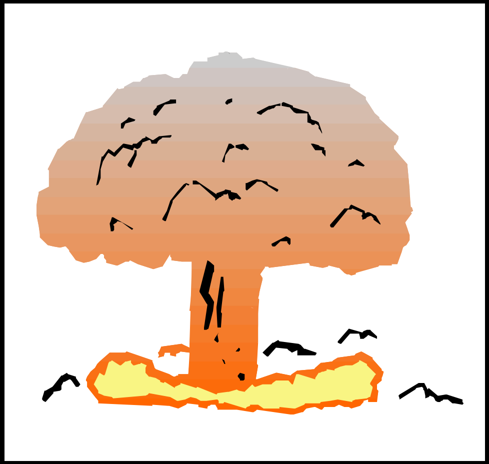
FIRES AND EXPLOSIONS



FUNDAMENTALS and DESIGN CONSIDERATIONS

Harry J. Toups LSU Department of Chemical Engineering with significant material from SACHE 2003 Workshop presentation by Ray French (ExxonMobil)

The Fire Triangle

- Oxidizers
  - Liquids
  - Gases
    - Oxygen, fluorine, chlorine
    - hydrogen peroxide, nitric acid, perchloric acid
  - Solids
    - Metal peroxides, ammonium nitrate

- Fuels:
  - Liquids
    - gasoline, acetone, ether, pentane
  - Solids
    - plastics, wood dust, fibers, metal particles
  - Gases
    - acetylene, propane, carbon monoxide, hydrogen

- Ignition sources
  - Sparks, flames, static electricity, heat

Liquid Fuels – Definitions

- **Flash Point**
  - Lowest temperature at which a flammable liquid gives off enough vapor to form an ignitable mixture with air
- **Flammable Liquids (NFPA)**
  - Liquids with a flash point < 100°F
- **Combustible Liquids (NFPA)**
  - Liquids with a flash point $\geq$ 100°F

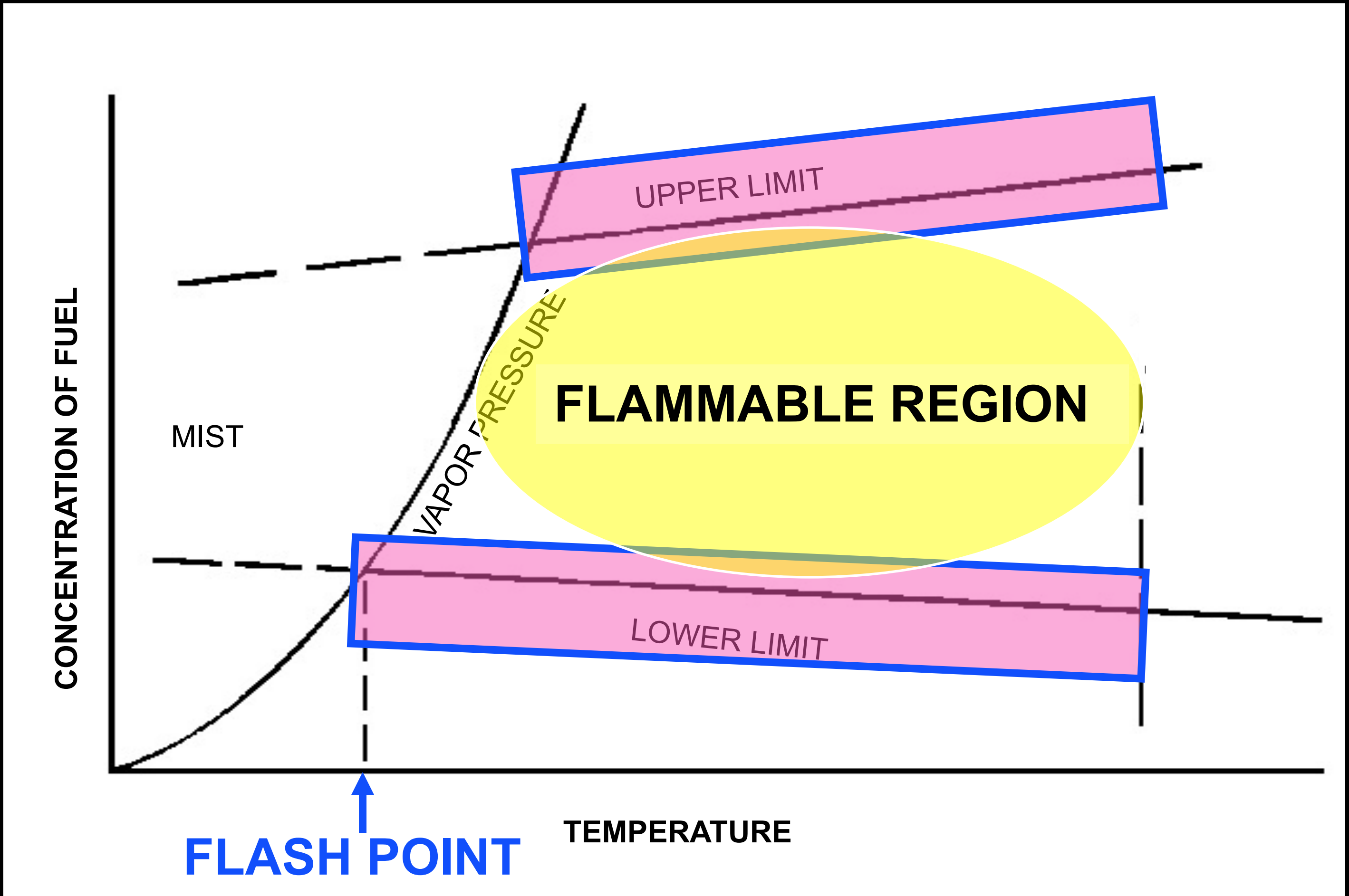
Vapor Mixtures – Definitions

- **Flammable / Explosive Limits**
  - Range of composition of material in air which will burn
    - UFL – Upper Flammable Limit
    - LFL – Lower Flammable Limit
    - HEL – Higher Explosive Limit
    - LEL – Lower Explosive Limit

  (LFL, HEL, LEL bracketed:) **SAME**

- **Measuring These Limits for Vapor-Air Mixtures**
  - Known concentrations are placed in a closed vessel apparatus and then ignition is attempted

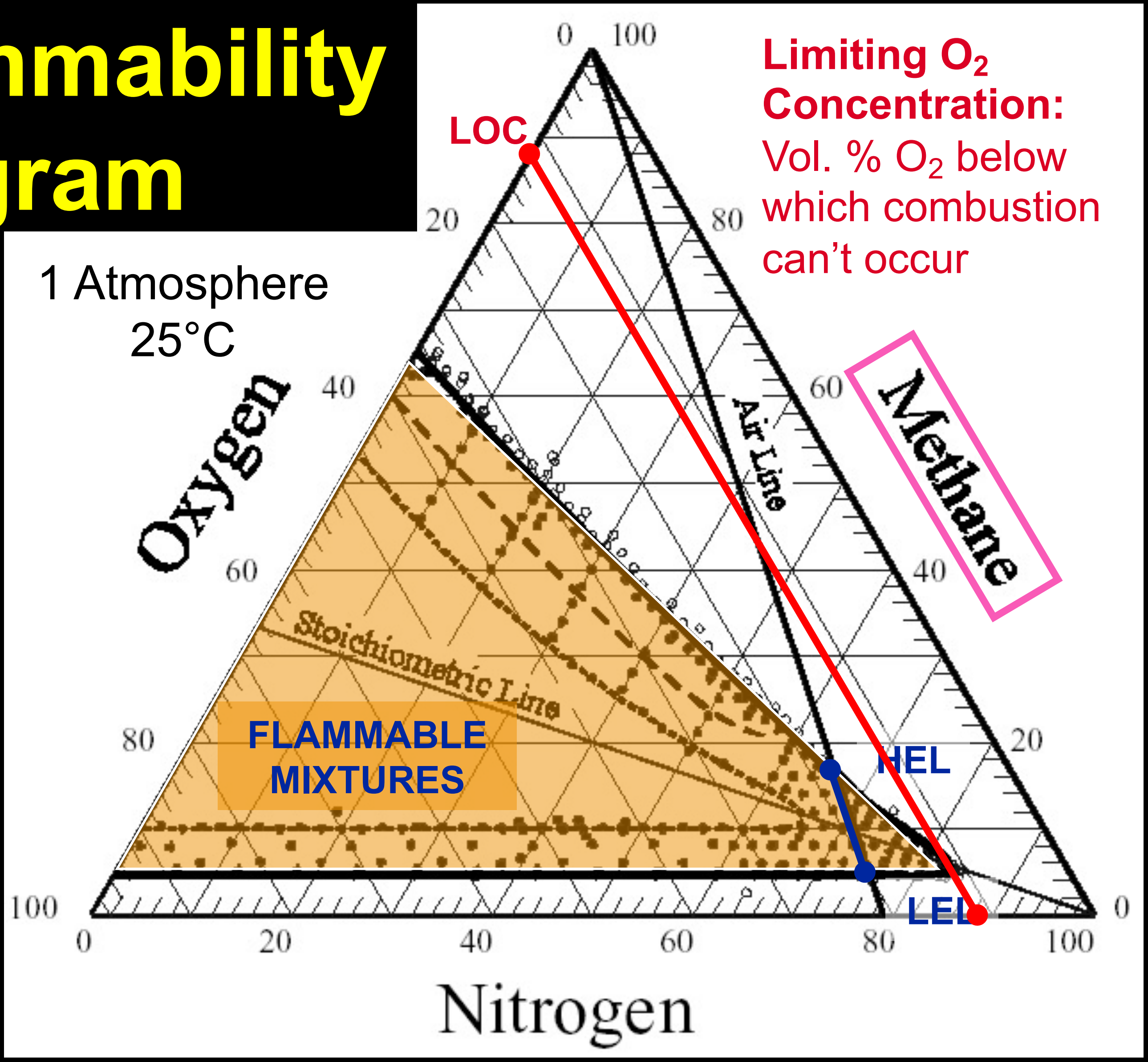
Flammability Relationships



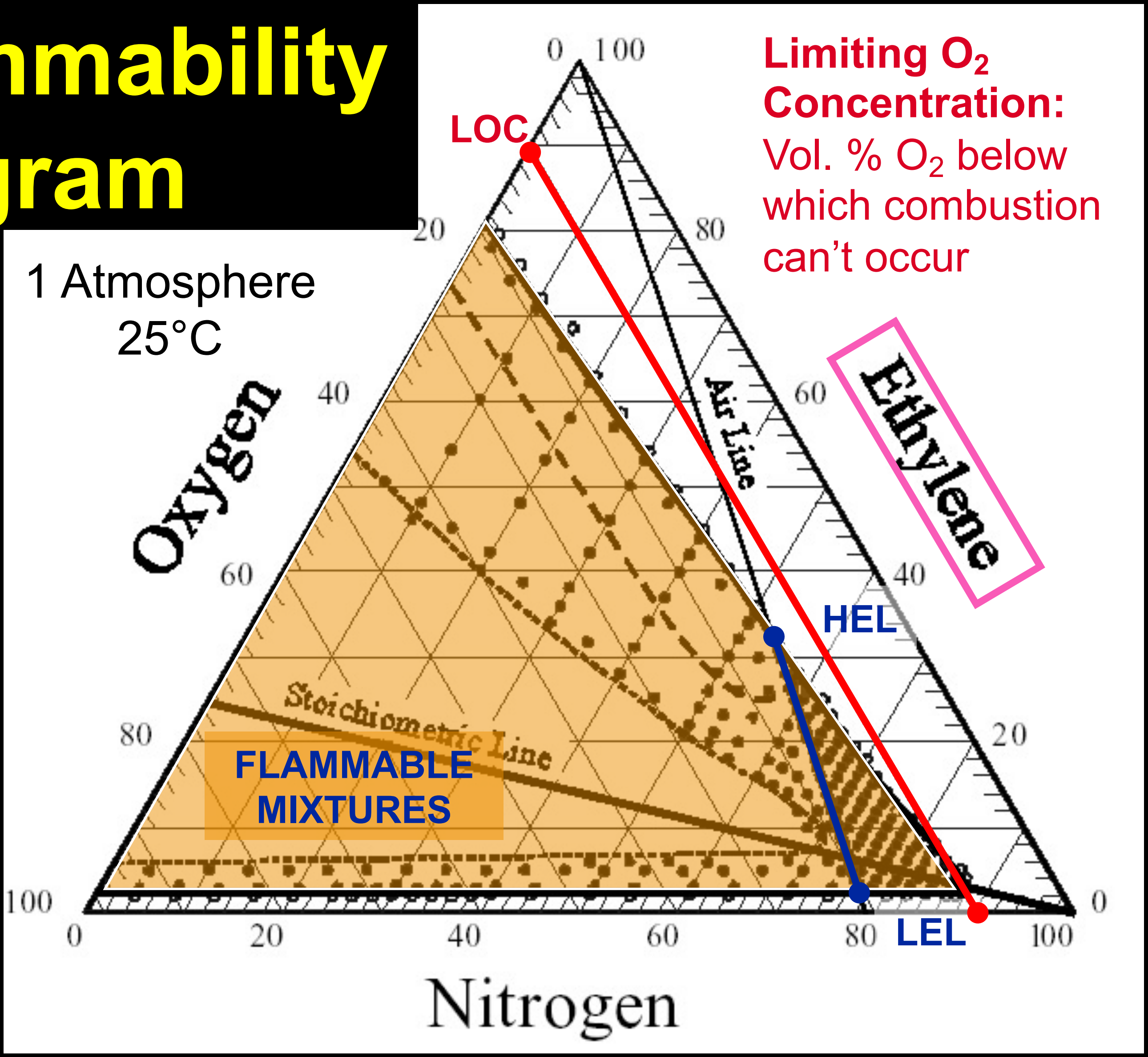
Flash Point From Vapor Pressure

- **Most materials start to burn at 50% stoichiometric**
- **For heptane:**
  - $C_7H_{16} + 11\ O_2 = 7\ CO_2 + 8\ H_2O$
  - Air = 11/ 0.21 = 52.38 moles air /mole of C_7H_{16} at stoichiometric conditions
  - At 50% stoichiometric, C_7H_{16} vol. % ≅ 0.9%
  - Experimental is 1.1%
  - For 1 vol. %, vapor pressure is 1 kPa temperature = 23° F
  - Experimental flash point temperature = 25° F

Flammability Diagram



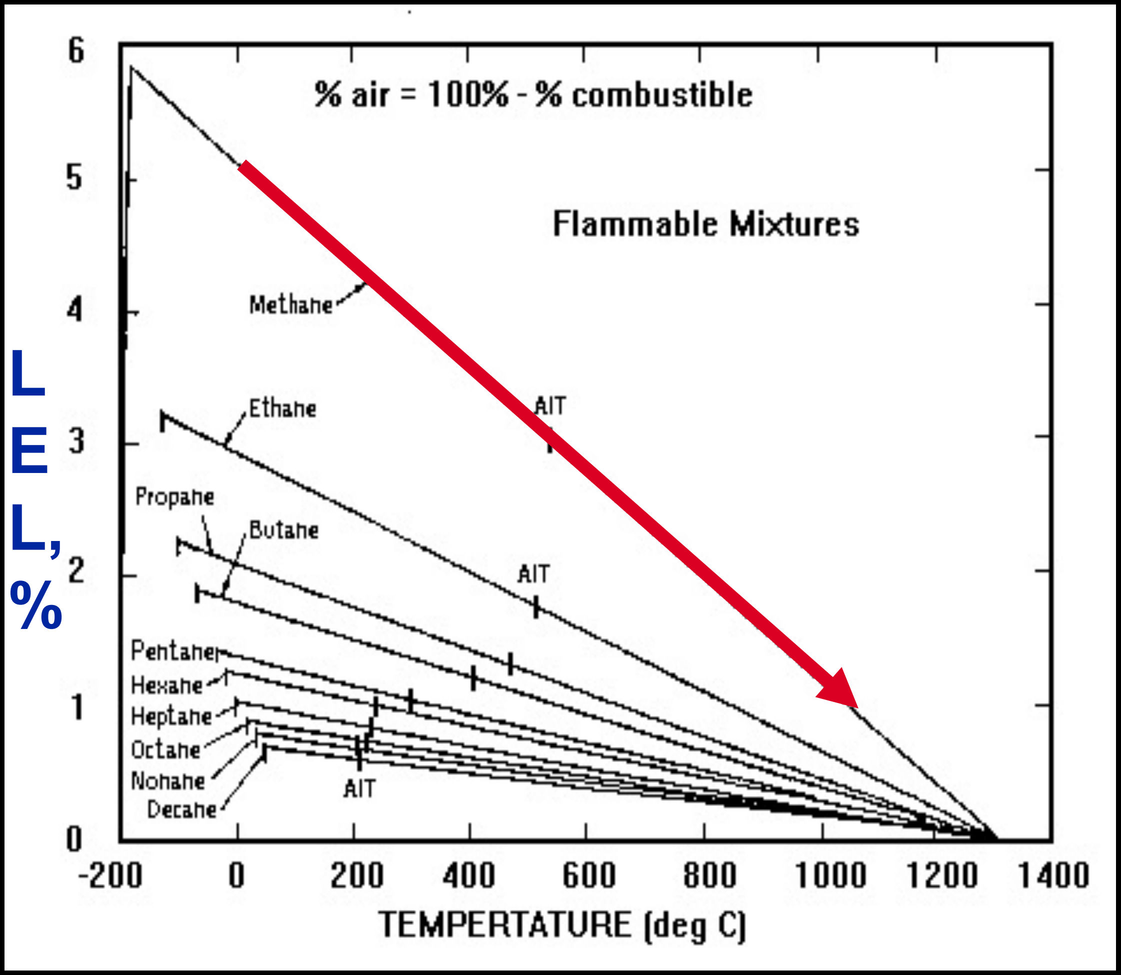
Flammability Diagram



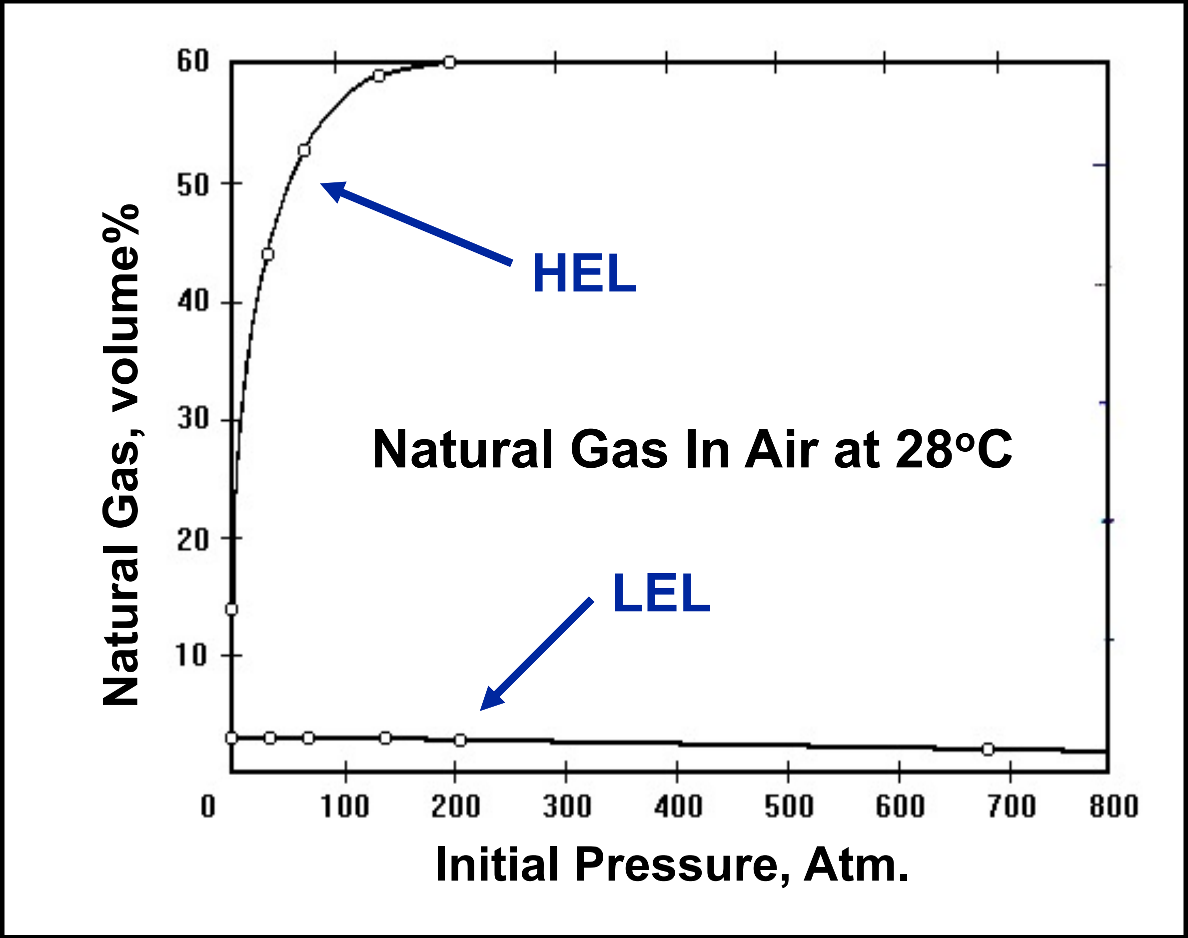
Flammable Limits Change With:

- Inerts
- Temperature
- Pressure

Effect of Temperature on Lower Limits of Flammability



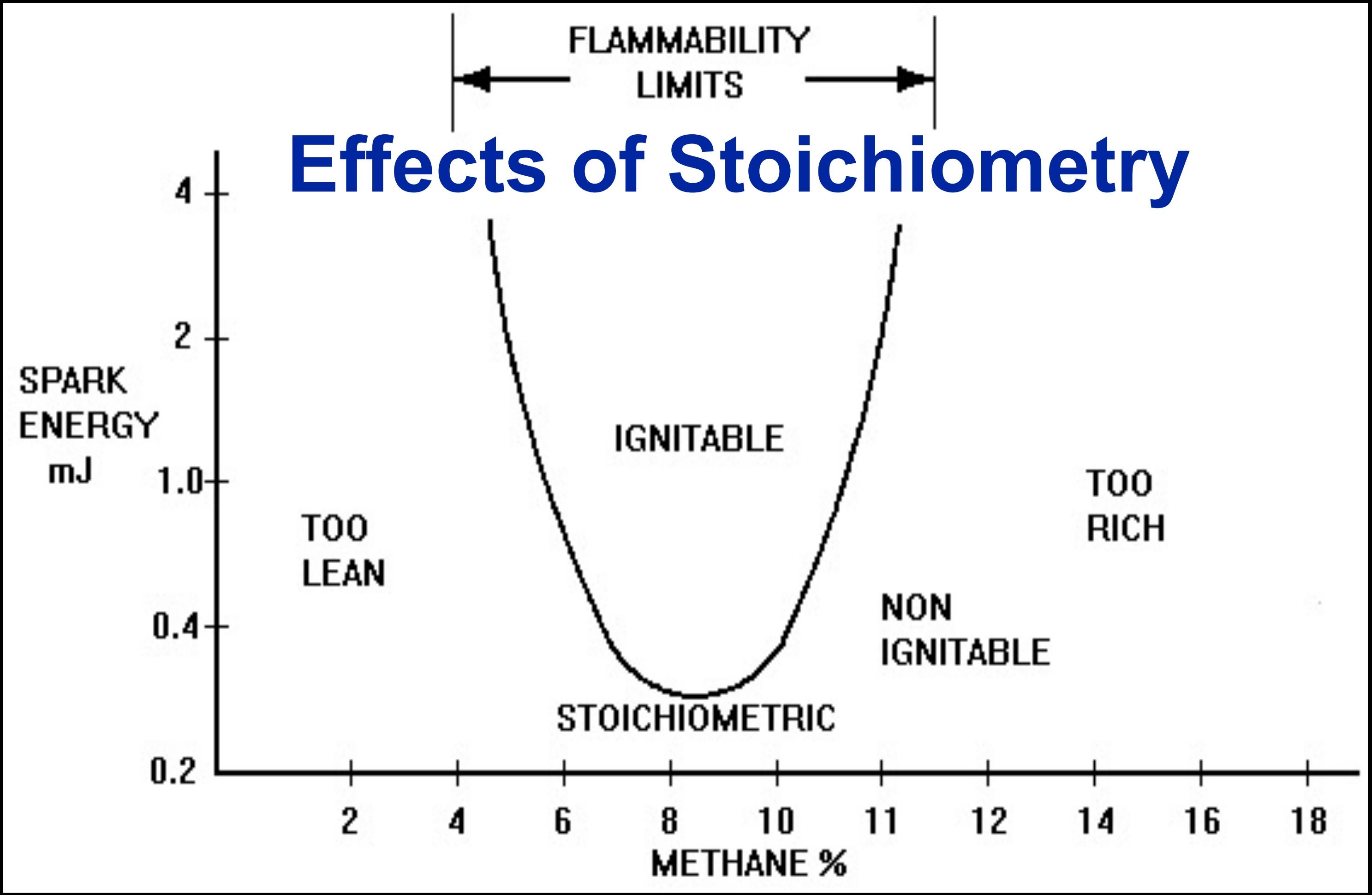
Effect of Pressure of Flammability



Minimum Ignition Energy

- Lowest amount of energy required for ignition
  - Major variable
  - Dependent on:
    - Temperature
    - % of combustible in combustant
    - Type of compound

Minimum Ignition Energy

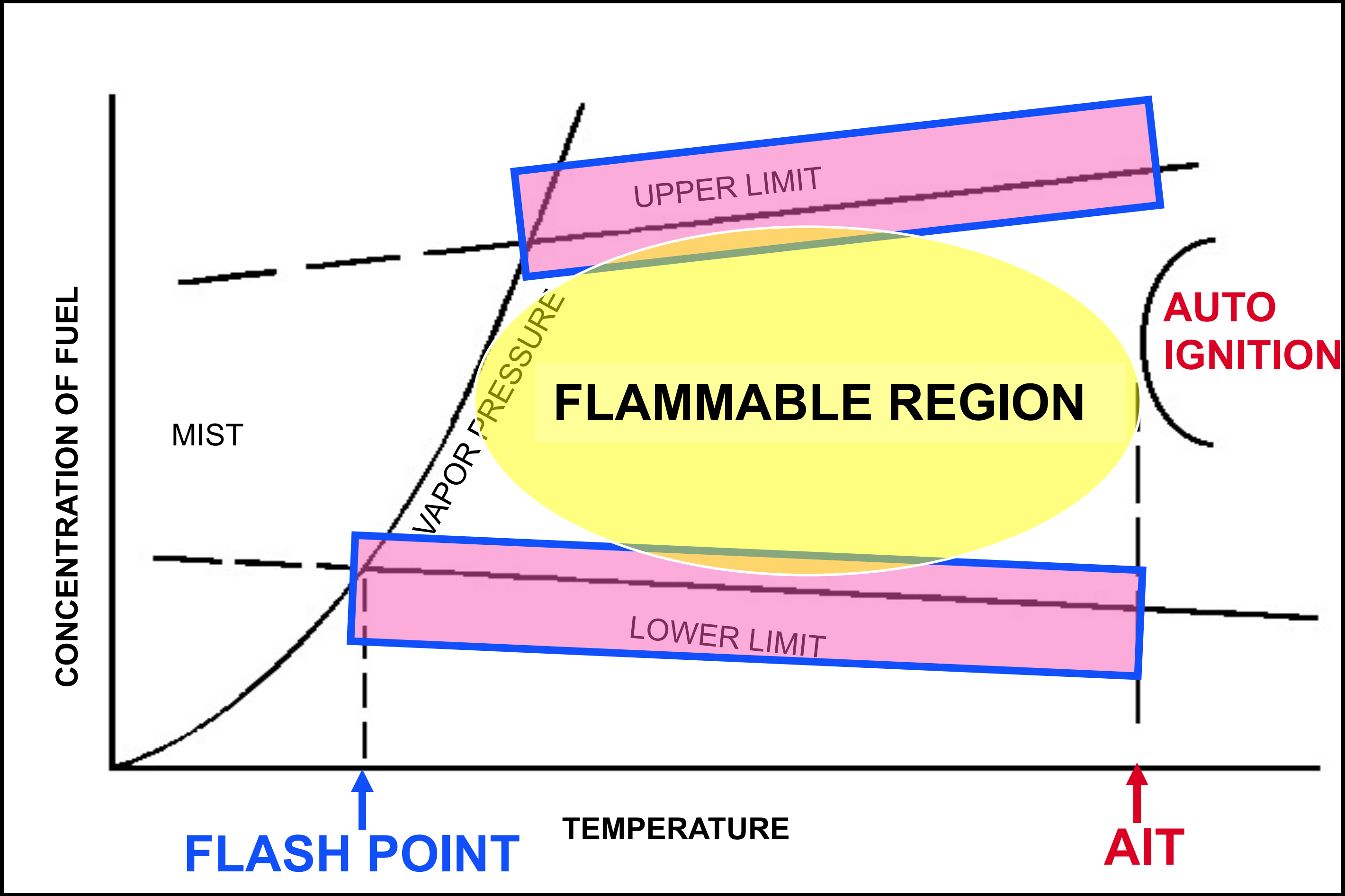


Autoignition Temperature

- Temperature at which the vapor ignites spontaneously from the energy of the environment

- Function of:
  - Concentration of the vapor
  - Material in contact
  - Size of the containment

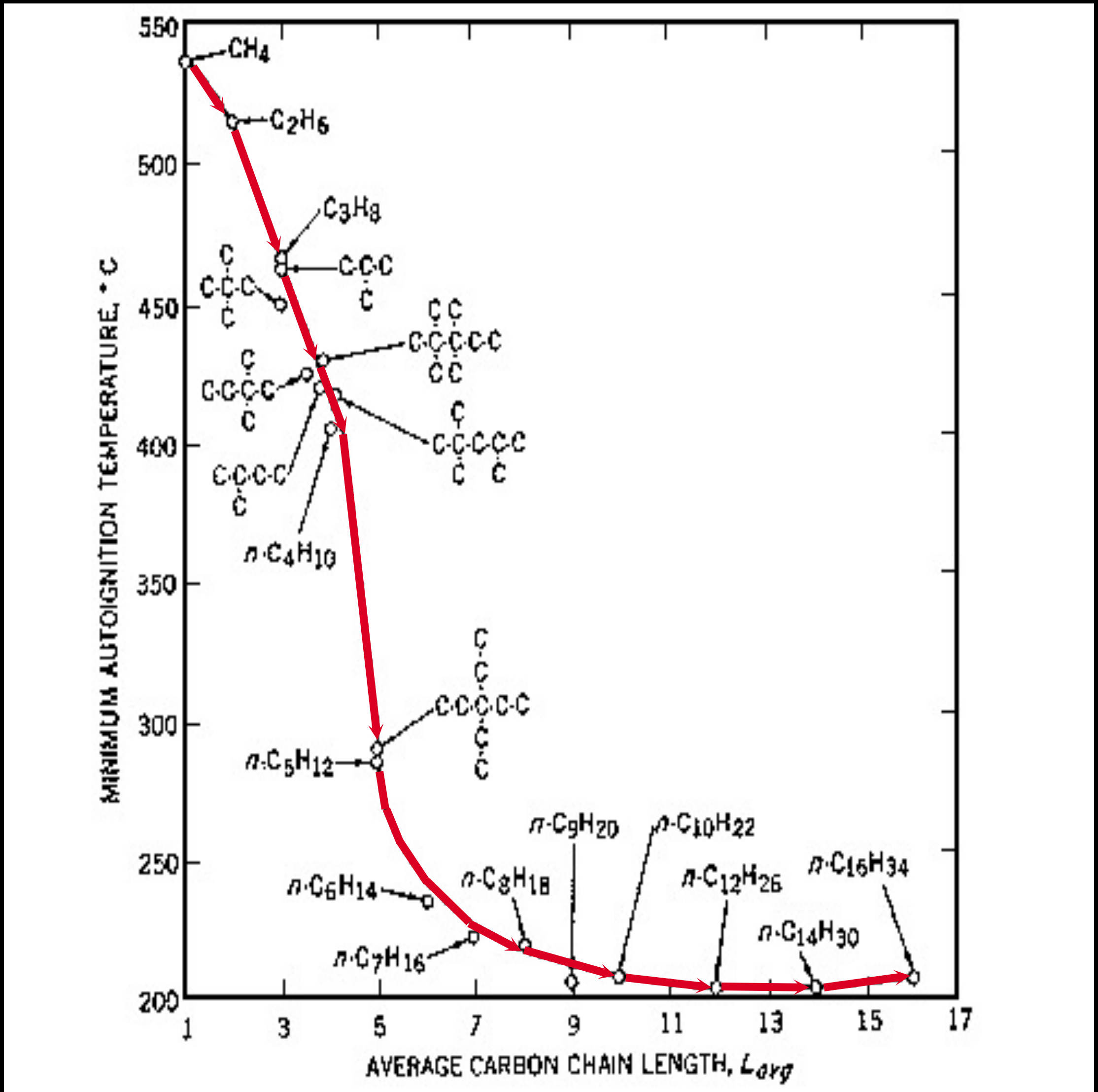
Flammability Relationships



Autoignition Temperature

Material	Variation	Autoignition Temperature
Pentane in air	1.50% 3.75% 7.65%	1018 °F 936 °F 889 °F
Benzene	Iron flask Quartz flask	1252 °F 1060 °F
Carbon disulfide	200 ml flask 1000 ml flask 10000 ml flask	248 °F 230 °F 205 °F

Autoignition Temperature



Auto-Oxidation

- The process of slow oxidation with accompanying evolution of heat, sometimes leading to autoignition if the energy is not removed from the system
- Liquids with relatively low volatility are particularly susceptible to this problem
- Liquids with high volatility are less susceptible to autoignition because they self-cool as a result of evaporation
- Known as **spontaneous combustion** when a fire results; e.g., oily rags in warm rooms; land fill fires

Adiabatic Compression

- Fuel and air will ignite if the vapors are compressed to an adiabatic temperature that exceeds the autoignition temperature
- Adiabatic Compression Ignition (ACI)
- Diesel engines operate on this principle; pre-ignition knocking in gasoline engines
- E.g., flammable vapors sucked into compressors; aluminum portable oxygen system fires

Ignition Sources of Major Fires

Source	Percent of Accidents
Electrical	23
Smoking	18
Friction	10
Overheated Materials	8
Hot Surfaces	7
Burner Flames	7
…	
Cutting, Welding, Mech. Sparks	6
…	
Static Sparks	1
All Other	20

More Definitions

- **Fire**
  - A slow form of **deflagration**
- **Deflagration**
  - Propagating reactions in which the energy transfer from the reaction zone to the unreacted zone is accomplished thru ordinary transport processes such as heat and mass transfer.
- **Detonation / Explosion**
  - Propagating reactions in which energy is transferred from the reaction zone to the unreacted zone on a reactive shock wave. The velocity of the shock wave always exceeds sonic velocity in the reactant.

Classification of Explosions

EXPLOSION = Rapid Equilibration of High Pressure Gas via Shock Wave

- Physical Explosions
- Chemical Explosions
  - Uniform Reactions
    - Thermal Explosions
  - Propagating Reactions
    - Thermal Explosions
    - Detonations (Shock Wave)
    - Deflagrations (Normal Transport)

Potential Energy

Stored Volumes of Ideal Gas at 20° C

PRESSURE, psig	TNT EQUIV., lbs. per ft^3
10	0.001
100	0.02
1000	1.42
10000	6.53

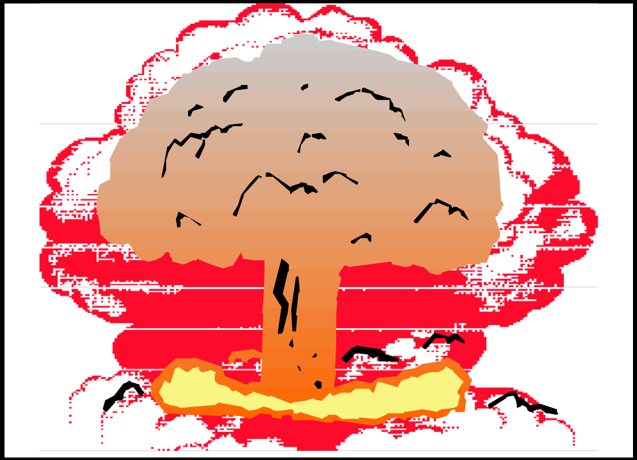
TNT equivalent = 5×10^5 calories/lb_m

Deflagration

- Combustion with flame speeds at non-turbulent velocities of 0.5 - 1 m/sec.
- Pressures rise by heat balance in fixed volume with pressure ratio of about 10.

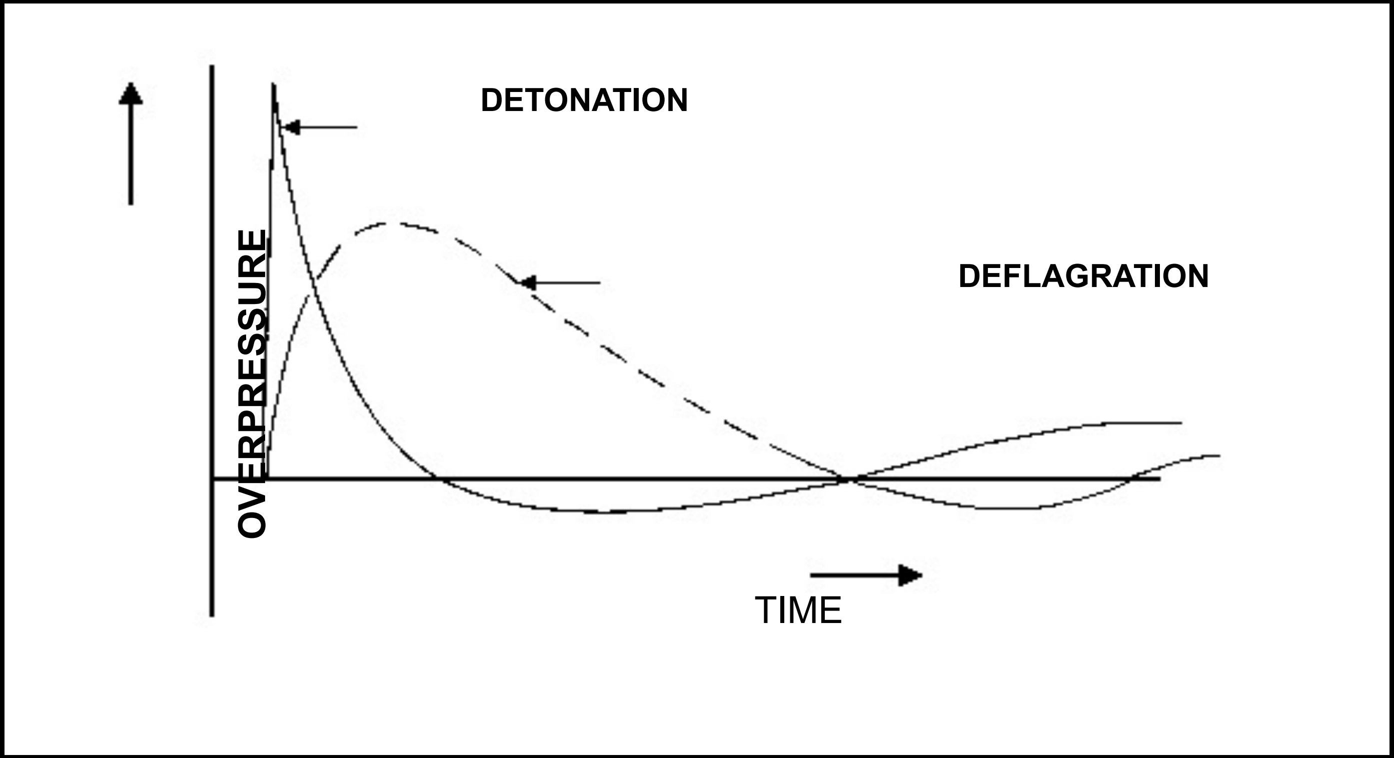
$CH_4 + 2\ O_2$	= $CO_2 + 2\ H_2O$ + 21000 BTU/lb
Initial Mols	= 1 + 2/.21 = 10.52
Final Mols	= 1 + 2 + 2(0.79/0.21) = 10.52
Initial Temp	= 298°K
Final Temp	= 2500°K
Pressure Ratio	= 9.7
Initial Pressure	= 1 bar (abs)
Final Pressure	= 9.7 bar (abs)

Detonation



- Highly turbulent combustion
- Very high flame speeds
- Extremely high pressures >>10 bars

Pressure vs Time Characteristics



CONSEQUENCES

Bayway, NJ
H-Oil Incident 1970

BAYWAY NO. 6 PIPESTILL "CONTROL HOUSE" - 1970

BAYWAY NO. 6 PIPESTILL "CONTROL HOUSE" - 1970

BAYWAY OFFICE BUILDING - 1970

Two Special Cases

- Vapor Cloud Explosion
- Boiling Liquid /Expanding Vapor Explosion

U V C E

U	V	C	E
N	A	L	X
C	P	O	P
O	O	U	L
N	R	D	O
F			S
I			I
N			O
E			N
D			S

- **An overpressure caused when a gas cloud detonates or deflagrates in open air rather than simply burns.**

What Happens to a Vapor Cloud?

- Cloud will spread from too rich, through flammable range to too lean.
- Edges start to burn through deflagration (steady state combustion).
- Cloud will disperse through natural convection.
- Flame velocity will increase with containment and turbulence.
- If velocity is high enough cloud will detonate.
- If cloud is small enough with little confinement it cannot explode.

What Favors Hi Overpressures?

- **Confinement**
  - Prevents escape, increases turbulence
- **Cloud composition**
  - Unsaturated molecules – ‘all ethylene clouds explode’; low ignition energies; high flame speeds
- **Good weather**
  - Stable atmospheres, low wind speeds
- **Large Vapor Clouds**
  - Higher probability of finding ignition source; more likely to generate overpressure
- **Source**
  - Flashing liquids; high pressures; large, low or downward facing leaks

Impact of VCEs on People

Peak Overpressure psi	Equivalent Wind Velocity mph	Effects
1		Knock personnel down
2	70	
5	160	Rupture eardrums
10	290	
15		Damage lungs
20	470	
30	670	
35		Threshold fatalities
50	940	50% fatalities
65		99% fatalities

Impact of VCEs on Facilities

Peak Overpressure psi	Typical Damage
0.5-to-1	Glass windows break
1-to-2	Common siding types fail: - corrugated asbestos shatters - corrugated steel panel joints fail - wood siding blows in
2-to-3	Unreinforced concrete, cinder block walls fail
3-to-4	Self-framed steel panel buildings collapse Oil storage tanks rupture
5	Utility poles snap
7	Loaded rail cars overturn
7-8	Unreinforced brick walls fail

Vapor Clouds and TNT

- World of explosives is dominated by TNT impact which is understood.
- Vapor clouds, by analysis of incidents, seem to respond like TNT if we can determine the equivalent TNT.
- 1 pound of TNT has a LHV of 1890 BTU/lb.
- 1 pound of hydrocarbon has a LHV of about 19000 BTU/lb.
- A vapor cloud with a 10% efficiency will respond like a similar weight of TNT.

Multi-Energy Models

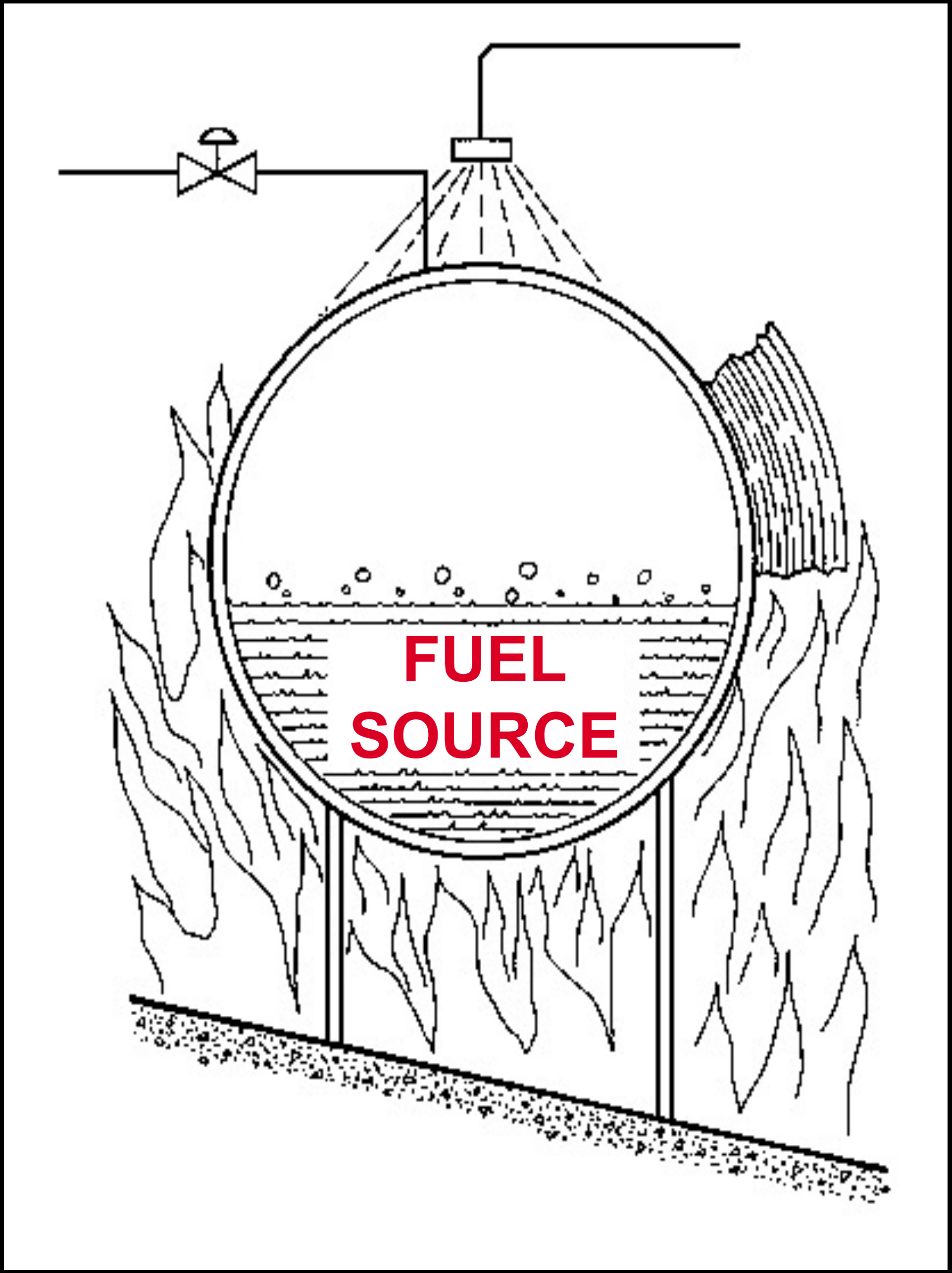
- **Experts plotted efficiency against vapor cloud size and … reached no effective conclusions. Efficiencies were between 0.1% and 50%**
- **Recent developments in science suggest too many unknowns for simple TNT model.**
- **Key variables to overpressure effect are:**
  - Quantity of combustant in explosion
  - Congestion/confinement for escape of combustion products
  - Number of serial explosions
- **Multi-energy model is consistent with models and pilot explosions.**

B L E V E

BOILING **L**IQUID **E**XPANDING **V**APOR **E**XPLOSIONS

- The result of a vessel failure in a fire and release of a pressurized liquid rapidly into the fire
- A pressure wave, a fire ball, vessel fragments and burning liquid droplets are usually the result

BLEVE



BLEVE Video Clip

Distance Comparison

INVENTORY (tons)	UVCE	BLEVE	FIRE
1	120	18	
2	150	36	
5	200	60	
10	250	90	20
20	310	130	30
50	420	200	36
100	530	280	50
200	670	400	60
500	900	600	100
1000	1150	820	130

Distance in Meters

DESIGN for PREVENTION

Eliminate Ignition Sources

Fire or Flames	Typical Control
Furnaces and Boilers	Spacing and Layout
Flares	Spacing and Layout
Welding	Work Procedures
Sparks from Tools	Work Procedures
Spread from Other Areas	Sewer Design, Diking, Weed Control, Housekeeping
Matches and Lighters	Procedures

Eliminate Ignition Sources

- Hot Surfaces
  - Hot Pipes and Equipment
  - Automotive Equipment
- Typical Control
  - Spacing
  - Procedures

- Electrical
  - Sparks from Switches
  - Static Sparks
  - Lightning
  - Handheld Electrical Equipment
- Typical Control
  - Area Classification
  - Grounding, Inerting, Relaxation
  - Geometry, Snuffing
  - Procedures

Inerting – Vacuum Purging

- Most common procedure for inerting reactors
- Steps
  1. Draw a vacuum
  2. Relieve the vacuum with an inert gas
  3. Repeat Steps 1 and 2 until the desired oxidant level is reached
- Oxidant Concentration after j cycles:

$$y_j = y_o\left(\frac{P_L}{P_H}\right)^j$$

where P_L is vacuum level
P_H is inert pressure

Inerting – Pressure Purging

- Most common procedure for inerting reactors
- Steps
  1. Add inert gas under pressure
  2. Vent down to atmospheric pressure
  3. Repeat Steps 1 and 2 until the desired oxidant level is reached
- Oxidant Concentration after j cycles:

$$y_j = y_o \left(\frac{n_L}{n_H}\right)^j$$

where n_L is atmospheric moles
n_H is pressure moles

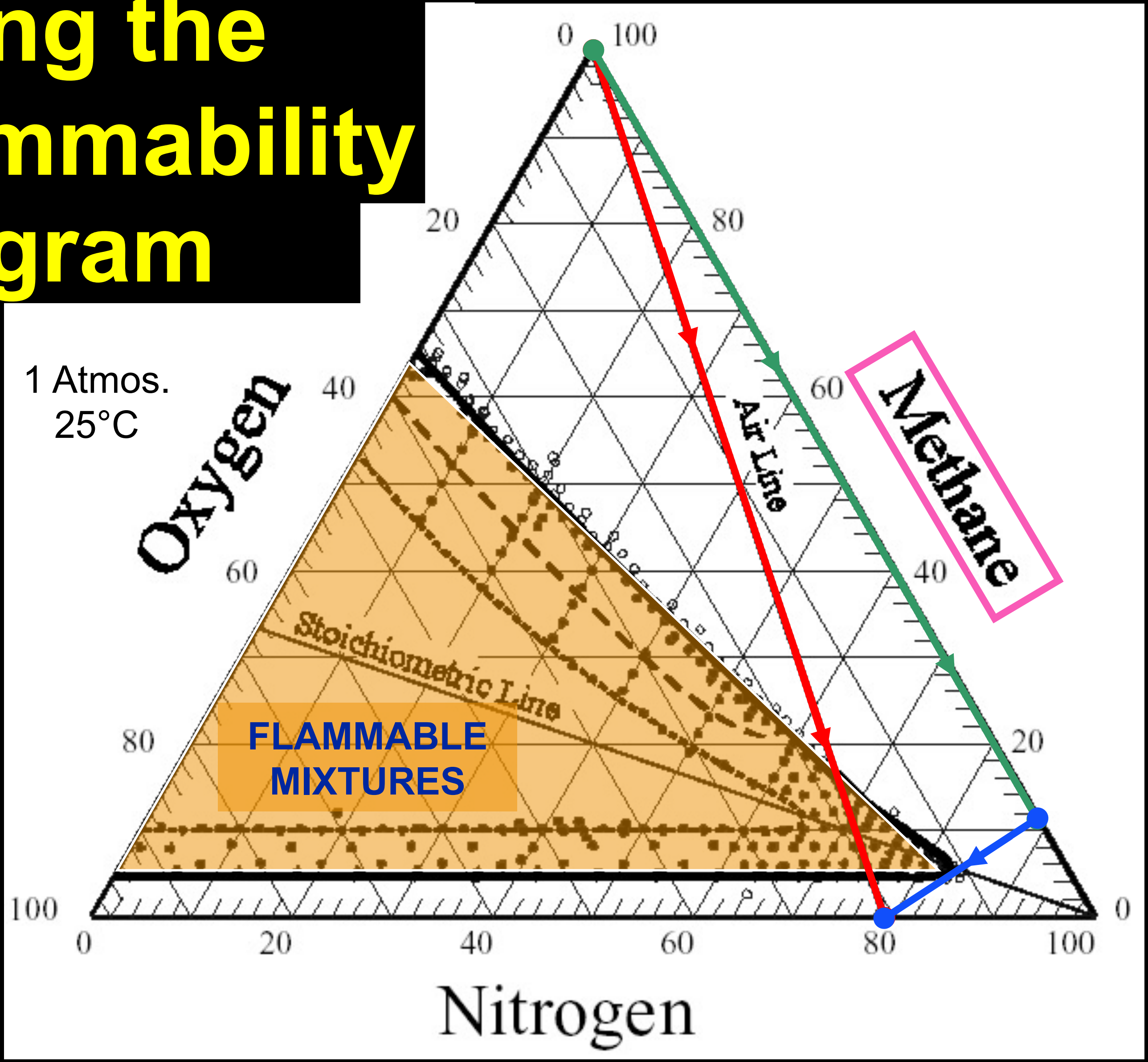
Vacuum? Pressure? Which?

- Pressure purging is faster because pressure differentials are greater (+PP)
- Vacuum purging uses less inert gas than pressure purging (+VP)
- Combining the two gains benefits of both especially if the initial cycle is a vacuum cycle (+ VP&PP)

Other Methods of Inerting

- **Sweep-Through Purging**
  - ‘In one end, and out the other’
  - For equipment not rated for pressure, vacuum
  - Requires large quantities of inert gas
- **Siphon Purging**
  - Fill vessel with a compatible liquid
  - Use Sweep-Through on small vapor space
  - Add inert purge gas as vessel is drained
  - Very efficient for large storage vessels

Using the Flammability Diagram



Static Electricity

- Sparks resulting from static charge buildup (involving at least one poor conductor) and sudden discharge
- Household Example: walking across a rug and grabbing a door knob
- Industrial Example: Pumping nonconductive liquid through a pipe then subsequent grounding of the container

Dangerous energy near flammable vapors	0.1 mJ
Static buildup by walking across carpet	20 mJ

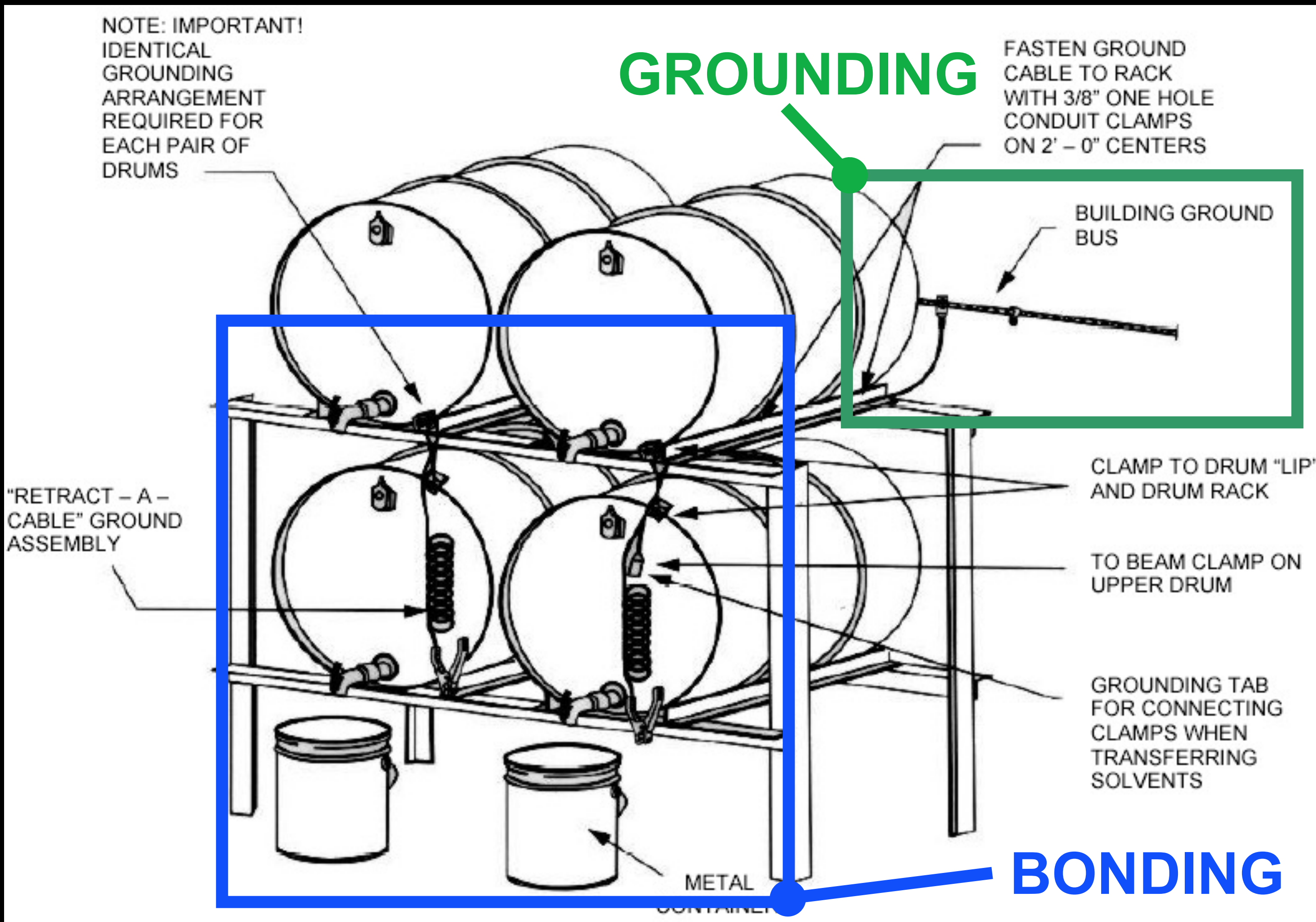
Double-Layer Charging

- **Streaming Current**
  - The flow of electricity produced by transferring electrons from one surface to another by a flowing fluid or solid
  - The larger the pipe / the faster the flow, the larger the current
- **Relaxation Time**
  - The time for a charge to dissipate by leakage
  - The lower the conductivity / the higher the dielectric constant, the longer the time

Controlling Static Electricity

- Reduce rate of charge generation
  - Reduce flow rates
- Increase the rate of charge relaxation
  - Relaxation tanks after filters, enlarged section of pipe before entering tanks
- Use bonding and grounding to prevent discharge

Controlling Static Electricity



Static Electricity – Real Life

Explosion Proof Equipment

- All electrical devices are inherent ignition sources
- If flammable materials might be present at times in an area, it is designated XP (Explosion Proof Required)
- Explosion-proof housing (or intrinsically-safe equipment) is required

Area Classification

- National Electrical Code (NEC) defines area classifications as a function of the nature and degree of process hazards present

Class I	Flammable gases/vapors present
Class II	Combustible dusts present
Class III	Combustible dusts present but not likely in suspension
Group A	Acetylene
Group B	Hydrogen, ethylene
Group C	CO, H2S
Group D	Butane, ethane
Division 1	Flammable concentrations normally present
Division 2	Flammable materials are normally in closed systems

VENTILATION

- Open-Air Plants
  - Average wind velocities are often high enough to safely dilute volatile chemical leaks
- Plants Inside Buildings
  - Local ventilation
    - Purge boxes
    - ‘Elephant trunks’
  - Dilution ventilation ($\geq$ 1 $ft^3/min/ft^2$ of floor area)
    - When many small points of possible leaks exist

Summary

- Though they can often be reduced in magnitude or even sometimes designed out, many of the hazards that can lead to fires/explosions are unavoidable
- Eliminating **at least** one side of the Fire Triangle represents the best chance for avoiding fires and explosions

END of PRESENTATION