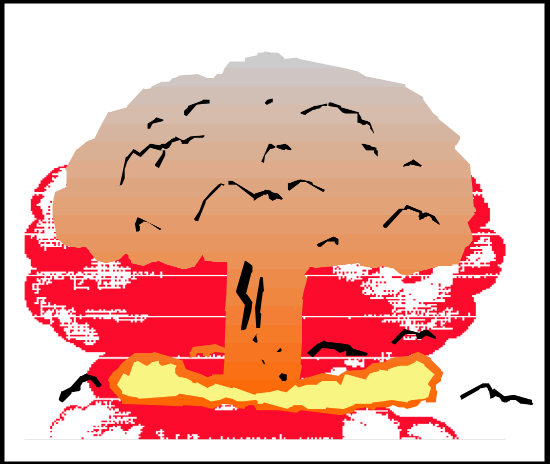
SAFETY ENGINEERING TECHNOLOGY

FUNDAMENTALS OF FIRES AND EXPLOSIONS



AIChE SACHE Faculty Workshop
Baton Rouge - Sep 29, 2003

What's Coming

- **Quiz**
- **Terminology & Definitions**
- **Flash Point**
- **Autoignition**
- **Minimum Ignition Energy**
- **Video - Flames & Explosions**
- **Ignition Sources**
- **Flammability Relationships**
- **Classification of Explosions**
- H-Oil Incident
- Video - Explosions & Detonations
- Unconfined Vapor Cloud Explosions
- Impact of UVCE
- Models
- BLEVE
- Impact of BLEVE
- Video - BLEVE
- Quiz Review

Quiz on Fundamentals of Fires and Explosions

1. What is the flash point of a liquid?

2. What is the fundamental difference between flammable and combustible stock?

3. What is the cut off point between a “flammable liquid” and a “combustible liquid” as defined by the NFPA standards?

4. What is the difference between the terms “lower explosive limit (LEL)” and “lower flammable limit (LFL)”?

5. A material whose flash point is 212°F (100°C) is being stored at 203°F (95°C). Is this treated as a flammable or combustible material under ExxonMobil practices?

6. There is a correlation of flash point with upper flammable limit (UFL) by means of the vapor pressure curve. (True/False)

7. A pipe whose surface temperature is 662°F (350°C) represents a likely source of ignition for a flammable vapor whose autoignition temperature (A.I.T.) is 608°F (320°C). (True/False).

Quiz on Fundamentals of Fires and Explosions

8. Pressure has a significant effect on the flammable range of most hydrocarbons. (True/False).

9. Deflagration is another word for detonation. (True/False)

10. Typical pressures reached in a confined deflagration are 6 to 8 times the initial pressure. (True/False)

11. Stoichiometric mixtures generally require higher ignition energies than other mixtures within the flammable range. (True/False)

12. The only factors that determine the strength of a vapor cloud explosion are the type of molecule and the amount released. (True/False)

13. The TNT model is still the best for modeling explosions. (True/False)

Terminology

- Auto Ignition Temperature
- BLEVE
- Combustible Liquids
- Deflagration
- Detonation
- Explosion
- Explosive Limits
- Fire
- Flammable Limits
- Flammable Liquids
- Flash Point
- High Flash Stocks
- Ignition Energy
- Intermediate Vapor Pressure Stocks
- Light Ends
- Low Flash Stocks
- Phyrophoric Materials
- Reid Vapor Pressure
- UCVE
- Vapor Pressure

Definitions

- **Flash Point**
  - Lowest temperature at which a flammable liquid exposed to air will burn when exposed to sparks or flame.
- **Auto Ignition Temperature**
  - Temperature above which spontaneous combustion can occur without the use of a spark or flame.
- **Ignition Energy**
  - Lowest amount of energy required for ignition.

Definitions

- **Flammable Liquids (NFPA)**
  - Liquids with a flash point $<$ 100F (38^o C)

- **Combustible Liquids (NFPA)**
  - Liquids with a flash point $\geq$ 100F (38^o C)

- **High Flash Stocks**
  - Liquids with flash point $\geq$ 130F (55^o C) or stored at least 15F(8^o C) below its flash point (Heavy Fuel Oil, Lube Oil)

- **Low Flash Stocks**
  - Liquid with flash point $<$ 130F (55^o C) or stored within 15F (8^o C) of its flash point (Kero, Diesel, etc.)

Definitions

- **Light Ends**
  - Volatile flammable liquids which vaporize when exposed to air. Design Practices defines as pentanes and lighter napthas of RVP > 15 PSIA.
- **Intermediate Vapor Pressure Stocks**
  - Low flash stocks heavier than light ends where the vapor space must be assumed to be mainly in the flammable range.
- **Pyrophoric Material**
  - Material which will spontaneously burn in air at ambient temperature.

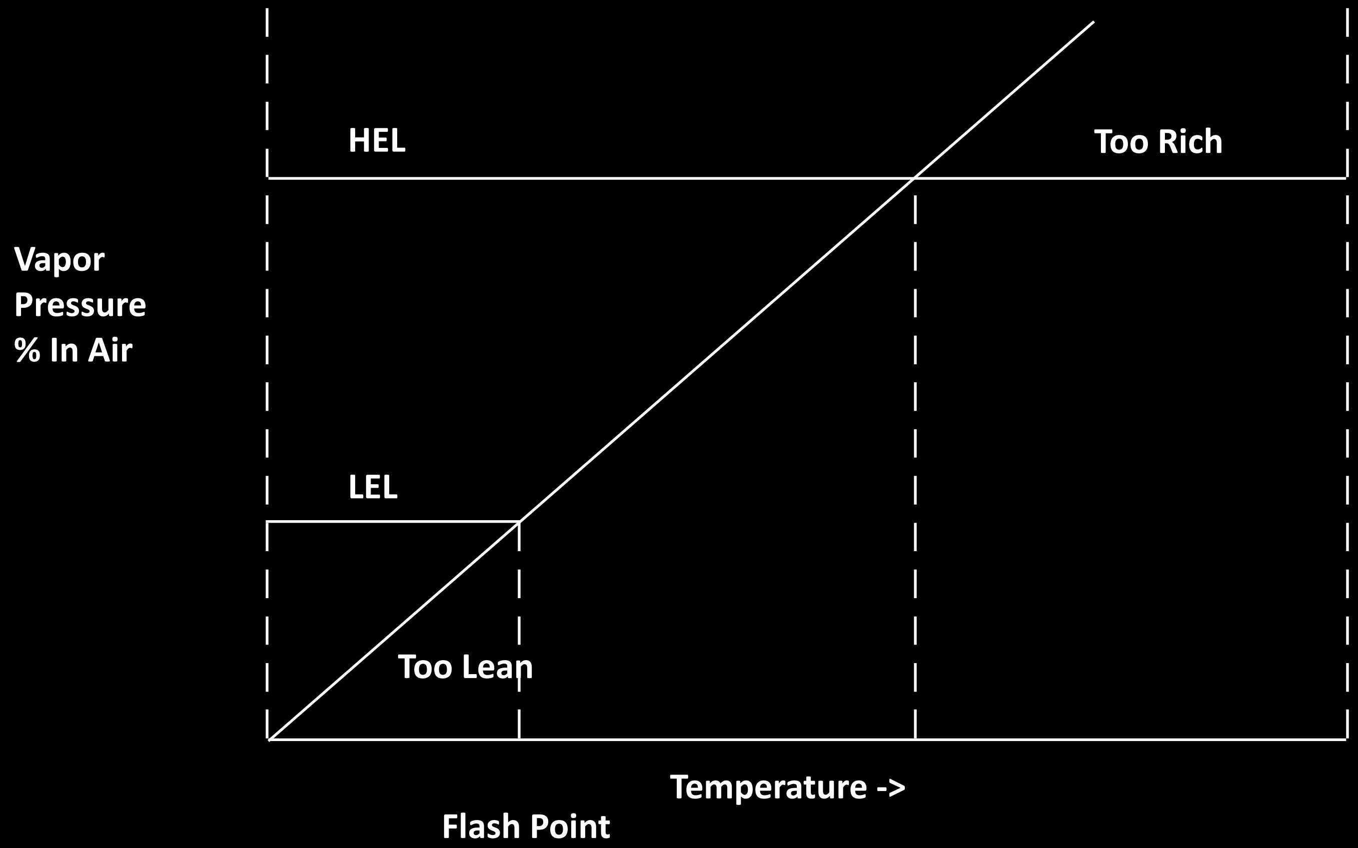
Definitions

- **Flammable Limits**
  - Range of composition of material in air which will burn.
    - U.F.L.........Upper Flammable Limit
    - L.F.L..........Lower Flammable Limit
- **Explosive Limits**
  - Same as flammable limits.
- **Vapor Pressure**
  - Pressure exerted by liquid on vapor space.
- **Reid Vapor Pressure**
  - Vapor Pressure measured at 100F (37.8^{o} C).

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/mole of heptane at stoichiometric conditions
    - At LEL with 50% stoichiometric, heptane is 0.5/52.38 = 1 vol. %
    - Experimental is 1.1%
    - For 1 vol. %, vapor pressure is 1 kPa temperature = 23^{o} F (-5^{o} C)
    - Flash point = 25^{o} F (-4^{o} C)

Flash Point Curve



Flash Point Determination Methods

- **Laboratory tests are:**
  - **Closed cup tag (ASTM D-65) for materials of 194°F (90 ° C) flash point or less**
  - **Pensky Martens (ASTM D-93) for materials of 194°F (90 ° C) flash point or more**
  - **Open cup tag (ASTM D-1310) or Cleveland (ASTM D-92)**

Auto Ignition Temperature

- Varies with:
  - size of containment
  - material in contact
  - concentration
- Is specific to a given composition
- Be careful of global numbers

Auto Ignition Temperature

- **Measured value very apparatus related, NFPA data:**

  - **Benzene in: quartz flask 1060° F (571°C)**
    iron flask 1252° F (678°C)

  - **CS_2 in: 200 ml flask 248° F (120°C)**
    1000 ml flask 230° F (110°C)
    10000 ml flask 205° F (96°C)

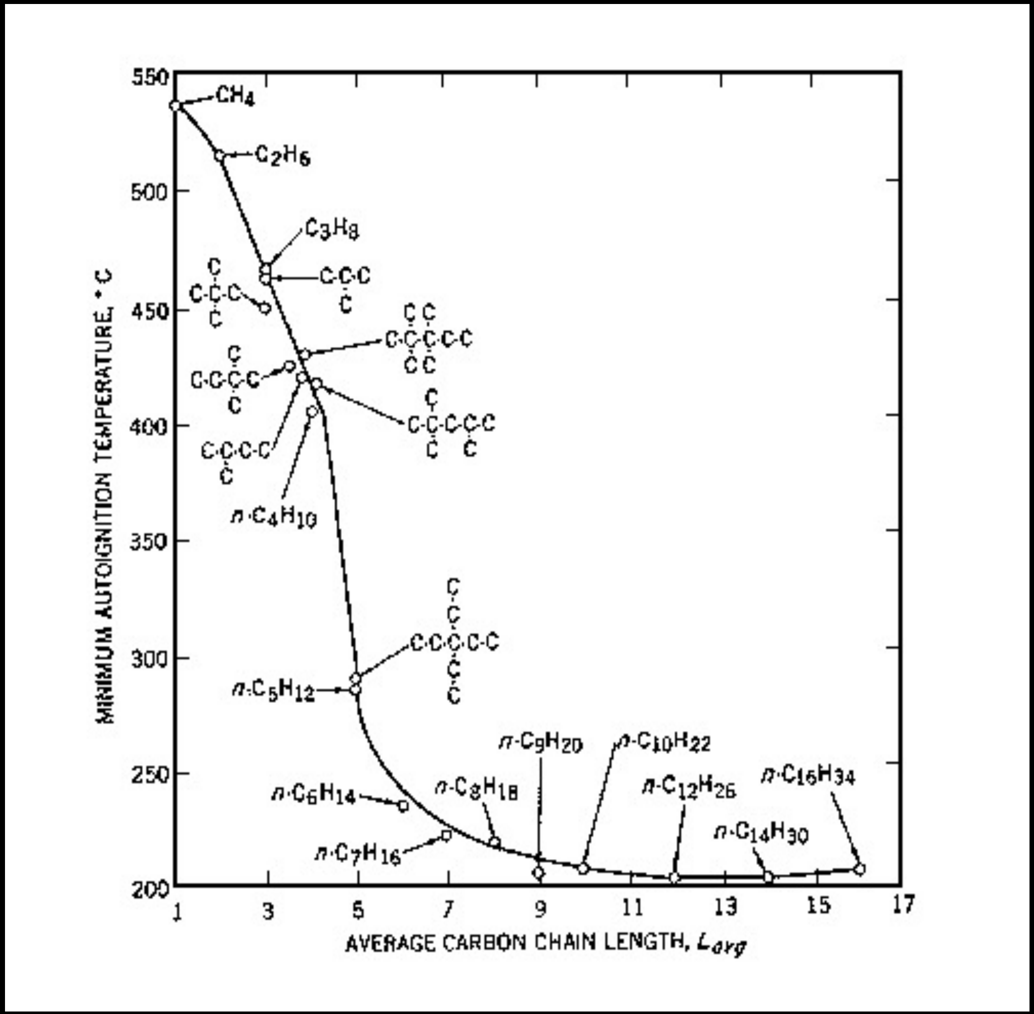
  - **Hexane with different apparatus: 437° F (225°C)**
    950° F (510°C)

Auto Ignition Temperature

- **Measured value also concentration dependent, NFPA data:**
  - **$C_5^=$ in air:**

$C_5^=$ in air:	**1.5%**	**1018° F (548°C)**
	3.75%	**936° F (502°C)**
	7.65%	**889° F (476°C)**

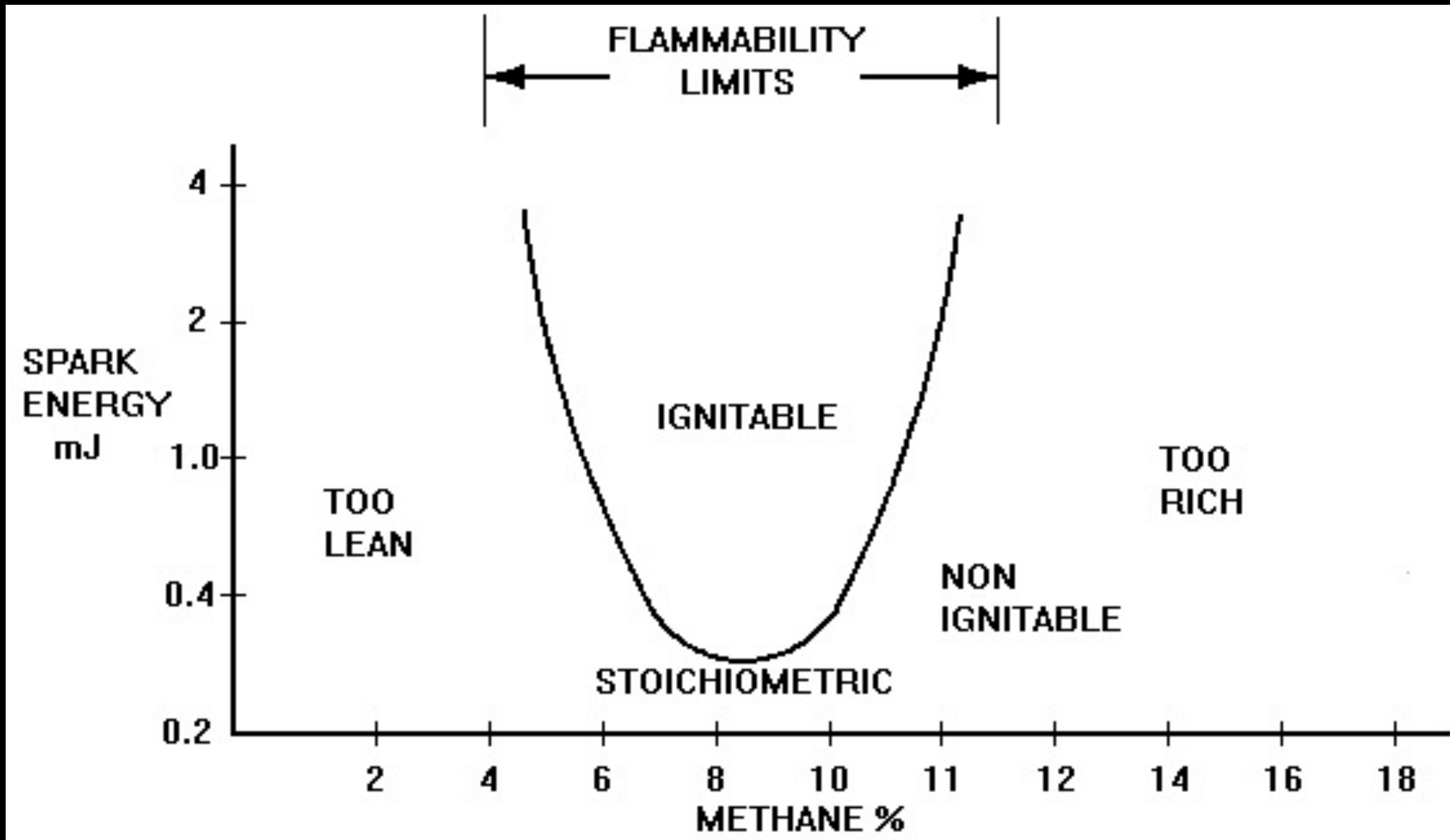
Auto Ignition Temperature



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
Effects of Stoichiometry



Minimum Ignition Energies

FLAMMABLE	MIN. IGNITION ENERGY mJ
CS_2	0.009
H_2	0.011
$C_2°$	0.017
$C_2^=$	0.07
CH_3OH	0.14
n- $C_6°$	0.22
n-$C_7°$	0.24
IPA	0.65
ACETONE	1.15
i-$C_8°$	1.35
"FINE" SULPHUR DUST	≈1.0
"NORMAL" DUSTS	>10.

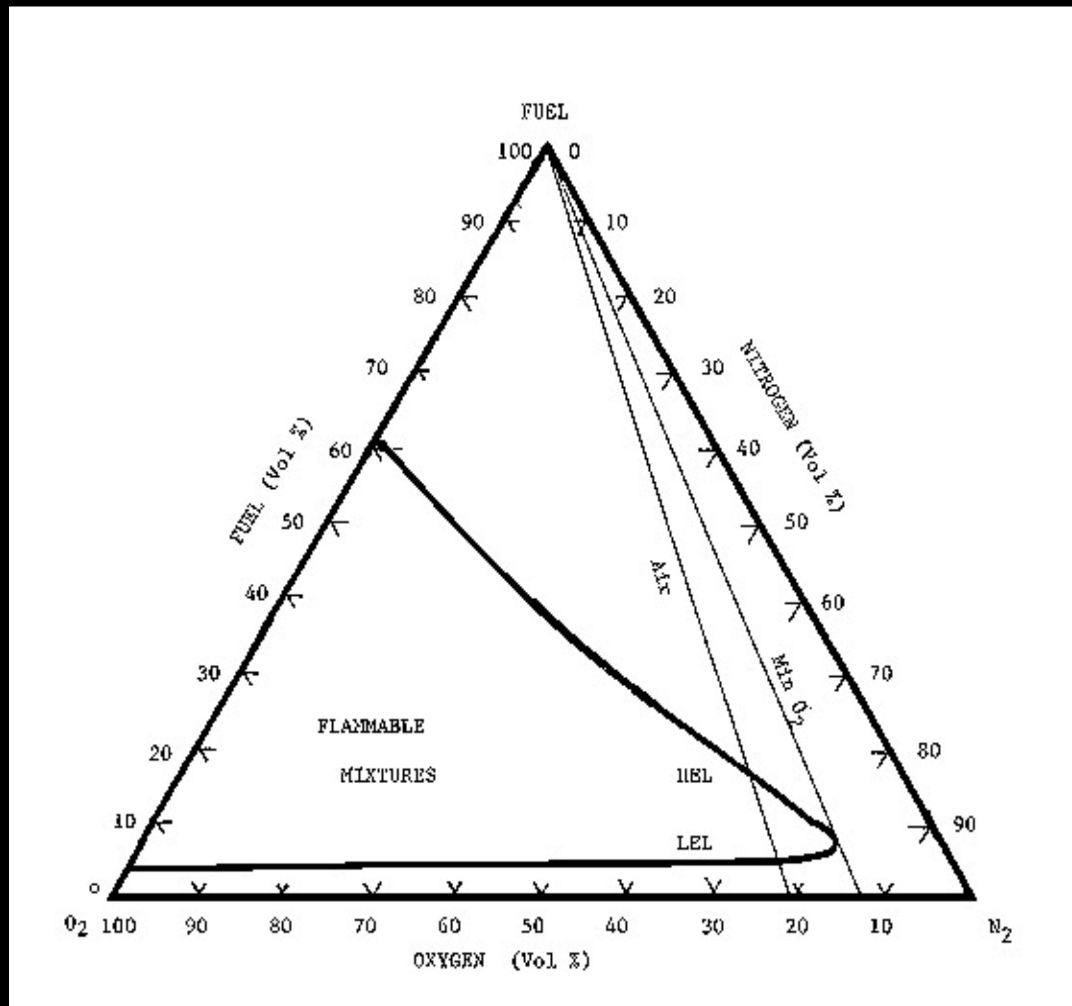
Video
Bureau of Mines
Flames & Explosions

COMMON IGNITION SOURCES	BASIC CONTROLS
Fire or Flames:	
– Furnaces and Boilers	Spacing & Layout
– Flares	Spacing & Layout
– Welding	Work Procedures
– Sparks from Tools	Work Procedures
– Spread from other Areas	Sewer Design, Diking, Weed Control, Housekeeping
– Matches and Lighters	Procedures

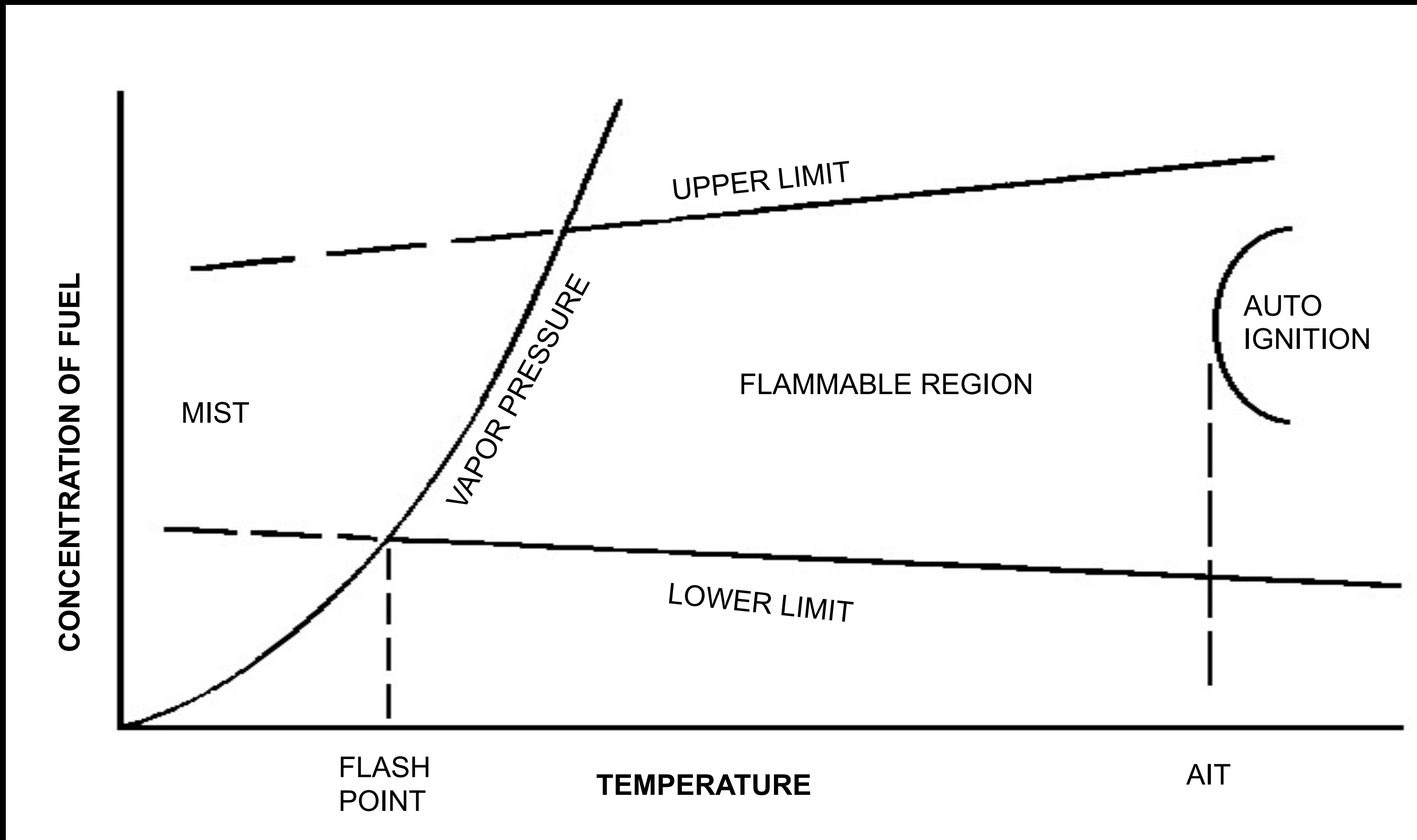
COMMON IGNITION SOURCES	BASIC CONTROLS
Hot Surfaces:	
– Hot Pipes and Equipment (>600 °F)	Spacing
– Automotive Equipment	Procedures

COMMON IGNITION SOURCES	BASIC CONTROLS
Electrical:	
– Sparks from Switches & Motors	Area Classification
– Static	Grounding, Inerting, Relaxation
– Lightning	Geometry, snuffing
– Hand Held Electric Equipment	Procedures

Flammability Diagram for the System Methane-Oxygen-Nitrogen at Atmospheric Pressure and 26°C



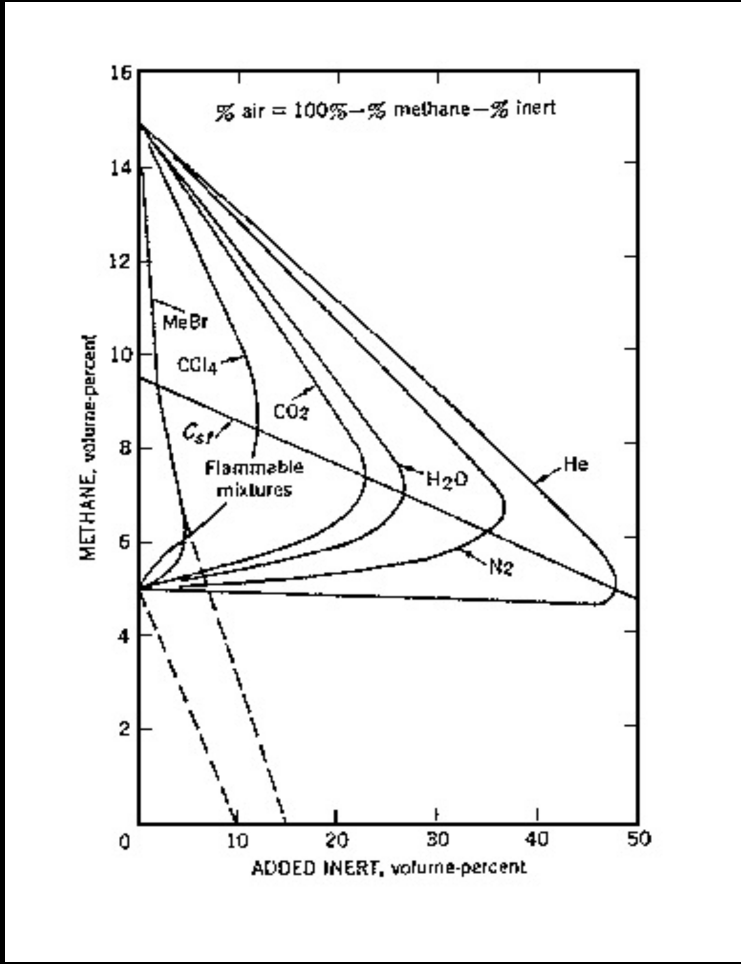
Flammability Relationships



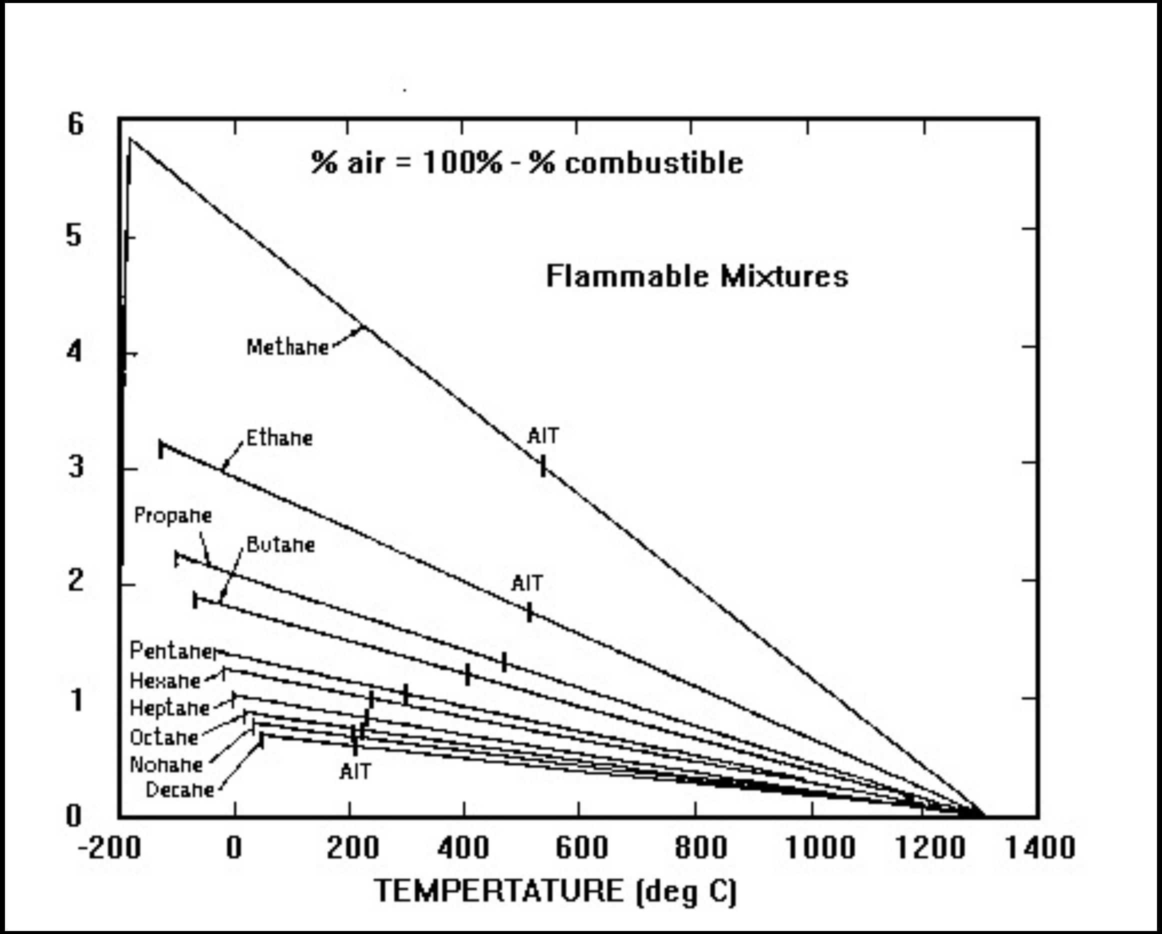
Flammable Limits Change With:

- Inerts
- Temperature
- Pressure

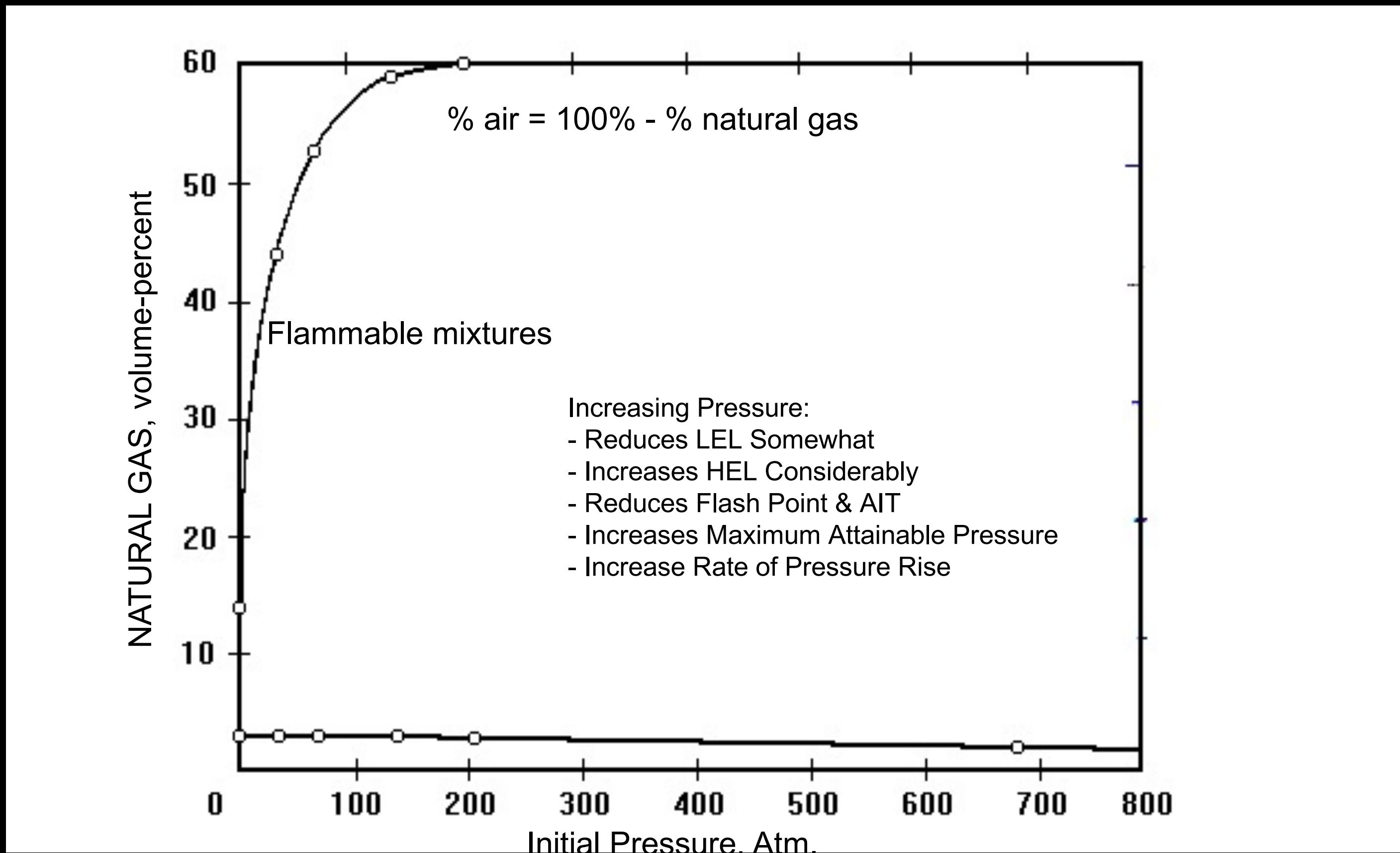
Limits of Flammability of Various Methane-Inert Gas-Air Mixtures at 25°C and Atmospheric Pressure



Effect of Temperature on Lower Limits of Flammability of Various Paraffin Hydrocarbons in Air at Atmospheric Pressure



Effect of Pressure of Flammability of Natural Gas In Air at 28^{o}C



More Definitions

- **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**
  - **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.**
- **Fire**
  - **A slow form of deflagration**

Classification of Explosions

EXPLOSION= Equilibration of high pressure gas with environment so rapid that energy is dissipated via shock wave.

Physical explosions result from dissipation of pre-existing potential energy (without chemical change).

Chemical explosions result from a chemical reaction creating the high pressure gas (may be confined or unconfined).

Uniform reactions occur (more or less) uniformly throughout the mass of reactants.

Propagating reactions start at a point and propagate as a front through the mass of reactants.

Thermal explosions result from exothermic reactions under confinement with inadequate dissipation of heat.

Deflgrations occur when energy transfer across the front is due solely to normal transport phenomena.

Detonations occur when energy transfer across the front is enhanced by reactive shock wave.

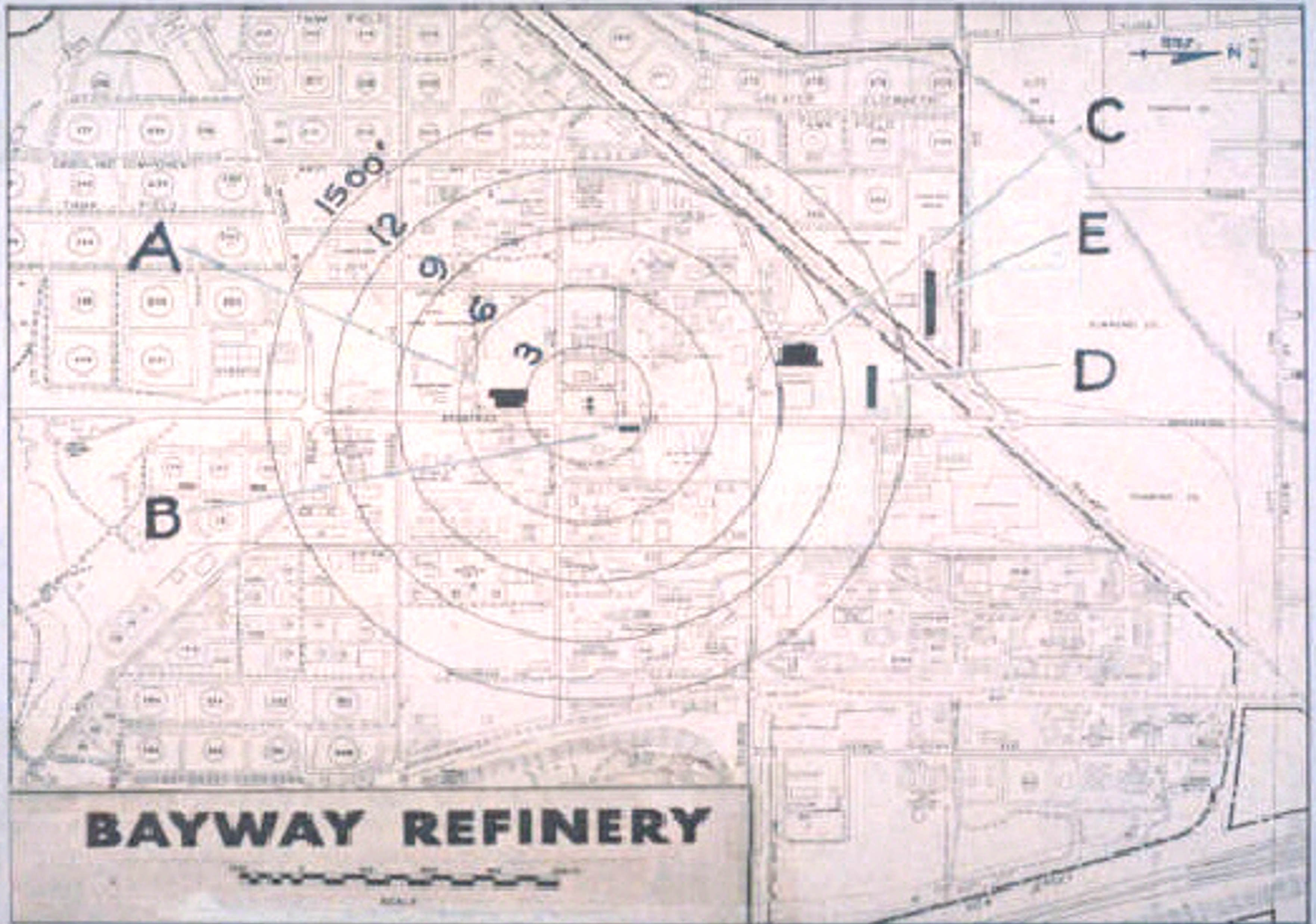
Potential Energy

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

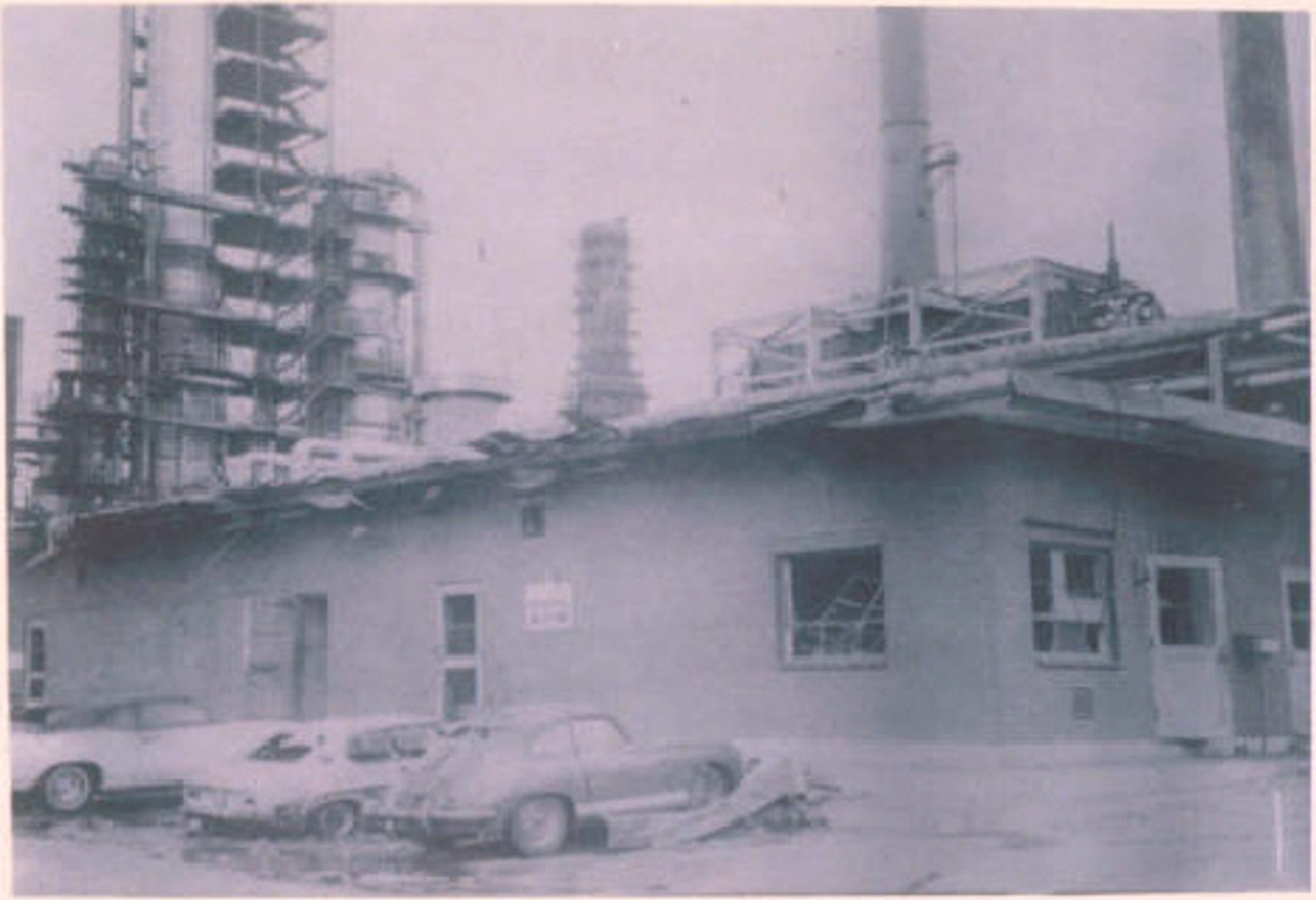
TNT equiv. = 5x 10^5 Calories/lb

Bayway, NJ
H-Oil Incident 1970



N
C
E
D
A
B
1500'
12
9
6
3
BAYWAY REFINERY

BAYWAY CAFETERIA BUILDING - 1970



BAYWAY NO. 6 PIPESTILL "CONTROL HOUSE" - 1970

BAYWAY NO. 6 PIPESTILL "CONTROL HOUSE" - 1970

BAYWAY OPERATIONS BUILDING - 1970

BAYWAY OFFICE BUILDING - 1970

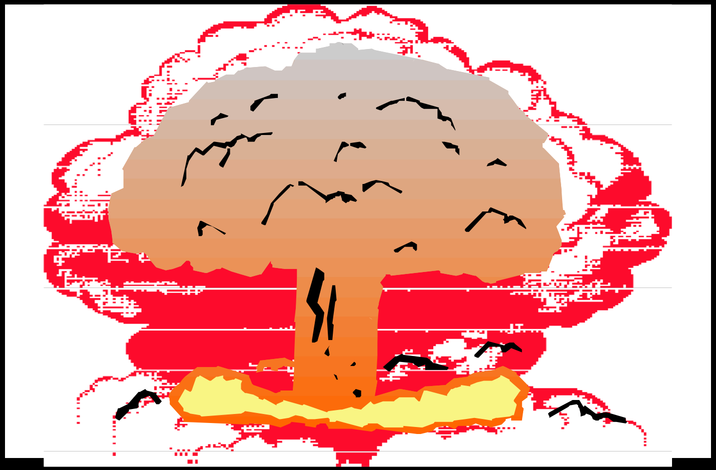
Video
Industrial Safety Series
Explosions and Detonations

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.**

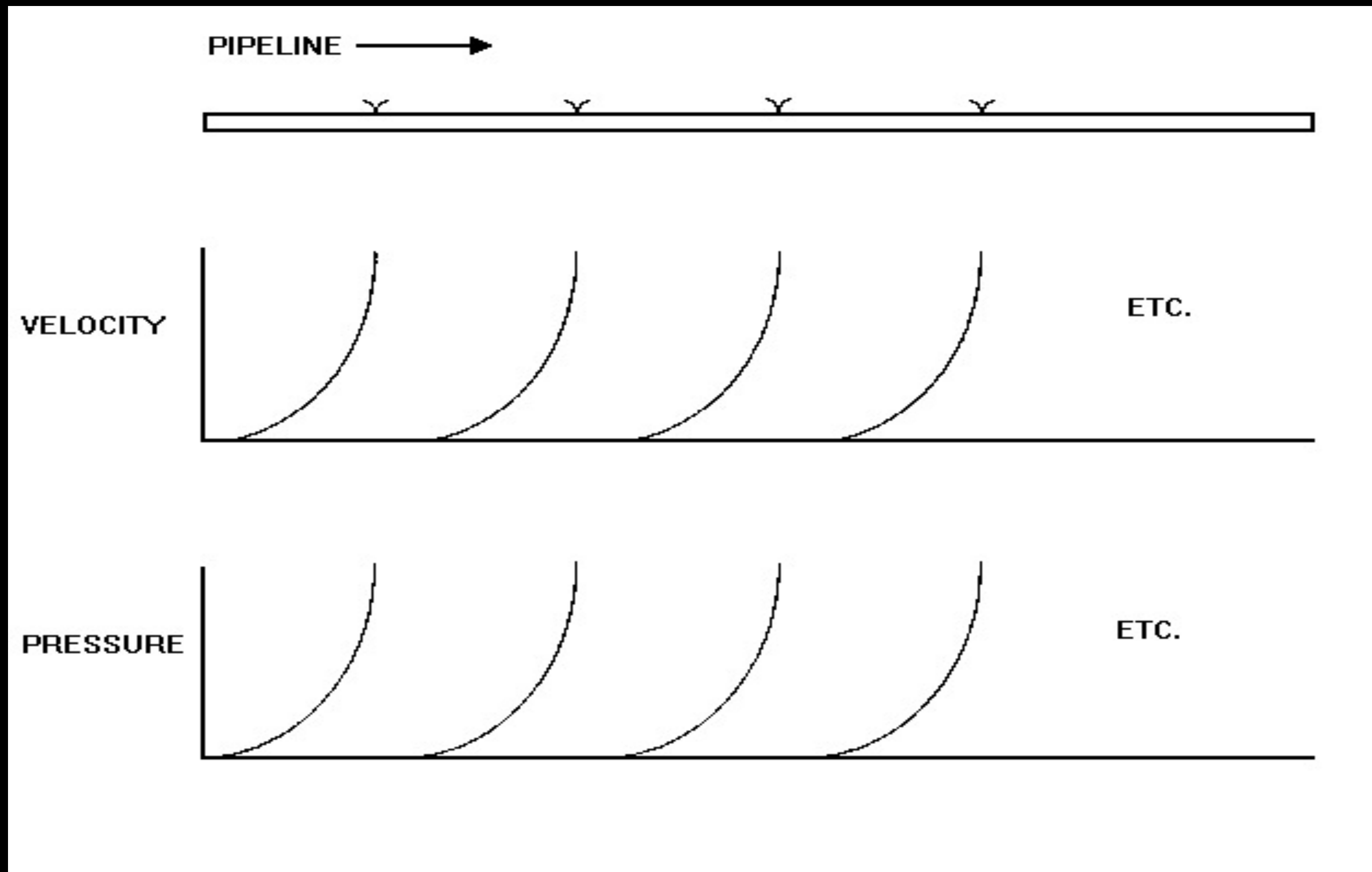
$CH_4 + 2\ O_2$	**= $CO_2 + 2\ H_2O$ + 21000 BTU/lb**
Initial Mols	**= 1 + 2/.21 = 10.52**
Final Mols	**= 1 + 2 + 2(0.79/0.21) = 10.52**
Initial Temp	**= 298°K**
Final Temp	**= 2500°K**
Pressure Ratio	**= 9.7**
Initial Pressure	**= 1 bar (abs)**
Final Pressure	**= 9.7 bar (abs)**

Detonation



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

Pipeline Detonation Mechanics



UVCE

U NCONFINED **V** APOR **C** LOUD **E** XPLOSIONS

- **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 Happens to a Vapor Cloud?

- Increasing unsaturation will increase chance of explosion (flame speeds higher).

  Guggan says “All ethylene clouds explode!”

- Effect of explosion readily modeled by analogy with TNT.

Factors Favoring High Over Pressures

- **Confinement**
  - **Prevents combustion products escaping, giving higher local pressures even with deflagration.**
  - **Creates turbulence, a precursor for detonation.**
  - **Terrain can cause confinement.**
  - **Onsite leaks have a much higher potential for UVCE than offset leaks.**

Factors Favoring High Over Pressures

- **Cloud composition**
  - **Highly unsaturated molecules are bad**
    - **High flammable range**
    - **Low ignition energy**
    - **High flame speeds**

    (Guggan says all ethylene clouds give high overpressures when they burn!)
    - **Most UVCE C_2 - C_6 light gases disperse readily, heavy materials do not form vapor clouds easily**

Factors Favoring High Over Pressures

- Weather
  - Stable atmospheres lead to large clouds.
  - Low wind speed encourages large clouds.

Factors Favoring High Over Pressures

- Vapor Cloud Size impacts on:
  - probability of finding ignition source
  - likelihood of generating any overpressure
  - magnitude of overpressure

Factors Favoring High Over Pressures

- **Source**
  - **flashing liquids seem to give high overpressure**
  - **vapor systems need very large failures to cause UVCE**
  - **slow leaks give time for cloud to disperse naturally without finding an ignition source**
  - **high pressure gives premixing required for large combustion**
  - **equipment failures where leak is not vertically upwards increases likelihood of large cloud**

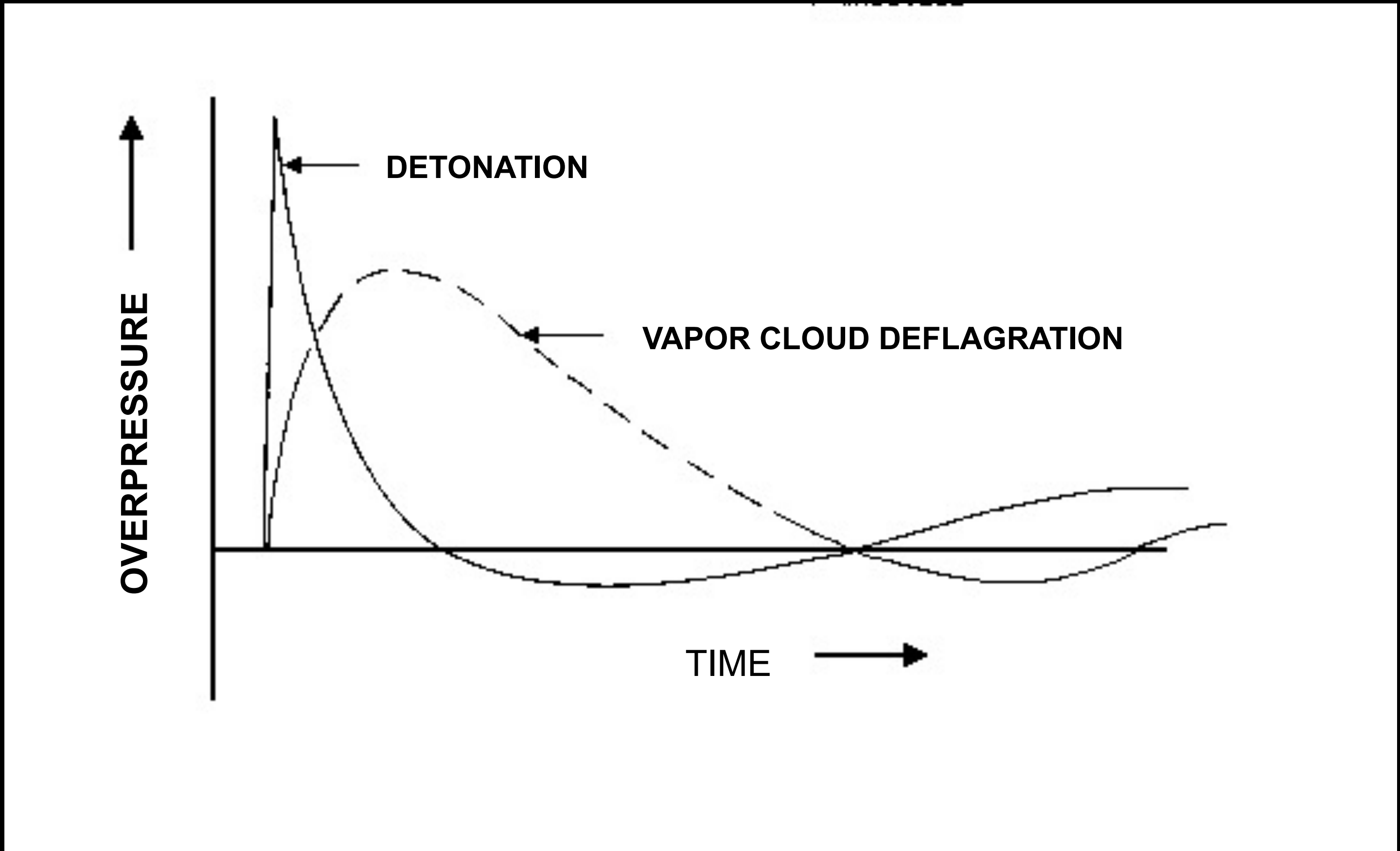
Impact of Vapor Cloud

- **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.**

Impact of Vapor Cloud

- Guggan analysis of vapor clouds plotted efficiency against cloud size and several other theoretical factors and reached no effective conclusions. Efficiencies were between 0.1% and 50%
- Traditional EMRE view was 3% for offsite leak and 10% for onsite leak
- Pressure is function of distance from the blast and $(\text{blast size})^{1/3}$

Pressure vs Time Characteristics



Impact of Vapor Cloud Explosions on People

PEAK OVERPRESSURE, psi	EFFECTS
1	Knock personnel down
5	Rupture eardrums
15	Damage lungs
35	Threshold fatalities
50	50% fatalities
65	99% fatalities

Damage from Vapor Cloud Explosions

Peak Overpressure (psi)	Typical Damage
0.5 - 1	Glass windows break
1 - 2	Common siding types fail - corrugated asbestos, shatters - corrugated steel, panel joints fail - wood siding, blows in
2 - 3	Unreinforced concrete or cinder block walls fail

Damage from Vapor Cloud Explosions

Peak Overpressure (psi)	Typical Damage
3 - 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

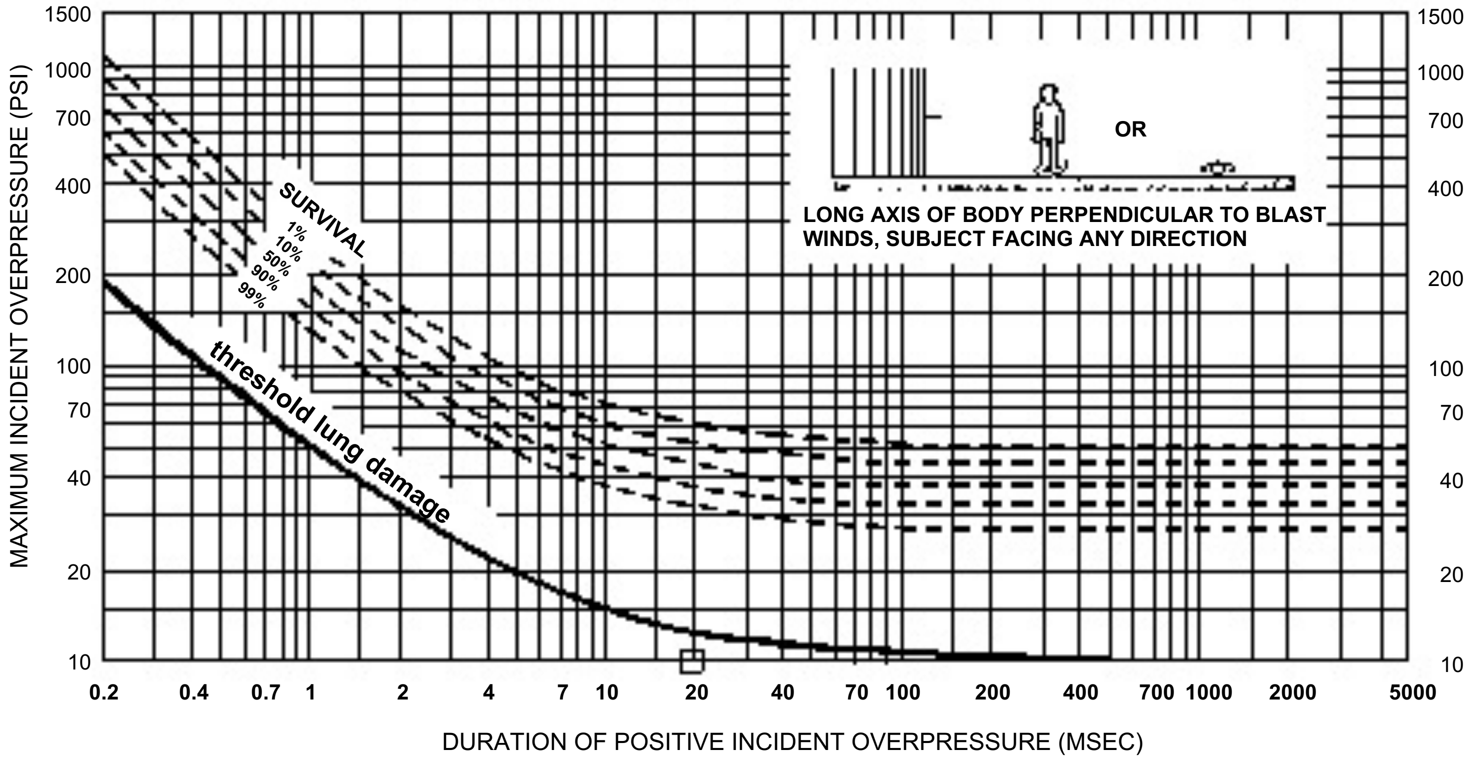
BATON ROUGE TREATING PLANT - 1951

Impact of Vapor Cloud Explosions

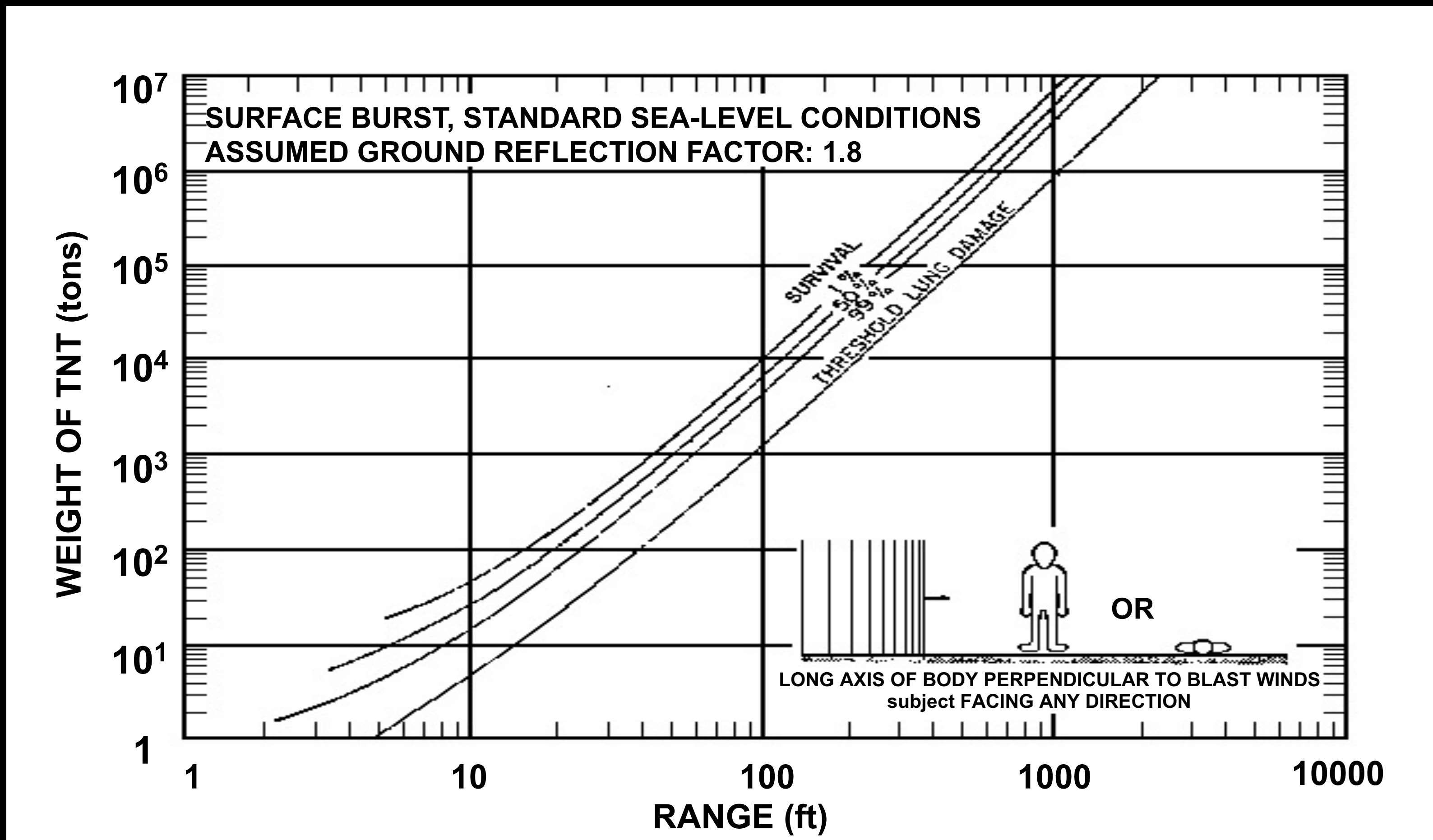
Equivalent Overpressure Wind Velocities

Peak Overpressure, psi	Wind Velocity, mph
2	70
5	160
10	290
20	470
30	670
50	940

Impact of Vapor Cloud Explosions



Impact of Vapor Cloud Explosions



Multi-Energy Models for Blast Effects

- Recent developments in science suggest too many unknowns for simple TNT model.
- Key variables to over pressure effect are:
  - Quantity of combustant in explosion
  - Congestion/confinement for escape of combustion products
  - Number of serial explosions
- This is key to EMR&E basis for calculation of impact.
- Multi-energy is consistent with models and pilot explosions.

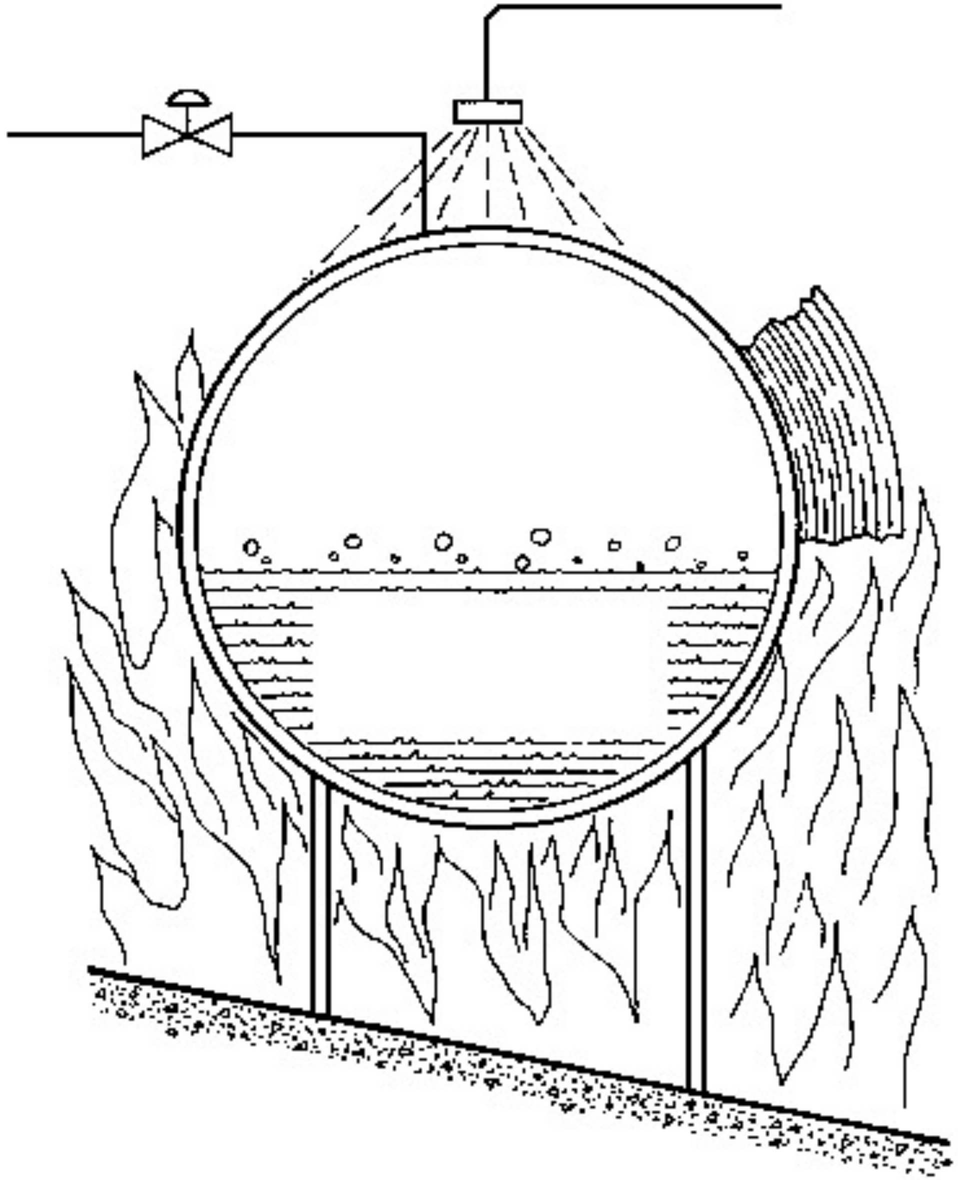
Video

BP LPG

B L E V E

- **B**OILING
- **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.**



Flammability Consequence Comparison

Limits selected:

- BLEVE - 1% lethality
- UVCE - 1 PSI over pressure, 3% efficiency
- Fire - 1 meter deep bund, 3 KW/m^2 flux.

Distance Comparison

(meters)

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

Video

BLEVE

Conclusions

- **We know directionally what factors cause UVCE.**
- **We can estimate roughly what the damage is from a UVCE.**
- **We can take precautions to minimize damage.**
- **We can make emergency plans to ameliorate offsite damage.**

We must take all reasonable measures to prevent significant leaks from our plant and adhere to high levels of design, inspection, maintenance and operation.

Quiz Review

Answers to Quiz on Fundamentals of Fires and Explosions

1Q. What is the flash point of a liquid?

1A. Flash point is the lowest temperature at which a liquid exposed to the air gives off sufficient vapor to form a flammable mixture, or within the apparatus used, that can be ignited by a suitable flame. More precisely, it is the temperature of a liquid at which the partial pressure of its vapor reaches the lower flammable limit when the liquid is heated in air.

Answers to Quiz on Fundamentals of Fires and Explosions

2Q. What is the fundamental difference between flammable and combustible stock?

2A. Flammable stock is capable of being ignited without having to be heated. Combustible material must be heated by some external source in order to be capable of burning.

Answers to Quiz on Fundamentals of Fires and Explosions

3Q. What is the cut off point between a "flammable liquid" and a "combustible liquid" as defined by the NFPA standards?

3A. NFPA defines a flammable liquid as one having a flash point below 100^{o}F (37.8^{o}C). A combustible liquid is one with a flash point of 100^{o}F (37.8^{o}C) or above.

Answers to Quiz on Fundamentals of Fires and Explosions

4Q. What is the difference between the terms "lower explosive limit (LEL)" and "lower flammable limit (LFL)"?

4A. None. The terms are synonymous.

5Q. A material whose flash point is 212^{o}F (100^{o}C) is being stored at 203^{o}F (95^{o}C). Is this treated as a flammable or combustible material under ExxonMobil practices?

5A. Flammable (Stored within 15^{o}F (10^{o}C) of its flash point.

Answers to Quiz on Fundamentals of Fires and Explosions

6Q. There is a correlation of flash point with upper flammable limit (UFL) by means of the vapor pressure curve. (True/False)

6A. False. The correlation is with the lower flammable limit (LFL).

Answers to Quiz on Fundamentals of Fires and Explosions

7Q. A pipe whose surface temperature is 662°F (350°C) represents a likely source of ignition for a flammable vapor whose autoignition temperature (A.I.T.) is 608°F (320°C). (True/False).

7A. False. In order to be a source of ignition in open air, a hot line would have to be at least 220°F (105°C) higher than the AIT. This has been found by experiment. Apparently, natural convection prevents the vapor from remaining in contact with the pipe long enough to cause ignition.

Answers to Quiz on Fundamentals of Fires and Explosions

8Q. Pressure has a significant effect on the flammable range of most hydrocarbons. (True/False).

8A. True. Flammable range widens with increasing pressure.

9Q. Deflagration is another word for detonation. (True/False)

9A. False. Deflagration is characterized by sub-sonic flame velocities, whereas detonation shock waves are supersonic.

Answers to Quiz on Fundamentals of Fires and Explosions

10Q. Typical pressures reached in a confined deflagration are 6 to 8 times the initial pressure. (True/False)

10A. True.

11Q. Stoichiometric mixtures generally require higher ignition energies than other mixtures within the flammable range. (True/False)

11A. False. They require lower energies.

Answers to Quiz on Fundamentals of Fires and Explosions

12Q. The only factors that determine the strength of a vapor cloud explosion are the type of molecule and the amount released. (True/False)

12A. False. Other factors are confinement, weather, and source consideration.

13Q. The TNT model is still the best for modeling explosions. (True/False)

13A. False. Although explosions are still reported as "tons of TNT equivalent", the Multi-Energy Model is more accurate in most cases.