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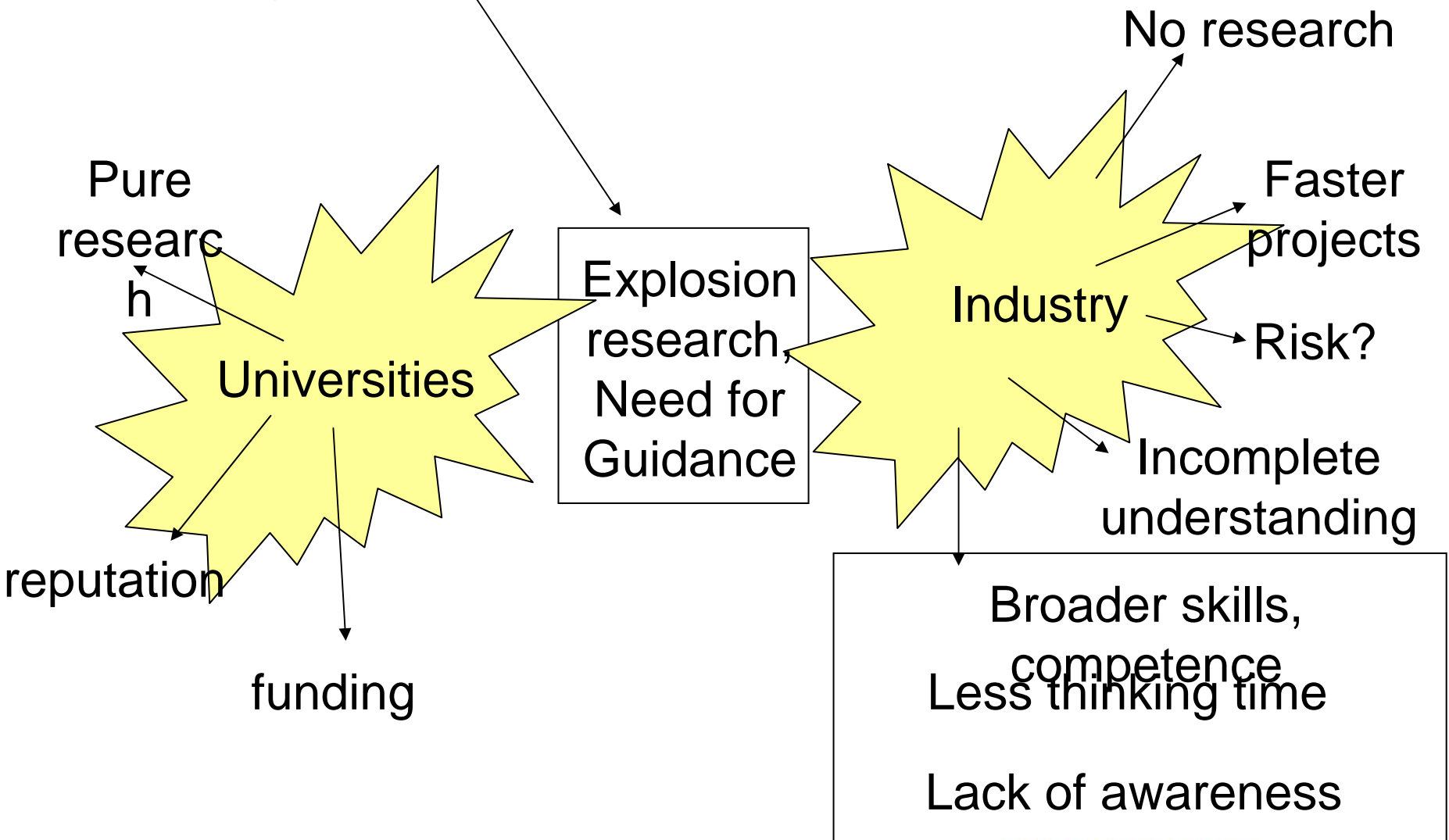# Bridging the gap between explosion research and industrial need.
An Industrial Perspective

UKELG, Sept 10 2008, Loughborough University.

Geoff Chamberlain, Shell GS UK.

The "gap"?

No research

Pure research

Faster projects

Universities

Explosion research, Need for Guidance

Industry

Risk?

Incomplete understanding

reputation

funding

Broader skills, competence

Less thinking time

Lack of awareness

Some explosion topics with "gaps"

- Autoignition.

- Low temperature oxidation, safe operating conditions in oxidation processes.

- Aerosol explosions.

- Sub grid modelling – the PDR assumption.

- DDT in congestion, high energy jet ignition.

- Blast wave/flame front interactions.

- Explosion loading – response of structures.

- Modelling variations in stoichiometry in real clouds.

- Modelling the clouds in the first place!

API RP 581 Risk Based Inspection – what a shocker!

Table A.3.3 – Specific Event Probabilities – Continuous Release Auto Ignition Likely

Final Liquid State – Processed Above AIT

Fluid	Probability of Ignition	Probabilities of Outcome				
		VCE	Fireball	Flash Fire	Jet Fire	Pool
$C_1 - C_2$						
$C_3 - C_4$						
C_5						
$C_6 - C_8$	1				1	
$C_9 - C_{12}$	1				1	
$C_{13} - C_{16}$	1				0.5	0.5
$C_{17} - C_{25}$	1				0.5	0.5
$C_{25} +$						1
H_2						
H_2S						
Styrene	1				1	

Final Gas State – Processed Above AIT

Fluid	Probability of Ignition	Probabilities of Outcome				
		VCE	Fireball	Flash Fire	Jet Fire	Pool Fi
$C_1 - C_2$	0.7				0.7	
$C_3 - C_4$	0.7				0.7	
C_5	0.7				0.7	
$C_6 - C_8$	0.7				0.7	
$C_9 - C_{12}$	0.7				0.7	
$C_{13} - C_{16}$						
$C_{17} - C_{25}$						
$C_{25} +$						
H_2	0.9				0.9	
H_2S	0.9				0.9	
Styrene	1				1	

Notes:
1. Shaded area represent outcomes that are not possible
2. Must be processed at least 27°C (80°F) above AIT

Table A.3.5 – Specific Event Probabilities – Continuous Release Auto Ignition Not Likely

Final Liquid State – Processed Below AIT

Fluid	Probability of Ignition	Probabilities of Outcome				
		VCE	Fireball	Flash Fire	Jet Fire	Pool Fire
$C_1 - C_2$						
$C_3 - C_4$	0.1					
C_5	0.1				0.02	0.08
$C_6 - C_8$	0.1				0.02	0.08
$C_9 - C_{12}$	0.05				0.01	0.04
$C_{13} - C_{16}$	0.05				0.01	0.04
$C_{17} - C_{25}$	0.02				0.005	0.0015
$C_{25} +$					0.005	0.0015
H_2						
H_2S						
DEE	1.0				0.18	0.72
Methanol	0.4				0.08	0.32
PO	0.4				0.08	0.32

Table A.3.5 – Specific Event Probabilities – Continuous Release Auto Ignition Not Likely

Final Gas State – Processed Below AIT

Fluid	Probability of Ignition	Probabilities of Outcome				
		VCE	Fireball	Flash Fire	Jet Fire	Pool Fire
$C_1 - C_2$	0.2	0.04		0.06	0.1	
$C_3 - C_4$	0.1	0.03		0.02	0.05	
C_5	0.1	0.03		0.02	0.05	
$C_6 - C_8$	0.1	0.03		0.02	0.05	
$C_9 - C_{12}$	0.05	0.01		0.02	0.02	
$C_{13} - C_{16}$						
$C_{17} - C_{25}$						
$C_{25} +$						
H_2	0.9	0.4		0.4	0.1	

API RP581 – what can we conclude

- No VCEs for liquids.
- No VCEs for gases above their AIT.
- No Texas City incident!

- TNT equivalence is recommended. TNO-ME and Baker-Strehlow mentioned but dismissed as "too complex"!
- Credit is taken for mitigation of VCEs by blowdown, fire water and foams!

Aerosol explosions

- Mists can explode below flash point.
- Mists should be in the right droplet size range and concentration.
- What is the risk, severity?
- Crank cases, hot oil pumps, boilers.
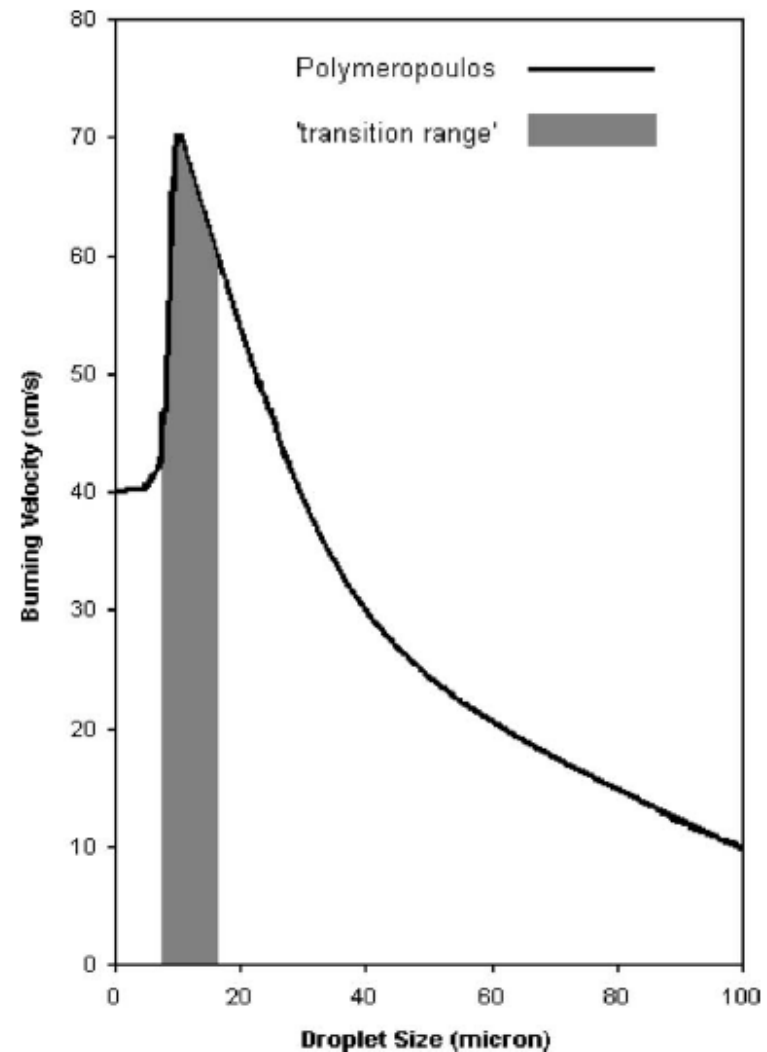- Are regulations (DSEAR, ATEX) adequate/over the top?

Fig. 2. Burning velocity predictions vs. aerosol droplet size [6].

Factory Mutual Engineering and Research (FME&R) statistics for a recent 10 year period shows 54 fires and explosions involving HTFs, resulting in US$ 150 million in losses. A large number of these resulted in fires, but it is the explosions that caused larger monetary losses. One such recent incident directly attributed to an HTF aerosol explosion resulted in a US$ 500,000 loss [2].

Explosion hazard modelling

- The PDR assumption.
- Modelling real clouds – assume all stoichiometric and uniform? Initial turbulence? Equivalent stoichiometric cloud size?
- The DDT in congested but unconfined areas.
- Flame front/blast wave interaction ignored.
- Simple models can over- or under- predict.
- What about the more exotic fuels? EO, PO, CS_2, mixtures.
- There is no alternative but to use complex models for complex geometries. Need for fast, accurate screening tools.

Modelling Congested Vapour Cloud Explosions

CFD, e.g. EXSIM

NS Equations with Porosity/Distributed Resistance (PDR)

Parameterisation of interaction of flow and flame with sub-grid obstacles is crucial

The resolution problem

- The CAD representation of an offshore platform may contain 100,000 objects
- Pipes down to dimensions of 50mm or less can have a significant effect on the flame surface area, hence the rate of combustion, hence explosion development
- Using a million computational cells, we can typically use a cell size of about 0.5 m
- Fully-resolved computations would require cells 100 times smaller (linear). So would perhaps need computers with a million times greater capacity
- Hence the use of sub-grid modelling – "PDR"

Porosity/distributed resistance

- **Area porosities** in the mass and diffusion fluxes

- **Volume porosities** in appropriate source and transient terms

- Sub-grid **obstacle resistance** source term in momentum equations

- Sub-grid obstacle **turbulence source** term in k- ε equations

- Sub-grid **flame area source** term enhances combustion (*in addition to* effect of turbulence increase)

Sub-grid terms in , e.g. continuity and momentum equations

$$\frac{\partial}{\partial t}\left[\beta_v \rho\right] + \frac{\partial}{\partial x_i}\left[\beta_i \rho u_i\right] = 0$$

Resistance due to sub-grid obstacles

Volume porosity

Area porosity

$$\frac{\partial}{\partial t}\left[\beta_v \rho u_i\right] + \frac{\partial}{\partial x_j}\left[\beta_j \rho u_j u_i\right] + \beta_v \frac{\partial p}{\partial x_i} - \beta_v \rho g_i = \frac{\partial}{\partial x_j}\left[\beta_j \sigma_{ij}\right] + R_i$$
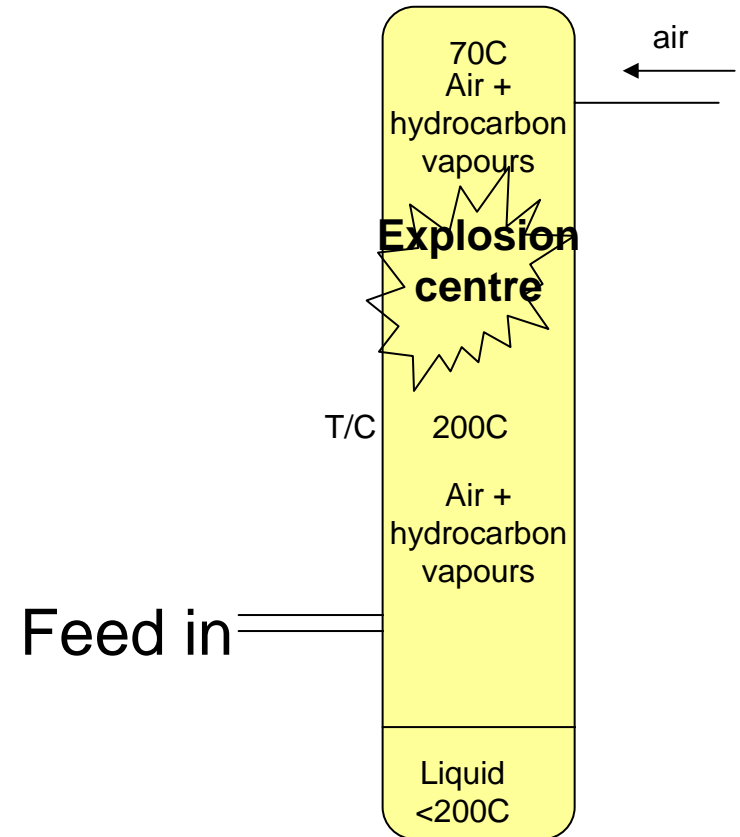
A Refinery Incident

- Explosion in a solvent vacuum distillation column.

- 2 pumps at bottom failed. Feed (kerosene) stopped. Liquid drained to a downstream vessel.

- Air entered column via atmospheric vent (vac pump not strong enough and non-return valve passing).

- 15 hours remaining liquid feed at 200C at bottom. Pumps repaired. Then 2 hours with heat to >200C. 50-100C at top of column.

- Add new feed, "BOOM".

641PRC1
0 barg
Safe location
- 0,7 barg
C4101
E4106 Airfans
V4101 Topaccumulator
MOV
NRV
641PRCV001
641PRCV002
P4106 vacuumpump
V4104

Normal gasflow

Standardsituation

Feed in C4101
Heatoil in C4101
supply of inertgas
P4106 in service
641PRC1 controlling pressure via 641PRCV001/2

641PRC1
0 barg
Safe location
- 0,7 barg
C4101
Airfans
V4101 Top accumulator
MOV
NRV
641PRCV001
641PRCV002
P4106 in service
V4104

It is an incorrect assumption that as long as the vacuum pump is lined-up and running, there will always be a positive displacement from the discharge of the pump to the atmospheric vent. A positive displacement will only occur if there is a constant supply of inert gases from the column - which is only possible when there is a continuous input of feed and heat.

When air entered the unit, the feed and to the column and the hot oil to the reboilers had been stopped; the vacuum pump was running 'idle'. When the pump's recycle valves opened, the pump's capacity was not large enough to cope with the volume of air entering the vent (as a result of the pressure differential between the column and the atmosphere). Consequently, the pump simply circulated the air over the two recycle valves. the pressure differential between the column and the atmosphere allowed air to enter the column despite the fact that the vacuum pump was still running.

Air-ingress route
Gascirculation

Situation at air-ingress

Feed out
Heatoil out
No inertgas
P4106 in service
641PRCV001 / 2 open
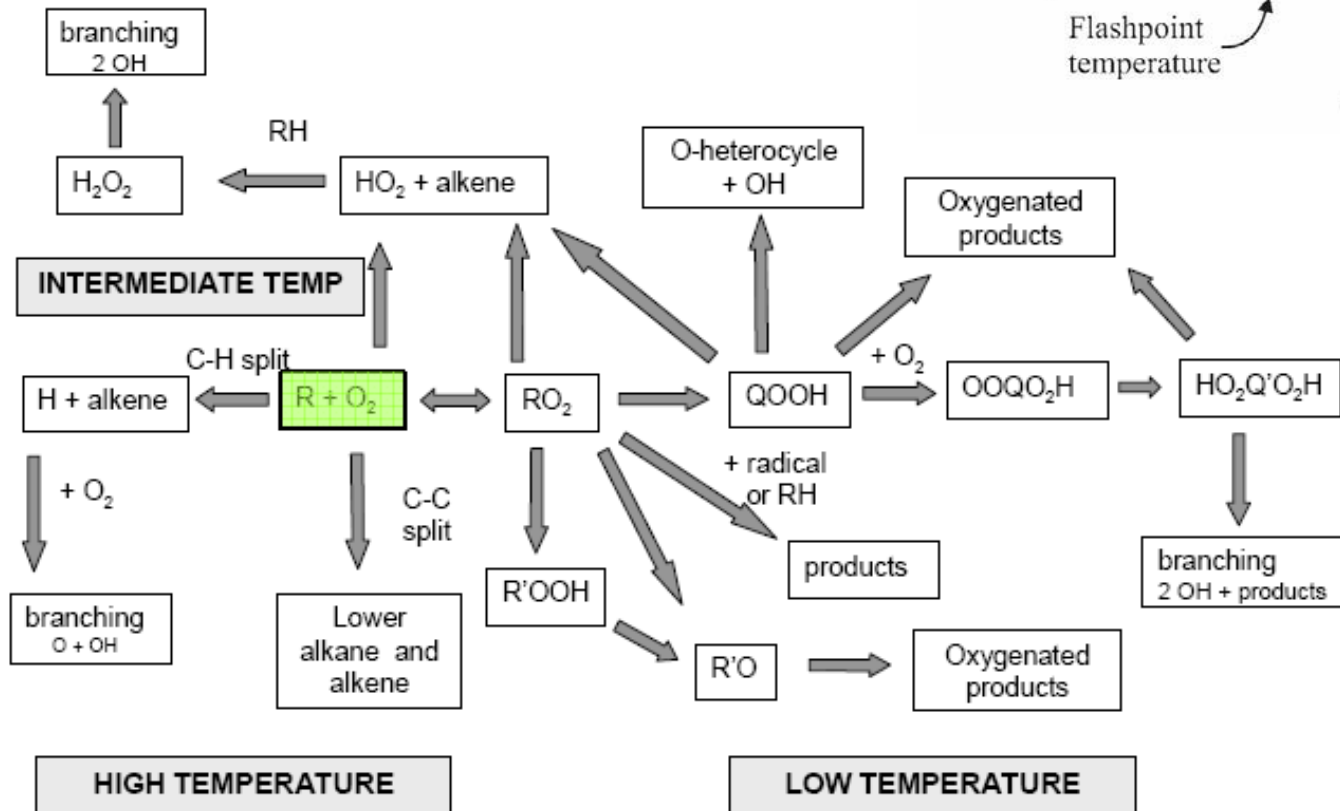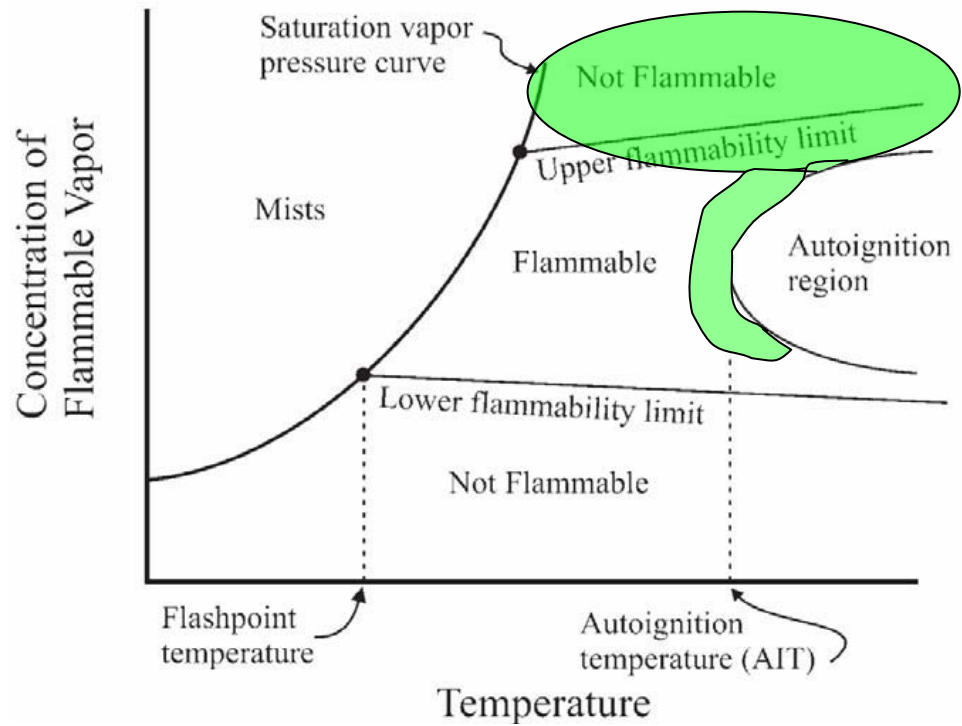
A Refinery Incident, cont.

- Kerosene below AIT but undergoes pre-ignition reactions. Slow oxidation starting at about 140C.

- Cold feed causes P drop, and movement of O_2 rich mixture down the column + mixing into higher T region.

Feed in

70C
Air + hydrocarbon vapours

air

Explosion centre

T/C 200C

Air + hydrocarbon vapours

Liquid <200C

A Refinery Incident, summary

- Modifications to the vac system led to situation where air could enter the column.

- Scenario not considered.

- Air ingress followed by pre-ignition reactions, probably led to cool flames followed by explosion.

- Potential for this in other vac systems.

- Many engineers not aware of LTO and assume min AIT.

Flammability diagram showing areas (green) where spontaneous combustion reactions may occur leading to flame propagation or explosion.

Saturation vapor pressure curve

Not Flammable

Upper flammability limit

Mists

Flammable

Autoignition region

Lower flammability limit

Not Flammable

Flashpoint temperature

Autoignition temperature (AIT)

Concentration of Flammable Vapor

Temperature

General reaction paths. All start at green.

branching 2 OH

H_2O_2

RH

HO_2 + alkene

O-heterocycle + OH

Oxygenated products

INTERMEDIATE TEMP

C-H split

H + alkene

$R + O_2$

RO_2

QOOH

$+ O_2$

$OOQO_2H$

$HO_2Q'O_2H$

+ radical or RH

+ O_2

C-C split

branching O + OH

Lower alkane and alkene

R'OOH

products

branching 2 OH + products

R'O

Oxygenated products

HIGH TEMPERATURE

LOW TEMPERATURE

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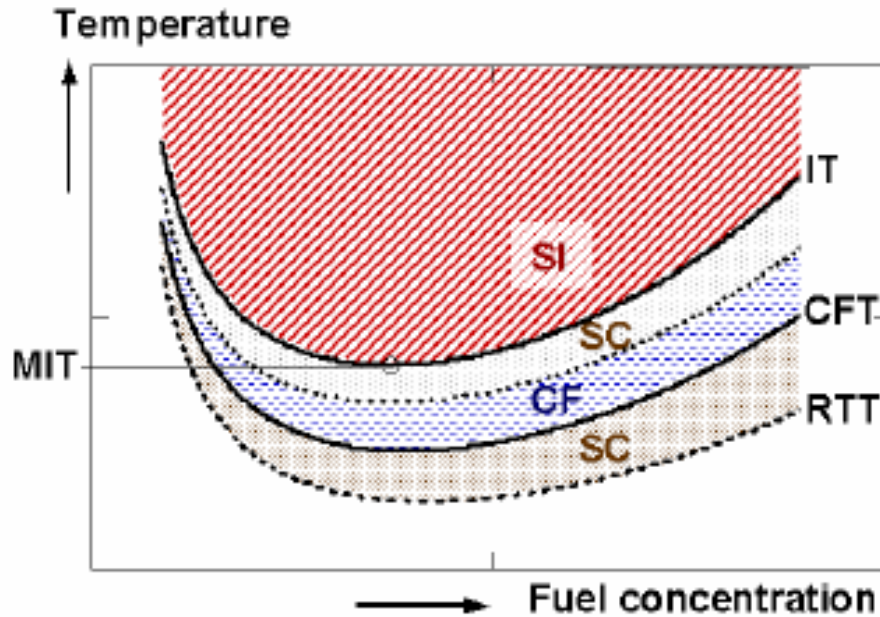# Schematic representation of oxidation phenomena below the AIT

Figure 3. Conceptual presentation of oxidation phenomena below the autoignition regime, SI – Self-Ignition, SC – Slow Combustion, CF – Cool Flame, MIT – Minimum Ignition Temperature (former named as AIT – AutoIgnition Temperature), CFT – cool flame temperature, RTT – Reaction threshold temperature, LFL – Lower Flammability Limit, UFL – Upper Flammability Limit.

!. Comparison of AutoIgnition Temperatures (AIT) with Cool Flame Temperature at atmospheric pressure [3].

	AIT [°C]	CFT [°C]
Methylethylketone	515	265
Methylisobutylketone	460	245
iso-Propylalcohol	400	360
n-Butylacetate	420	225

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In traditional explosion theory, phenomena such as induction time and cool flames may not be covered sufficiently in all applications. Operation outside the (traditional) flammability regime and below AIT may seem safe but slow oxidation may lead to unexpected explosion behaviour.

Flame arrestors

- Min. exptl safe gap (MESG) determination for mixtures at elevated temperatures.

- E.g.

Component	Name	Worst case
		% mole
H2		20.62
CH4		28.53
C2H4		26.31
C2H6		8.04
C3H6	propene	9.72
C4H6	1,3-butadiene	2.36
C4H8	1-butene	2.00
C5H10	1-pentene	1.56
C6H6	benzene	0.86
Sum		100.00

Explosion group	Maximum Experimental Safe Gap [mm]	NEC/ NFPA	Reference Substances
I	$1{,}14 = MESG$		Methane
IIA	$0{,}9 < MESG$	D	Propane
IIB	$0{,}5 \leq MESG \leq 0{,}9$	C	Ethene / Hydrogen
subcategorized as			
IIB1	$0{,}85 \leq MESG \leq 0{,}9$	C	Ethene
IIB2	$0{,}75 \leq MESG < 0{,}85$	C	Ethene
→ IIB3	$0{,}65 \leq MESG < 0{,}75$	C	Ethene
IIC	$MESG < 0{,}5$	B	Hydrogen

Probability of ignition inside process vessels

- Scenario, EO vapour concn exceeds threshold of flammability.

- Vessel contains stirrer and various sensors.

- Operating pressure is around 3-4 barg. However, the vessel MAWP is only about 5 barg, so if vapor-phase decomposition of EO begins, it would most likely exceed the vessel pressure rating.

- Need for information on MIE to answer this question.