Modeling Tools for Flammability Ranking of Low-GWP Refrigerant Blends

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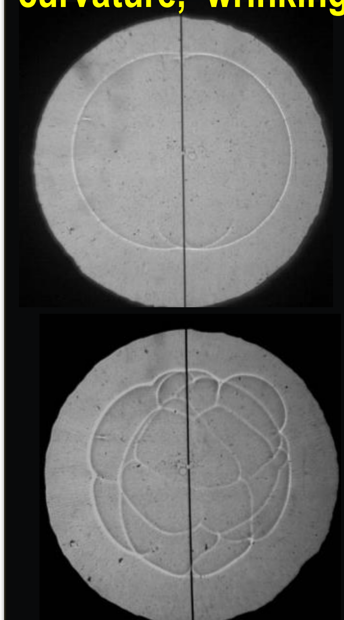
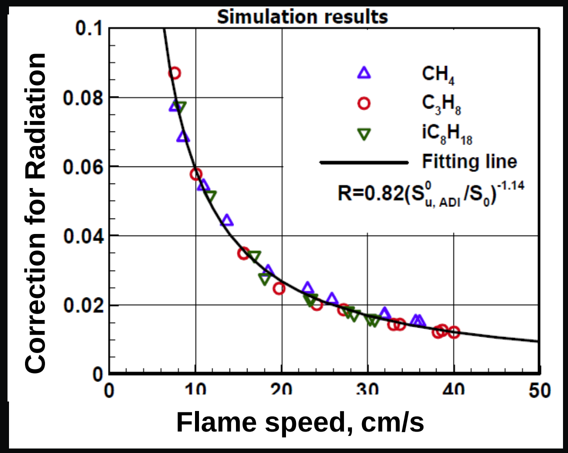
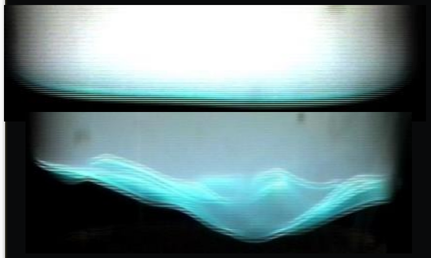
Flame Stretch, curvature, wrinking



Radiation Heat Losses



Buoyancy



Flame stretch, radiation heat losses, and buoyancy affect flame behavior.

A proper ranking of flammability and an understanding of the full-scale behavior must account for these effects.

* Yu et al. CNF, 2014

**Takizawa et al.

Project Summary

Timeline:

Start date: Oct. 1, 2016

Planned end date: Sept. 30, 2019

Key Milestones

1. Burning velocity data/predictive tool for HFCs (9/17) and HFOs (9/18).
2. Generalized burning velocity predictive tool for blends (9/19)
3. Input into codes and standards test method development (9/19).

Budget:

Total Project $ to Date:

- DOE: $1350k
- Cost Share: $700k (NRC post-doc, NIST equip. grant, ½ Greg's Salary)

Total Project $:

- DOE: $2000k
- Cost Share: $875k

Key Partners:

AHRI	ITV, RWTH Aachen (Pitsch)
ASHRAE	Northeastern Univ. (West)
ISO	Univ. of So. Cal. (Egolfopoulos)
UTRC	W.P.I. (Jayachandran)
Gexcon	Peking Univ., China (Chen)
UMd (Sunderland)	AIST, Japan (Takizawa)

Project Outcome:

1. Develop predictive tools for the laminar burning velocity of low-GWP refrigerants, so that blends can be optimized by industry to maximize performance while minimizing flammability.
2. Build and validate kinetic mechanisms (full and reduced) to allow for DNS modeling of fire threats.
3. Provide technical input into the codes and standards development process to facilitate the safe implementation of low-GWP, mildly flammable refrigerants.

Team

NIST:

G. Linteris : Project Manager, past experience with HFCs for fire suppression, experiment/modeling

V. Babushok*, D. Burgess* : kinetic model development

J. Manion* : shock-tube measurements of elementary rates, mechanism development

R. Burrell (NRC post-doc): burning velocity measurement, constant volume and constant pressure methods (leaving spring 2019; replacement to be found).

M. Hegetschweiler: 1D, 2D numerical modeling

Universities:

H. Pitsch* (ITV, RWTH Aachen Univ.): simultaneous schlieren/PIV measurements, 3D modeling, flame dynamics

R. West (Northeastern Univ.): mechanism optimization, reduction

F. Egolfopoulos* (Univ. So. Cal.): thermo. modeling of constant-volume experiments

J. Jayachandran (WPI) : HTDR/TORC modeling of constant-volume experiments

Z. Chen*, Peking Univ. : ASURF modeling of 1D, unsteady, spherical flames with radiation

P. Sunderland (UMd) : evaluation of existing flammability test methods (ASTM E681)

Industry / Goverment:

Gexcon : Explosion modeling, burning velocity expts.

AHRI : coordination with industry.

Army Research Lab: ARL, APG, ATC, SERDP.

Standards Organizations:

ASHRAE (Standard 34, T.C. 3.1)

ISO

* World leader in their respective field.

Challenge

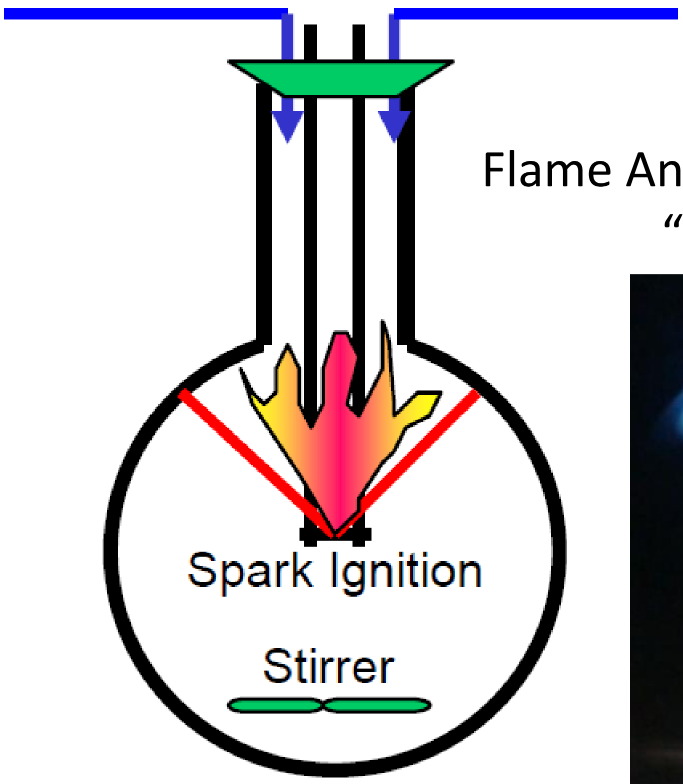
Problem Definition: Existing HFC working fluids for vapor compression HVAC systems have high GWP and will be phased out per the Kigali Agreement. The implementation of this agreement, according to the Natural Resources Defense Council, is equivalent (with regard to radiative forcing) to stopping all fossil-fuel combustion for two years.

New low-GWP fluids have been, and are being, developed; however, they are flammable and the lack of codes and standards for their safe use is a major obstacle to their rapid adoption. The US HVAC industry is onboard with adoption of the low-GWP compounds, although flammable working fluids in residential and commercial settings is a new concern for them; hence, they need help ranking and understanding the flammability risk of different options.

To achieve the performance and GWP goals, industry will use blends (up to five components). To optimize the blends, techniques exist to predict the thermodynamic performance and GWP; however, there are no methods to predict the flammability.

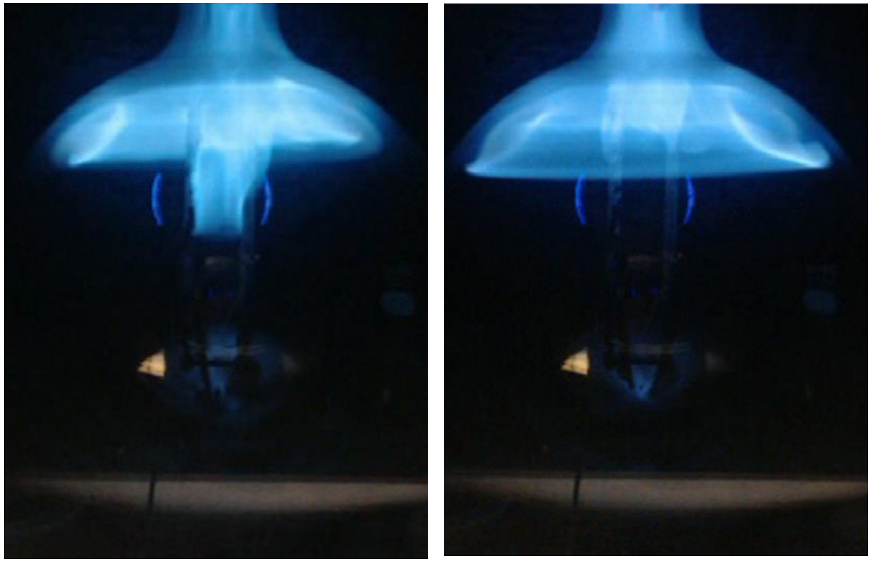
Challenge

ASTM E681 Apparatus



Flame Angle: 85° 95°

"non-flammable" "flammable"



This flammability test depends upon burning velocity (buoyant flow ↑ , flame speed ↔)

Can this test result be predicted? Yes!

Can full-scale flammability behavior be understood better? Yes!

Approach

Laminar Burning Velocity (LBV) is foundational: much fire behavior depends upon it.

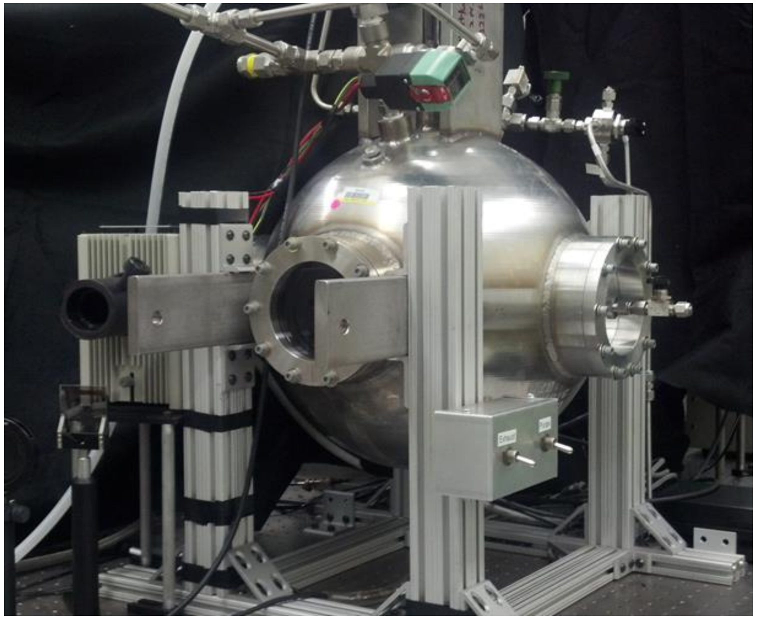
Goals:

- To develop the ability to predict the laminar burning velocity LBV of an arbitrary blend so that industry can optimize the blends with regard to flammability.
- To model and understand the burning velocity/flammability test methods so that industry has an accurate and relevant standard test method.
- Improve the understanding of full-scale flame behavior to reduce flammability risks.

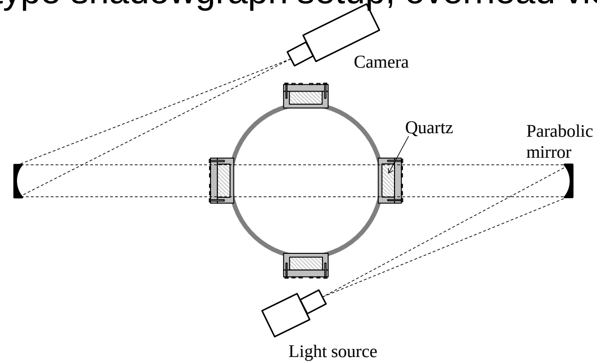
1. Assemble team (experimental, modeling, kinetics).
2. Get experimental LBV data for select pure compounds, over range of fuel/air mixtures.
3. Build kinetic models (shock-tube studies, quantum mechanical calculations, etc.).
4. Get flame modeling tools. (1-D, 2-D, time-dependent, spherical, with radiation).
5. Understand what's modelled and what's measured.
6. Compare experiments with model (validate model).
8. Develop predictive tool, f(humidity, T_{init}, P_{init}), pure compounds, mixtures, humidity).
9. Outputs:
   a.) Predictive tool for the burning velocity of refrigerants.
   b.) Validated kinetic mechanisms (full and reduced).
   c.) Technical input to standards development.

Experiments

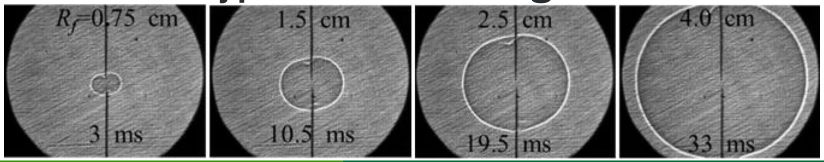
Constant Pressure Method, 30 L chamber



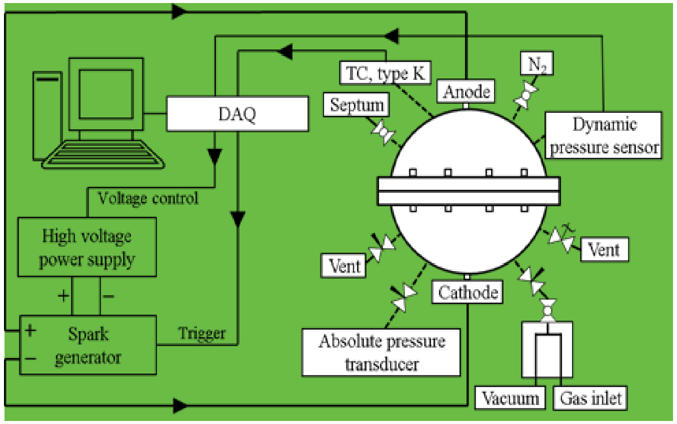
Z-type shadowgraph setup, overhead view.



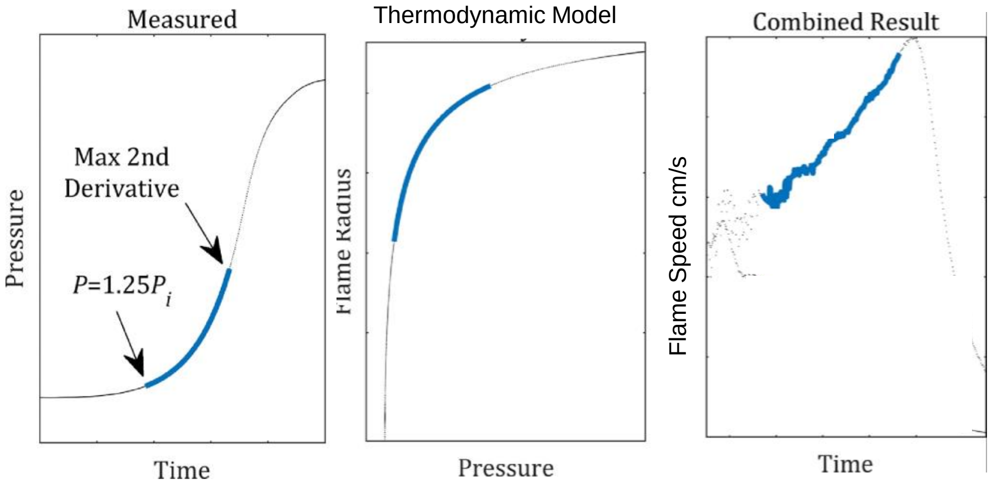
Typical Flame Images



Constant Volume Method, 1.8 L Chamber



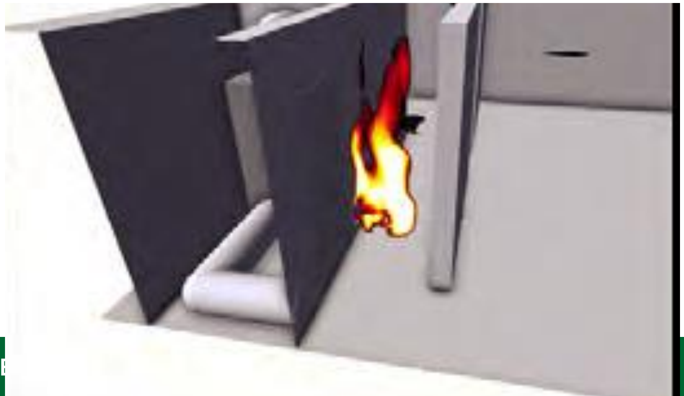
Schematic diagram.



Other State-of-the-Art Approaches:

1. Practical refrigerant release flammability experiments:
   a.) essential to get an overview of the behavior.
   b.) are mostly build-it and burn it empirical tests.
   c.) little interpretation of reasons for observed behavior.
   d.) too many parameters to get a full assessment of the range of risks.
   e.) costly and time-consuming to perform.
   f.) controlling parameters not systematically varied.
2. Scenario modeling using numerical fire models (e.g. FLACS)
   a.) requires input: - burning velocity data over a range of equivalence ratio
   - response of flame to stretch and transition to turbulence
   b.)can be used to cover more cases and wider range of conditions.
   c.) depends upon the accuracy of the model.
   d.) currently, not validated by experiments.

Full-scale numerical simulations of the behavior of refrigerant-air flames cannot currently predict the experimental behavior.



Impact

Directly supports BTO Emerging Technologies 2016-20 MYPP

Goal : Enable 45% reduction in building EUI in 2030 vs. 2010 EUI HVAC/WH/Appliances

Strategy 1: Near-Term Technology Improvement

Unique Comparative Advantage:

1. Existing approaches for understanding refrigerant flammability are largely empirical and inadequate.
2. Present approach is based on fundamental, detailed kinetics.
3. Numerical simulations of the flame structure are used to to uncover role of ancillary effects (buoyancy, stretch, radiation).
4. Can employ various levels of fidelity depending upon the need: (approx. kinetics; simplified radiation; planar vs. spherical flames, etc.)

Realization of Impact:

1. The goal is a usable design tool that can predict the fundamental laminar burning velocity of refrigerant blends.

2. Full-scale numerical simulations of the behavior of refrigerant-air flames, which are required to cover the range of possible scenarios, depend upon accurate burning velocity data and the response of the flame to stretch. The present project will provide those, enabling better full-scale numerical simulations.

Progress (project is ¾ through time, 2/3 through money)

Accomplishments:

1. Experiments

   a.) obtained comprehensive burning velocity data for R32 and R152a (over range of equivalence ratio and oxygen concentration) for mechanism development.

   b.) modified data reduction technique to now account for the effects of thermal radiation on the inferred burning velocity from the constant volume experiments.

   c.) assessed the role of flame stretch (i.e., curvature) and radiation on the inferred burning velocity from the constant pressure experiments.

2. Kinetic Mechanisms

   a.) New shock-tube data for key elementary rates

   b.) quantum mechanical calculations to extend literature elementary rates to T, P of flames.

   b.) Initial mechanisms for:

   - C_1, C_2 HFCs (R32, R41, R125, R134, R134a, R143, R134a, R152, R152a, R161).
   - fluoropropenes (R1234yf, R1234ze(E), R1243zf)

   b.) Comprehensive mechanisms for:

   - R32 (complete)
   - R152a (complete)
   - R125, R134a, R1234yf, R1234ze(E) (in work)

Progress (project is ¾ through time, 2/3 through money)

Accomplishments:

3. Numerical Modeling

a.) Performed DNS simulations (1D, unsteady, spherical flames with detailed chemistry and radiation heat losses) for experiments with the constant pressure method CPM and constant volume method CVM.

b.) Modeled the effects of stretch and radiation on the inferred burning velocity for:

- R32-air flames CPM (complete)
- R1234y-air flames CPM (in-work)
- R32-air flames CPV (in-work)
- R1234y-air flames CPV (in-work)

c.) Performed DNS simulations (2D, unsteady, buoyant flames with reduced chemistry) for diluted flames of CH_4-air and H_2-air with LBV of about 5 cm/s to explore the role of buoyancy and the assumptions in the data reduction techniques typically used in the standard test methods in development for refrigerant-air flames.

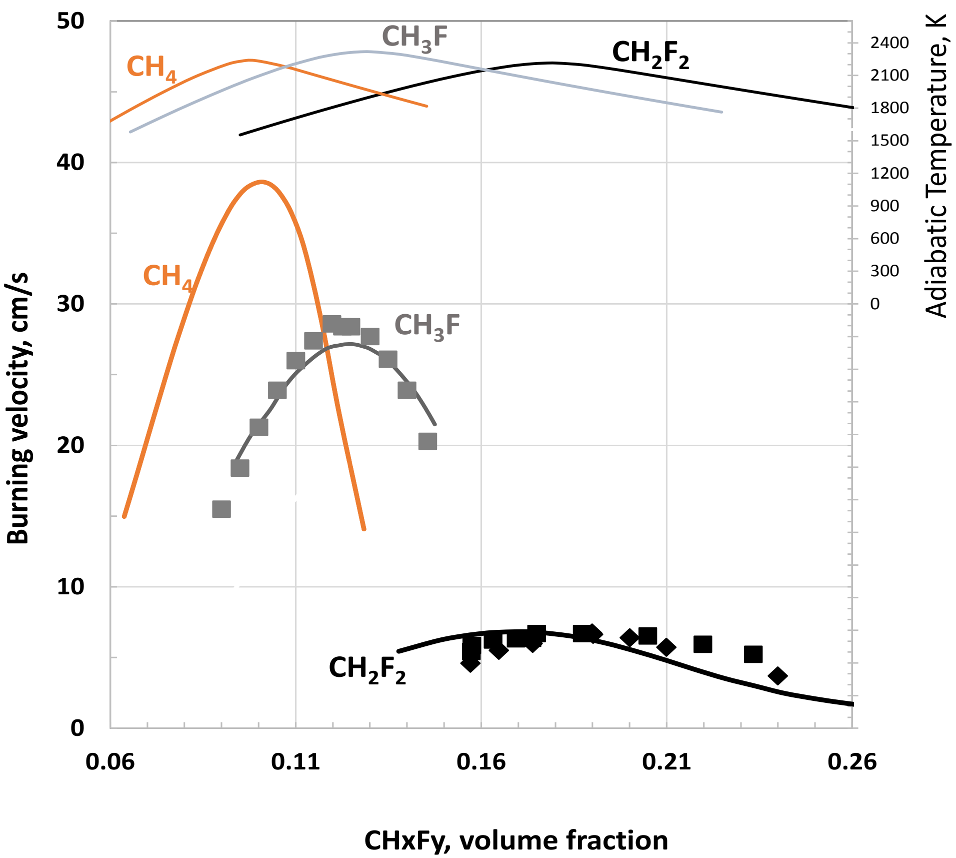
d.) Performed 1D, steady, planar flame speed simulations for a wide range of refrigerants, oxidizers, etc. and compared with above 1D and 2D unsteady simulations.

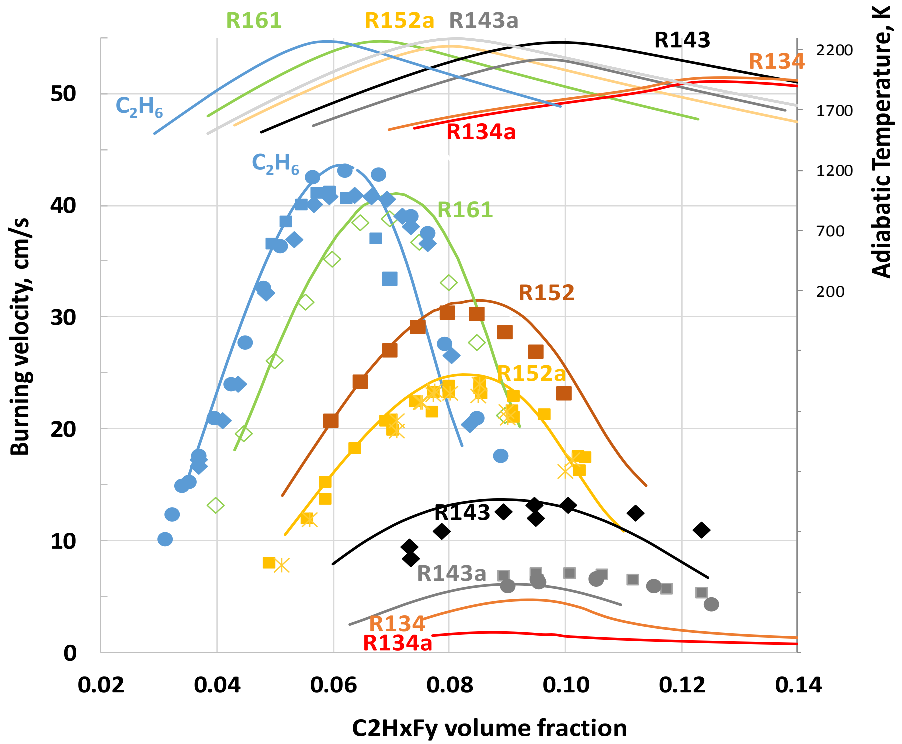
4. Generalized Burning Velocity Predictive Model

a.) Wrote a platform-independent GUI front-end, mimicking the NIST software package REFPROP, for use in user-friendly determinations of laminar burning velocity, adiabatic flame temperature, overall chemical reaction rate, etc. for an arbitrary initial conditions (refrigerant mixtures, Tin, Pin, humidity, oxidizer type, etc.).

b.) Constructed an empirical model for refrigerant flammability (blends) based on Tad and F/H ratio, that matches ASHRAE Standard 34 database, for use in screening studies until our more detailed LBV predictive tool is ready.

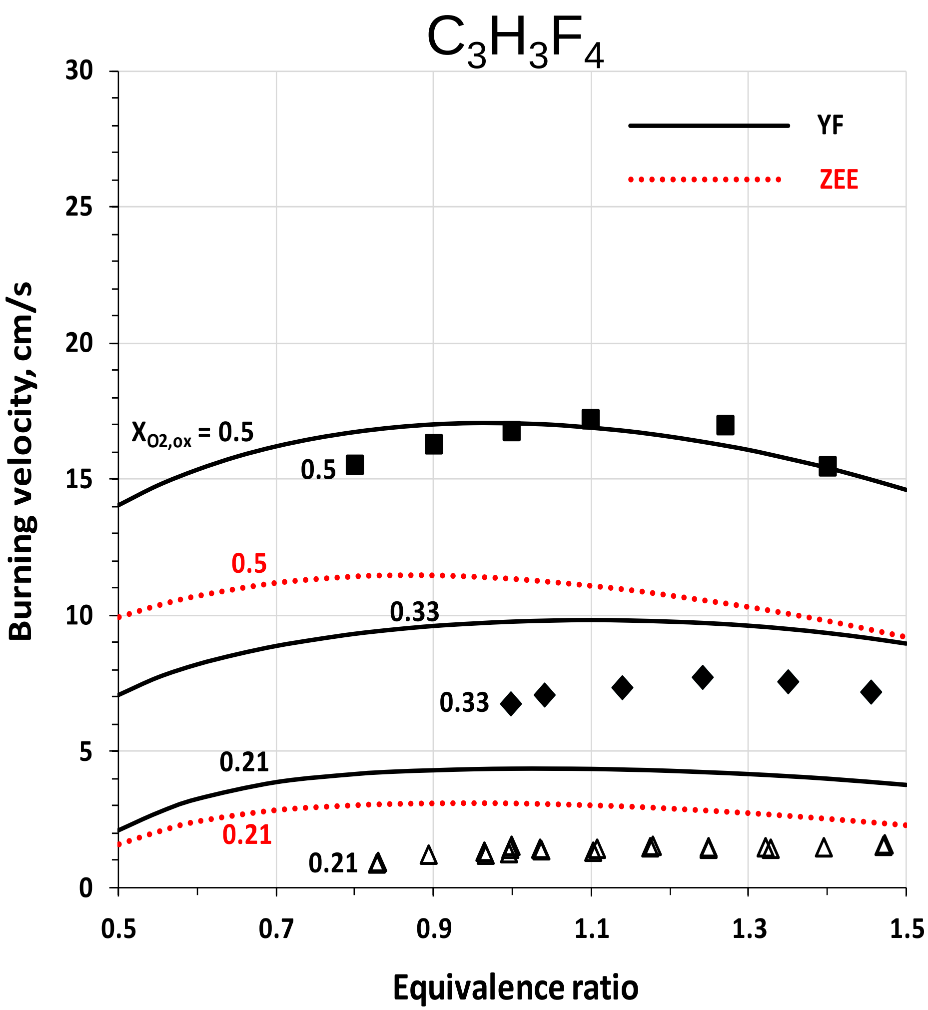
Predicted Burning Velocity of C_1, C_2 Fluorocarbons*

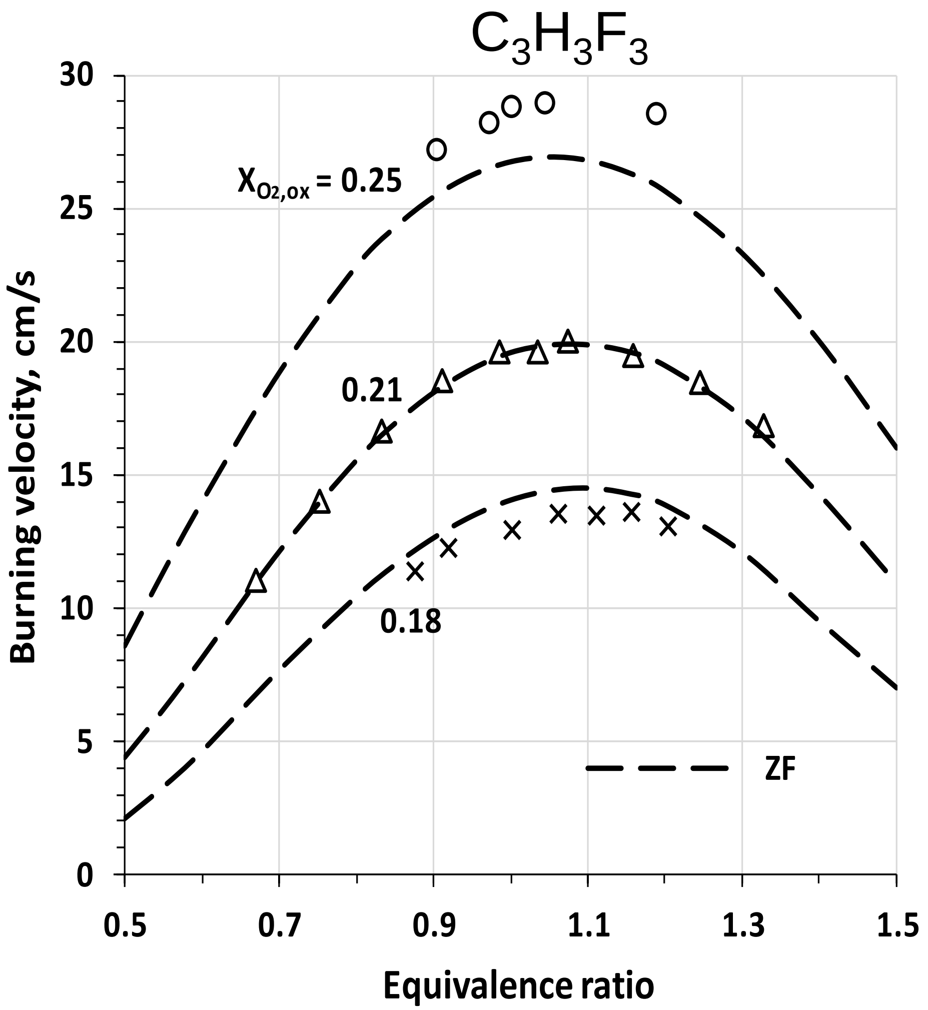




*Experimental data of: K. Takizawa, et al.

Predicted Burning Velocity of Flouropropenes*

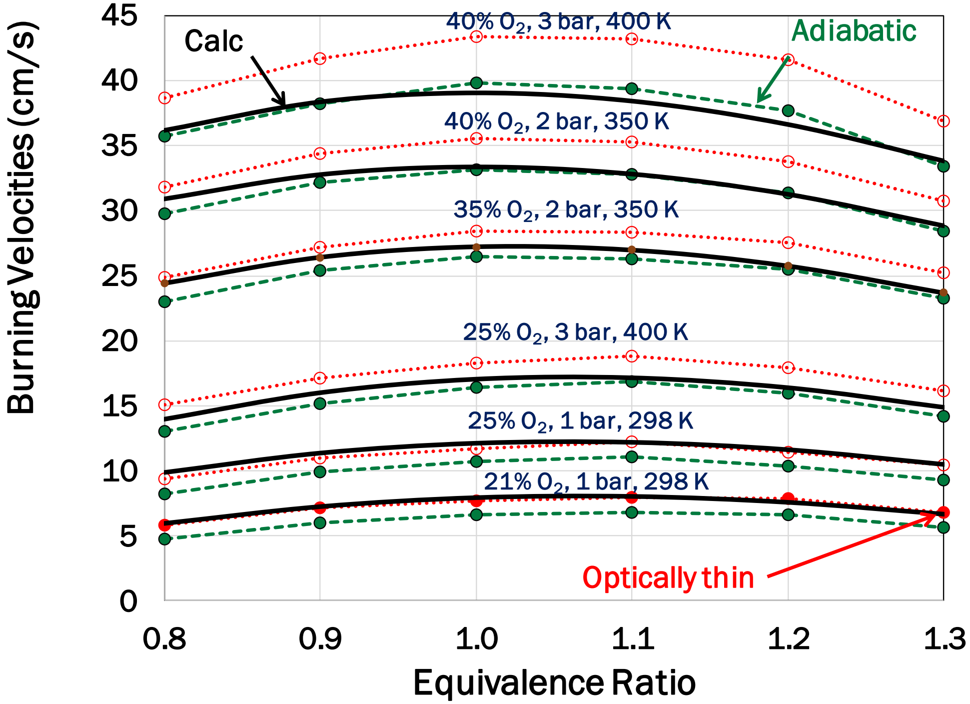




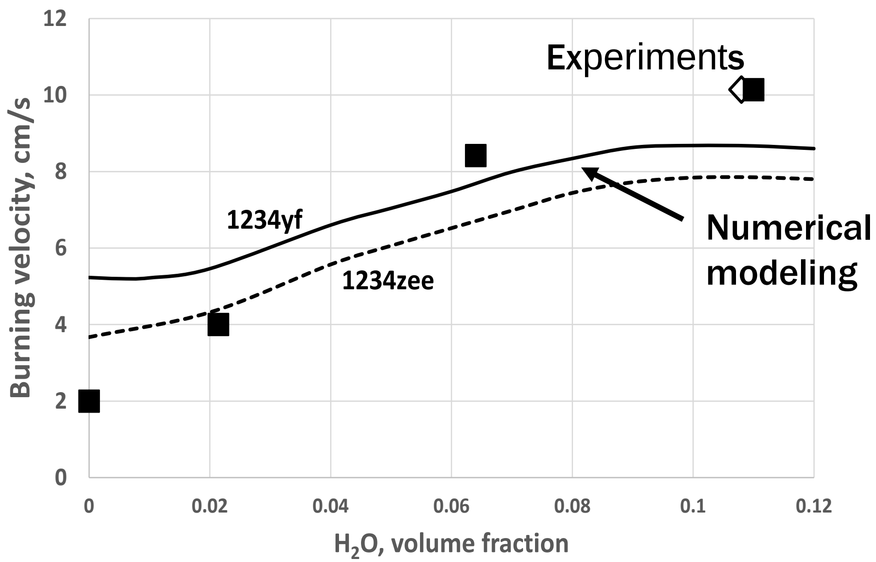
*Experimental data of:
K. Takizawa, K. Tokuhashi, S. Kondo, Flammability assessment of CH2=CFCF3: Comparison with fluoroalkenes and fluoroalkanes, Journal of Hazardous Materials 172 (2009) 1329-1338.

Predicted Burning Velocities

R32



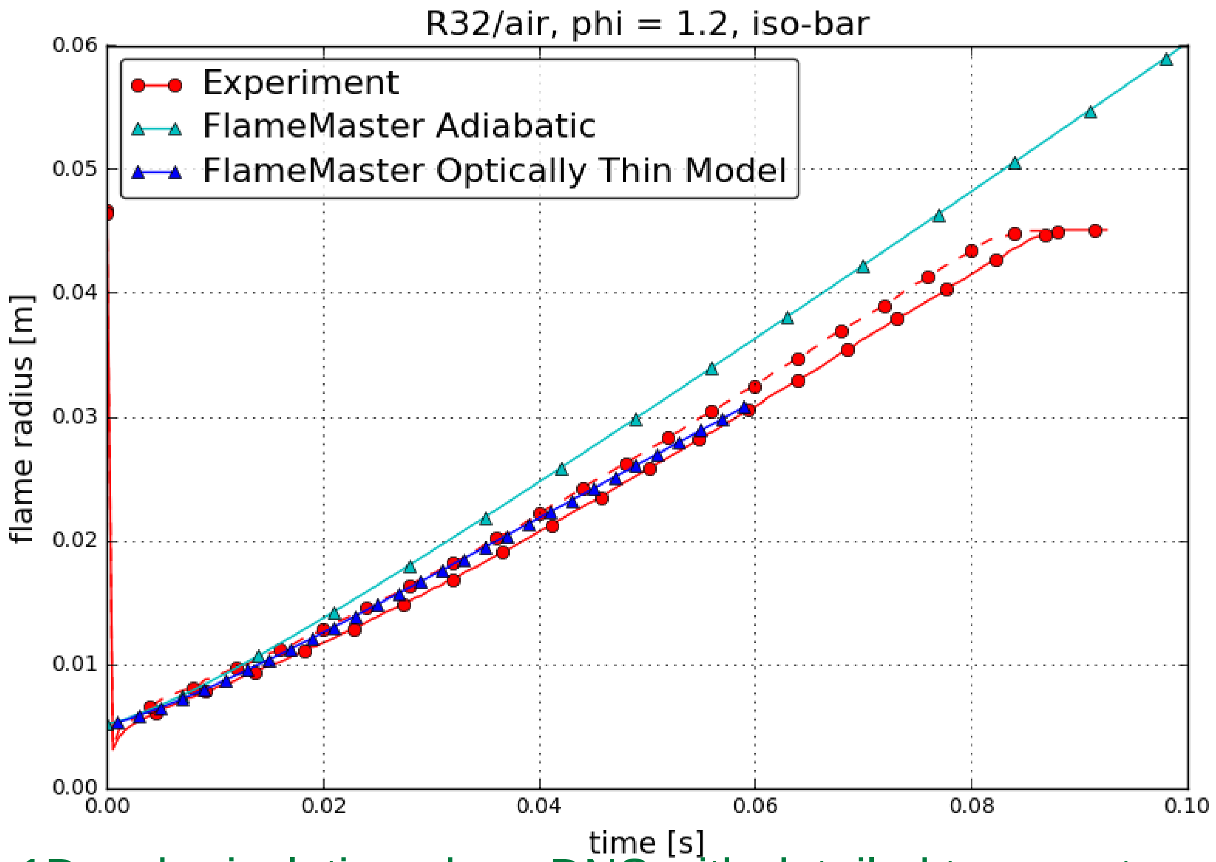
R1234yf and 1234ze(E)

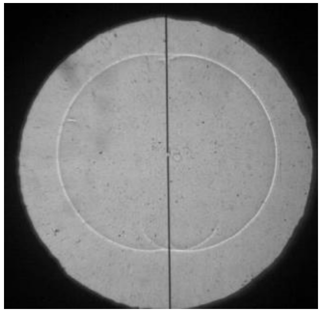


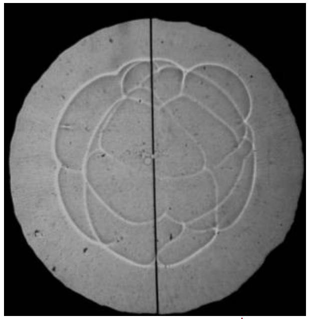
- Mechanism works very well for R32.
- Calculated LBV agrees with adiabatic assumption for high P, T (as expected).
- " " " " " " " optically thin " " low " " "

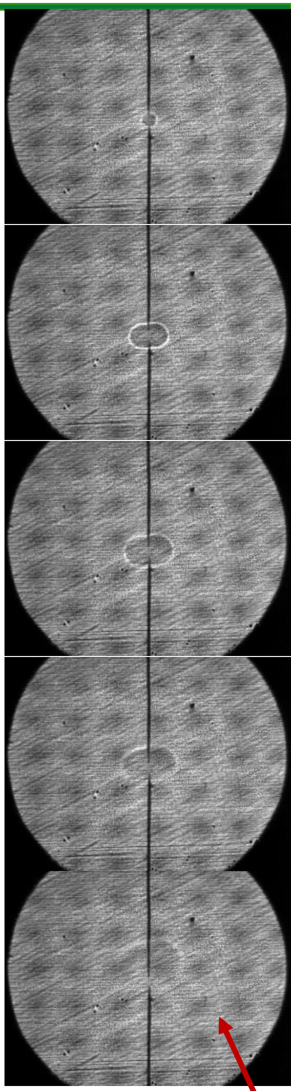
- With initial mechanism for R1234yf and R1234ze(E): effect of water vapor is captured.

DNS Predicted Flame Radius vs time R32









1D, spherical, time dep., DNS with detailed transport and full chemistry:
=> Effects of radiation and flame curvature are accurately modeled.
(change in slope with time is due to effect of flame curvature).

Thermal radiation and response to stretch influence flame acceleration and extinction, which are important in full-scale behavior.

Stakeholder Engagement (project is in mid-late stage)

Dr. Linteris is a member of committees addressing refrigerant flammability in AHRI, ASHRAE, and ISO. He actively collaborates with other refrigerant flammability researchers at the Army Research Laboratory, Univ. of Md, United Technologies Research Ctr., Advanced Institute of Science and Technology (Japan), Honeywell, and Gexcon. Through these relationships he communicates his research findings to the standards, testing, modeling, and industrial partners.

<u>ASHRAE</u>

- Member T.C. 3.1: Refrigerants and Secondary Coolants, Research Subcommittee.
- Active in SSPC 34, Flammability Subcommittee
- Member of Project Management Subcommittee for ASHRAE-1806
- To be a member of Project Management Subcommittee for new HF formation project
- Active presenter at ASHRAE meetings

<u>AHRI</u>

- Member AHRI Flammable Refrigerants Subcommittee. Helping to identify and guide new research on refrigerant flammability.

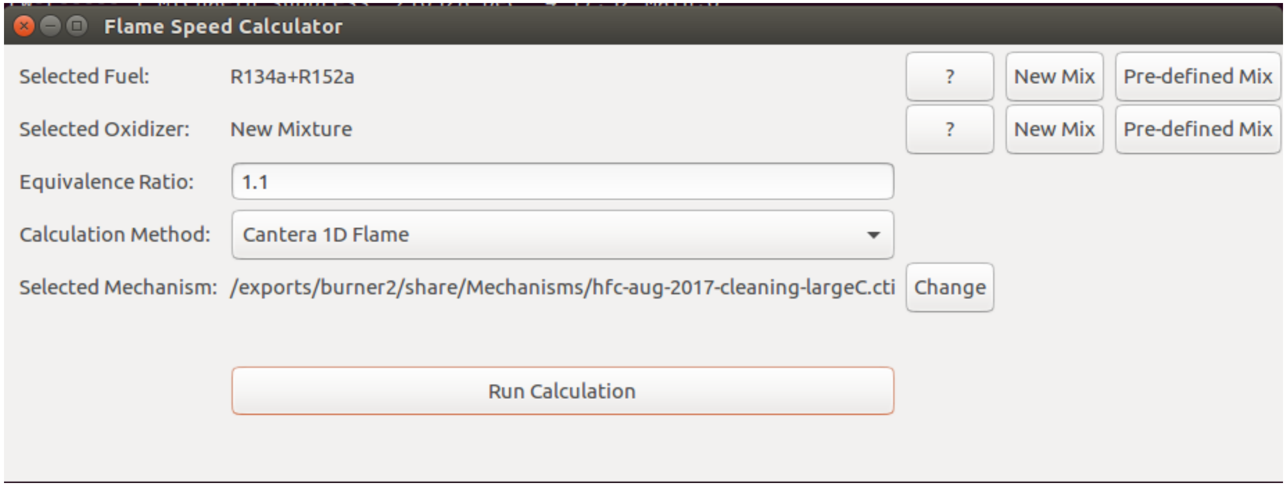
<u>ISO</u>

- Member of TC86, SC 8 / WG8: Burning Velocity Test Methods
- Providing on-going detailed input to new ISO standard test methods on LBV using constant

<u>Army Research Laboratory / SERDP</u>

- Active collaborator with researchers/engineers at ARL, APG, ATC.

Front-end GUI for use by industry to estimate flammability of refrigerant blends.



1. Idea based on existing NIST tools: Ref Prop, Ref Leak: refrigerant thermodynamic properties for blends, leakage rates for blends.

2. Will allow users to estimate the LBV of refrigerant blends at arbitrary composition, initial temperature, pressure, and humidity.

3. Currently uses Cantera or Sandia 1D premixed flame calculation.

4. Can estimate LBV using stirred reactor overall rate.

5. Hope to extent it to have: - lookup tables for existing experimental data

Stakeholder Engagement

Relevance in the face of advances in the market and competitive forces:

Because this project is fundamentally based, it can be modified as new refrigerants come to market. For example, a recent application to ASHRAE Standard 34 is a blend based on the compound CF_3I. We can adopt and improve the existing kinetic mechanisms for CF_3I, updated recently for its use as a fire suppressant, so that our burning velocity predictive tool could be used for refrigerant blends containing it.

The ability to predict the flammability behavior of a blend of agents will be very useful to industry. As an interim step until our work is complete, we have developed and published a method of predicting the flammability rating as determined by the ASRHAE Standard 34 test and have validated it against existing ASHRAE refrigerant database (see ref. [2] and [3] below).

Remaining Project Work

Kinetic Mechanisms:

a.) Comprehensive mechanisms for R125, R134a are nearly finished; those for R1234yf and R1234ze(E) are in work.

b.) Integration of these two separate mechanisms (that for C_1-C_2 HFCs and for fluoropropenes) is in work.

c.) More experimental data on mixtures needs to be collected and then used to validate the predictions. We expect it to compare well.

Flame Modeling:

a.) Current results indicate that radiation is very important for slow flames (LBV < 6 cm/s), and could make a large difference in the inferred LBV from the experiments; i.e., the literature data for very slow burning refrigerants may be wrong by a factor of 2 or 3. Hence, we need to verify that, and then develop a means to correct for radiation effects—without the need for 1D time-dependent DNS modeling.

b.) ongoing DNS results with buoyancy should give us a good idea of whether the current industry standard experimental data reduction method is correct.

Remaining Project Work

Generalized Burning Velocity Predictive Model:

a.) The software tools need to make the predictions are complete. We are fairly close to predicting the laminar, steady, planar, 1D burning velocity of the compounds originally stipulated; however, to be sure it's working, we need to have high-quality experimental data—that is corrected for the effects of stretch, buoyancy and radiation. Through numerical modeling, we are converging on a good understanding of these effects, and their influence on the burning velocity data.

b.) These findings are central to helping industry develop a suitable standard test method for burning velocity, since for fair comparison of different refrigerants, the effects of stretch, buoyancy, and radiation on the LBV needs to be quantified.

Thank You

National Institute of Standards and Technology (NIST)
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REFERENCE SLIDES

Publications

Journal Publications:

[1] R. Burrell, J.L. Pagliaro, G.T. Linteris, **Effects of stretch and thermal radiation on difluoromethane-air burning velocity measurements in constant volume spherically expanding flames**, *Proc. Combust. Inst.* 37(3) (2019) 4231-4238.

[2] G.T. Linteris, I. Bell, M.O. McLinden, **An empirical model for refrigerant flammability based on molecular structure and thermodynamics**, *International Journal of Refrigeration* to be accepted (2019).

[3] I. Bell, P.A. Domanski, G.T. Linteris, M.O. McLinden, **Evaluation of binary and ternary refrigerant blends as replacements for R134a in an air-conditioning system**, *International Journal of Refrigeration* to be accepted (2019).

[4] G.T. Linteris, V.I. Babushok, **Predicted Burning Velocities of C_1 and C_2 Hydrofluorocarbon Refrigerant Flames with Air**, *International Journal of Refrigeration* submitted (2019).

[5] M.J. Hegetschweiler, G.T. Linteris, J.L. Pagliaro, **Effects of stretch and radiation on the laminar flame speed of CH_2F_2 (R32) - Air mixtures**, *Combust. Flame* to be submitted (2019).

Conference Papers:

[6] G.T. Linteris, V.I. Babushok, **Predicted Burning Velocities of C_1 and C_2 Hydrofluorocarbon Refrigerant Flames with Air**, *2018 Eastern States Section Meeting of the Combustion Institute*, The Combustion Institute, State College, PA, 2018.

Publications

Conference Papers (cont.):

[7] D.R. Burgess Jr, J.A. Manion, R. Burrell, V.I. Babushok, M.J. Hegetschweiler, G.T. Linteris, **Development and validation of a mechanism for flame propagation in R-32/air mixtures**, *2018 Eastern States Section Meeting of the Combustion Institute*, The Combustion Institute, State College, PA, 2018.

[8] G.T. Linteris, I. Bell, M.O. McLinden, **An empirical model for refrigerant flammability based on molecular structure and thermodynamics**, *17th International Refrigeration and Air Conditioning Conference at Purdue, July 9-12, 2018*, Purdue University, West Lafayette, IA, 2018.

[9] I. Bell, P.A. Domanski, G.T. Linteris, M.O. McLinden, **Evaluation of binary and ternary refrigerant blends as replacements for R134a in an air-conditioning system**, *17th International Refrigeration and Air Conditioning Conference at Purdue, July 9-12, 2018*, Purdue University, West Lafayette, IA, 2018.

[10] G.T. Linteris, V.I. Babushok, **Numerically-Predicted Burning Velocities C_1 and C_2 Hydrofluorocarbon Refrigerants with Air**, *17th International Refrigeration and Air Conditioning Conference at Purdue, July 9-12, 2018*, Purdue University, West Lafayette, IA, 2018.

[11] V.I. Babushok, M.J. Hegetschweiler, G.T. Linteris, **Flame Propagation in Mixtures of Moist O_2/N_2 Oxidizer with Fluorinated Propene Refrigerants (CF_3CFCH_2, CF_3CHCHF, and CF_3CHCH_2)**, *11th U. S. National Combustion Meeting, March 24, 2019 - March 27, 2019*, The Combustion Institute, Pasadena, CA, United states, 2019.

Publications

Conference Papers (cont.):

[12] D.R. Burgess, J.A. Manion, R.R. Burrell, V.I. Babushok, M.J. Hegetschweiler, G.T. Linteris, **Validated Model for Burning Velocities of R-32/O_2/N_2 Mixtures over a Wide Range of Conditions**, *11th U. S. National Combustion Meeting, March 24, 2019 - March 27, 2019*, The Combustion Institute, Pasadena, CA, United states, 2019.

[13] R.R. Burrell, M.J. Hegetschweiler, D.R. Burgess Jr, J.A. Manion, V.I. Babushok, G.T. Linteris, **R-152a/air and R-134a/oxygen constant volume spherical flame burning velocity measurements**, *11th U. S. National Combustion Meeting, March 24, 2019 - March 27, 2019*, The Combustion Institute, Pasadena, CA, United states, 2019.

[14] L. Berger, R. Hesse, K. Kleinheinz, A. Attili, J. Beeckmann, H. Pitsch, **A DNS study of the impact of gravity on spherically expanding premixed flames**, The 9th European Combustion Meeting (ECM 2019), The Combustion Institute, Lisbon, Portugal, 2019.

Reports:

[15] J.L. Pagliaro, G.T. Linteris, **Burning Velocities of Marginally-Flammable Refrigerant-Air Mixtures**, NIST Technical Note 1988,*National Institute of Standards and Technology*, Gaithersburg, MD, 2018, p. 17.

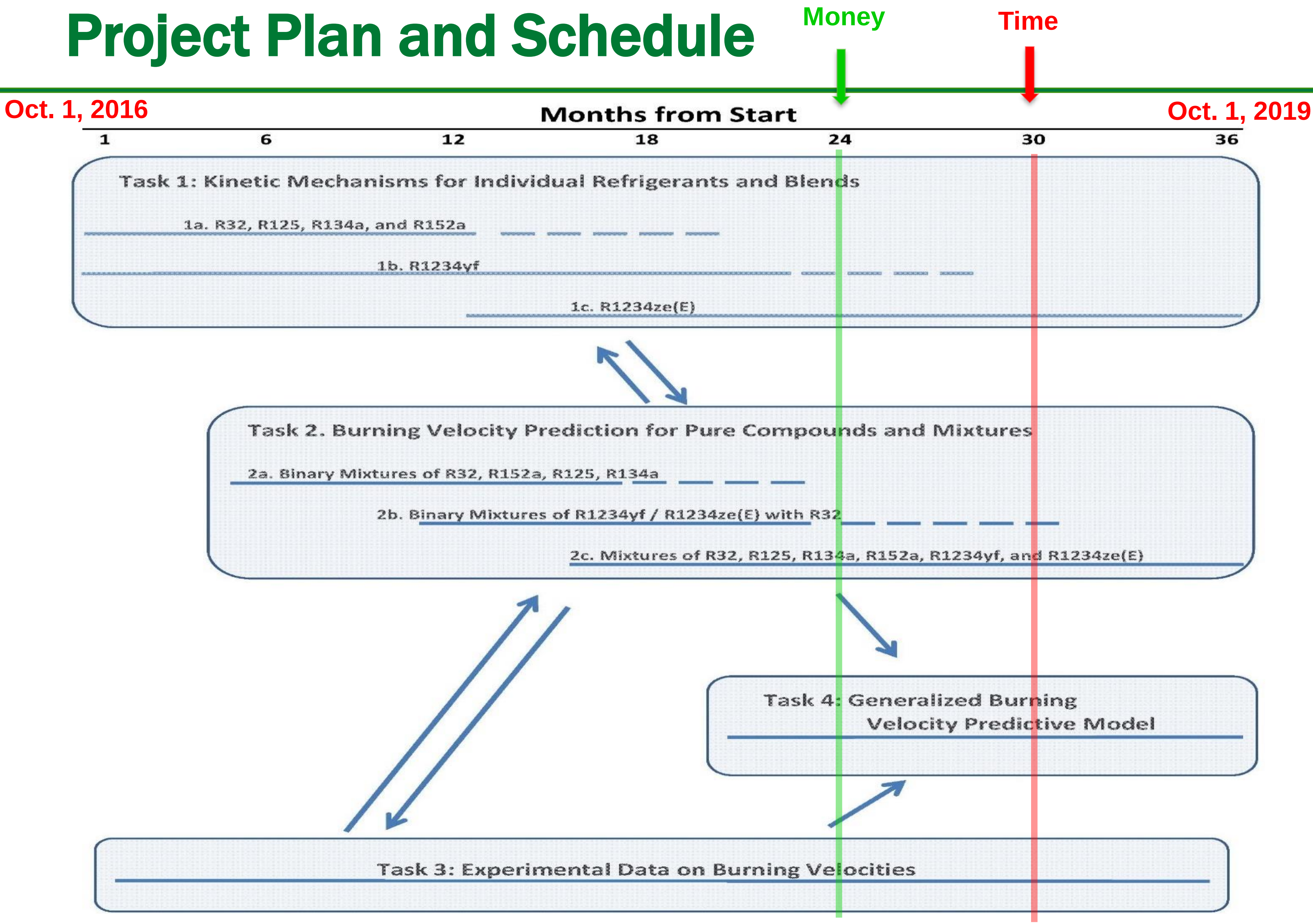
[16] P.A. Domanski, M.O. McLinden, I.H. Bell, G.T. Linteris, **Low-GWP Alternative Refrigerant Blends for HFC-134a**, NIST Technical Note 2014,*National Institute of Standards and Technology*, Gaithersburg, MD, 2018, p. 30.

Project Budget

Project Budget: $2000k
Variances: None.
Cost to Date: $1350k
Additional Funding: $875k (Cost-share NIST, NRC, equip.); possibly SERDP.

Budget History					
Oct. 1, 2016 – FY 2018 (past)		FY 2019 (current)		FY 2020 – N/A (planned)	
DOE	Cost-share	DOE	Cost-share	DOE	Cost-share
$1400k	$700	$600	$875		

Project Plan and Schedule



Effects of Radiation