800 s^{-1} for inerting (i.e., lower rxn rate by 5x)

Whereas with added R125, Novec, or 2-BTP, the overall reaction rate must be lowered to about 20 s^{-1} for FAA-ACT extinction (i.e., 100x lower reaction rate than in the turbulent zone).

Return

Strain rate varies over chamber domain



Fuel discharge port
(propane/ethanol/water)

Arcing igniter

The core region near the fuel spray is **high strain**, and easy to extinguish.

Secondary reaction of the agents with air occurs at **low strain**, and is hard to extinguish.

Air - agent mixture

=> Adding a mildly flammable agent creates low-strain regions that are harder to extinguish

Moral of the Story

These mixtures, nearly pure suppressant and air, were burning at conditions at which their burning velocity was only about 1 cm/s*.

If you have something that is mildly flammable, and you get it burning with some other strong ignition source, it can burn, even at very low S_L, if the conditions are right, and create overpressure.

=> Does this matter for the safe use of 2L refrigerants?

⇒ Does this matter in the use of fire suppressants in systems other than aircraft cargo bays? (e.g., engine nacelles, flammable liquid storage areas, battery backup rooms, energized electrical equipment, etc.)

⇒ Simple analyses based on fundamental thermodynamic and kinetic considerations can teach us a lot about the dynamics of these systems.

* More calculations are necessary to really pin down this number.

Reduced-Scale Experiments for Screening, Model Validation and Understanding Full-Scale Results of Marginally-Flammable Mixtures

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A. JAMES CLARK
SCHOOL OF ENGINEERING

BOEING

NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

Outline

1. **Experiments**
    a. Devices
    b. Results
    c. Screening

2. **Model Validation**
    a. Models
    b. Approach
    c. Results

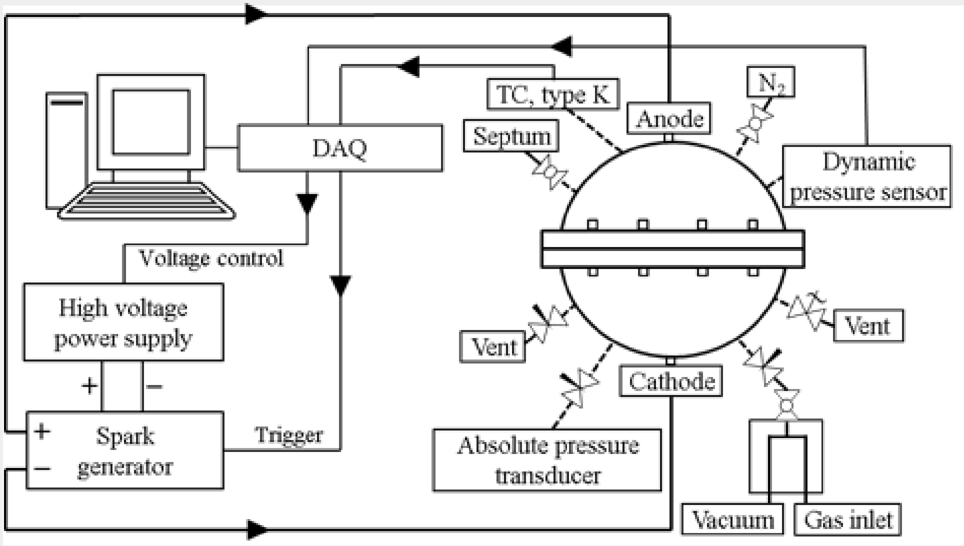
2 L Constant V Chamber => Pressure Rise

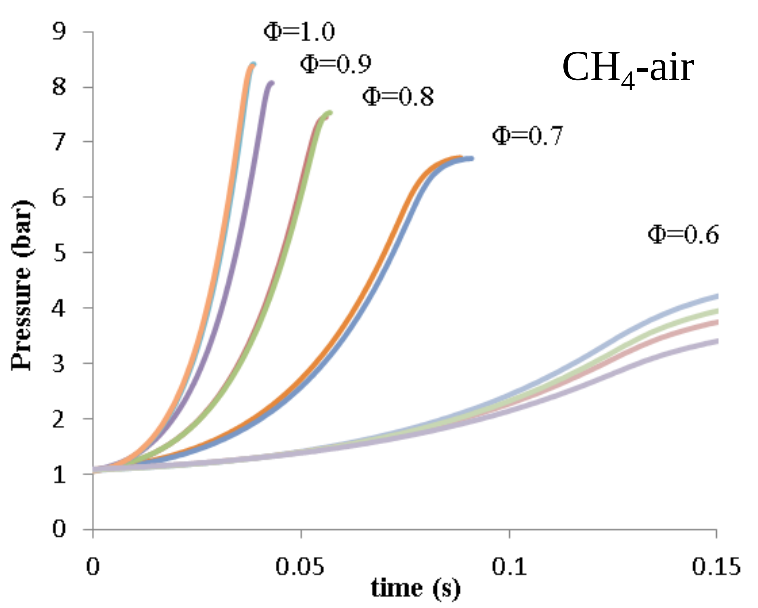
Used to measure:

1. Flammability limits
2. Max explosion pressure
3. Rate of pressure rise (dP/dt)
4. S_L

S_L determined from the pressure-time trace

$$S_L = \frac{R}{3}\left[1-(1-x)\left(\frac{P_0}{P}\right)^{1/\gamma_u}\right]^{-2/3}\left(\frac{P_0}{P}\right)^{1/\gamma_u}\left(\frac{dx}{dt}\right)$$





Ignition methods:

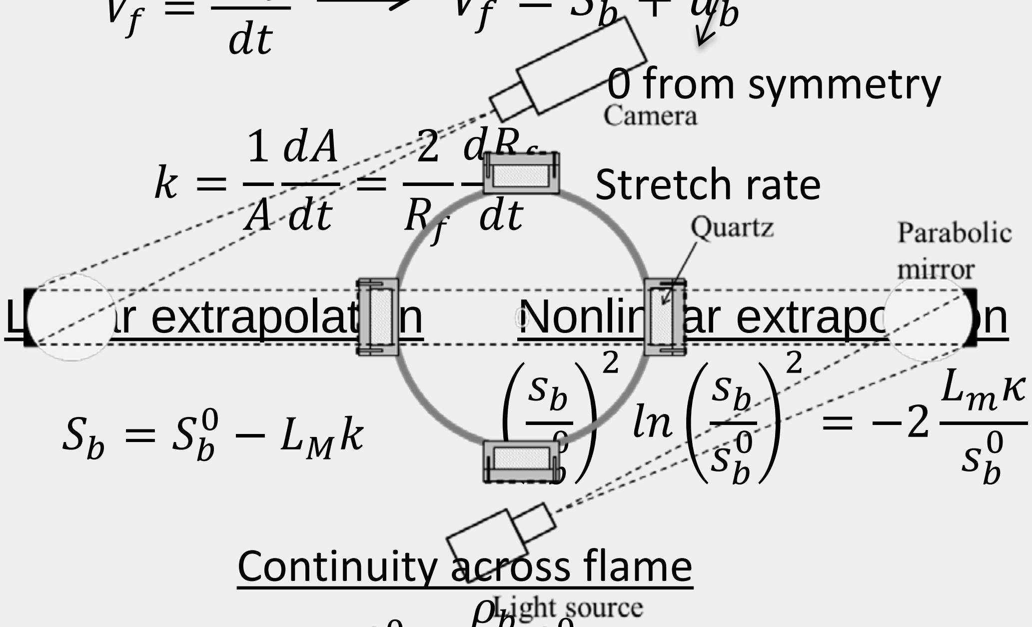
1. Variable cap discharge
2. Fused wire

Pros:

1. Provides burning velocity for a range of temperature and pressure from one experiment

30 L Chamber: Shadowgraph Image of Flame => S_L

S_b from flame front tracking



$$V_f = \frac{dR_f}{dt} \longrightarrow V_f = S_b + \cancel{u_b}$$

0 from symmetry

$$k = \frac{1}{A}\frac{dA}{dt} = \frac{2}{R_f}\frac{dR_f}{dt}$$ Stretch rate

<u>Linear extrapolation</u>

$$S_b = S_b^0 - L_M k$$

<u>Nonlinear extrapolation</u>

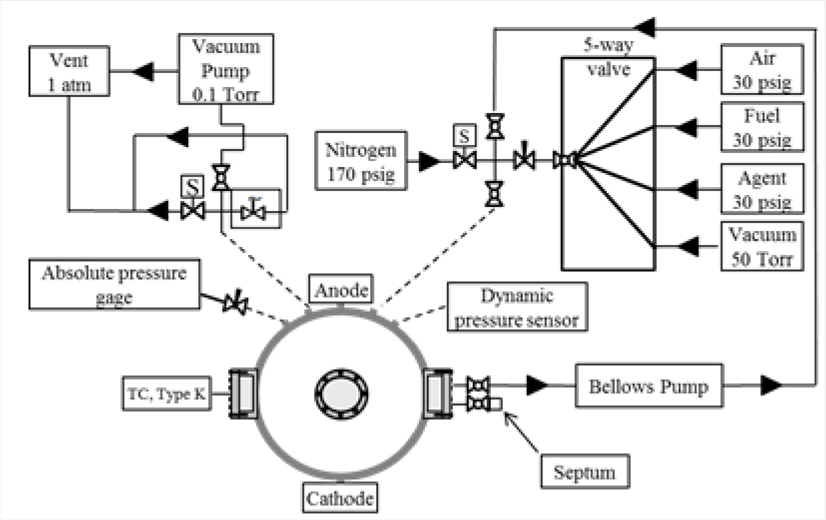
$$\left(\frac{s_b}{s_b^0}\right)^2 ln\left(\frac{s_b}{s_b^0}\right)^2 = -2\frac{L_m \kappa}{s_b^0}$$

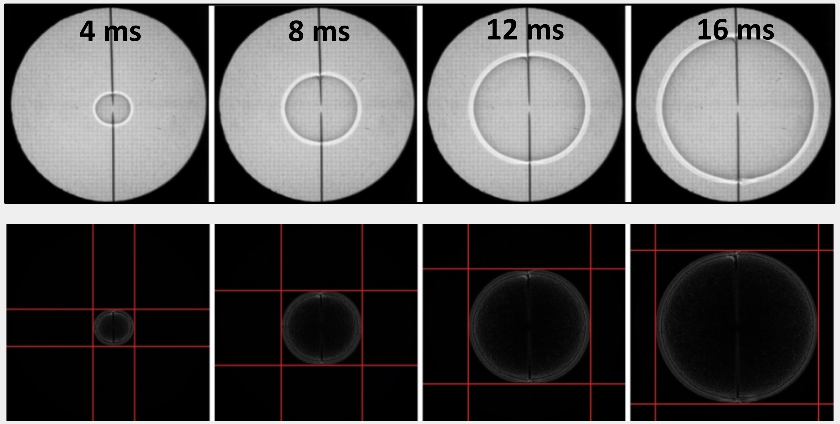
<u>Continuity across flame</u>

$$S_u^0 = \frac{\rho_b}{\rho_u} S_b^0$$

<u>Pros:</u>

1. Straightforward method for obtaining unstretched burning velocities and effects of stretch
2. Can go to lower S_L than 2 L chamber.



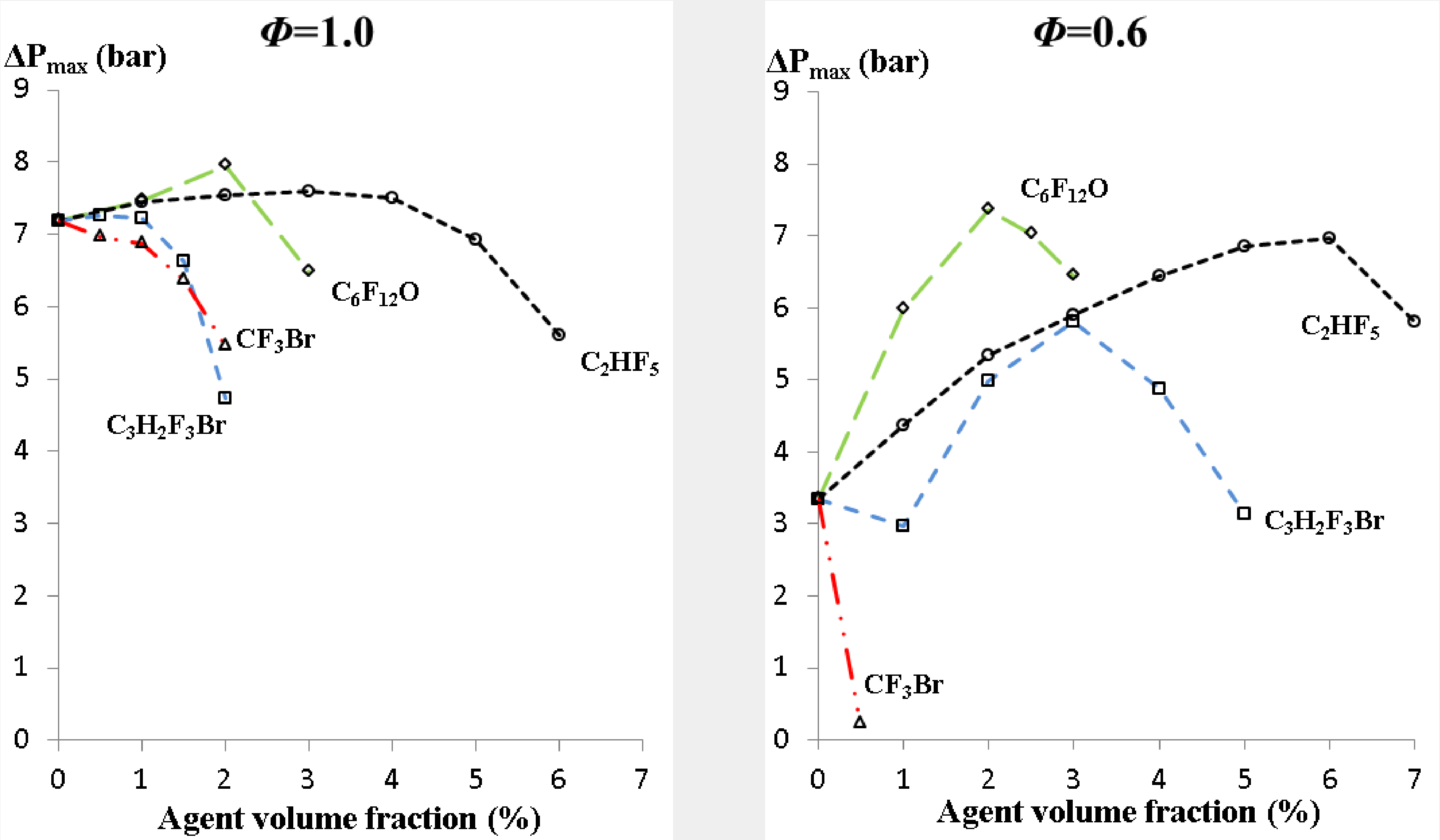


Flame front tracking illustration

Adding Fire Suppressants can Increase Pressure Rise

Agents added to premixed CH_4-air at Φ = 1.0 and 0.6

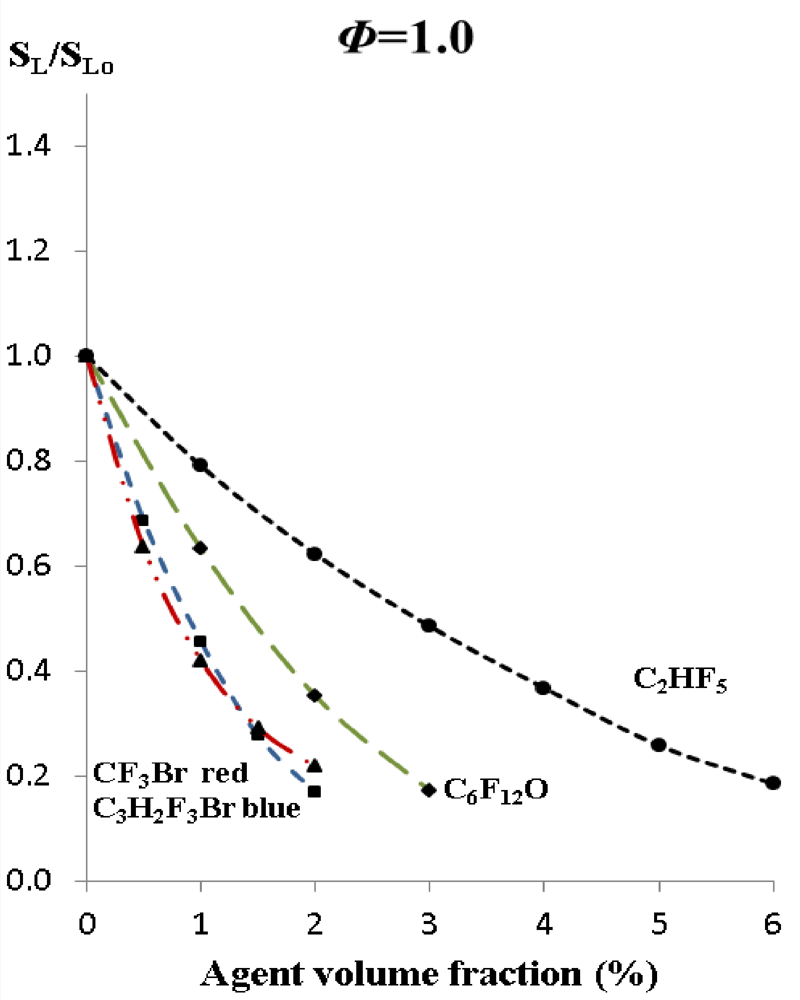
T=298 K and P=1 bar

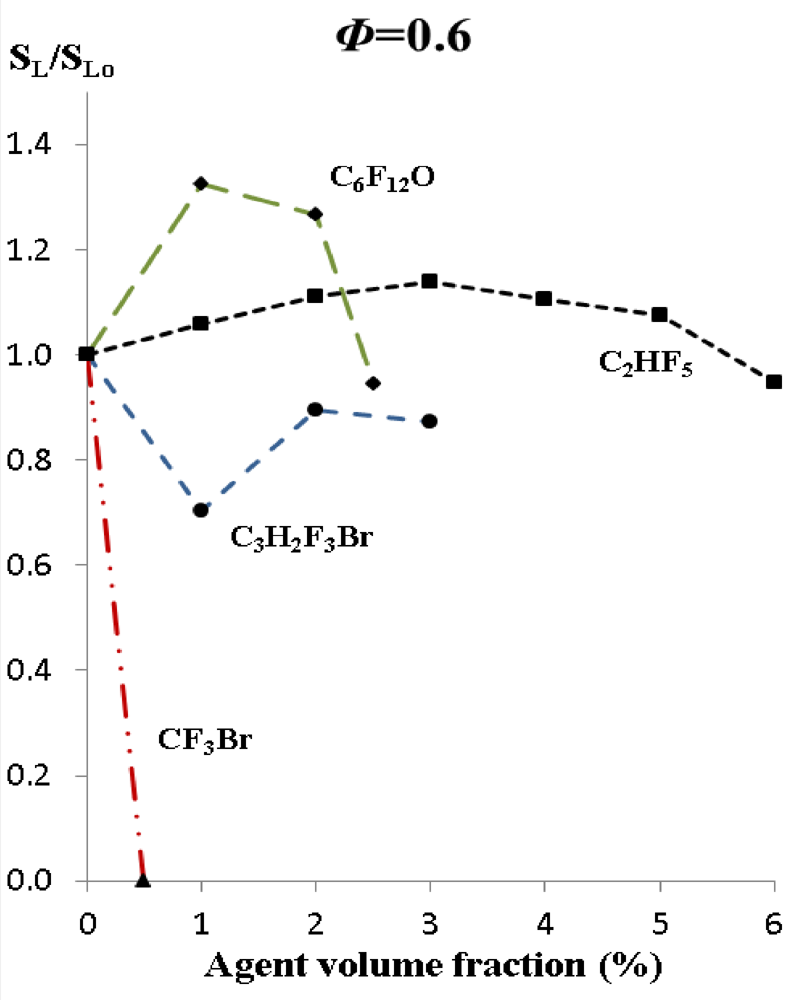


Adding Fire Suppressants can Increase Burning Velocity

Agents added to premixed CH_4-air at Φ = 1.0 and 0.6

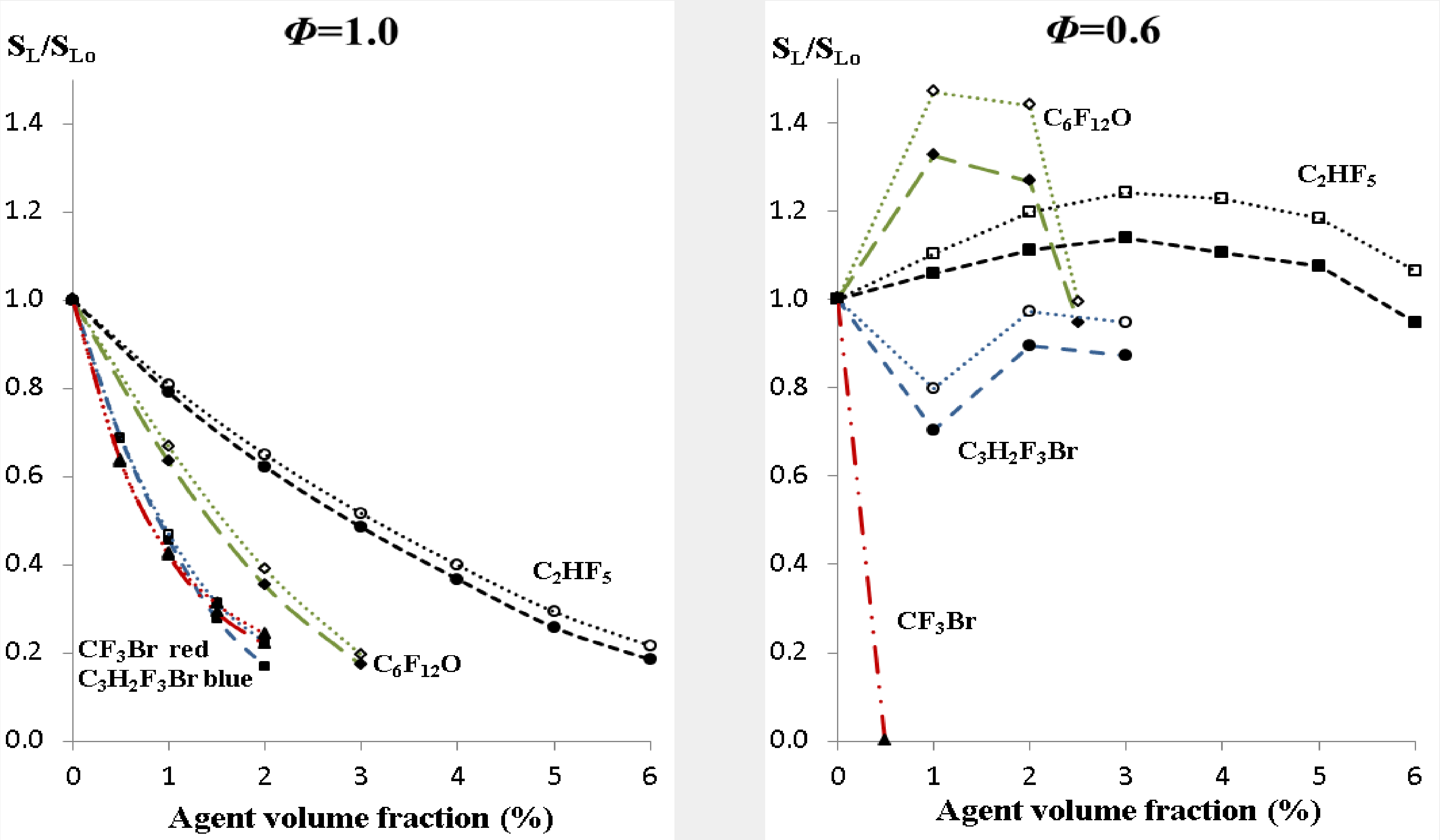
T=298 K and P=1 bar





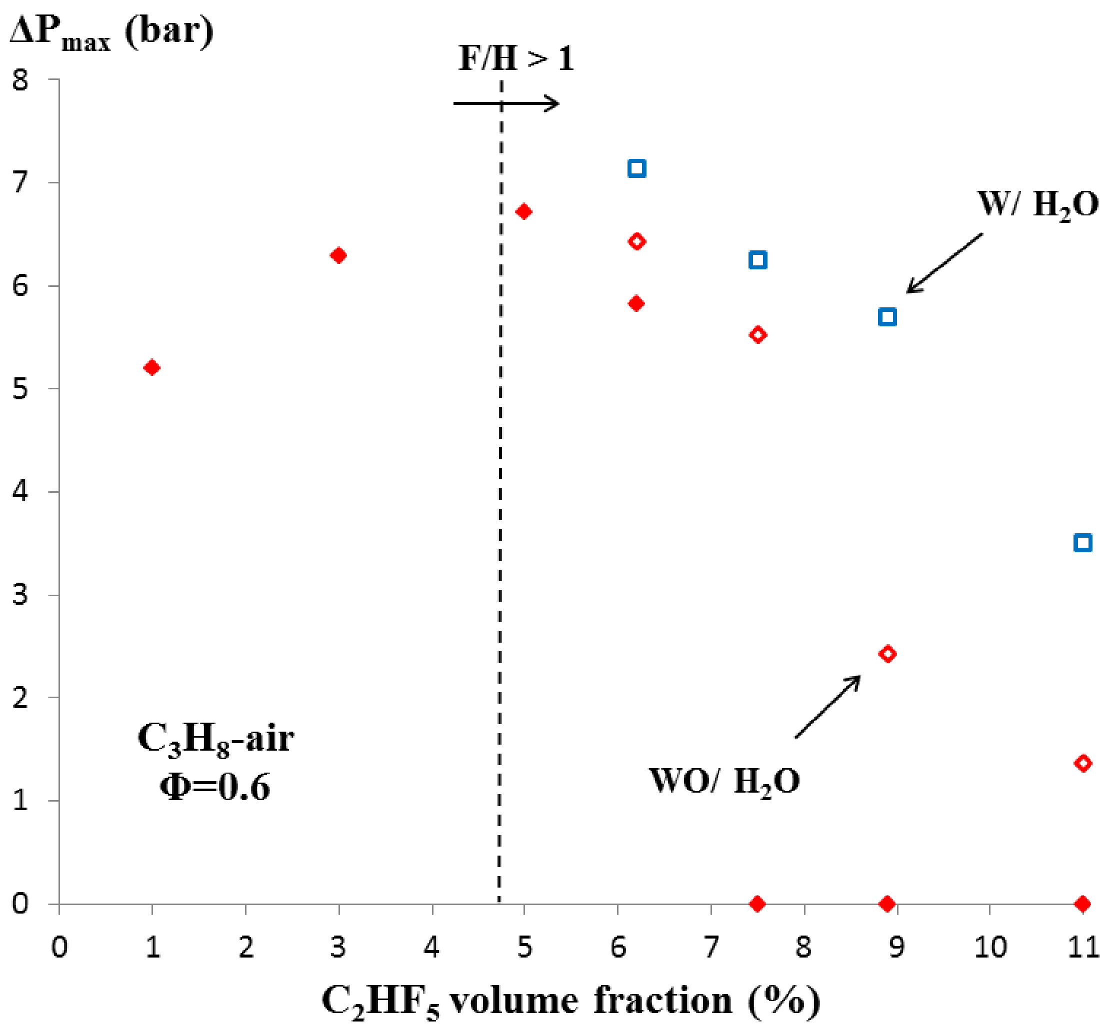
Higher Initial Temperature Reduces Effectiveness

Agents added to premixed CH_4-air at Φ = 1.0 and 0.6
T=400 K and P=3 bar



H_2O increases pressure rise at certain conditions

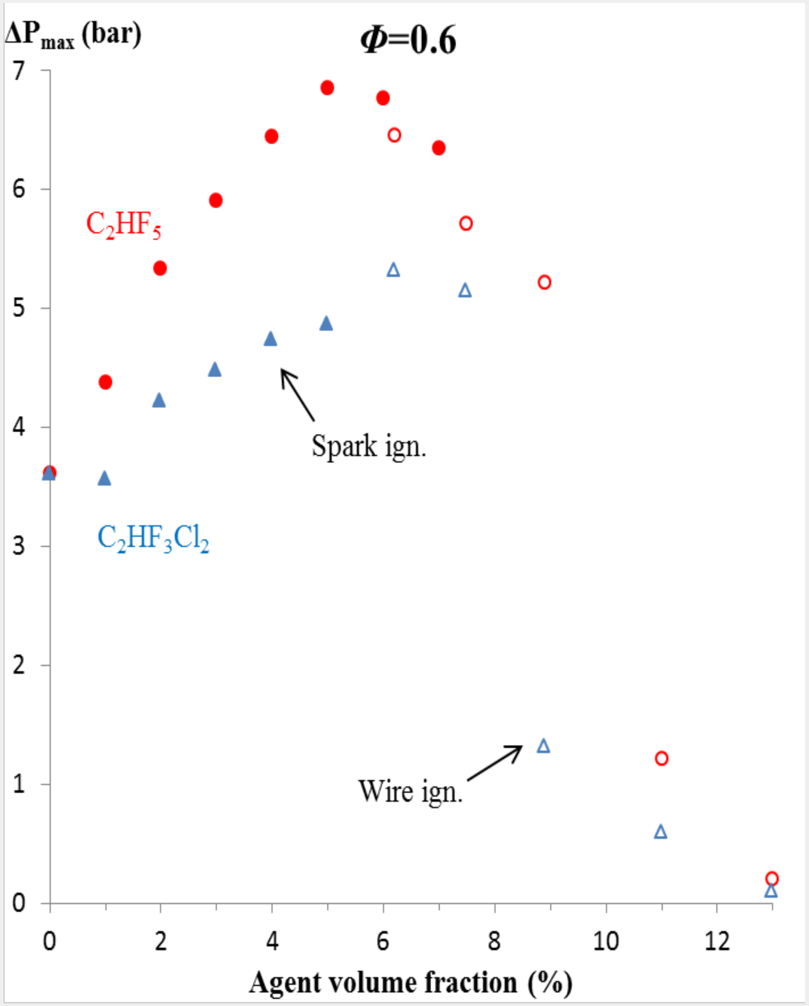
C_3H_8-air, Φ=0.6 with added C_2HF_5 (R-125)

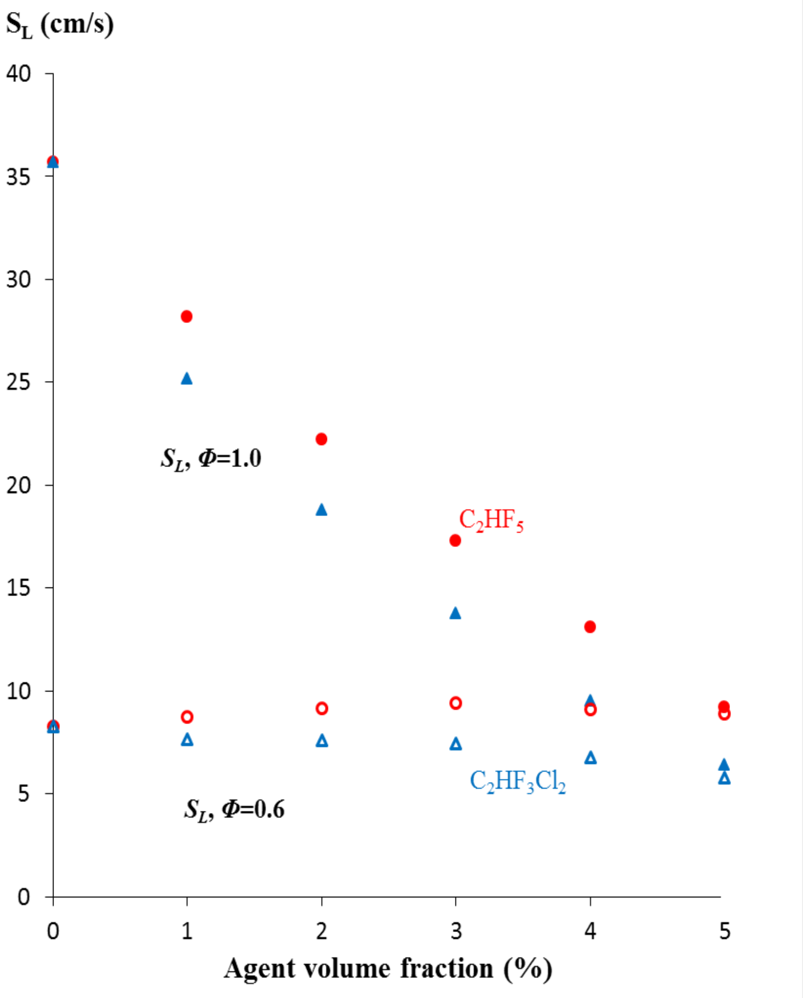


Screening technique

Agents added to premixed CH_4-air at Φ = 1.0 and 0.6

T=298 K and P=1 bar





Outline

1. Experiments
    a. Devices
    b. Results
    c. Screening

2. **Model Validation**
    a. Models
    b. Approach
    c. Results

Models

Aerosol Can Test Kinetic Model	Species	Reactions	Type
C_3-C_4 Hydrocarbon mechanism (Wang et al.) with C_2H_5OH reactions (Dryer et al.)	116	820	Acquired
NIST C_1, C_2 HFC, for hydrocarbon flame inhibition + update for pure flames	171	1467	Updated, Developed
FM200	178	1504	Updated
Novec 1230	181	1513	Developed
CF_3Br	181	1568	Updated
CF_3I	181	1563	Updated
2-BTP	188	1609	Developed
HCFC-123	242	1959	Developed

Can use S_L to validate mechanisms

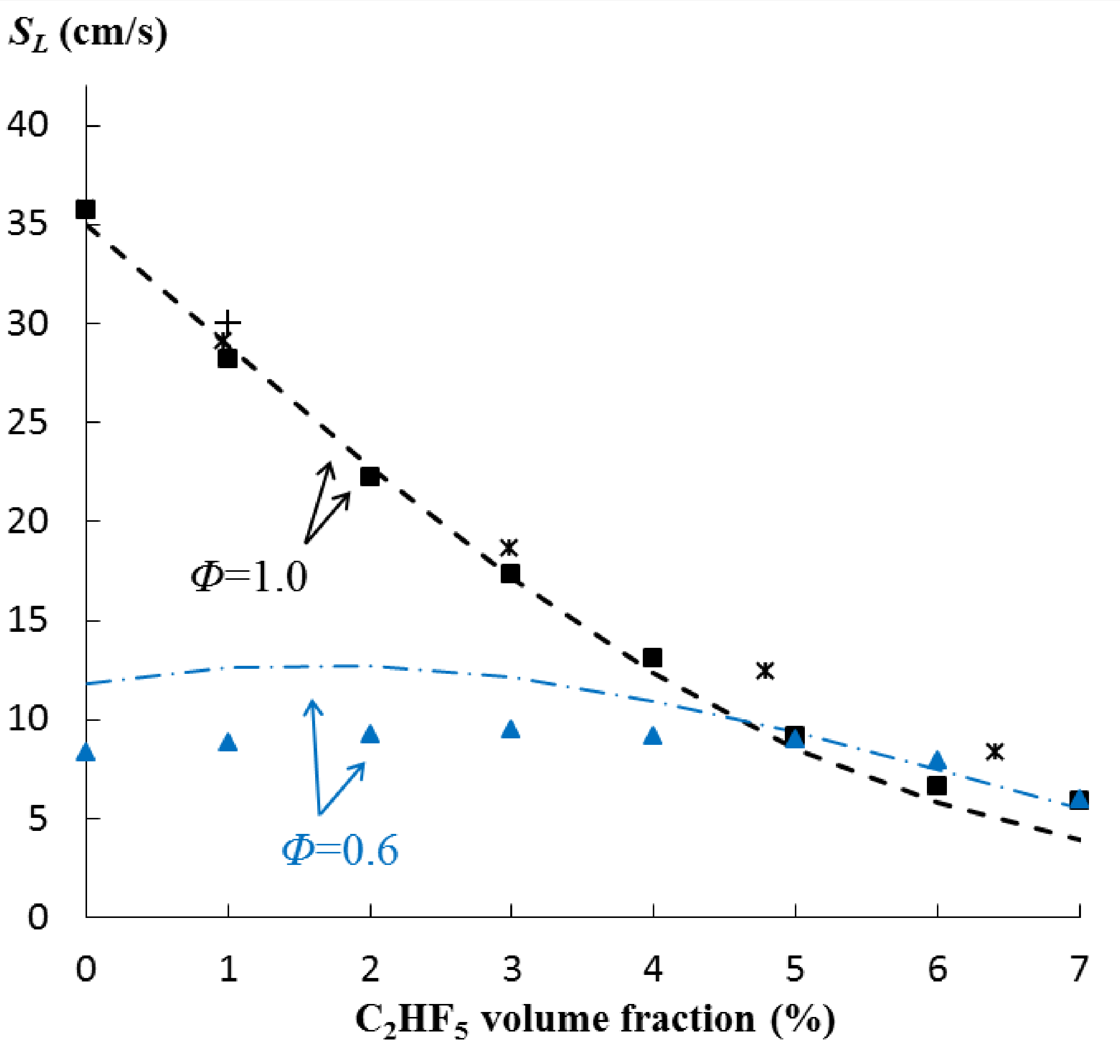
S_L is:

- A distinct property of a combustible mixture
- A measure of reactivity, diffusivity, and exothermicity
- steady, 1-D, planar, adiabatic flame

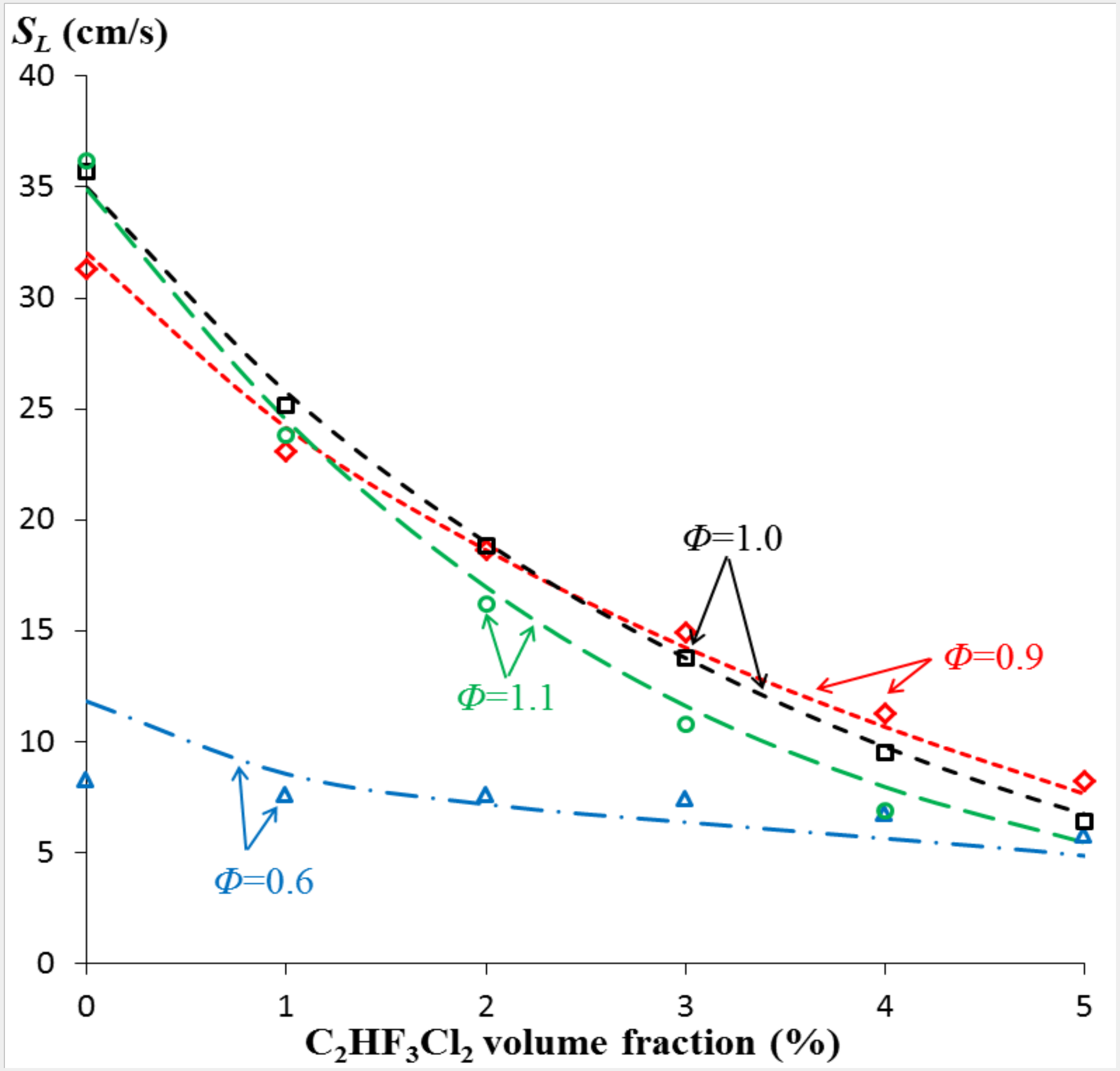
Can solve the steady, 1-D flame equations with full chemistry (Chemkin PREMIX)

Can measure S_L and compare with calculation

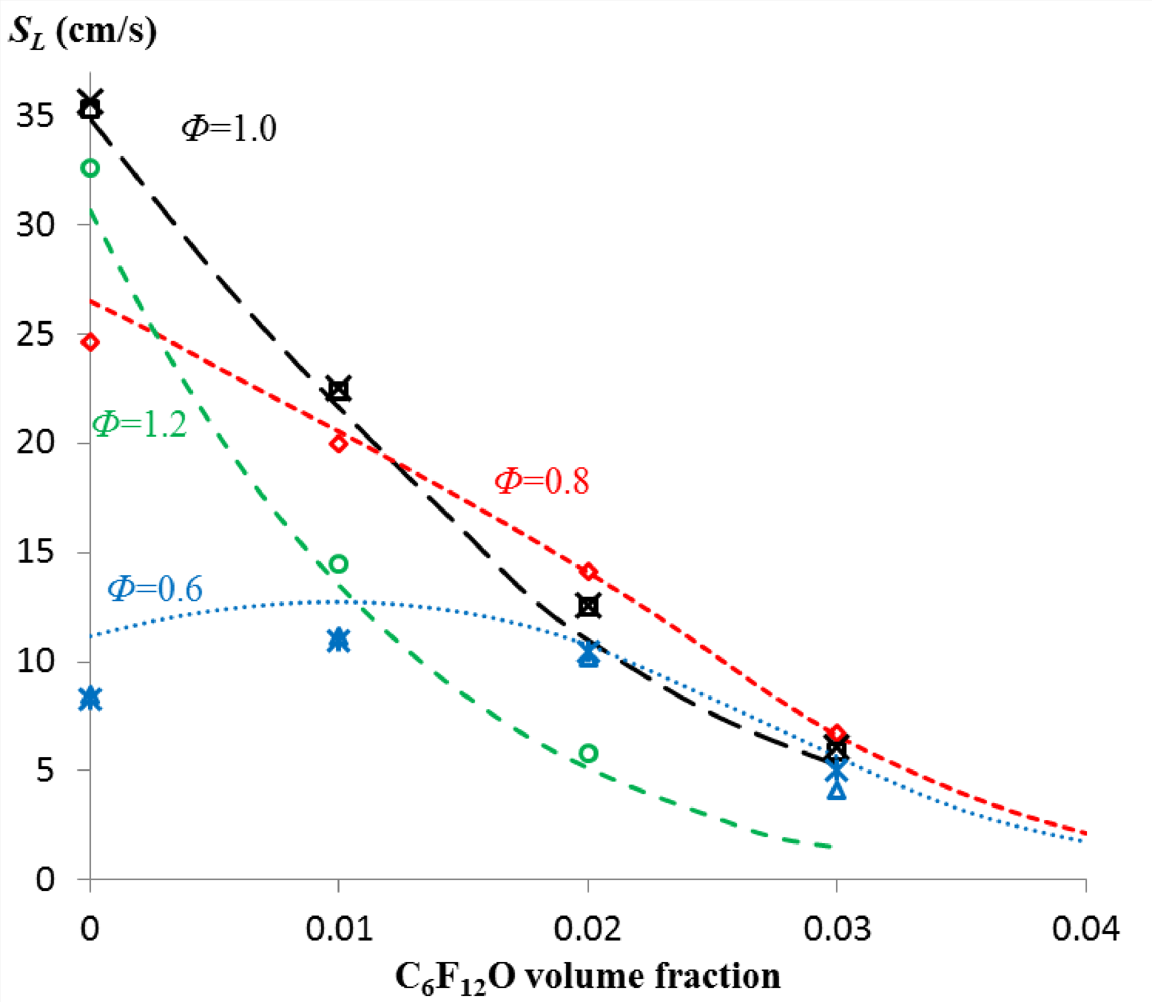
Model Validation – CH_4-air + C_2HF_5 (R-125)



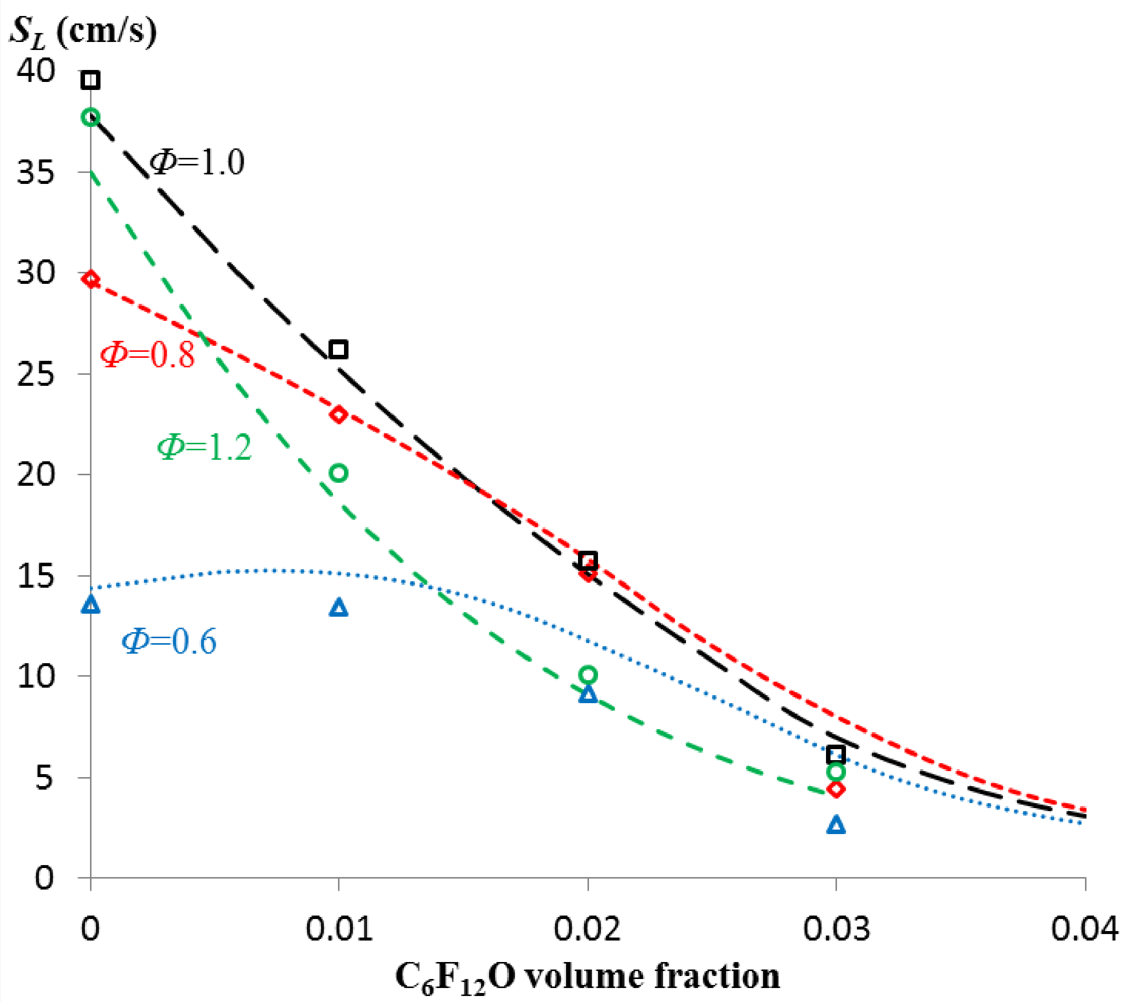
Model Validation – CH_4-air + $C_2HF_3Cl_2$ (R-123)



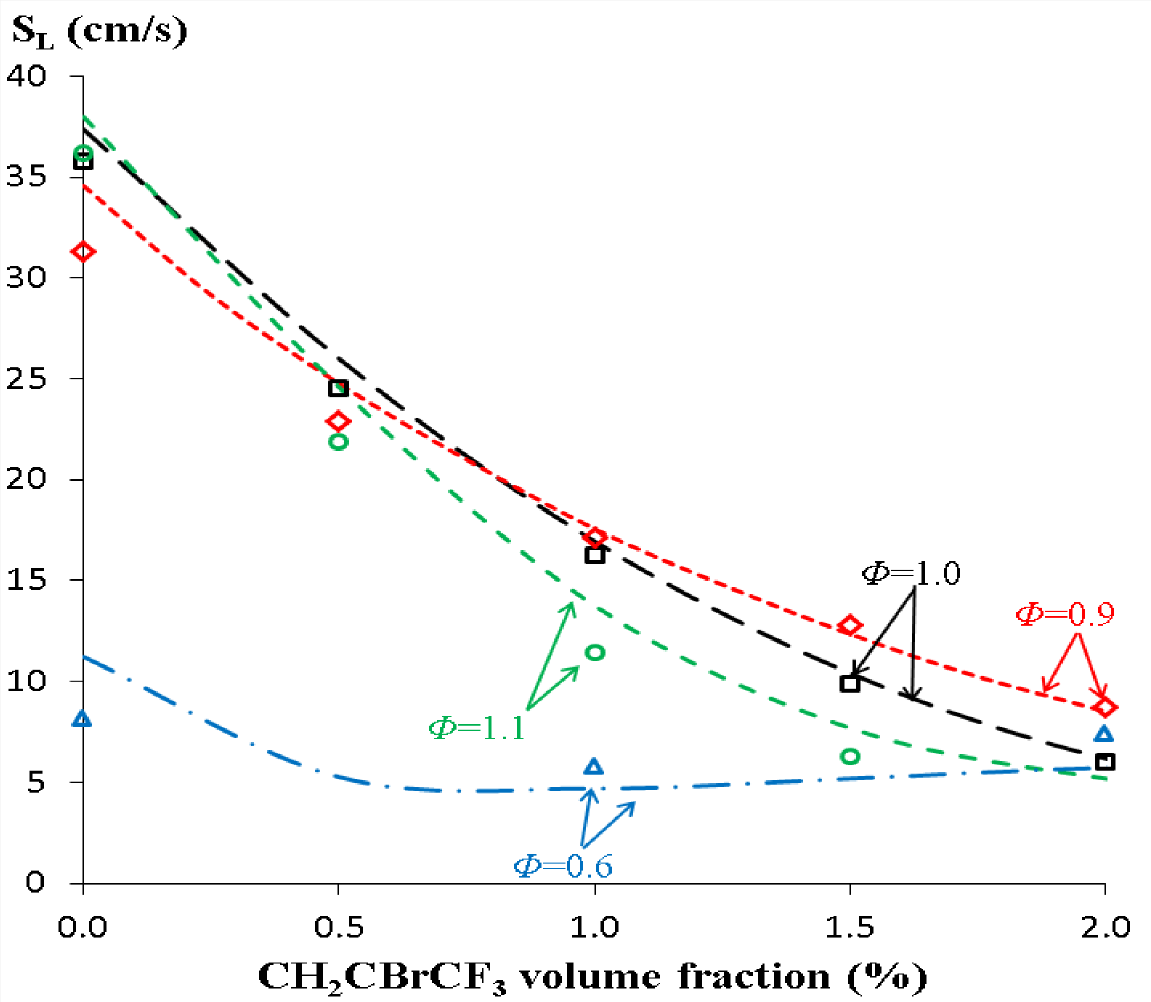
Model Validation – CH_4-air + $C_6F_{12}O$ (Novec 1230)



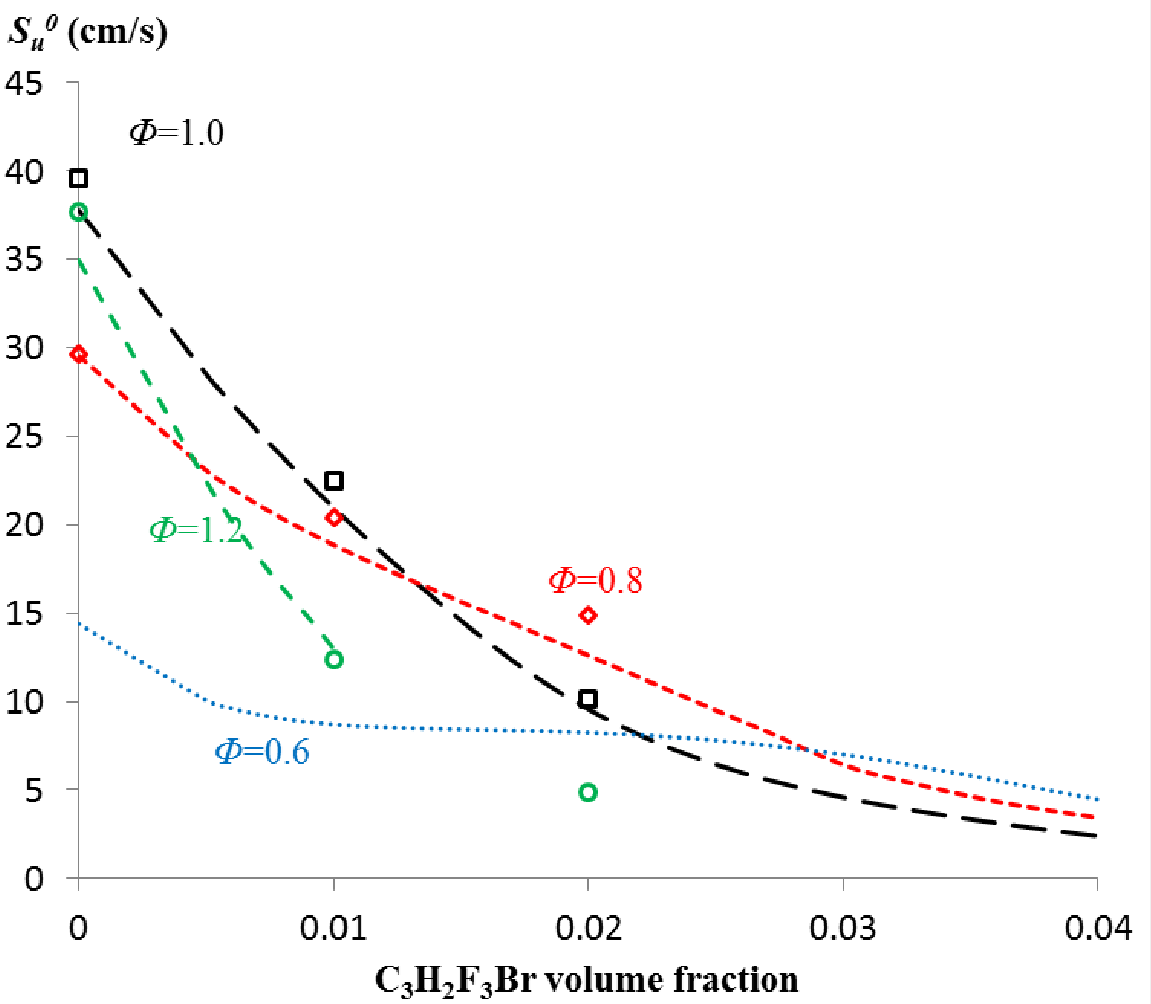
Model Validation – C_3H_8-air + $C_6F_{12}O$ (Novec 1230)



Model Validation – CH_4-air + $C_3H_2F_3Br$ (2-BTP)



Model Validation – C_3H_8-air + $C_3H_2F_3Br$ (2-BTP)



Conclusions

Similar overpressures as observed in the FAA-ACT were seen in small-scale premixed tests, particularly at lean conditions

Constant-volume spheres offer screening potential for agent performance in the FAA cargo bay test

Adding R-125 and Novec 1230 to lean mixtures not only increases heat release, but reactivity (S_L) as well

Suppressant influence on reactivity of lean flames is even worse at elevated temperature

Validation data is in excellent agreement with models considering they are not "tuned"

Now that mechanisms have been tested, we have improved confidence in the previous findings and in what we can learn from them in the future

Measurements & Data for Fundamental Kinetic Modeling of Halocarbon Flammability

Jeffrey A. Manion

Contributors: David Sheen, Don Burgess, Iftikhar Awan,
Valeri Babushok, Greg Linteris

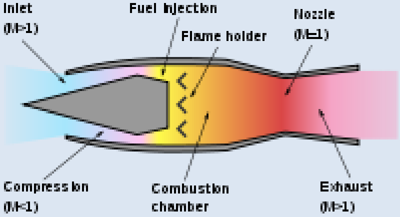
National Institute of Standards and Technology
Gaithersburg, MD 20899

Workshop on the
Flammability of Halogenated Hydrocarbons
Gaithersburg, Maryland
October 28, 2014

Challenges of Multi-Scale Problems

System-level

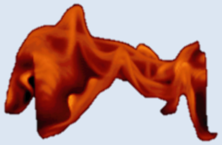
Microscopic



$$\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \mathbf{u} = 0$$

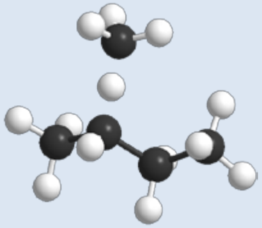
$$\rho \frac{\partial \mathbf{u}}{\partial t} + \left(\rho \mathbf{u} \cdot \nabla \right) \mathbf{u} = -\nabla p + \mu \nabla^2 \mathbf{u}$$

$$P = \frac{\rho R T}{\bar{M}}$$



$$\frac{\partial Y_k}{\partial t} + \left(\mathbf{u} \cdot \nabla \right) Y_k = \frac{1}{\rho} \nabla \cdot \mathbf{u}_k \rho Y_k + \omega_{k,\text{chem}}$$

$$\frac{\partial e}{\partial t} + \left(\mathbf{u} \cdot \nabla \right) e = \frac{1}{\rho} \left(\nabla \cdot \lambda \nabla \right) T - \frac{1}{\rho} \sum_k \nabla \cdot \mathbf{u}_k e_k \rho Y_k + \sum_k e_k \omega_{k,\text{chem}} - \dot{w}$$



$$\mathrm{X} + \mathrm{Y} \rightarrow \mathrm{C} + \mathrm{D}$$

$$\frac{d[\mathrm{X}]}{dt} = \omega_{X,\text{chem}} = -[\mathrm{X}][\mathrm{Y}] A T^n \exp\left(\frac{-E}{T} \right)$$

Can we predict (or develop useful insight on) the behavior of a human-scale system based on fundamental molecular properties?

Understanding Flammability – The Role of Fundamental Chemical Kinetic Models & Data

- **Engineers require design tools to answer technological questions.**
  - **<u>Fire Suppressants: H</u> are the failure modes?**
    What happ
  - **<u>Refrig</u> ed?**
    Can I de
  - **What happens if …?**

- Best designer is probably the one with the best tools
- More realistic, accurate models will be developed
- Question is when and by whom?
- <u>**How can NIST help**?</u>

- **Engineering tools have an wide range of sophistication:**
  - **Empirical approaches & correlations (Edisonian)**
  - **Fundamental understanding and science-based insight**
  - **Realistic accurate computer based models of complex systems**

Outline

- Some Fundamental Property Databases at NIST
- Data Informatics
- Development of a chemical kinetic model for 2-BTP
- Strategies for improving models
- Concluding Remarks

Some Fundamental Property Databases at NIST

- **General Chemical Properties.**
  - **NIST Webbook: (Peter Linstrom) webbook.nist.gov**
- **Physical Properties:**
  - **REFPROP (Fluid Properties): (Eric Lemmon) www.nist.gov/srd/nist23.cfm**
- **Molecular Properties.**
  - **TRC Thermodynamics Database: (Michael Frenkel) trc.nist.gov**
  - **Gas Phase Kinetics: (Jeff Manion) kinetics.nist.gov**
  - **Quantum Chemical Calculations: (Russ Johnson) cccbdb.nist.gov/**

Data Standards & Informatics – Organizing and Mining Chemical Kinetic Information

- **NIST Kinetics Database (60,000+ rate constants)**
  - **<u>How to search for relationships and evaluate the data?</u>**
- **InChI-ER: New unique electronic identifier for <u>elementary reactions</u>:**

  $HOCH_2CH_3$ is the same as CH_3CH_2OH

  - **Extension of existing InChI: a computer-generated slash delimited string**

    InChI String $\xrightleftarrows{\text{algorithm}}$ **Molecular Structure**

  - **InChI-ER is a unique identifier for reaction identification and classification,**
  - **Will facilitate data sharing, data mining, evaluation, model comparison**

“*Data Formats for Elementary Gas Phase Kinetics: Part 1. Unique Representations of Species at the Molecular Level*” D.R. Burgess, J.A. Manion, and C.J. Hayes, Intern. J. Chem. Kinetics. 46(10), 640-650, 2014.
“*Data Formats for Elementary Gas Phase Kinetics: Part 2 Unique Representations of Reactions*” D.R. Burgess, J.A. Manion, and C.J. Hayes, submitted IJCK, under peer review, 2014.
“*Data Formats for Elementary Gas Phase Kinetics: Part 3. Reaction Classification*” D.R. Burgess, J.A. Manion, and C.J. Hayes, submitted IJCK, under peer review, 2014.

Outline

- Some Fundamental Property Databases at NIST
- Data Informatics
- **Development of a chemical kinetic model for 2-BTP**
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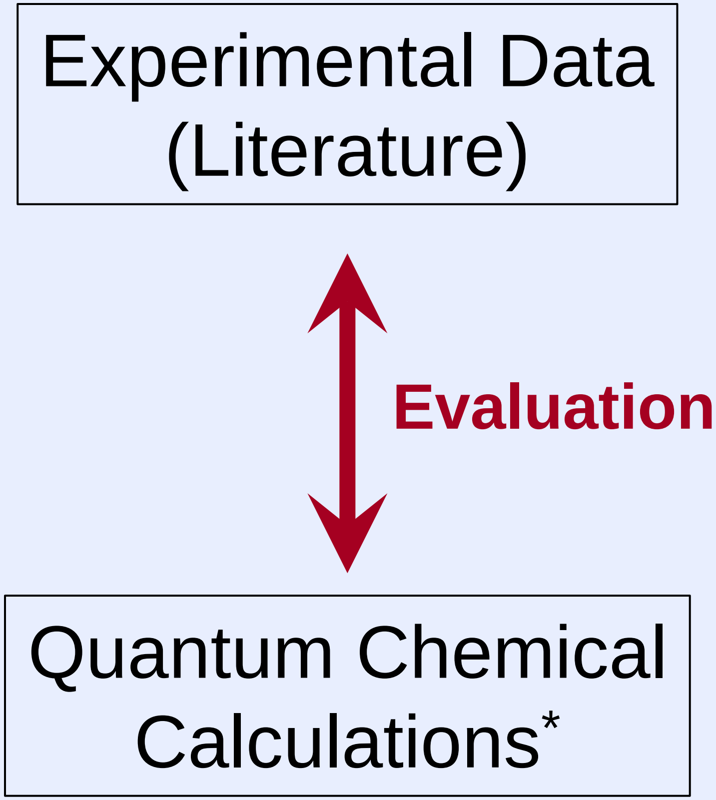
Chemical Data Needs for Detailed Kinetic Models

- **Chemical Properties.**
  - **Thermochemistry of Molecules:**
  - **Kinetics: *k*(T, P)**
  - **Mechanism (Reaction Set)**
- **Physical Properties:**
  - **Transport properties, etc.**

Thermochemistry



Experimental Data (Literature)

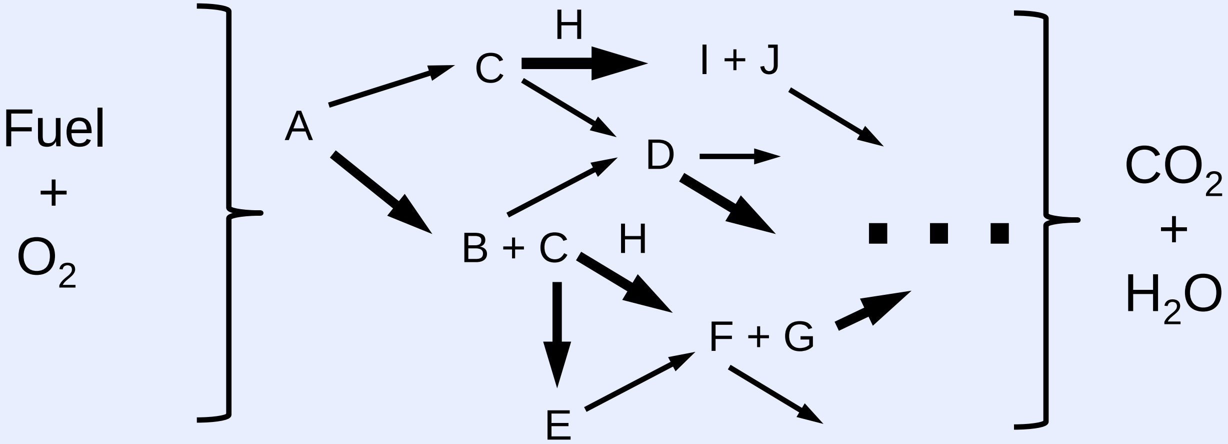
Evaluation

Quantum Chemical Calculations*

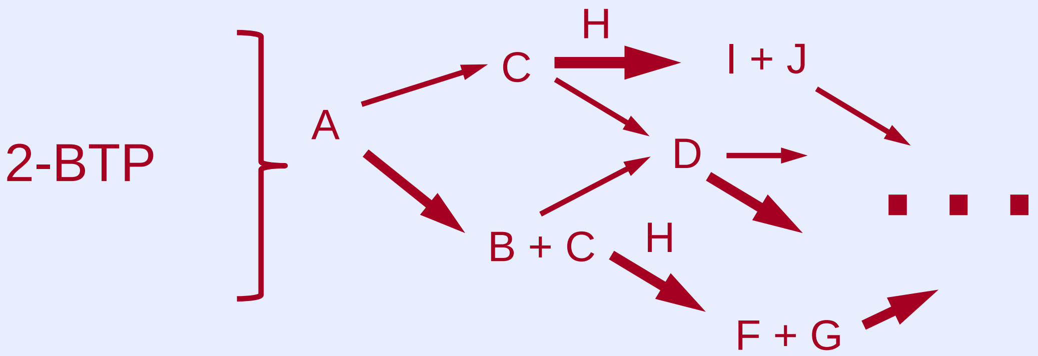
Good & Bad ways of doing this!

* 2-BTP Model: Don Burgess

Halocarbon Combustion and Inhibition: 2-BTP Mechanism Development



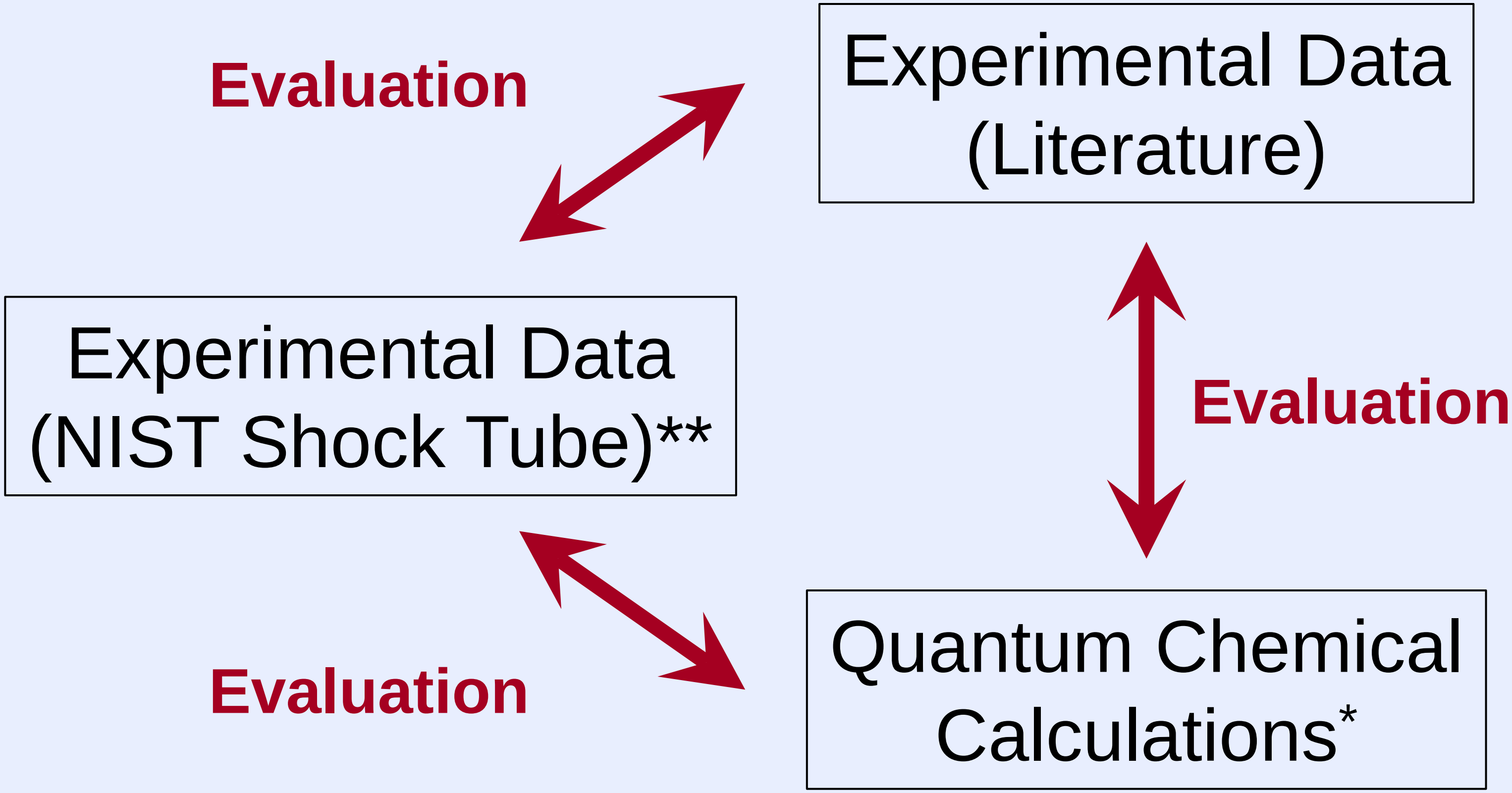
Fuel Combustion models exist



- Halocarbon chemistry partly known
- Augment with:
  - Theory
  - Experiment

"*A Chemical Kinetic Mechanism for 2-Bromo-3,3,3-trifluoropropene (2-BTP) Flame Inhibition*" D.R. Burgess, V.I. Babushok, G.T. Linteris, J.A. Manion, submitted to Intern. J. of Chem. Kinetics

Kinetics for 2-BTP



Evaluation

Experimental Data
(Literature)

Experimental Data
(NIST Shock Tube)**

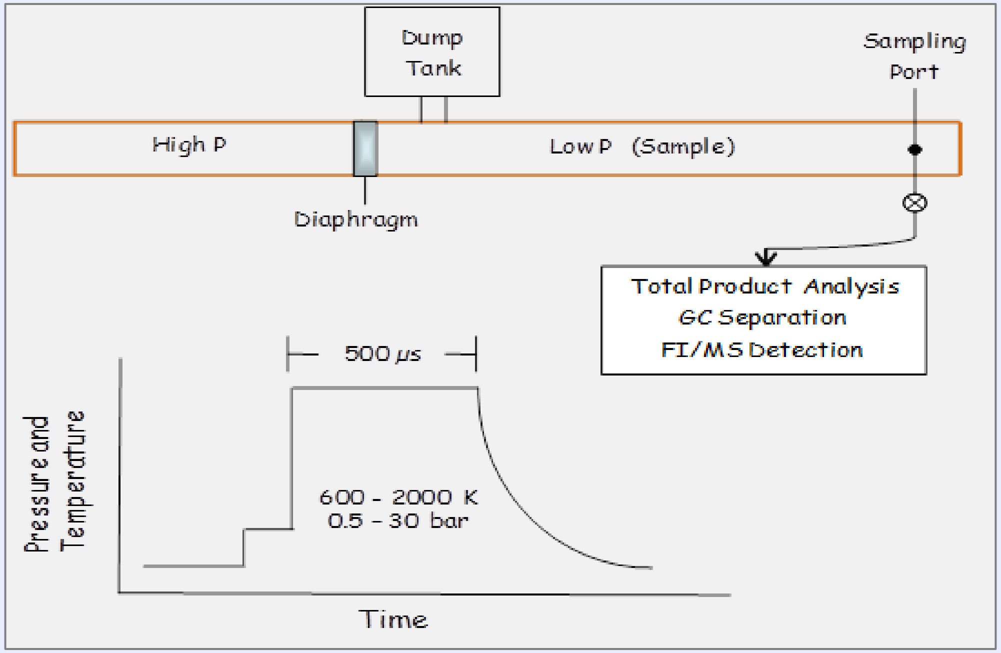
Evaluation

Evaluation

Quantum Chemical
Calculations*

2-BTP Model: * Don Burgess; **Awan & Manion

Shock Tube – A Pulse Heater for Gases

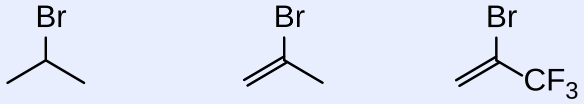


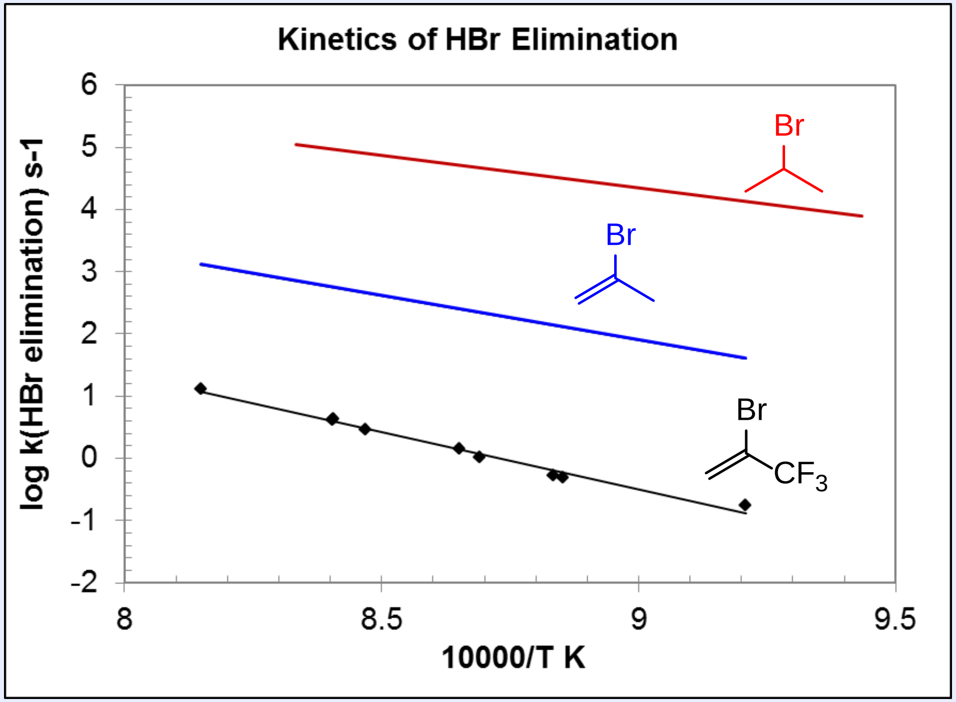
Characteristics:

- Pulse short duration heater – no surface induced interference
- Allows isolation of *initial* gas phase processes (not global reactions)
- Accurate product monitoring at sub-ppm levels (see all products)

Unimolecular Decompositions – 2-BTP and Related

Studies of structure/rate effects





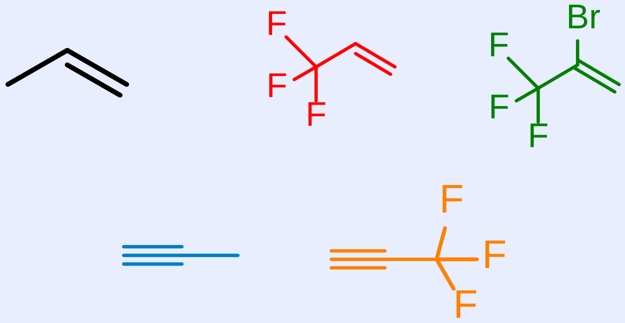
Shock Tube Measurements :

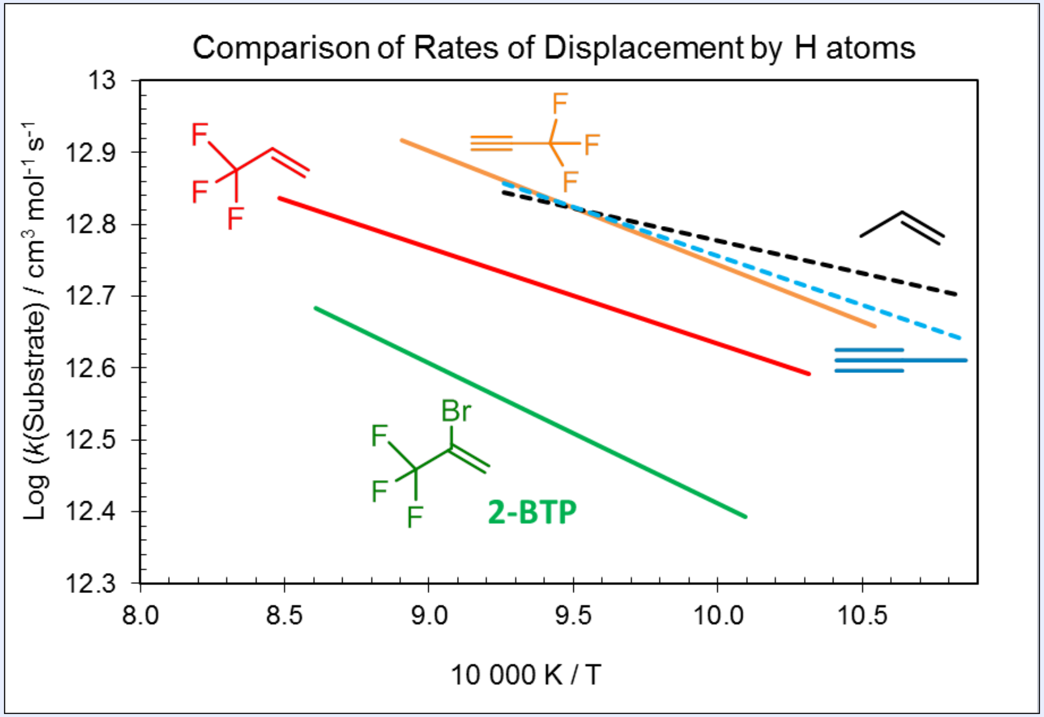
- Double bond lowers *k* by 100x
- CF_3 lowers *k* an additional 100x

- 2-BTP is very stable (most stable compound to HBr elimination yet measured)
- Experimental reference data: *needed to validate computational kinetics*

Bimolecular Attack by H atoms – 2-BTP and Related

Studies of structure/rate effects





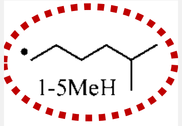
Shock Tube Measurements :

- Only small variations; rates within about 3x at 1000 K.

➢ H atom induced decomposition of 2-BTP is similar to hydrocarbons

➢ Experimental reference data: *validate computational kinetics*

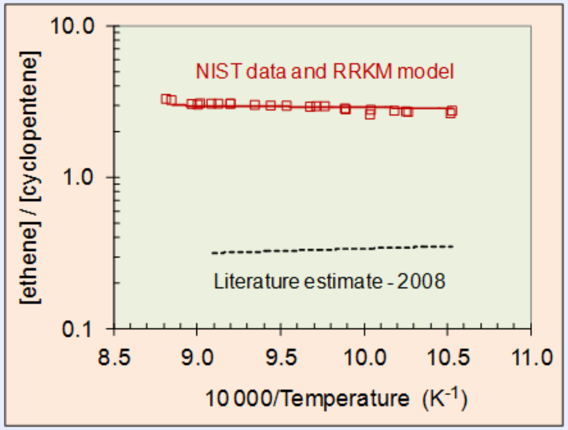
Decomposition of Fuel Radicals



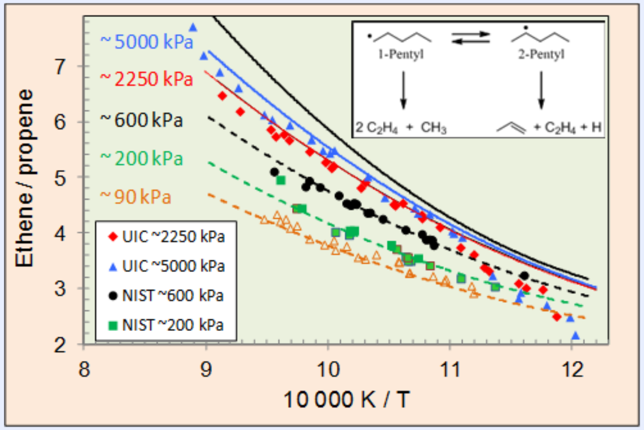
Our technique resolves complex behavior and minor channels

NIST Reference Data – Fuel Radical Fragmentation Patterns

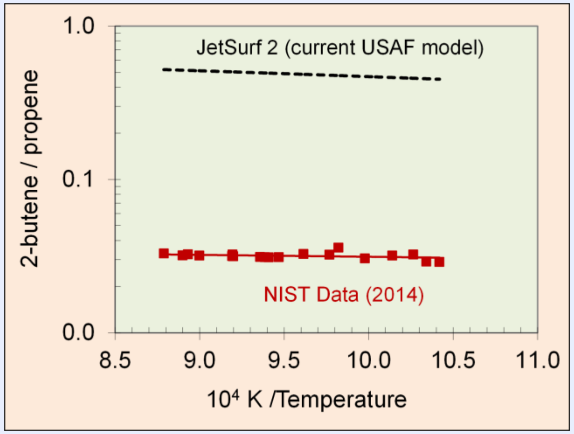
Product ratio: cyclopentyl



Product ratio: *n*-pentyl



Product ratio: *2*-butyl



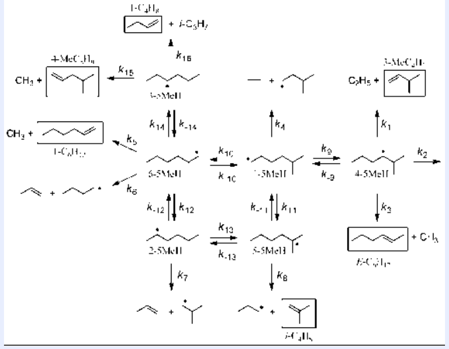
Focus is reference data to fill data gaps

Precise measurements - uncertainties are (5 to 10)% compared with (300 to 400)%.

NIST studies are the ONLY direct measurements of fragmentation patterns at high *T*

Raw Measurements to Reliable Rates

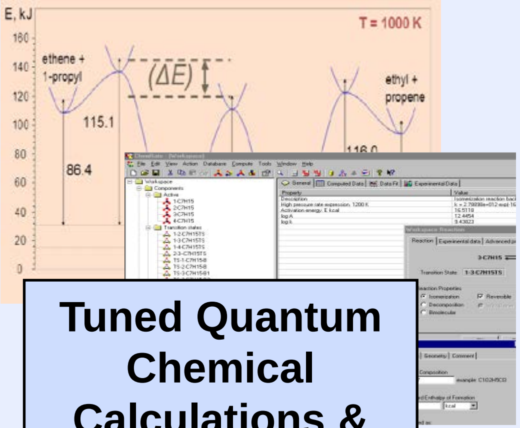
Lab Experiments



Can't measure everything:

Measure for prototypical species

Extend by reaction class



Tuned Quantum Chemical Calculations & RRKM Analysis

Reaction	$\log_{10}$ A (s^{-1})	*n*	E_a/R K
k_1: c-$C_6H_{11} \longrightarrow$ c-C_6H_{10} + H	12.97	0.8422	16381
k_2: 1-C_6H_{11}-6 $\longrightarrow C_2H_4 + C_4H_7$-4	14.06	- 0.2308	14899
k_3: 4-C_6H_{11}-3 $\longrightarrow$ 1,3-C_5H_8 + CH_3	13.29	- 0.2662	18201
k_4: 1-C_6H_{11}-3 $\longrightarrow$ 1,3-C_4H_6 + C_2H_5	14.28	-0.3962	17866
k_5: c-C_5H_9-$CH_2 \longrightarrow CH_2$-c-$C_5H_8$ + H	11.98	1.283	15490
k_6: 1-CH_3-c-C_5H_8-3 $\longrightarrow$ 4-CH_3-c-C_5H_7 + H	12.69	0.8105	16861
k_7: 1-CH_3-c-C_5H_8-3 $\longrightarrow$ 3-CH_3-c-C_5H_7 + H	12.66	0.8104	16808
k_8: 1-C_6H_{11}-5 $\longrightarrow C_3H_6 + C_3H_5$ (allyl)	13.89	- 0.3622	12029
k_9: 2-CH_3-4-C_5H_8-1 $\longrightarrow C_3H_6 + C_3H_5$(allyl)	13.78	- 0.6942	11831
k_{10}: 1-C_6H_{11}-6 $\longrightarrow$ c-C_6H_{11}	7.54	1.7491	2433
k_{-10}: c-$C_6H_{11} \longrightarrow$ 1-C_6H_{11}-6	12.33	1.004	13605
k_{11}: 1-C_6H_{11}-6 $\longrightarrow$ 1-C_6H_{11}-3	8.83	2.596	6510
k_{-11}			
k_{12}			
k_{-12}			
k_{13}			
k_{-13}			
k_{14}			
k_{-14}			
k_{15}			
k_{-15}			

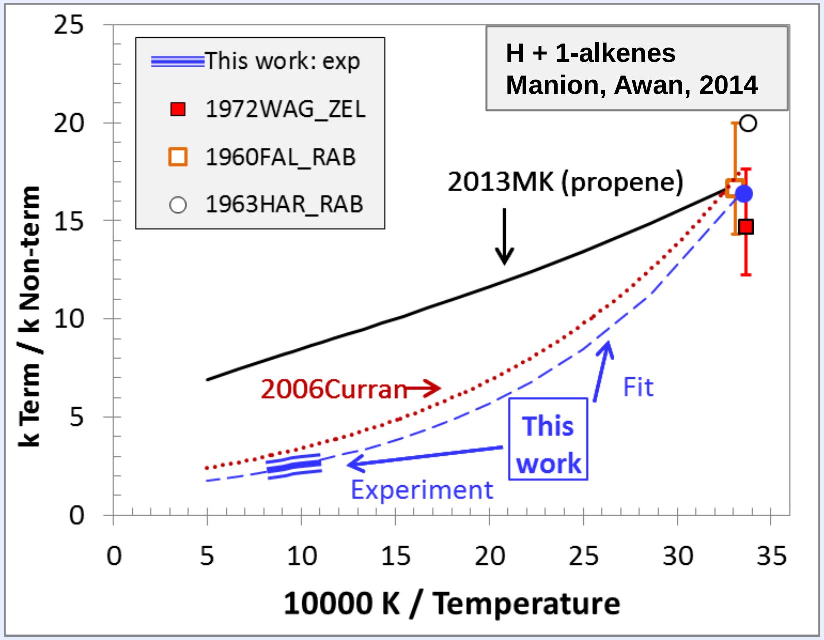
Kinetics over
P, T
500 to 2500 K
0.5 to 500 bar

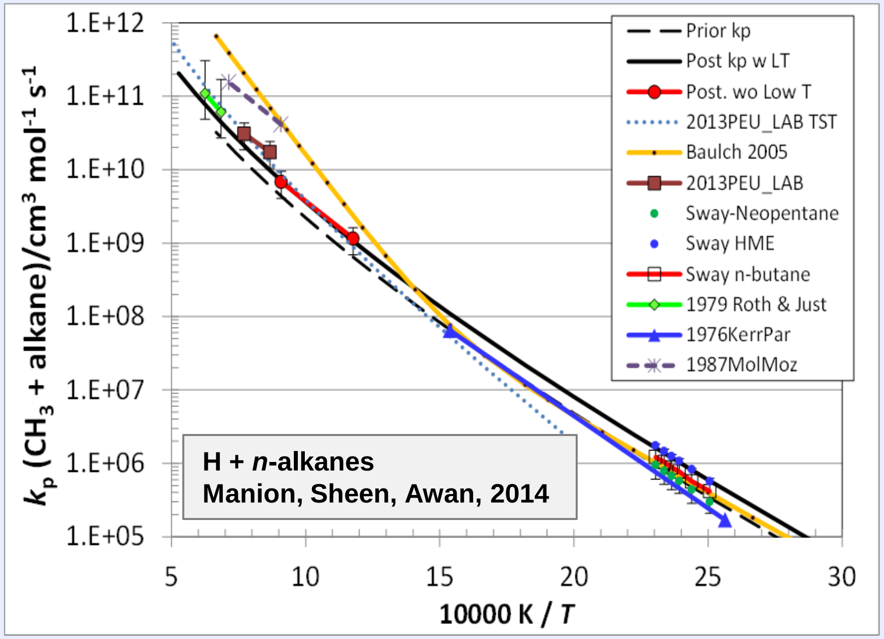
Team: Jeff Manion, Don Burgess, Iftikhar Awan

Outline

- Some Fundamental Property Databases at NIST
- Data Informatics
- Development of a chemical kinetic model for 2-BTP
- **Strategies for improving models**
- Concluding Remarks

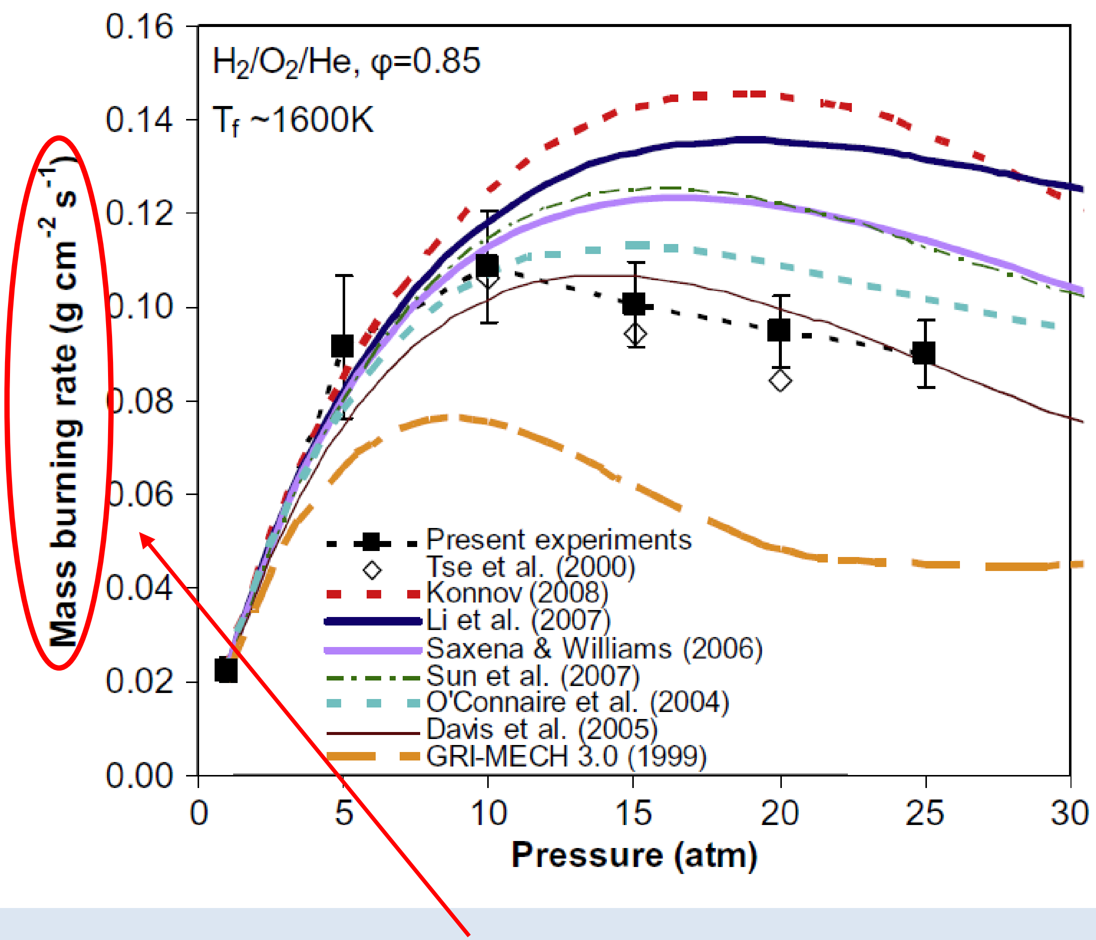
Data Evaluation – When the data disagree





- ➢ Evaluation of data is an important process
- ➢ NIST shock-tube experiments can provide validating kinetic reference data

Models and Uncertainty – What Do We Really Know?



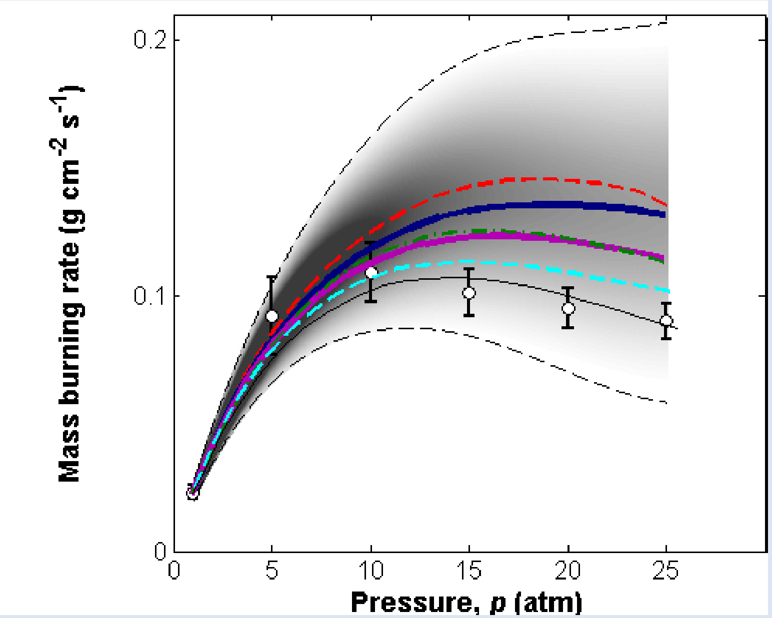
- Many models, none agree with each other or with experiment
- Without understanding uncertainty, model development is a non-converging process

= Density x Laminar Flame Speed

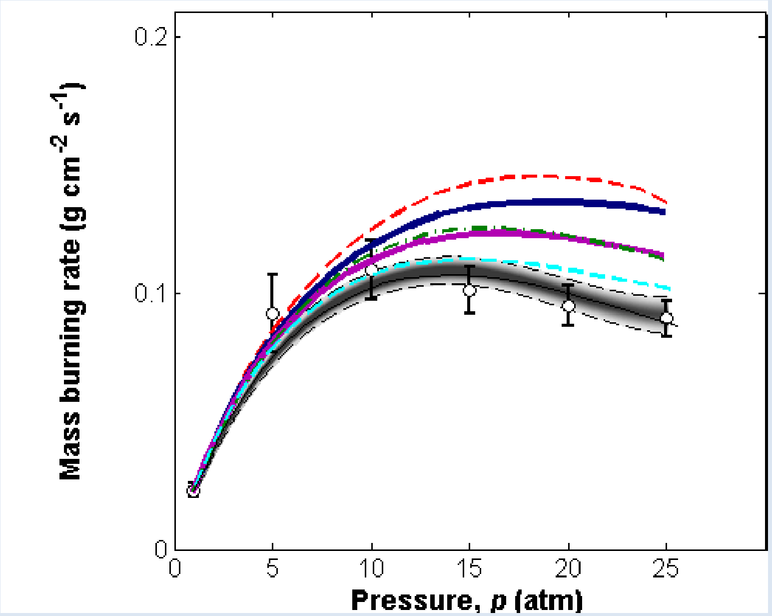
Burke, et al., 2010

Working Smarter – Better Models Through Uncertainty Analysis

Forward Uncertainty Quantification
(Propagation)



Inverse Uncertainty Quantification
(Constraint)



Experimental Design through Differential Information (1)

Every measurement has

- measurement uncertainty σ^{obs}
- model uncertainty σ^{*}

Define an information sensitivity

$$S_{H,ij} = \frac{\partial \sigma_j^{*}}{\partial \sigma_i^{\text{obs}}} \frac{\sigma_i^{\text{obs}}}{\sigma_j^{*}}$$

cf. Information entropy (Shannon 1948)

This is the sensitivity of the model uncertainty in prediction *j* to uncertainty in measurement *i*

Effect of other experiments' experimental uncertainty on simulated uncertainty of *r*

Effect of experimental uncertainty of *r* on other experiments' simulated uncertainty

$\Phi_r > 0$ ↔ More information going out from measurement *r* to other conditions

$\Phi_r < 0$ ↔ More information coming in from other measurements to condition *r*

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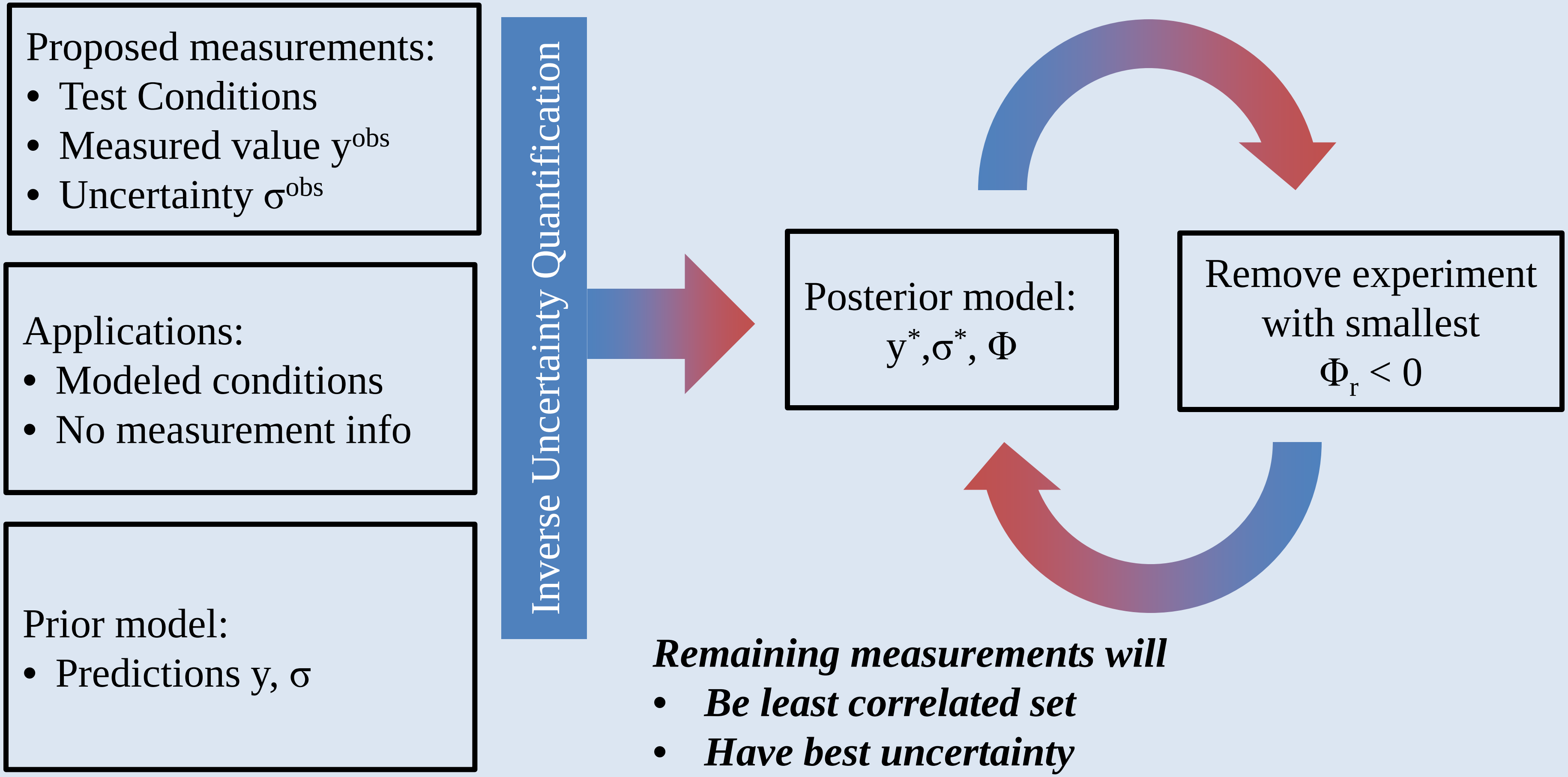
Experimental Design through Differential Information (2)



Proposed measurements:
- Test Conditions
- Measured value y^{obs}
- Uncertainty σ^{obs}

Applications:
- Modeled conditions
- No measurement info

Prior model:
- Predictions y, σ

Inverse Uncertainty Quantification

Posterior model:
y^*, σ^*, Φ

Remove experiment with smallest
$\Phi_r < 0$

Remaining measurements will
- ***Be least correlated set***
- ***Have best uncertainty***
- ***Target chemistry relevant to applications***

Sheen & Manion, J. Phys. Chem. A, **118**, 4929, 2014

Experimental Design through Differential Information (3)

Application of EDDI

- We have applied to complex chemical kinetic models and shock tube experiments
- **However**, method is general - applicable to any system with uncertain model parameters
- May help answer "what experiments to do?"

Sheen & Manion, J. Phys. Chem. A, **118**, 4929, 2014

Recap

- Some Fundamental Property Databases at NIST
- Data Informatics
- Development of a Chemical Kinetic Model for 2-BTP
- Strategies for Improving Models
- Concluding Remarks

Applying Fundamental Models to Flammability

- **Fundamental Data / Models – What would be useful?**
  - **Standard Fuel Combustion Models?**
  - **Standard Models for Combustion of Refrigerants/Suppressants?**
  - **Standard Tests?**
  - **Databases – what data, properties, etc.?**

…?

Assorted Properties of Mildly Flammable Systems

NIST Workshop on the Exothermic Reaction of Halogenated Hydrocarbons
Gaithersburg, MD Nov. 27-28, 2014

	Greg Linteris*,		*NIST Fire Research*
Kinetics	Jeff Manion / Wing Tsang / Don Burgess,		*NIST Chemical Kinetics*
	Valeri Babushok,	Flame modeling	*(NIST GR)*
	Vish Katta,		*Innovative Scientific Sol. Inc.*
	Fumi Takahashi,		*Case Western Reserve Univ.*
	Peter Sunderland, John Pagliaro	Experiments	*Univ. of Maryland*

**Presenter*

The work was supported by The Boeing Company, NIST Internal Funds, ARRA Grant.

What we learned*

Low-strain regions can support low reactivity flames.

Once you get a flame going (e.g., with a stronger hydrocarbon-air flame), very weak mixtures can burn vigorously.

Adding a suppressant to lean mixture beyond its flammability limit can make it flammable.

Adding a suppressant to cup-burner flame can increase the heat release.

The flammability behavior depends a lot on the ignition source.

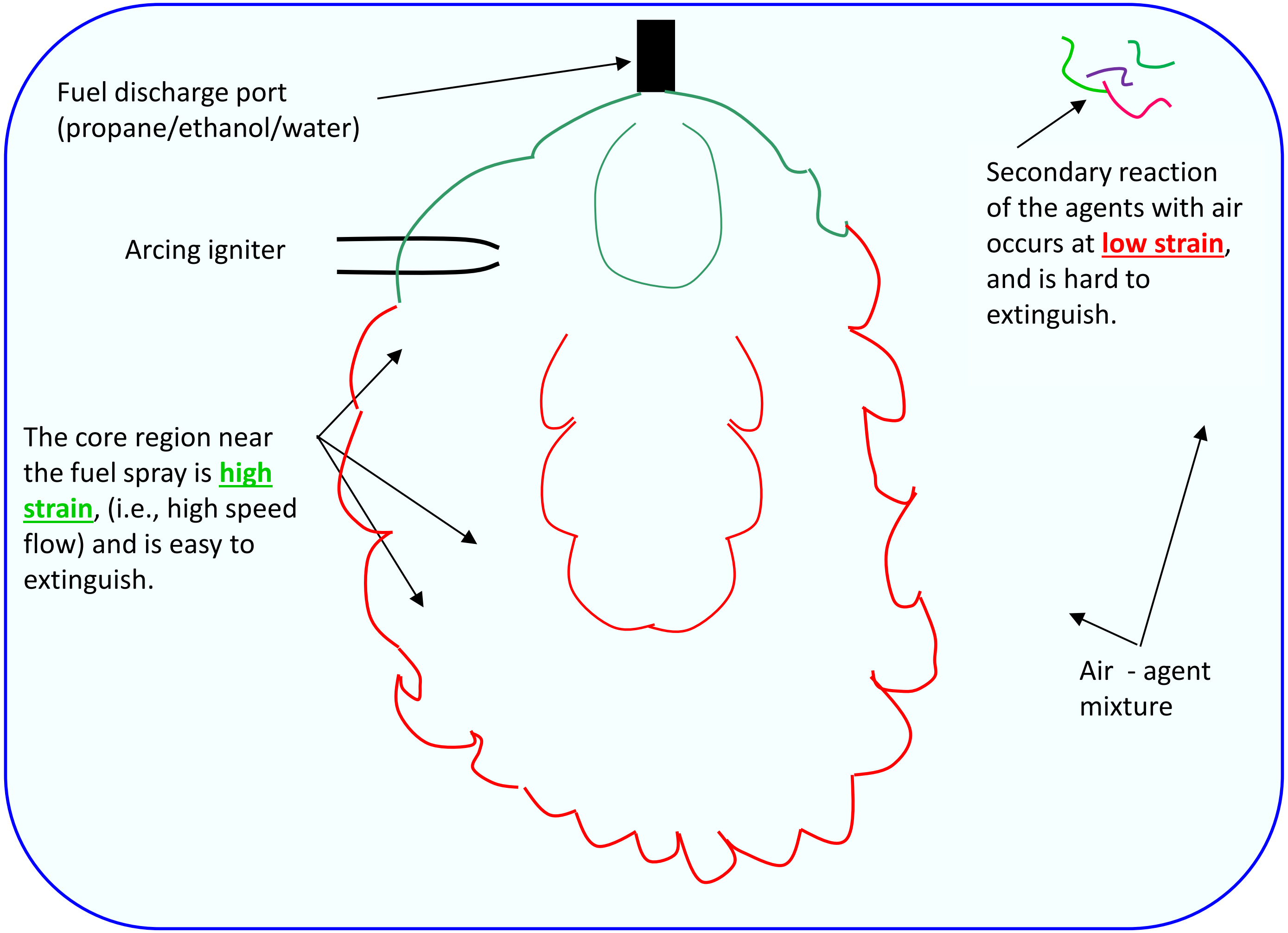
Water vapor has a significant effect on halogen-rich systems.

If this is all true for some fire suppressants, then it is even more true for mildly-flammable refrigerants.

⇒ The behavior of a mildly-flammable compound depends a lot on the environment it is in (ignitions source, other flammables, flow-field, clutter, turbulence, etc.)

*Does this matter for the safe use of 2L refrigerants and fire suppressants?

Low-strain regions can support very weak flames.



Fuel discharge port (propane/ethanol/water)

Arcing igniter

Secondary reaction of the agents with air occurs at **low strain**, and is hard to extinguish.

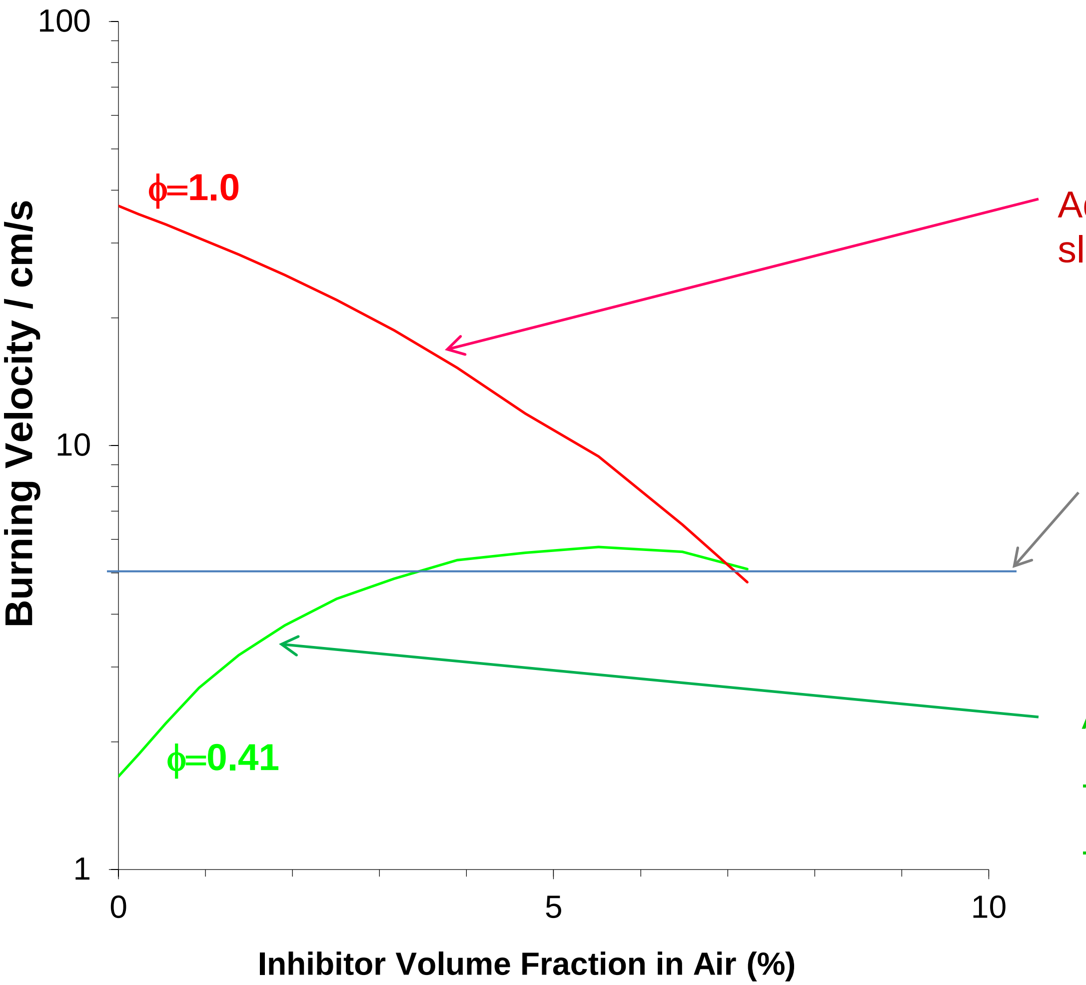
The core region near the fuel spray is **high strain**, (i.e., high speed flow) and is easy to extinguish.

Air - agent mixture

=> Adding a mildly flammable agent creates low-strain regions that are harder to extinguish

Suppressant added to lean mixture beyond its flammability limit can make it flammable

HFC-125 with Aerosol Can Test Fuel, T_{init}=298 K



Adding suppressant to a stoichiometric flame slows the burning velocity.

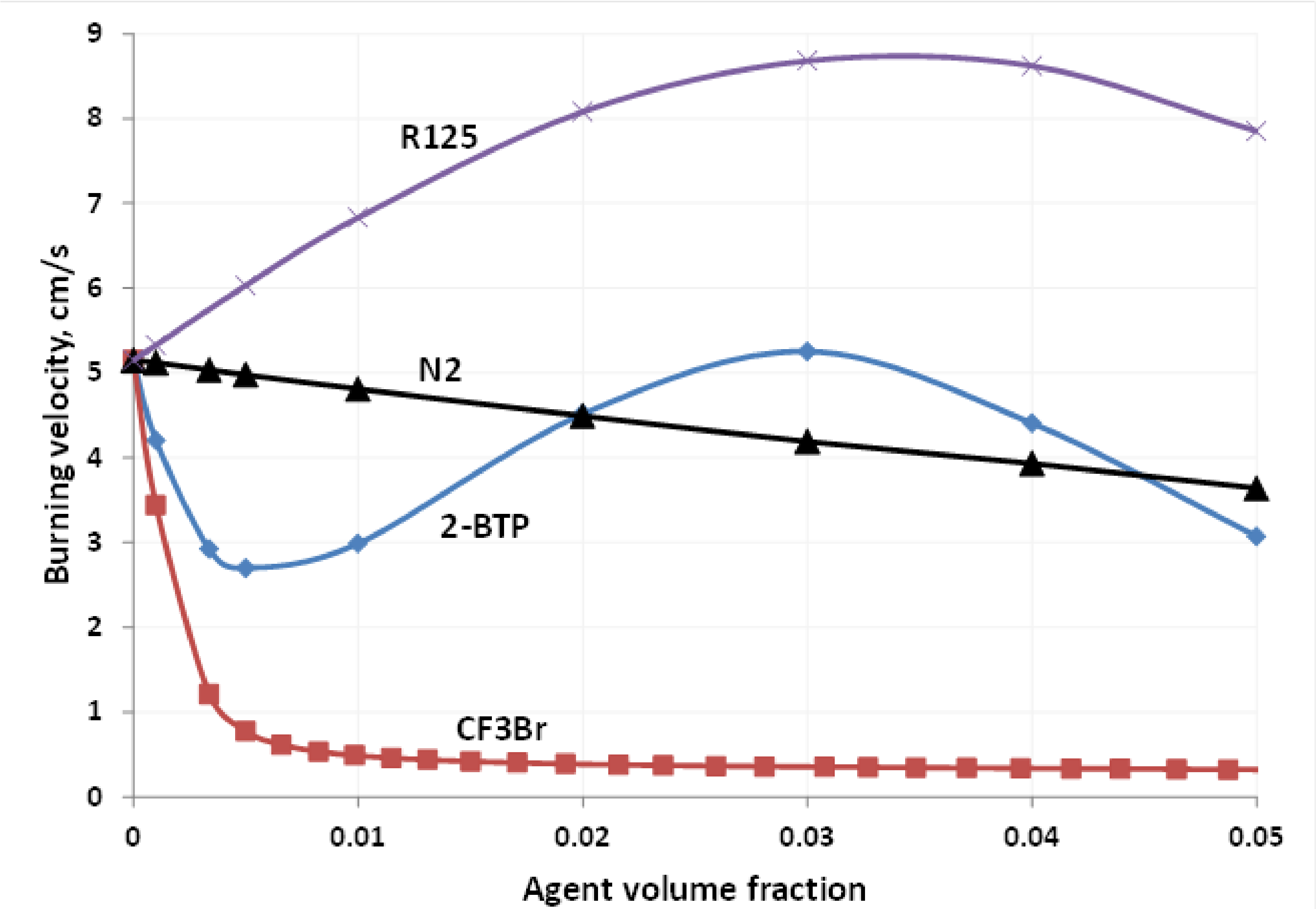
A burning velocity of 5 cm/s is sometimes considered a criterion for the flammability limit.

Adding suppressant to a lean mixture can:

- increase the burning velocity, and
- bring the mixture into a flammable regime.

Return

Effect of suppressant on lean flames (CH_4-air, ϕ=0.5) varies with the agent type



turn

Adding a suppressant to cup-burner flame can increase the heat release.

Computational Method (UNICORN)

- Time-dependent axisymmetric governing equations

⇒ Mass, momentum, species, energy conservation equations

⇒ Thermo-physical properties from polynomial curve fits

⇒ Optically thin-media radiation from CO_2, H_2O, CH_4, CO, and CF_2O, and soot

⇒ Implicit QUICKEST scheme (momentum)

- Comprehensive reaction mechanism (177 species/2986 rxns)

⇒ 4-carbon hydrocarbon mechanism by Wang et al. (111 species/1566 rxn.)

⇒ Ethanol reactions by Dryer et al. (5 species/72 rxns)

⇒ CF_3Br inhibition by Babushok et al. (10 additional species/148 rxns)

⇒ A subset of NIST HFC mechanism (51 species/1200 rxns)

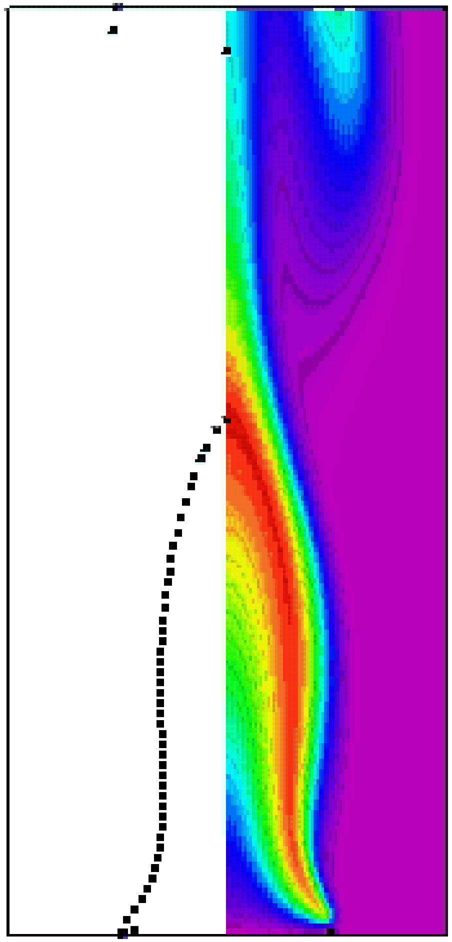
- Validation

⇒ Validated for various flame-flow phenomena, including couterflow flame extinction, vortex-flame interaction, blowoff, and suppression

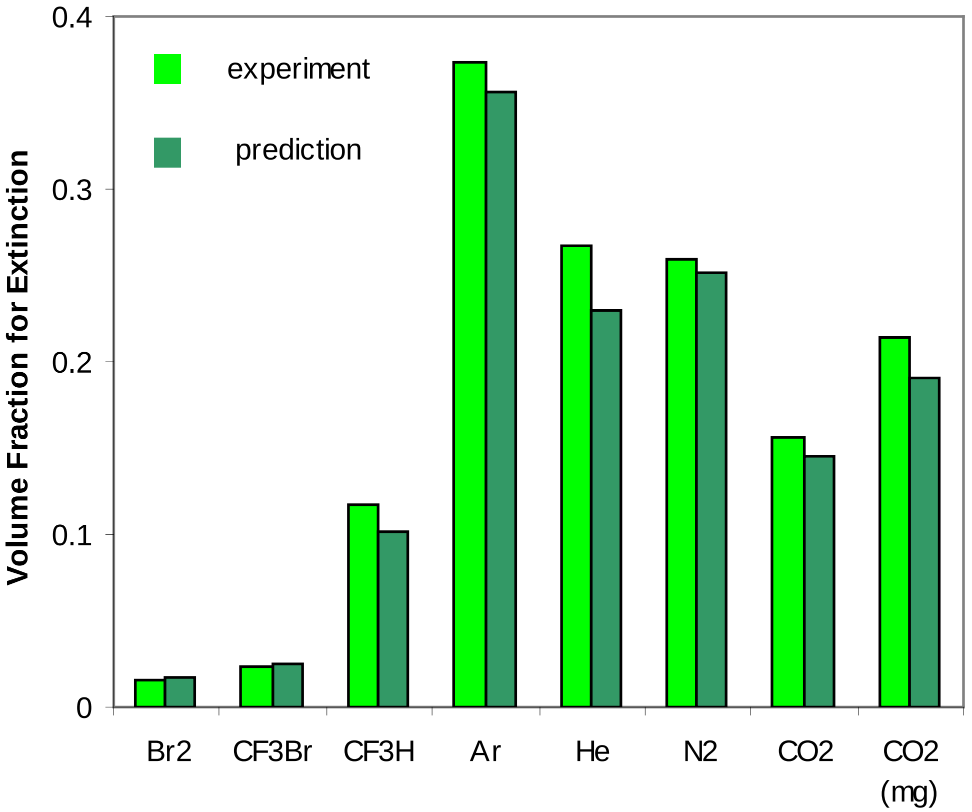
⇒ The predicted extinction strain rates for propane-air counterflow diffusion flames were within 7.5% of the measured values.

Cup Burner Flame Simulations

1. Detailed numerical simulation (solves Navier-Stokes equations) with full kinetics (177 species, 2986 reactions).
2. Time dependent, 2-D, axi-symmetric, full transport, gray thin-limit radiation model.

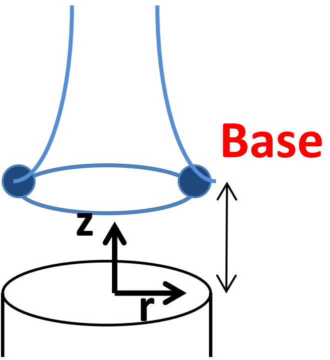


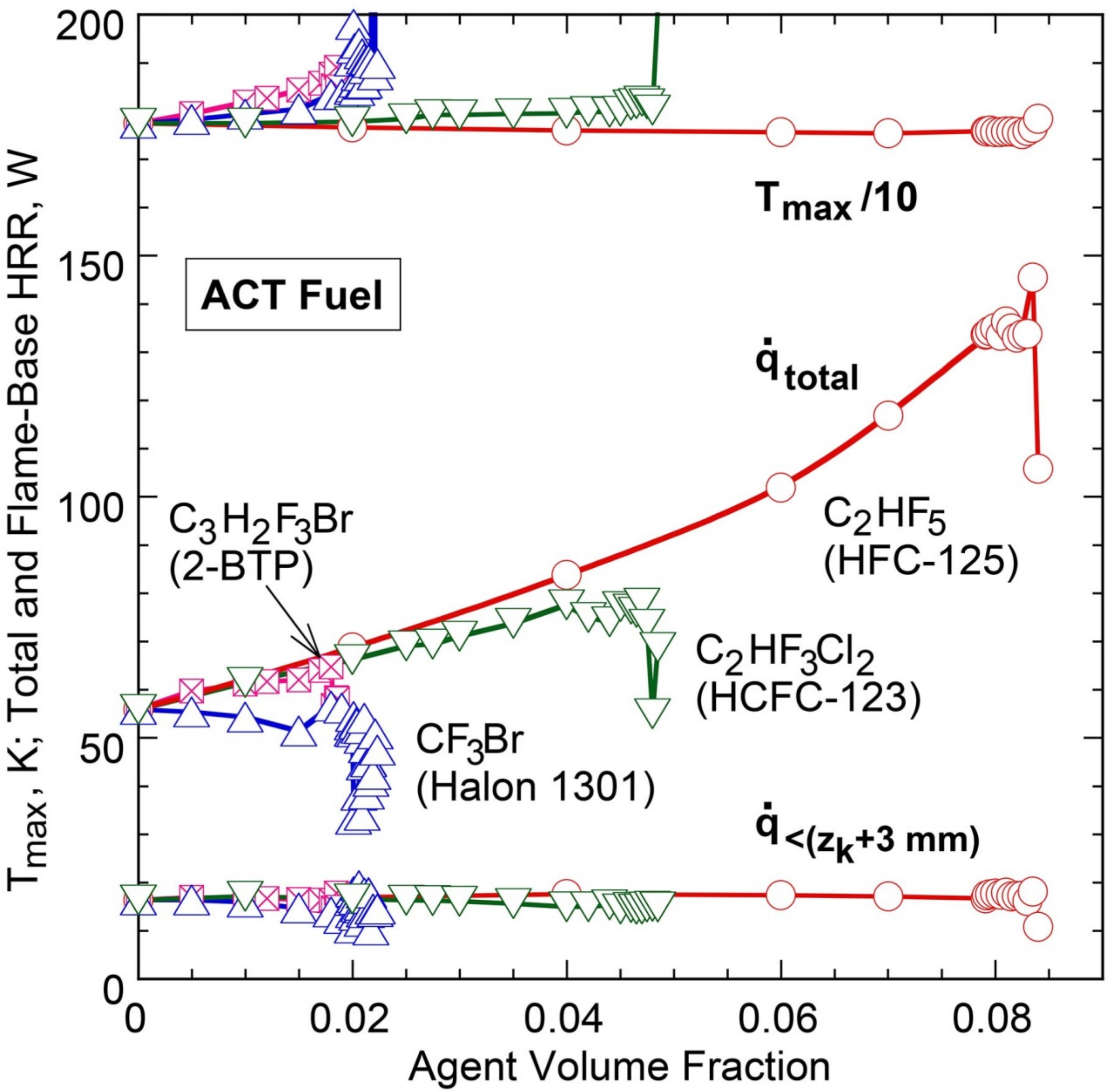
1. The model has can predict extinction of the cup burner.



Return

Cup Burner Flame: T_{max}, and Heat Release (total and at base)

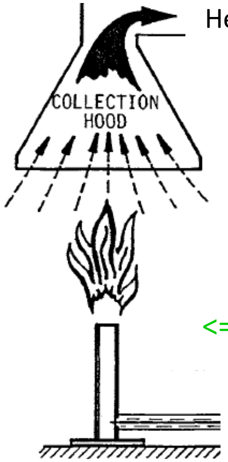




Air+agent added to co-flow

ACT Fuel: U_{fuel}=0.853 cm/s **Air + Agent:** U_{ox}= 10.7 cm/s

HFCs added to Propane-air Flame Increases Heat Release, but HCFCs do not.

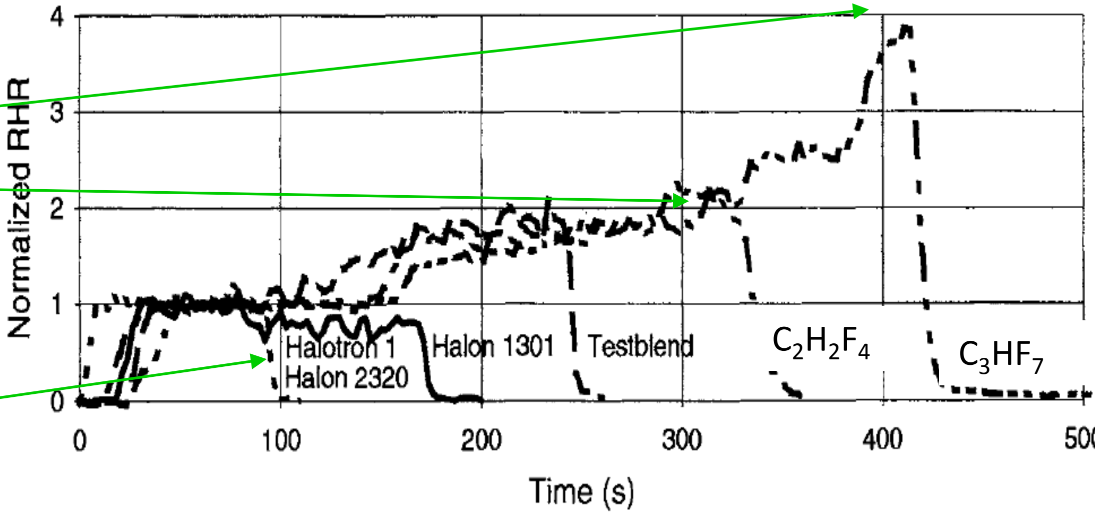


Heat Release Rate Measurement

<= air and agent input (Increase agent concentration in air linearly in time.)

<= propane

From: Holmstedt et al. 1994



⇒ Total heat release increases (≈2 to 4 times) for $C_2H_2F_4$ (HFC-134a)

or C_3HF_7, (HFC-227ea)

at concentrations just below extinction,

=> but does not increase for Halotron 1

(mostly $C_2HCl_2F_3$; i.e., R-123).

=> So this test <u>also</u> indicates that R-123 may work in FAA Aerosol Can Test.

Exothermic reaction of pure agents in air

Calculated Temperature and Burning Velocity of fire suppressant/air stoichiometric mixtures (1 bar)

(Premixed burning velocity is a measure of the mixture’s overall reaction rate.)

Agent	Formula	Oxidizer	Initial Temperature, K	Peak Adiabatic Flame Temperature K	Burning Velocity, cm/s
HFC-23	CF_3H	air	400	1751	0.567
HFC-125	C_2F_5H	air	400	1858	1.56
HFC-227ea	C_3F_7H	air	400	1874	2.48
2-BTP	$C_3H_2F_3Br$	air	400	2033	2.14
Novec 1230	$C_3F_7COC_2F_5$	air	400	1864	0.367
Triodide	CF_3I	oxygen	500	1528	1.33
halon-1301	CF_3Br	oxygen	500	1485	<0.15

(values down to ≈1 cm/s can be measured.)

- some fire suppressants themselves may support flames (although very weak) in air at elevated temperatures.

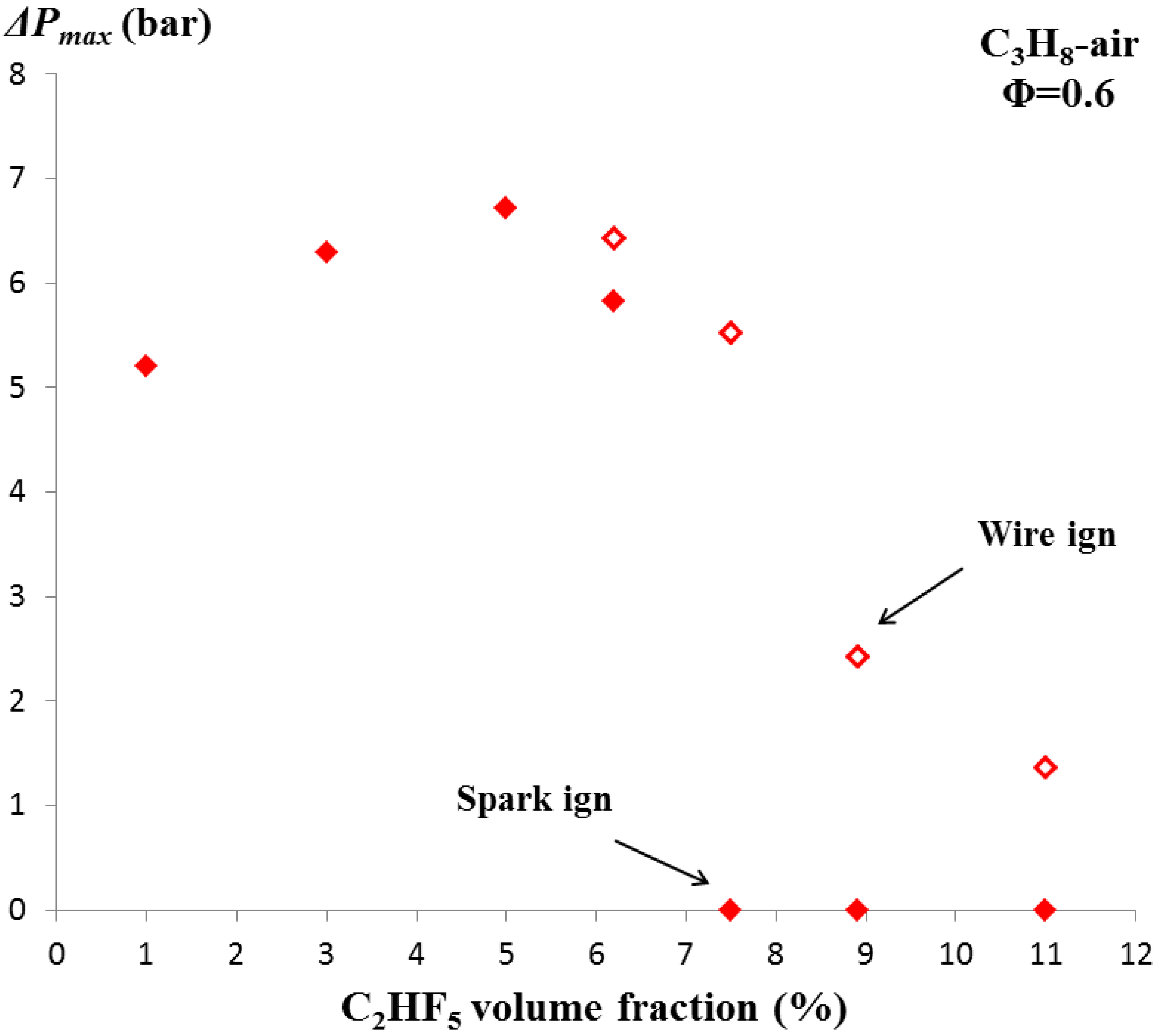
- burning velocity of CF_3Br is < 0.15 cm/s at 500 K with O_2 oxidizer.

Return

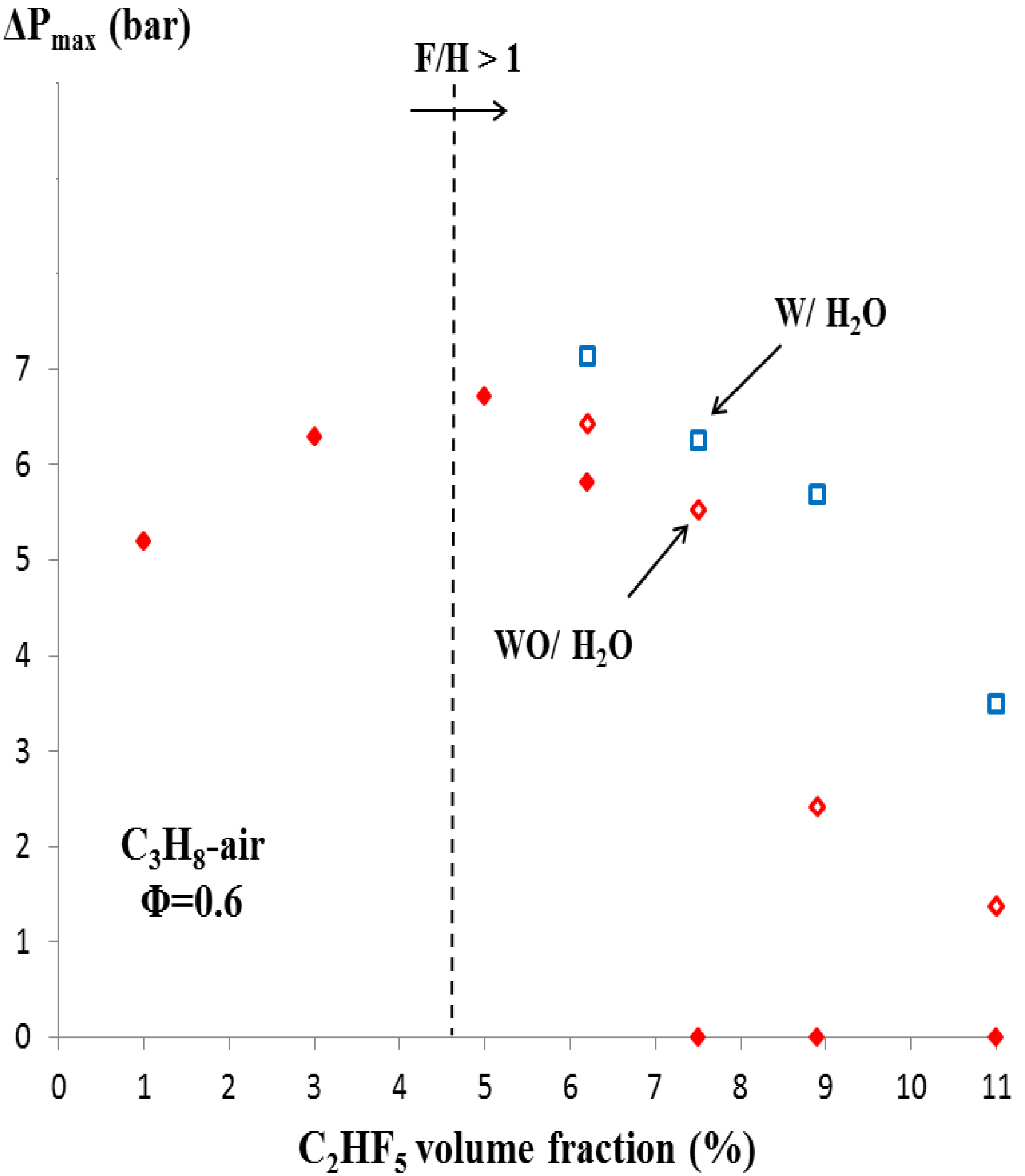
The flammability behavior depends a lot on the ignition source.

⇒ To ignite mixtures that were burning in the FAA-ACT, we had to go to the Pt wire igniter. Could not do it with the high energy spark ignition.

⇒ That igniter implies different flammability limits (e.g. C_3H_8-air flame with 125)



Water Vapor Can Have a Significant Effect



Point of this talk:

This is what we learned from interpreting the FAA_ACT.

Does any of this matter for suppressants in other scenarios (than cargo bay)?

Are there any scenarios for refrigerants in which these properties matter?
(Oil burner, leak in A/C coil, etc.)

What is the limiting S_L for inertion? What is the value of S_L for safe use of the compounds and what are the environmental conditions that influence that value?