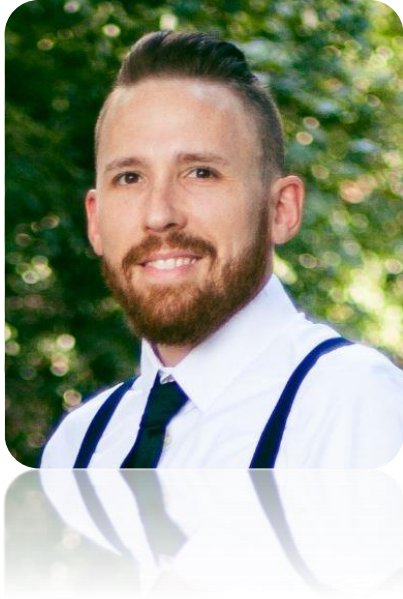




Challenges in Flammability Testing and Application

BIO – ROBERT BELLAIR



The Dow Chemical Company (Freeport, TX) (2010-present)

- Flammability Technical Leader
- Reactive Chemicals Subject Matter Expert
 - ✓ Specialization in flammability, acrylic monomer stability and reactivity, thermokinetic modeling, emergency response

■ Education:

- PhD: Materials Science & Engineering - Wayne State University
- BS: Chemical Engineering - Wayne State University

■ Secretary of the ASTM E27 Technical Committee on Hazard Potential of Chemicals

■ Member of the Texas A&M Mary K O'Connor Process Safety Center Technical Advisory Committee

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WIN THE BID WITH A MORE VERSATILE & COST-EFFICIENT BINDER

BREAKING NEWS
Dow's Dr. Robert Bellair Recognized as 2015 National Safety Council Rising Star of Safety

08.17.15

Dr. Robert Bellair, EH&S associate research scientist for Reactive Chemicals in the Analytical

RELATED CONTENT

- Covestro Plans for Succession of CEO



OBJECTIVES FOR THIS SEMINAR

Challenge #1 Defining Flammability

- What does “flammable” really mean?
- What defines the boundary between flammable and non-flammable?
- Why is there so much variability in literature flammable limits?
- Can we truly “standardize” flammability testing?
- What do we gain and lose through standardization?

Challenge #2 Measuring and Applying Flammability Data

- Examples where measurement by standardized test methods produces non-conservative data
- Examples where careful consideration of testing methodology must be done



What is fire?

Fire - Rapid oxidation of a material releasing heat, light, and various reaction products

Flame –a hot glowing body of ignited gas that is generated by something on fire



SOUNDS SIMPLE RIGHT??

We know what it means when something burns, but how do we define which things will burn and which will not?

How do we define “flammable”?

Ambiguity abounds

Flammable:

- Websters: **Capable** of being set on fire and of burning **quickly**
- Dictionary.com: **Easily** set on fire; combustible; inflammable
- OSHA: When vapors of a material are mixed with air in the proper proportions in the presence of **a source of ignition**, **rapid** combustion or an explosion **can** occur
- Collins Dictionary: **Liable** to **catch fire**; **readily** combustible
- NFPA (18 definitions in the different standards):
 - NFPA 556 (Flammable): (1) **Capable** of burning with a flame under specified conditions, or (2) when used to designate high hazard, subject to **easy** ignition and **rapid** flaming combustion
 - NFPA 1126(Flammable): A combustible that is **capable** of **easily** being ignited and **rapidly** consumed by fire.
 - NFPA 921(Flammable): **Capable** of burning with a flame
 - NFPA 780(Flammable Air-Vapor Mixtures): Flammable vapors mixed with air in proportions that will cause the mixture to burn **rapidly** when ignited
 - NFPA 55,1,2,56,5000 (Flammable gas): A material that is **ignitable** at an absolute pressure of 14.7 psi (101.3 kPa) when in a mixture of 13 percent or less by volume with air, or that has a flammable range at an absolute pressure of 14.7 psi (101.3 kPa) with air of at least 12 percent, regardless of the lower limit.



Challenge #1: Determining What Flammability MEANS

For something to be flammable, it must be **easily** set on fire and combust **rapidly**

Vague definition with no scientific criteria defining exactly when something is considered flammable:

- What do we mean by “easily” set on fire? How easily?
- What do we mean by combusts “rapidly”? How rapid?
- What is considered “an ignition source”?
- Does the fire have to be able to spread throughout the material or can it stay localized to the ignition source?
- Does the material need to be able to sustain a fire as long as fuel and oxygen are present?

After more than 100 years of investigating the flammability of materials, researchers, regulatory bodies, and test standard committees are still unable to clearly agree on what “flammable” means



What Does “Flammable” Mean?

Is wood flammable?

- It doesn't just catch fire the second you expose it to flame...

Is octane flammable?

- It will not ignite at ambient temperatures in West Lafayette, Indiana between November to March.

Is gasoline flammable?

- It will not ignite in a closed container at room temperature and atmospheric pressure...

“Flammable” is used as a classification for regulatory purposes, measured under standardized conditions

Flammable Classification should be used with caution as it may not reflect the conditions under which a material is being handled!!

Flashpoint	-7C	23C	35C	37.8C	60C	93C	No FP	
NFPA 30	Flammable			Combustible			Non Flammable	
	Class IA (BP<37.8C) Class IB (BP>37.8C)		Class IC	Class II	Class IIIA	Class IIIB		
NFPA 704	4		3		2		1	0
OSHA	Flammable			Combustible				
	Category1 (BP<35C) Category2 (BP>35C)		Category 3		Category 4			
ANSI	Extremely Flammable Liquid	Extremely Flammable Liquid (BP<35C) Flammable Liquid (BP>35C)			Combustible Liquid			
DOT	Flammable Liquid				Combustible Liquid			
GHS	Category1 (BP<35C) (Class3/Group I) Category2 (BP>35C) (Class3/Group II)		Category 3 (Class3/Group III)		Category 4 (Combustible Liquid)			
HAZMAT	Flammable Class 3			Flammable Class 3 if sustains fire otherwise combustible		Combustible		
CLP (Europe)	Category1 (BP<35C) (Class3/Group I) Category2 (BP>35C) (Class3/Group II)		Category 3 (Class3/Group III)					
EPA (RCRA)	Flammable Liquid							

And more broadly

“Flammable” is used to describe whether or not a material will sustain or propagate combustion under any specific set of conditions



LET'S PLAY "IS IT FLAMMABLE?"

Iron

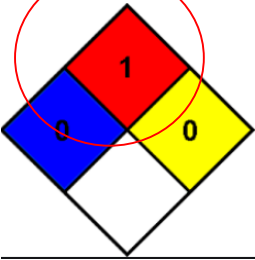


R134a refrigerant



Hint?

Hydraulic oil

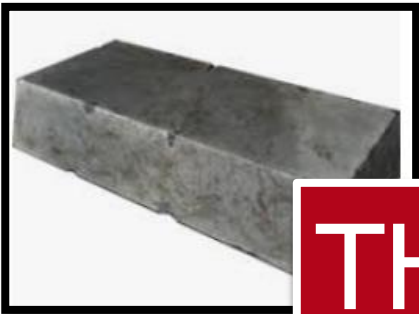


Hint?



LET'S PLAY "IS IT FLAMMABLE?"

Iron



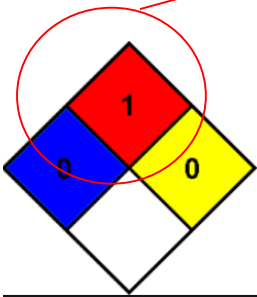
R134a refrigerant



Hydraulic oil



Hint?



THE CONDITIONS MATTER!!!



Pyrophoric if
ground fine
enough



Flammable at
250C



Flammable when
in fine
droplets/spray



Defining Flammability

Whether a material will propagate a flame is a function of:

- Temperature
- Pressure
- Oxidizer identity (usually oxygen) and concentration
- Inert identity (usually nitrogen) and concentration
- Fuel concentration
- Vessel shape (sphere, cylinder etc.), volume, and whether it is a sealed or open vessel
- Type, geometry, energy, and energy density of ignition source
- Turbulence
- And other variables.....



Defining Flammability Limits

Beyond the variables that can affect the flammability of a material is the uncertain definition of when a material transitions from non flammable to flammable.... It is not a clearly demarked line!

- % combustion or propagation: If 1% of the material combusts is it flammable? How about if 10% combusts? 100%?
- Probability of ignition: If only 1 out of three ignition attempts results in a deflagration for a given set of conditions, does that meet the requirement that the material “easily ignites”? What about if is one time out of 10 attempts?

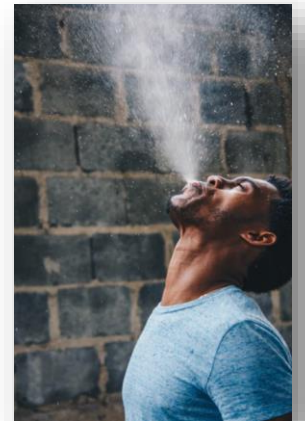


Clearly
Flammable



Where do we draw
the line?

Clearly Not
Flammable



Challenges – Definition of flammability

What Is considered “Flammable”? 4 possible definitions (and infinite gradations):

1. Any combustion outside of the ignition zone
 1. How do we define the “ignition zone”? This limit will be dependent on ignition source/type/dynamics
 2. How do we measure infinitely small amounts of combustion? Visually? Temperature? Compositional analysis?
2. X inches of flame propagation in a specified direction(s)
 1. What direction? Do we focus on upward propagating flames or downward? If a thin ribbon of material combusts in that direction is that sufficient?
3. Y% of material combusted
 1. How do we define “combustion” and the amount that combusted? How much Combustion is “enough”?
4. Complete flame propagation/combustion throughout the mixture
 1. Will be dependent on the vessel size/dimensions and ignition location

1&4 are the only two that truly define a “limit” (when tested in a large vessel). Unfortunately, 1 is too conservative and 4 is too non-conservative for any realistic use in industry



Debate #1: Where Does Gray “Begin”?

ASTM E681 – visual identification of upward and outward propagation of flame to the walls (~100mm) in a 5L spherical glass flask

ASTM E681A1 – visual identification of upward and outward propagation of flame to the walls (~140mm) making an angle >90 degrees in a 12L spherical glass flask

ASTM E918 – 7% pressure rise upon ignition in a steel vessel >1L in volume

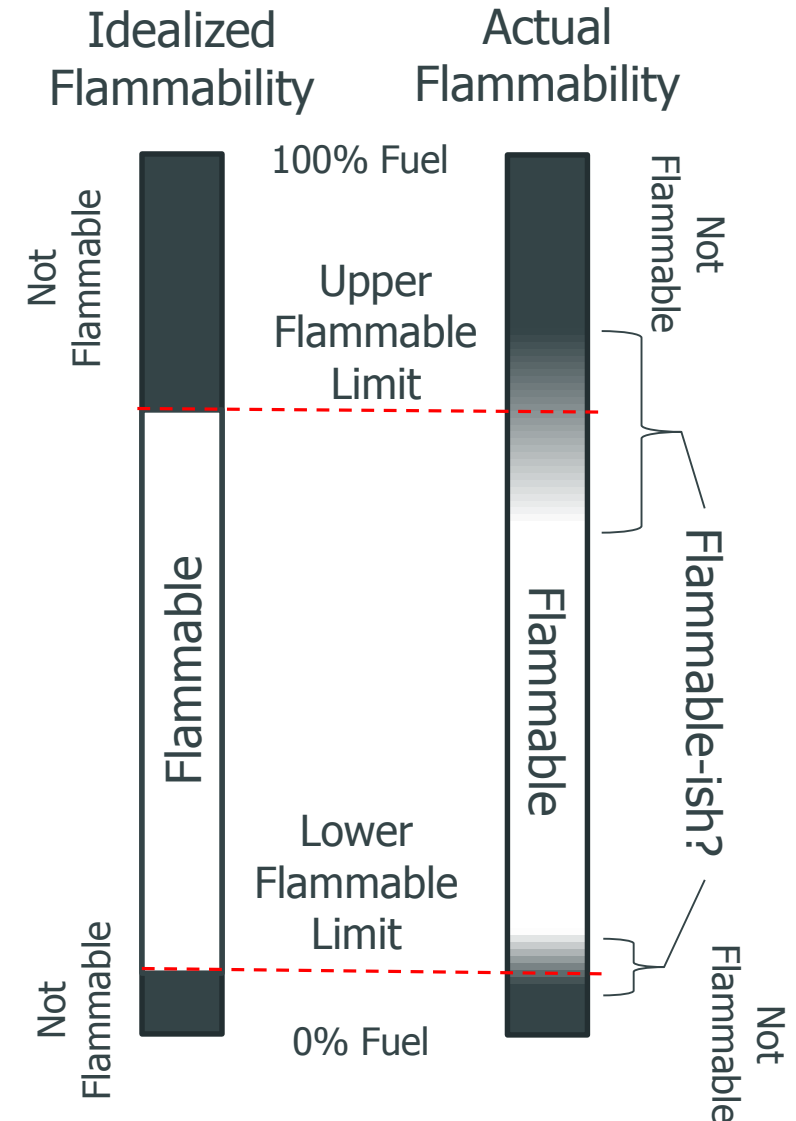
EN 1839 – visual identification of flame detachment from ignition source and upward propagation of >100mm in a 80mm ID vertical glass tube

EN 1839B – 5% pressure rise upon ignition in a spherical steel vessel >5L in volume

These methods also use varying ignition sources



- No Flame Propagation
- Complete Flame Propagation



Pop Quiz

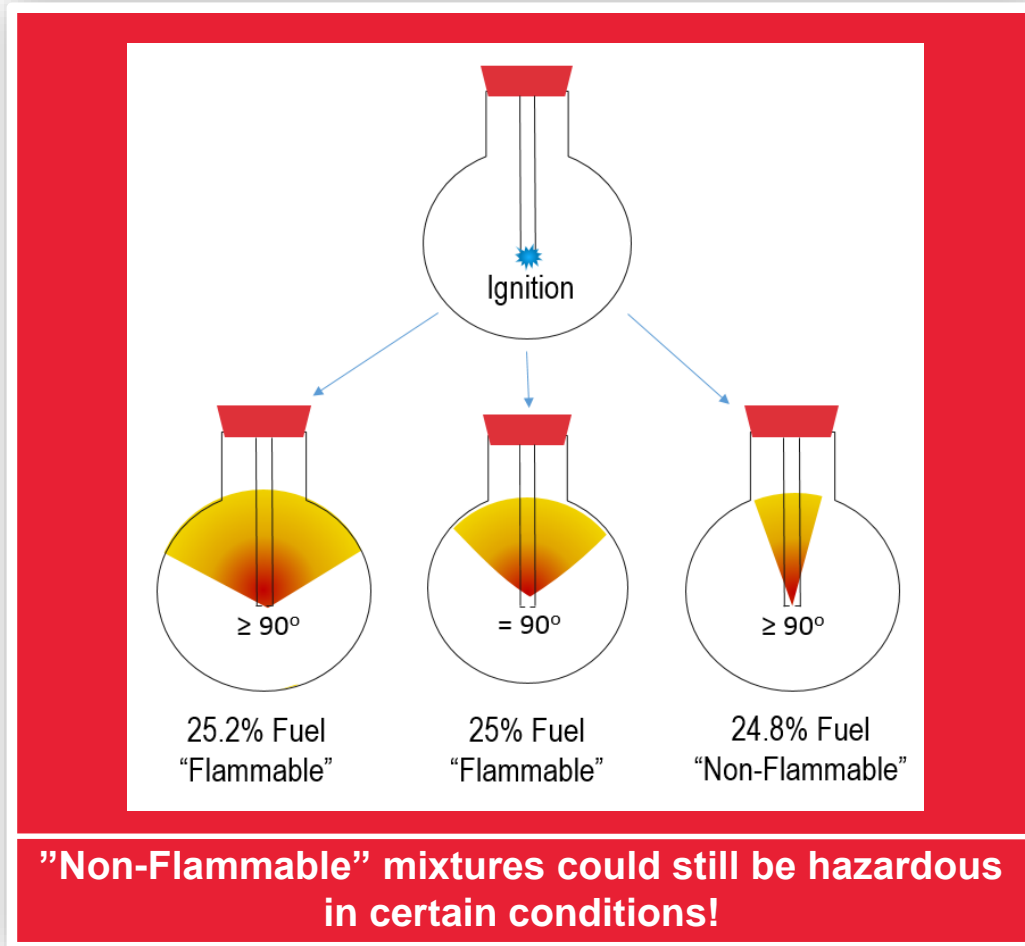
Lets say that a gas was tested for its flammability, and the upper flammable limit was found with high confidence (many repeat tests were done) by the ASTM E681A1 test method to be exactly 25%.

- What would you expect to observe if this material was mixed at 24.8% with air and an ignition source applied?
- What would you expect to observe if this material was mixed at 25.2% with air and an ignition source applied?

Criteria for ignition in ASTM E681A1: Flame propagation is defined as flames that having spread upward and outward to the walls of the flask, are continuous along an arc that is greater than that subtended by an angle equal to 90° , as measured from the point of ignition to the walls of the flask



The Answer is Clear as Mud



Results:

- Partial flame propagation at 24.8%
- Partial flame propagation at 25%
- Partial flame propagation at 25.2%

In General:

- Concentrations further from stoichiometric will propagate the flame less far on average, and positive ignitions will be less frequent
- Concentrations closer to stoichiometric will propagate the flame further on average, and positive ignitions will be more frequent

Debate #1: Where Does Gray “Begin”?

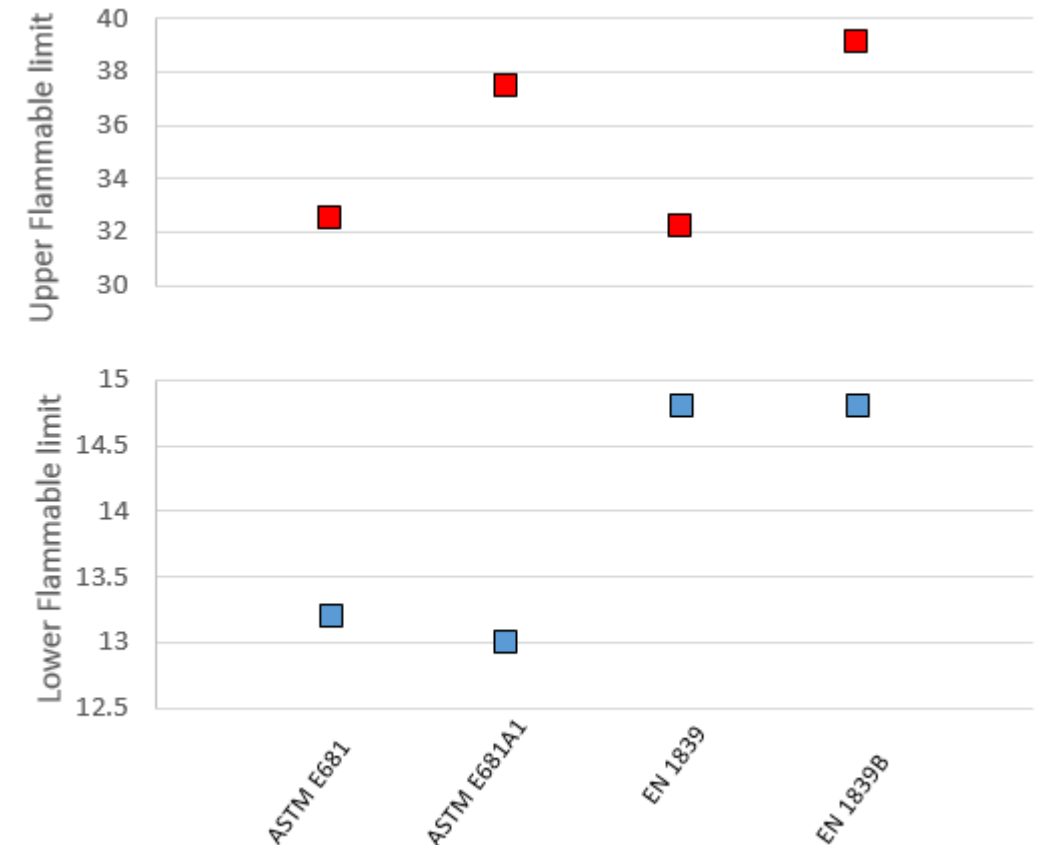
Visual Criteria:

- Enough of the vessel must be clear that a visual assessment must be made
- Makes testing at elevated temperatures and pressure difficult or challenging
- Due to low pressure handling of glass vessels, they must be vented, which can artificially influence the results of low burning velocity materials
- Evaluation of flame propagation can be a bit of an art due to some subjectivity in the evaluation

Pressure Criteria:

- May get different limits in different size vessels
- No visual confirmation of actual flame propagation
- Some hazard involved with having a sealed vessel for deflagration testing

Ammonia Flammability



Challenges – Effect of T&P

At elevated Temps and Pressures, the appearance of “cool flame” regions occur along the upper flammable limit

Traditionally, the accepted UFL should not fall in the cool flames region

- pressure criteria method tends to give values in this range.
- Flame propagation criteria is hard to evaluate in this region and is very observer dependent

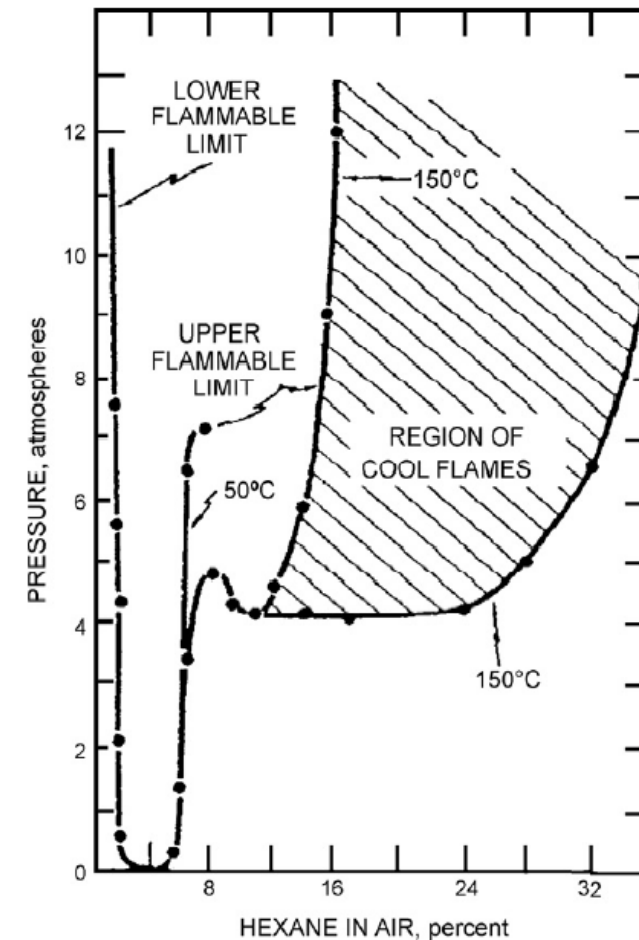
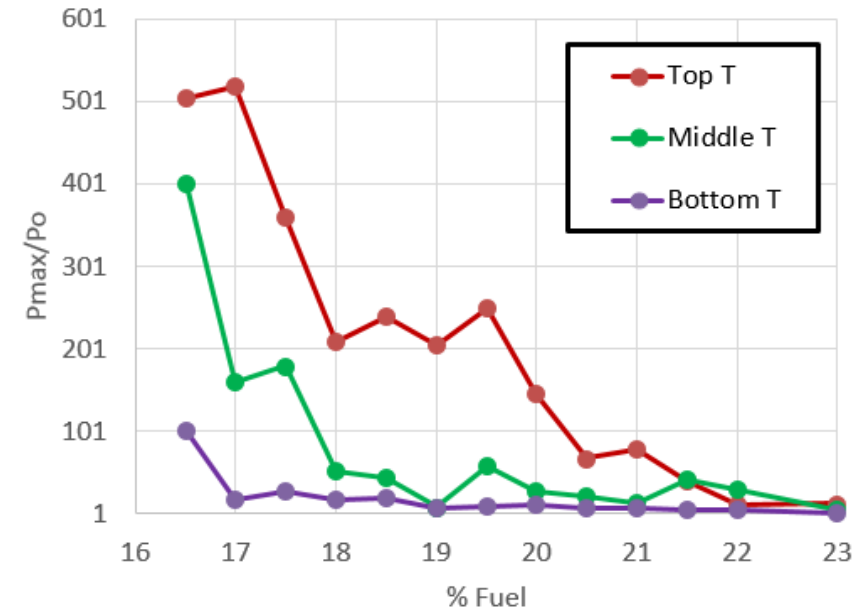
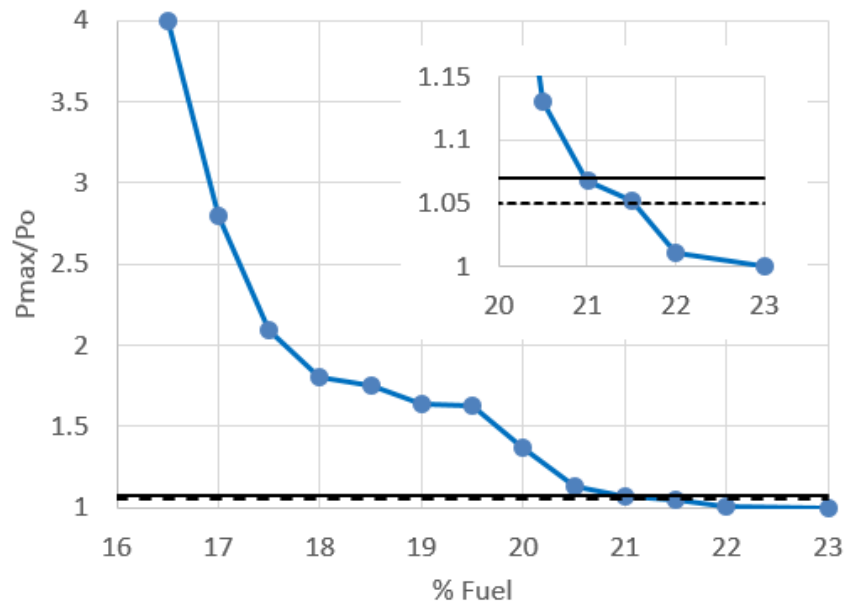
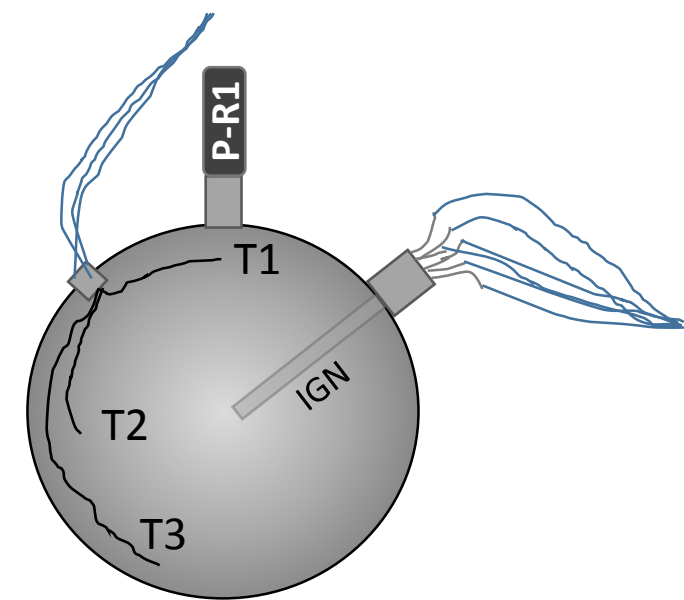


Fig. 1 – The cool flame and normal flame region for hexane air mixtures by Hsieh—reproduced by permission of The Royal Society of Chemistry.

Fuel Rich Example

Determining the Upper Flammable Limit for a set fuel/inert composition at elevated temperature and pressure



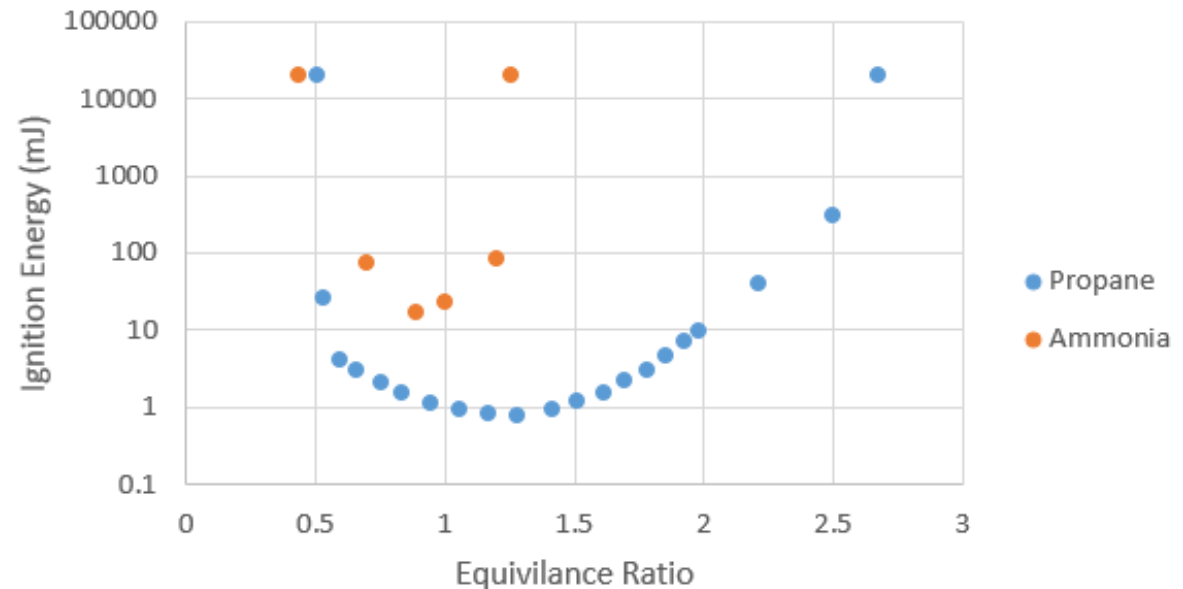
Debate #2: What Ignition Energy and Source is the “Right” One?

Ignition sources used for flammability testing range considerably in the energy density, size of the ignition region, rate of energy release and duration, as well as can have additional catalytic effects:

- Capacitive sparks
- Inductive sparks
- Electrically triggered match heads
- Diffusion flames
- Premixed flames
- Exploding fuse wires
- Hot wires
- Chemical igniters (explosive squibs)

Differences in the properties and dynamics of these ignition sources can result in very different limits

Same ignition source but different energies



		10 mJ igniter	20 J igniter
Propane	LFL	2.4%	2.1%
	UFL	7.6%	10.5%
Ammonia	LFL	no ignition	14.8%
	UFL	no ignition	33.5%

Debate # 3: What is the Right Size/Shape of Vessel?

Most common real world conditions:

- Large cylindrical vessels, with a variety of L/D ratios
- Pipes, horizontal or vertical (Various flowing and stagnant conditions)
- Open atmosphere (vapor cloud)

Unrealistic to test flammability in very large vessels as cost, complexity, time, and hazard level of testing exponentially increases with size

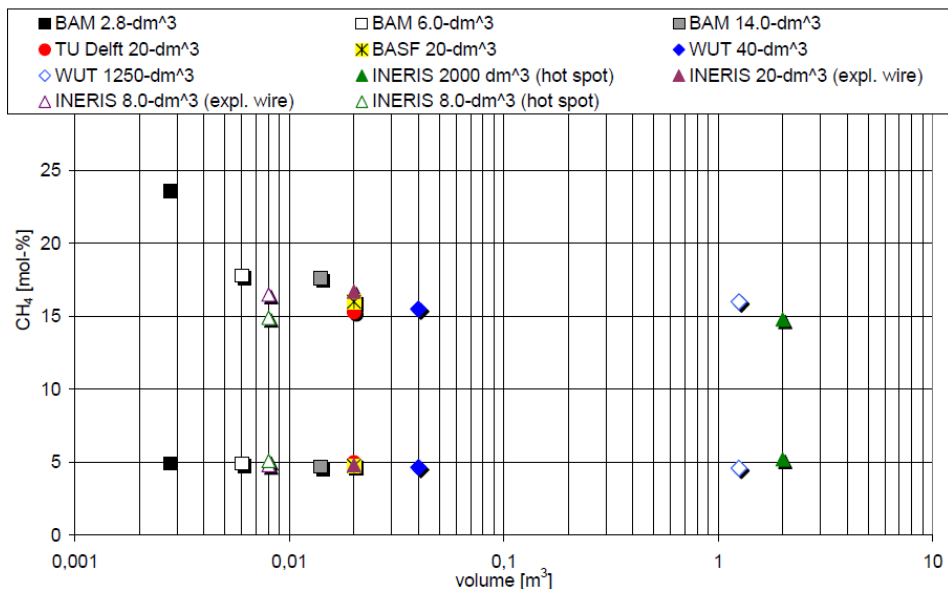
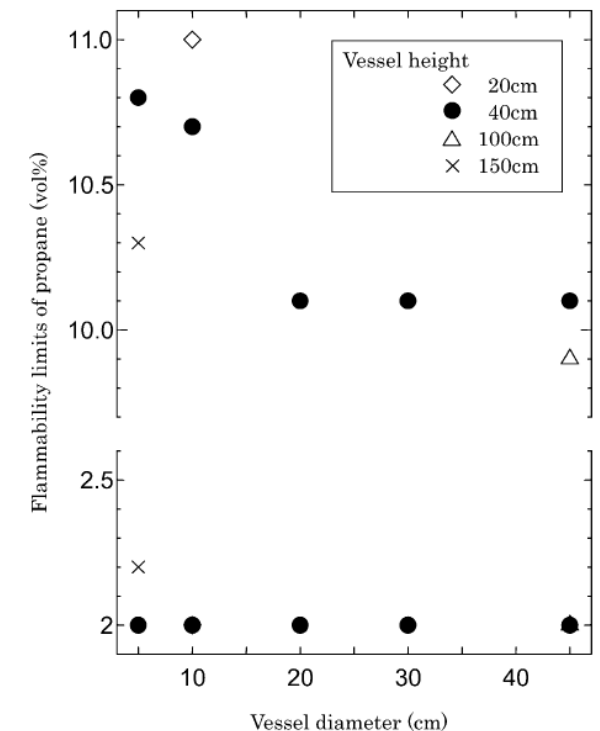


Fig. 72: Volume dependence of the explosion limits of methane/air mixtures at an initial pressure of 1 bara and an initial temperature of 20 °C

Holtappels, Kai.; *Federal Institute for Materials Research and Testing (BAM), Contract No. EVG1-CT-2002-00072* (2006).

Takahashi, Akifumi, et al.; *Journal of hazardous materials* 105.1-3 (2003): 27-37



DOW RESTRICTED Experimental flammability limits of propane measured in vessels of various sizes.

Additional Debates

- Should testing be done under quiescent (still) or turbulent conditions?
- How tightly controlled should the oxygen concentration be?
- How many repeat tests at a given composition need to be done?
- Should the ignition be done towards the top, middle or bottom of the vessel?
- Where do we set the flammable limit relative to the closest go/no-go concentrations?
- How carefully should temperature be controlled?
- Can we use thermocouples inside the vessel to help differentiate between cool flames and normal flames or determine propagation direction in steel vessels?
- Should cool flames be considered “flammable”?

Similar Issues Exist For Dust Cloud Explosibility

Dust explosibility has the additional challenge of timing and turbulence.

- You cannot have a dust cloud generated without turbulence, but the amount of turbulence has an impact on the resulting explosibility and parameters.
- Changing the timing of the ignition will impact the turbulence at the time of ignition as well as the concentration of the dispersed dust at the time of ignition

Additionally, the criteria for dust cloud explosibility is pressure based so we need to determine how much combustion is needed to be “Flammable”.

Finally, dusts are generally much less ignition sensitive than vapors, so the type and energy of the ignition source is critical



Comparison of Dust Test Methodology

Test Method	EN 14034-2	ASTM E1226:	EN 14034-3	ASTM E1515
Measurement	Explosibility	Explosibility	Minimum Explosible Concentration	Minimum Explosible Concentration
Vessel Size	20L or 1 m ³ vessel	20L or 1 m ³ vessel	20L or 1 m ³ vessel	20L or 1 m ³ vessel
Criteria for ignition:	0.5 bar overpressure	100% pressure rise	0.5 bar overpressure	100% pressure rise
Ignition Source	Two 5 kJ pyrotechnic	Two 5 kJ pyrotechnic	Two 1 kJ pyrotechnic	One 2.5 or 5 kJ pyrotechnic

Test Method	EN 14034-2	ASTM E1226:
Measurement	Minimum Ignition energy	Minimum Ignition energy
Vessel Size	1.2L glass cylinder	1.2L glass cylinder
Criteria for ignition:	Visual Flame	Visual Flame
Ignition Source	Capacitive spark with 1-2 mH inductance	Capacitive spark

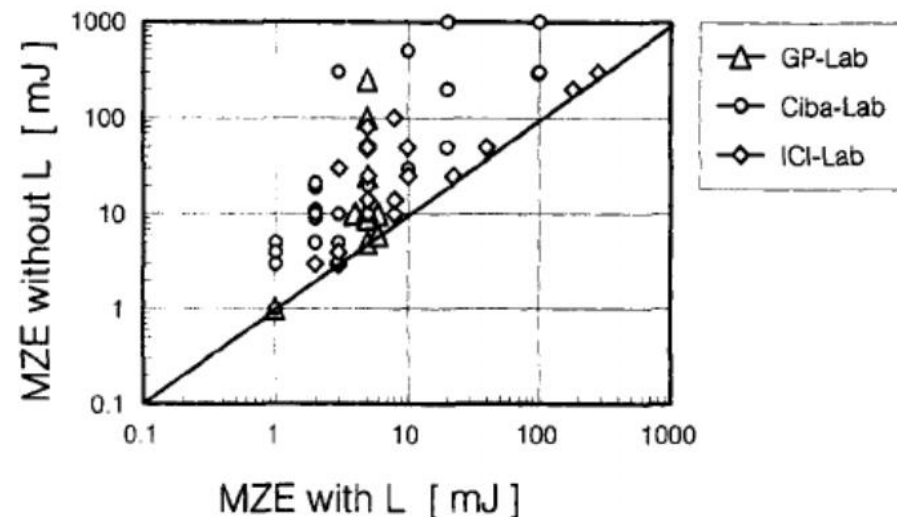


FIGURE 3. Influence of the inductance on the minimum ignition energy MIE.

Siwek, Richard, and Christoph Cesana; *Process safety progress* 14.2 (1995): 107-119

DOW RESTRICTED



Dust Layer Ignition

Many organics oxidize at elevated temperatures, releasing heat. Due to the very poor thermal conductivity and high surface area for oxidation in loose powder, this heat accumulates in the material resulting in a runaway reaction (fire).

Standardized test methods have been created to evaluate this property, however caution must be used when applying the results

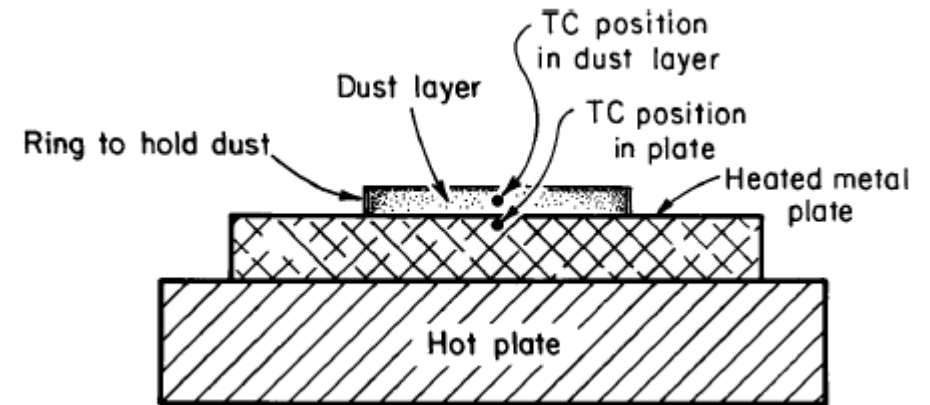


FIG. 1 Schematic of Hotplate Layer Ignition Apparatus

ASTM Standard E2021-09, 2013, "Hot-Surface Ignition Temperature of Dust Layers" ASTM International, West Conshohocken, PA, 2013

From ASTM E2021:

Data obtained from this test method provide a relative measure of the hot-surface ignition temperature of a dust layer

Dust Layer Ignition

The actual potential for a runaway oxidation at a given temperature depends **strongly** on the dimensions of the pile.

- While the ASTM standard makes multiple statements about this, the general practice followed in industry is to just test at the standard 20mm thickness and report that value

From ASTM E2021 (coal dust):

Layer Thickness, mm	Hot-Surface Ignition Temperature, °C
6.4	300
9.4	260
12.7	240
25.4	210

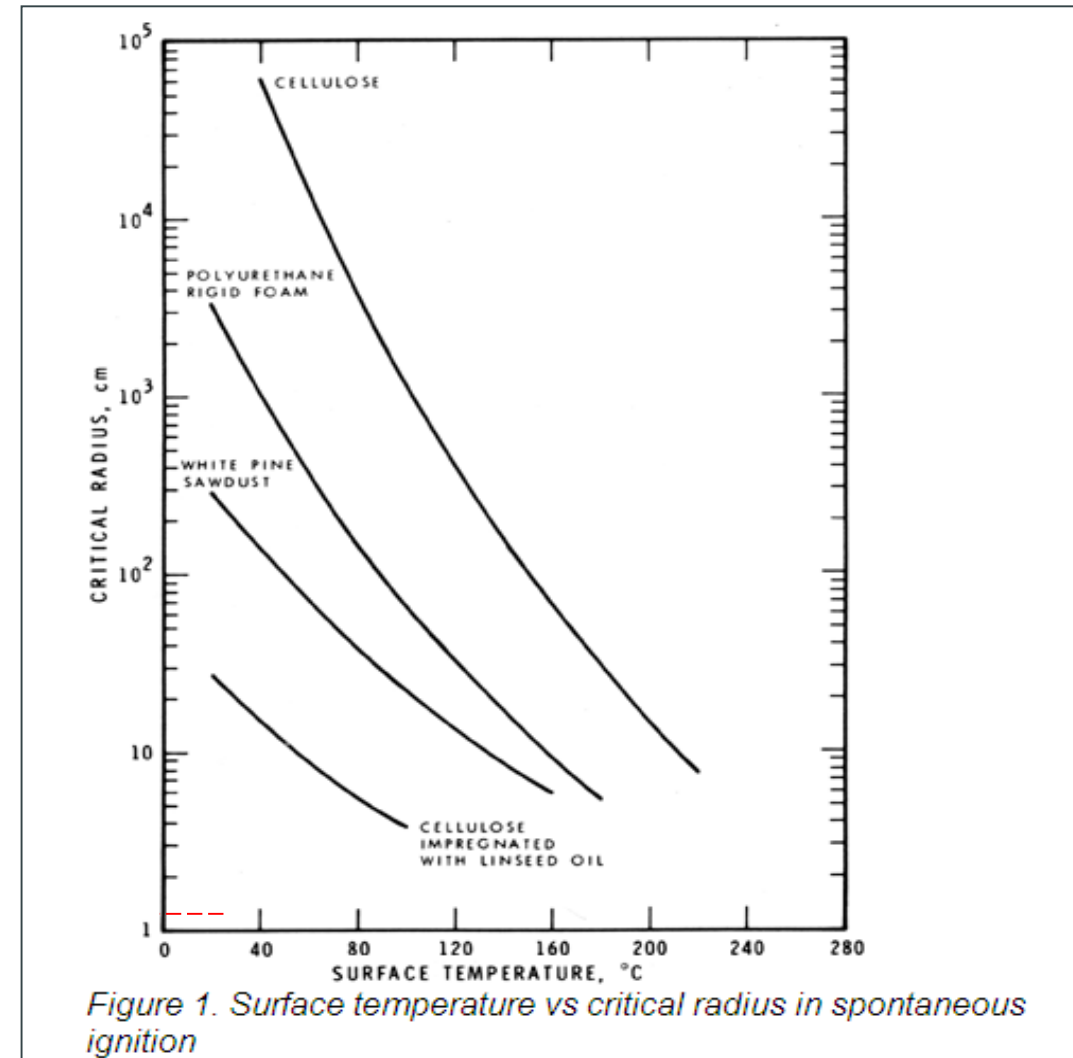


Figure 1. Surface temperature vs critical radius in spontaneous ignition

McGuire, J. H.; *Fire Technology* 5.3 (1969): 237-241.

Similar Issues Exist For Liquid Flammability

The flash point is just an approximation of the temperature limit of flammability, and has many of the same challenges that flammable limits measurement have. The small size vessel, non-equilibrium state, and flame or hot wire ignition systems in flash point apparatuses all have an impact on the measurement

Example: Methylene Chloride

Due to a large quenching diameter, methylene chloride will not exhibit a flash in the small cup of a flash point apparatus, however above 100C it does form a flammable vapor composition above the liquid



WHAT DO WE GAIN/LOSE THROUGH STANDARDIZATION

- Generally reproducible results
- Everyone using the same values/limits
- Consistent regulatory classification
- Reduced potential for bad data due to poor measurement science
- Decrease the expertise required to produce quality data

- Results that may not reflect the true hazard
- False sense of security
- Misunderstanding of the data applicability
- Reduced flexibility



Measuring and Applying Flammable Data

Why nitpick the details?

For a large fraction of flammable materials with sharply defined limits under atmospheric conditions, the small differences caused by different methods may be easily addressed by use of safety buffers/factors. However:

- Overlooking some of the details can result in seriously underestimated hazards
- Many processes need to operate as close as safely possible to the hazardous range in order to be profitable (example – partial oxidation processes)
- Variability in testing methodology or test conditions can result in the same material being regulated in different ways
- Strictly following standardized test methods can result in limits that are not at all applicable (and potentially hazardous) for a given use



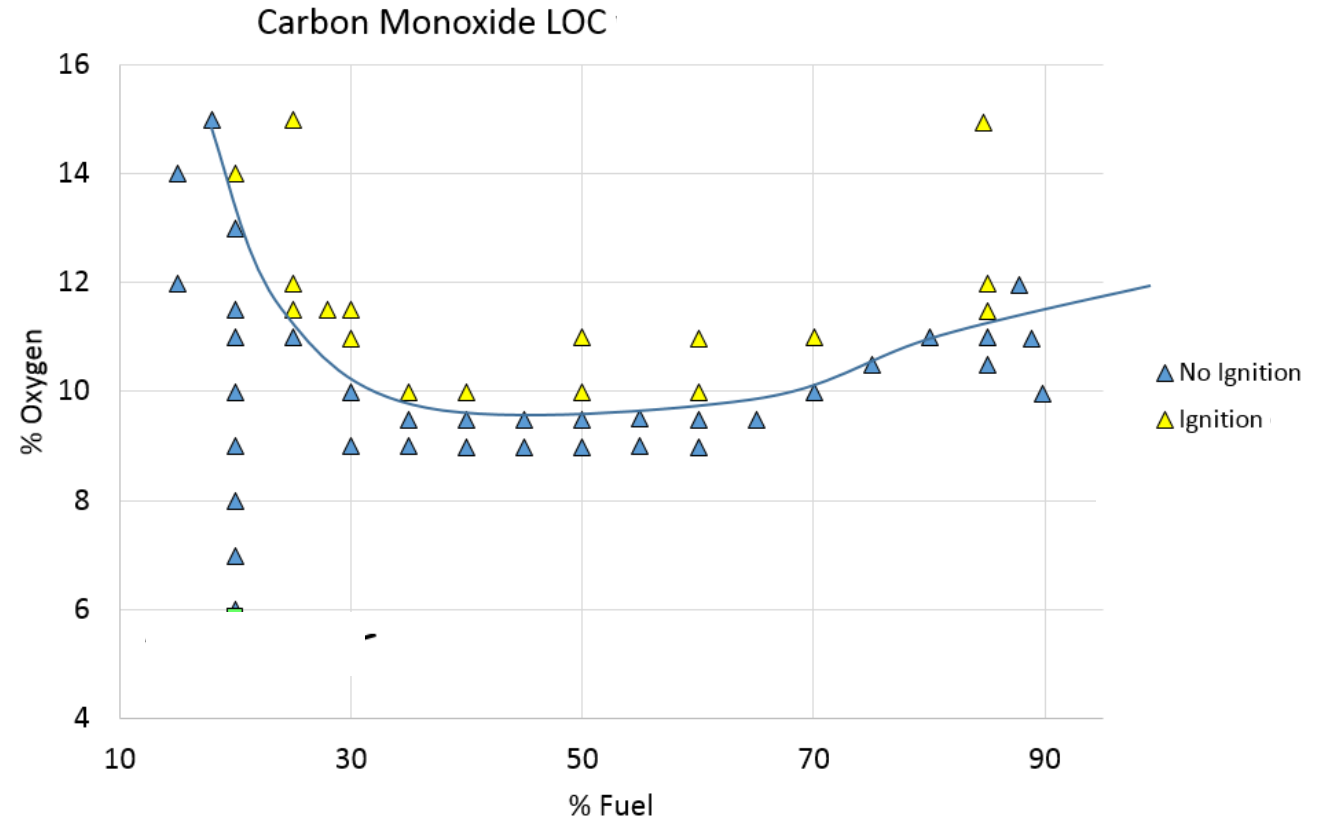
Gas Example – Carbon Monoxide

For most gases, tests using humid air would result in non-conservative flammable limits

- H_2O more effective inertant than N_2

For some gases, H_2O participates in the combustion reaction and makes the fuels more flammable

- Carbon monoxide, highly halogenated materials etc.

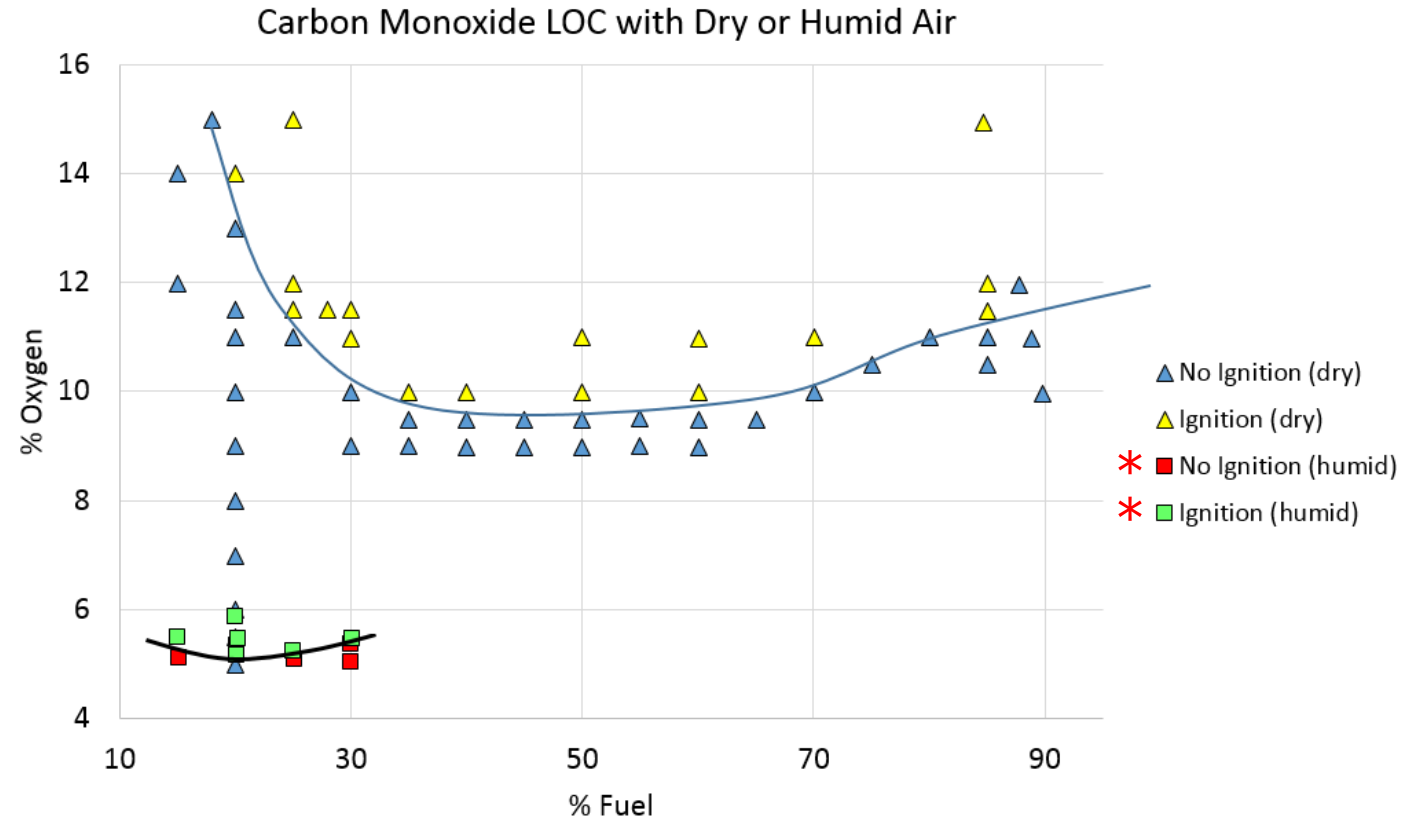


Gas Example – Carbon Monoxide

Most standardized test methods state you must use high purity dry air when doing testing.

- What should the reported LOC be?
- Likely, the first people to test CO did not know beforehand to include moisture

* Even with high quality test data, there is always a chance that we have unintentionally made a non-conservative assumption that makes the material more hazardous than we thought.



* I.A. Zlochower, G.M. Green; Journal of Loss Prevention in the Process Industries, Volume 22, Issue 4, 2009, Pages 499-505

Refrigerants



New regulations are requiring phasing out of high Global Warming Potential (GWP) refrigerants

Next gen refrigerants have lower GWP in part because they have shorter lifespans in the environment

The same chemistry changes that reduce their environmental lifespan, also make them more reactive and oxidizable

Due to their highly halogenated nature, they are often hard to ignite, have only borderline flammability under normal conditions, and require a certain amount of moisture to be present in order to be flammable

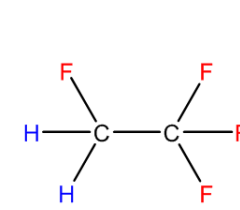


Refrigerants

Example: HFO-1234ze

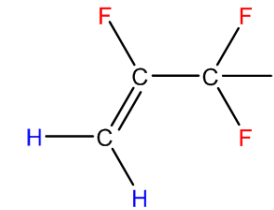
Data available says it is:

- Either flammable or not flammable at room temperature
- It either requires a high energy ignition source or it doesn't
- If it is flammable, its LFL falls somewhere between 4-9% and its UFL falls somewhere between 9-15%



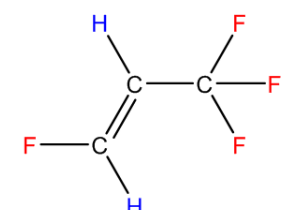
1,1,1,2-tetrafluoroethane
HFC-134a

	25C	60C
Dry	Not Flam.	Not Flam.
50% RH	Not Flam.	Flammable



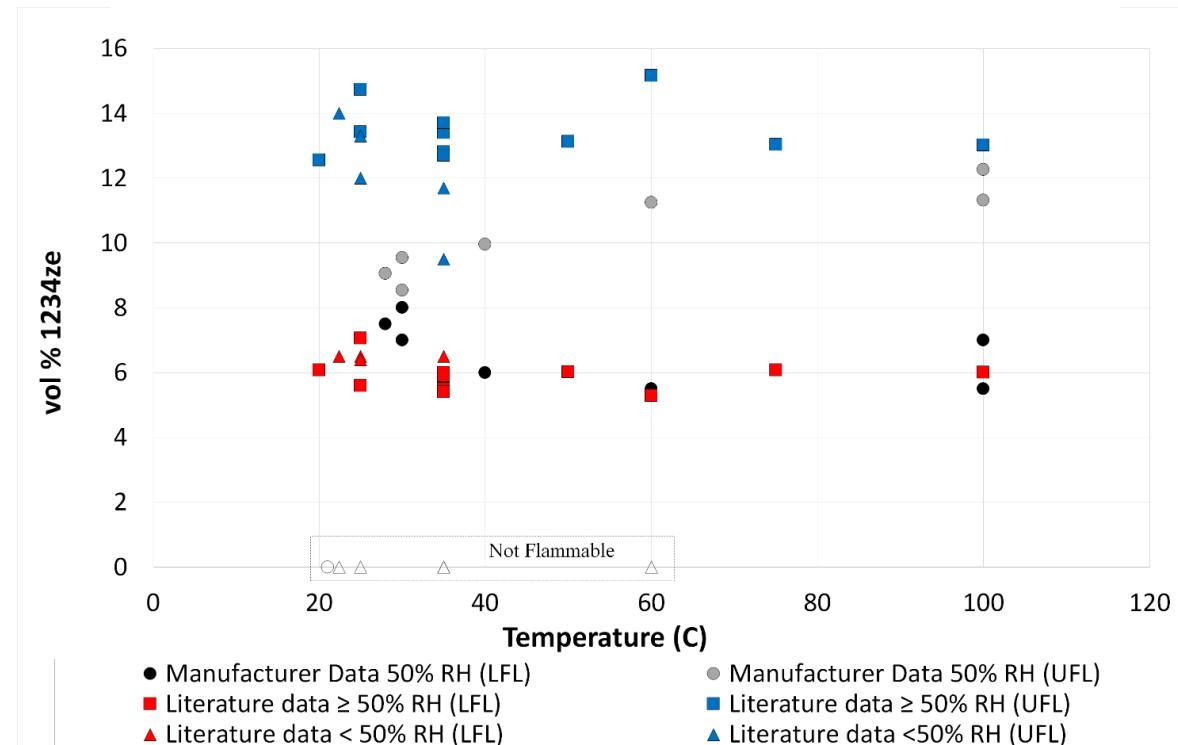
2,3,3,3-tetrafluoropropene
HFO-1234yf

	25C	60C
Dry	Flammable	Flammable
50% RH	Flammable	Flammable



1,3,3,3-Tetrafluoropropene
HFO-1234ze

	25C	60C
Dry	Conflicting Data	Conflicting Data
50% RH	Conflicting Data	Flammable



Bellair, Robert J., and Lawrence Hood; *Process Safety and Environmental Protection* 132 (2019): 273-284.

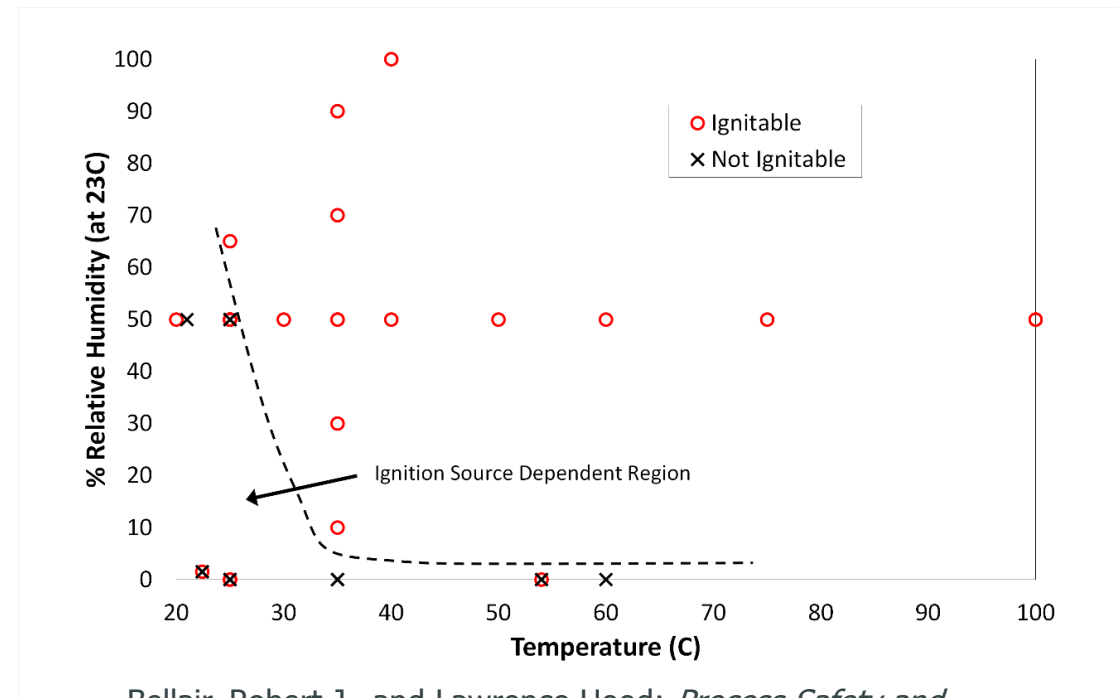
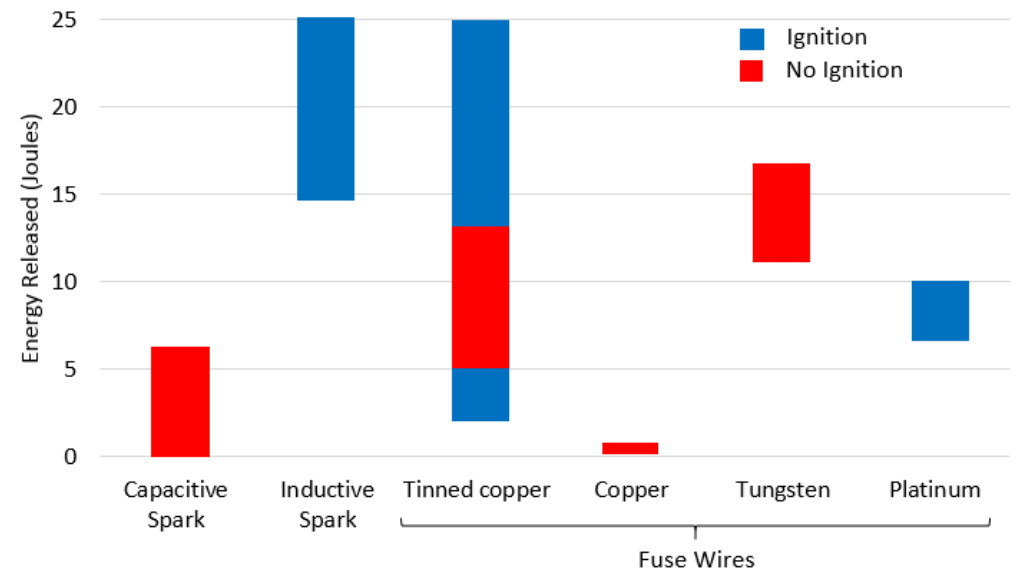


Refrigerants

Example: HFO-1234ze

It turns out that beyond the temperature, pressure, and humidity requirements, this material is particularly sensitive to the igniter type and dynamics

The electrode spacing for sparks, the metallurgy of the fuse wire, and the energy released (as well as the rate of energy release) all play a factor.



Bellair, Robert J., and Lawrence Hood; *Process Safety and Environmental Protection* 132 (2019): 273-284.



What's The Right Answer?

If a material has specific ignition source and moisture requirements at ambient temperature to make it flammable, should it be classified as flammable?

If not classified as flammable, how do we ensure that potential users understand the hazards?



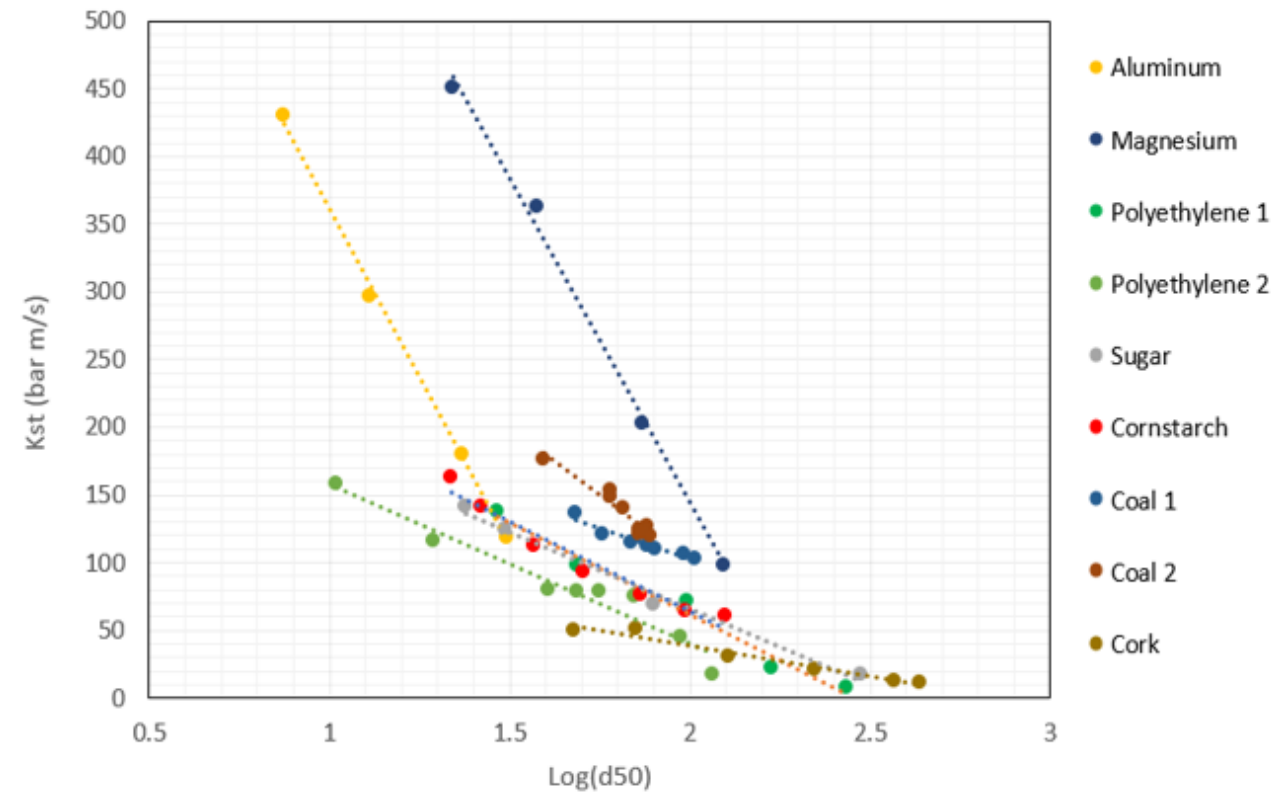
All Dusts Are Not Created Equal

Well known that particle, shape, surface area, aspect ratio and size distribution (polydispersity, skewedness etc) all impact dust explosion properties

However:

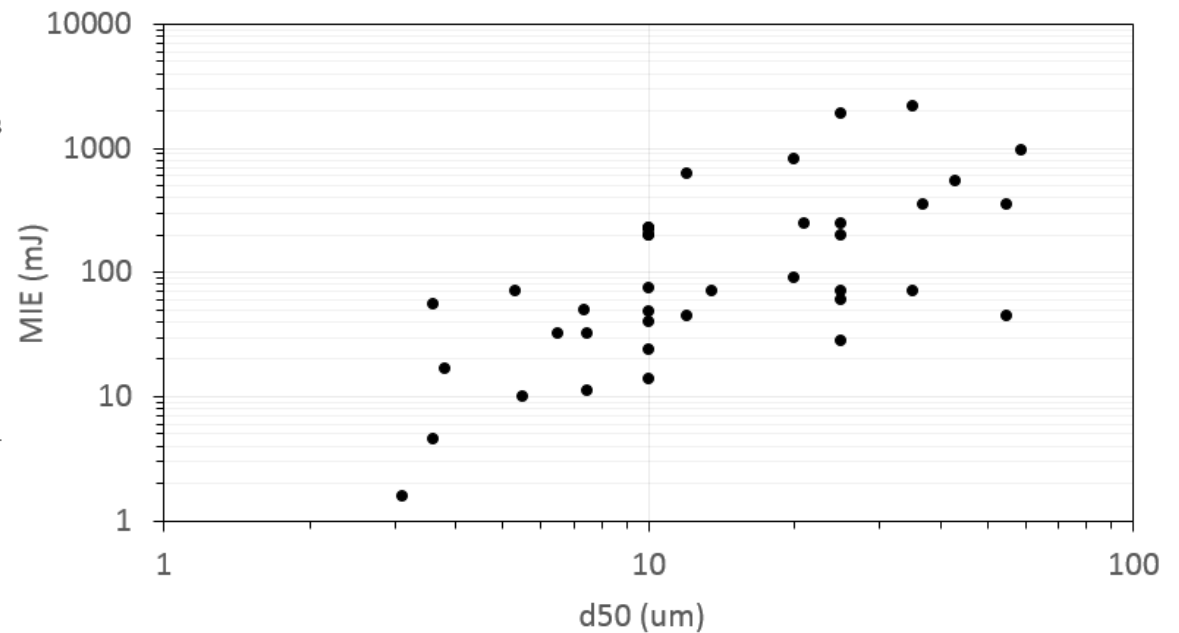
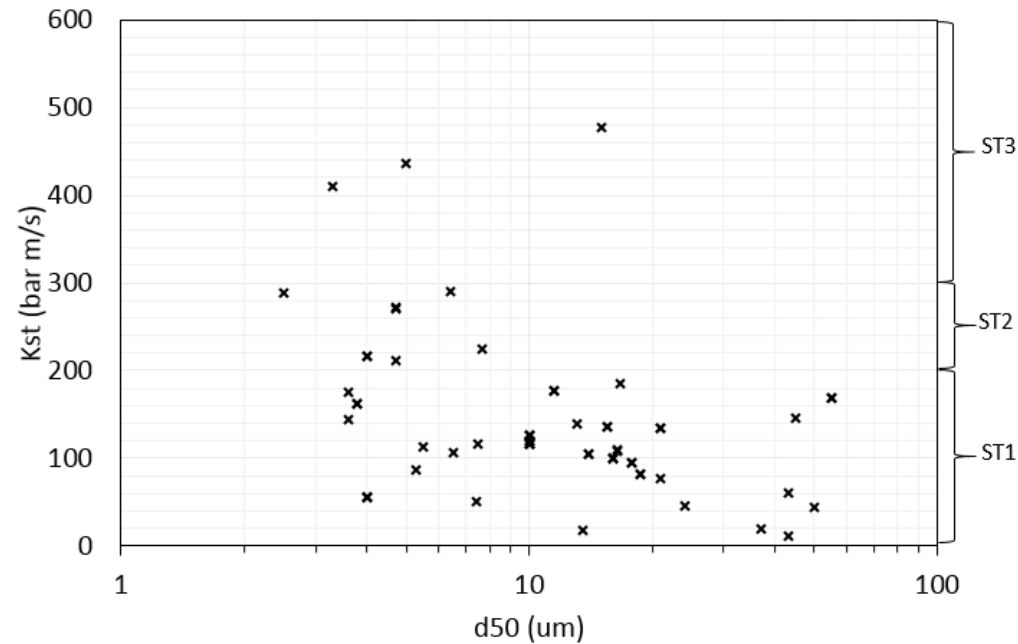
- Particle information is rarely published/provided with dust explosion data
- Reliance on a single set of dust explosion data taken at one moment is fairly common
- Often assumed a sample with the same median particle size will have the same dust explosion properties

Various Literature Studies Evaluating the Impact of Particle Size on Dust Explosibility



All Dusts Are Not Created Equal

Data compiled from the open literature on a single metal dust illustrates why just selecting a literature reference for dust explosion properties is not sufficient



Problems with Small Scale Testing: Dusts

In principle, the 1m³ dust explosion apparatus is the “industry standard” device for determining dust explosion properties

In practice, only a very tiny fraction of dust explosion testing is done in 1m³ apparatuses for a variety of reasons

The 20L vessel has been shown to give scalable data for a large fraction of materials, but is known to “underdrive” some materials.

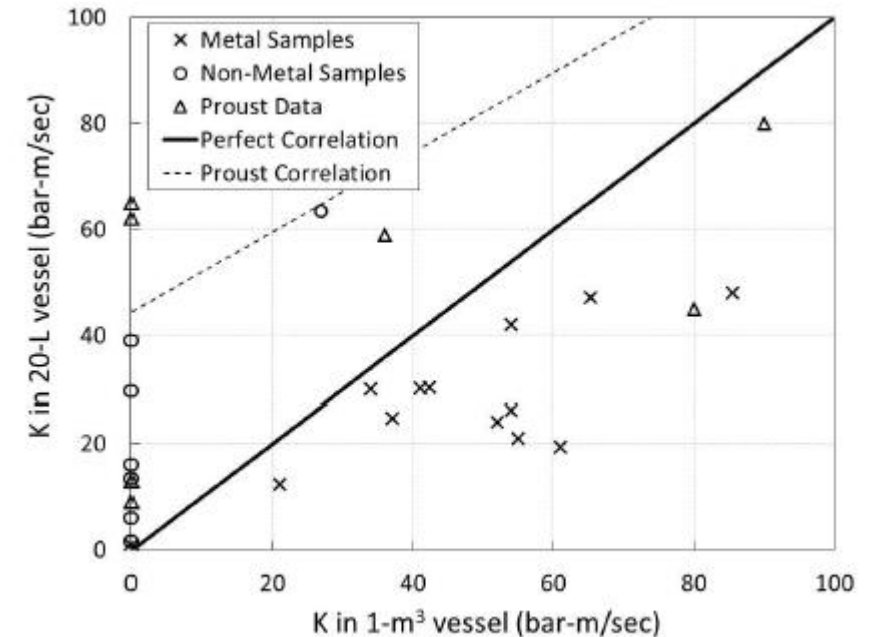


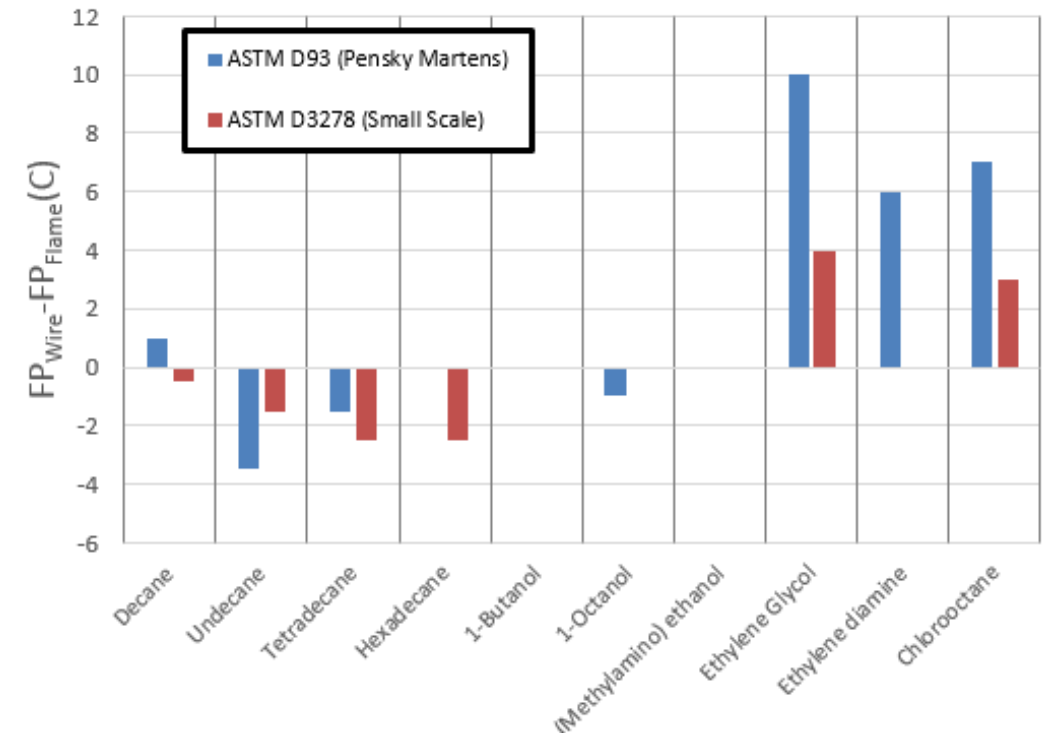
Figure 1: Comparison of K values between the 20-L and 1-m³ chambers.

Bucher, J., Ibarreta, A., Marr, K., Myers, T.; 15th Mary Kay O'Connor Process Safety Center International Symposium. 2012: p. 688-697. College Station, USA

Flash Point – Ignition Source

New generation flash point apparatuses have improved safety features including use of a hot wire instead of a hydrocarbon flame as the ignition source

- Some materials have different flash points when tested with the hot wire ignition source
- The regulatory classification (37.8C threshold) of ethylenediamine can depend on which ignition source was used to do the test



	ASTM D93 Flame Ethylenediamine	ASTM D93 Hot Wire Ethylenediamine
Run 1	36.5	42.5
Run 2	35.5	42.5
Run 3	39.5	44.5
Run 4	37.5	41.5
Run 5	37.5	42.5
AVG	37.3	42.7
STDEV	1.5	1.1

Flash Point Problem

- A new formulation of a product has been made and a flash point is needed to determine safe handling requirements and for regulatory purposes
- The flash point was tested, and the results are shown in the table.
- Is it safe to assume the material is “not flammable”?

Temp	Flash/No Flash
20	No Flash
25	No Flash
30	No Flash
35	No Flash
40	No Flash
45	No Flash
50	No Flash
55	boiled



Flash Point – Lack of Flash Does Not Mean “Non Flammable”

What if I told you the mixture was composed of:

- 95% acetone (FP= -20C)
- 5% of a low molecular weight polymer (FP>300C)

So why didn't it ignite then?

Temp	Flash/No Flash
20	No Flash
25	No Flash
30	No Flash
35	No Flash
40	No Flash
45	No Flash
50	No Flash
55	boiled

Acetone vapor pressure puts it above its upper flash point (UFL) at ambient temperature. It will typically not flash at room temperature in a closed cup method.

There are multiple products on the market right now touted to be “non-flammable” (despite the fact that every component in them is considered flammable), likely because they do not have a flash point from ambient up to their boiling point



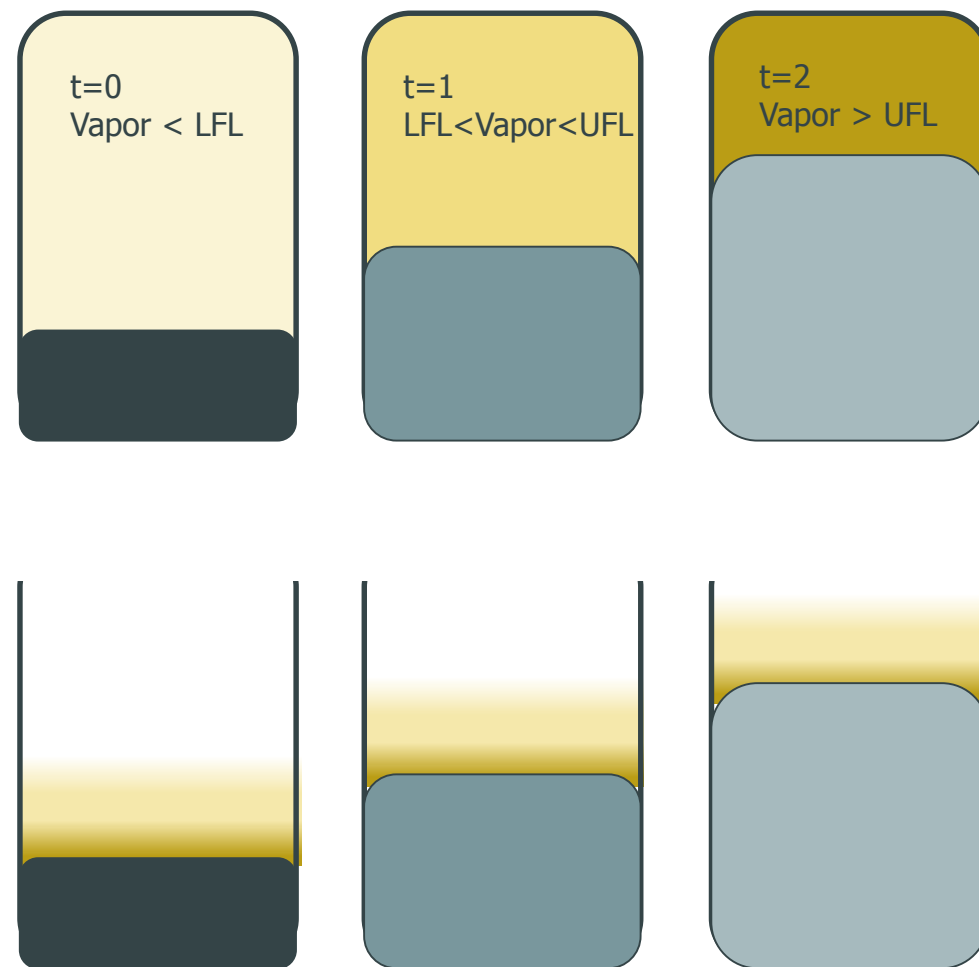
Foam Flammability

Some materials may not be assessable by any published test method

EXAMPLE: Two component foams that generate flammable gas or borderline flammable gas, or a mix of flammable and nonflammable gas

- *Closed system:* Flammability of the vapor space is a function of time. Headspace is compressed as gas is evolved and will often pass through the flammable range and even exceed the UFL
- *Open System:* Similar to open cup flash point, if a flammable composition exists it will exist at some short distance above the foam surface, however the location of that surface is changing as a function of time

What is the right way to evaluate the potential for a hazardous condition?



DOW RESTRICTED

Key Takeaways

- It is easy to assume a material is either “flammable” or it isn’t, however this mindset can create significant risk
- Blind use of standardized test methods or data generated by them can result in seriously under predicted risk
- Even if limits were generated under comparable conditions to how they will be applied, there is still uncertainty as to where “flammable” truly lies
- All flammability data should be closely assessed for applicability prior to applying it to a process/scenario



Questions?

