PROCESS SAFETY ENGINEERING (0905477)

11- FIRES AND COMBUSTION: GASEOUS FUELS

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The superior man, when resting in safety, does not forget that danger may come…. When all is orderly, he does not forget that disorder may come. Confucius (551 BC – 479 BC)

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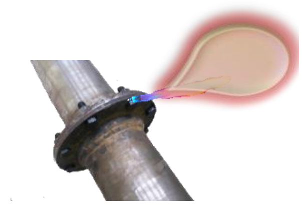
Outline

- Gaseous Fuels
  - Flammable (Explosive) Range
  - Implications for Process Plants
- Flammability Limits of Mixtures
- Flammability Limit Dependence on Temperature
- Flammability Limit Dependence on Pressure
- Estimating Flammability Limits
- Flammability Relationships
- Estimating LOC

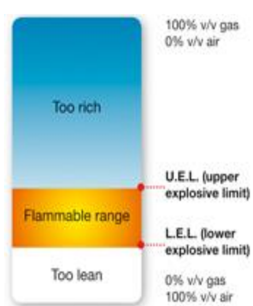
Gaseous Fuels

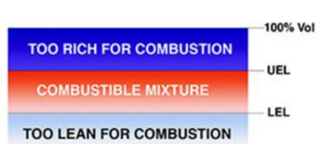
- Needs to mix with air
  - A **slow leak** will diffuse into air.
  - A **fast leak** will mix turbulently.
  - **Premixed** air and fuel can explode.
- Only a certain range of compositions can burn.
- Spreading gas clouds may have flammable regions

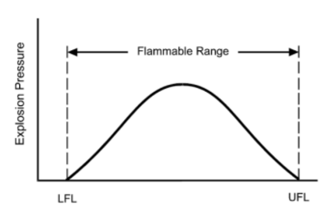


Flammable (Explosive) Range

- There is only a limited band of gas/air concentration which will produce a combustible mixture.
- This band is specific for each gas and vapour, or mixture,
  - Lower Explosive Limit (LEL), or Lower Flammable Limit (LFL) and
  - Upper Explosive Limit (UEL), or Upper Flammable Limit (UFL).
  - **Explosive Range = UEL - LEL**

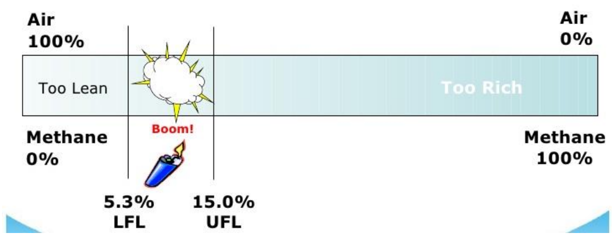






LEL and UEL (LFL and UFL)

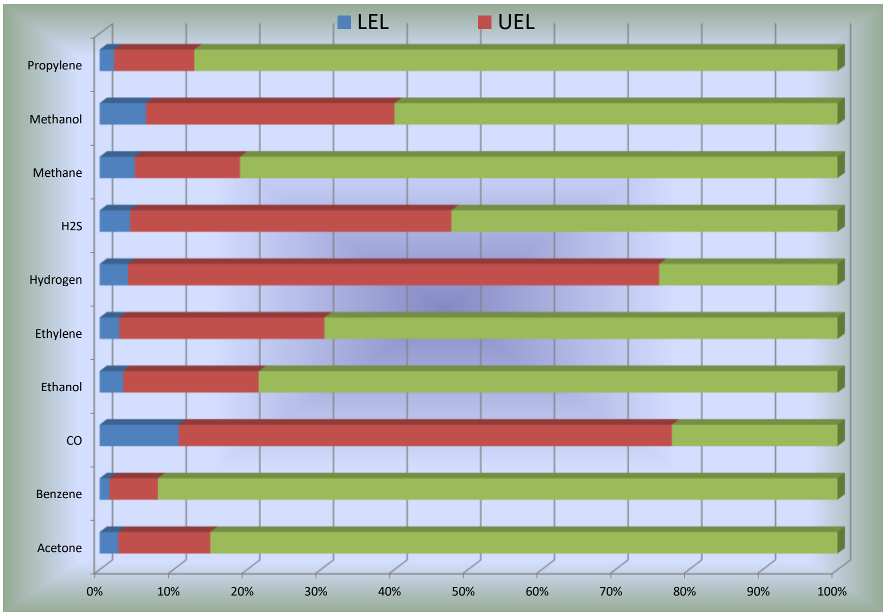
- At concentration levels below the LEL, there is insufficient gas to produce an explosion (i.e. the mixture is too '**lean**')
- Above the UEL, the mixture has insufficient Oxygen (i.e. the mixture is too '**rich**').
- The flammable range therefore falls between the limits of the LEL and UEL for each individual gas or mixture of gases.
- Outside these limits, the mixture is not capable of combustion.
- Usually, data is given for gases and vapors at normal conditions of pressure and temperature. An increase in pressure, temperature or oxygen content will generally broaden the flammability range.



Fuel gas	LEL (%)	UEL (%)	Fuel gas	LEL (%)	UEL (%)
Acetaldehyde	4	60	Gasoline	1.4	7.6
Acetone	2.6	12.8	Kerosine	0.7	5
Acetylene	2.5	81	Methane	5	15
Ammonia	15	28	Methyl alcohol	6.7	36
Arsine	5.1	78	Methyl chloride	10.7	17.4
Benzene	1.35	6.65	Methyl ethyl ketone	1.8	10
n-Butane	1.86	8.41	Naphthalene	0.9	5.9
Iso-butane	1.8	8.44	*n*-Heptane	1	6
Iso-butene	1.8	9	*n*-Hexane	1.25	7
Butylene	1.98	9.65	*n*-Pentene	1.65	7.7
Carbon disulfide	1.3	50	Neopentane	1.38	7.22
Carbon monoxide	12	75	Neohexane	1.19	7.58
Cyclohexane	1.3	8	*n*-Octane	0.95	3.2
Cyclopropane	2.4	10.4	Iso-octane	0.79	5.94
Diethyl esther	1.9	36	*n*-Pentane	1.4	7.8
Ethane	3	12.4	Iso-pentane	1.32	9.16
Ethylene	2.75	28.6	Propane	2.1	10.1
Ethyl alcohol	3.3	19	Propylene	2	11.1
Ethyl chloride	3.8	15.4	Silane	1.5	98
Fuel oil no. 1	0.7	5	Styrene	1.1	6.1
Hydrogen	4	75	Toluene	1.27	6.75
Isobutane	1.8	9.6	Triptane	1.08	6.69
Isopropyl alcohol	2	12	*p*-Xylene	1	6

Note: The limits indicated are for gas and air at 20°C and atmospheric pressure
Source: www.mathesontrigas.com/pdfs/products/Lower-(LEL)-&Upper-(UEL)-Explosive-Limits-.pdf

EXPOSIVE LIMITS OF COMBUSTIBLE GASES WHEN MIXED WITH AIR



Implications for Process Plants

- There would normally be no gases leaking into the surrounding area or, at worst, only a low background level of gas present.
- Detection and early warning system will only be required to detect levels from 0% of gas up to the lower explosive limit (LEL).
- By the time this concentration is reached, shut-down procedures or site clearance should have been put into operation. In fact this will typically take place at a concentration of less than 50% of the LEL value, so that an adequate safety margin is provided.
- In confined, enclosed or unventilated areas, a concentration in excess of the UEL can sometimes occur. At times of inspection, therefore, special care needs to be taken when operating hatches or doors, since the ingress of air from outside can dilute the gases to a hazardous, combustible mixture.
- This is particularly to be taken into consideration with hot work permits in confined space e.g., welding operations.

Flammability Limits of Mixtures

- Le Chatelier Rule (1891)

$$\mathrm{LFL}_{\mathrm{mix}} = \frac{1}{\sum_{i=1}^{n} \frac{y_i}{\mathrm{LFL}_i}} \qquad \mathrm{UFL}_{\mathrm{mix}} = \frac{1}{\sum_{i=1}^{n} \frac{y_i}{\mathrm{UFL}_i}}$$

- The number of combustible species is *n*.
- The mole fraction of component *i* on a combustible basis is y_i.

Assumptions:

1) Product heat capacities constant.
2) No. of moles of gas constant.
3) Combustion kinetics of pure species unchanged.
4) Adiabatic temperature rise is the same for all species.

Example 6-2

What are the LFL and UFL of a gas mixture composed of 0.8% hexane, 2.0% methane, and 0.5% ethylene by volume?

Solution

The mole fractions on a fuel-only basis are calculated in the following table. The LFL and UFL data are obtained from appendix B.

	Volume %	Mole fraction on combustible basis	LFL_i (vol. %)	UFL_i (vol. %)
Hexane	0.8	0.24	1.2	7.5
Methane	2.0	0.61	5.3	15
Ethylene	0.5	0.15	3.1	32.0
Total combustibles	3.3			
Air	96.7			

Equation 6-2 is used to determine the LFL of the mixture:

$$\mathrm{LFL}_{\mathrm{mix}} = \frac{1}{\sum_{i=1}^{n} \frac{y_i}{\mathrm{LFL}_i}} = \frac{1}{\frac{0.24}{1.2} + \frac{0.61}{5.3} + \frac{0.15}{3.1}}$$

$= 1/0.363 = 2.75\%$ by volume total combustibles.

Equation 6-3 is used to determine the UFL of the mixture:

$$\mathrm{UFL}_{\mathrm{mix}} = \frac{1}{\sum_{i=1}^{n} \frac{y_i}{\mathrm{UFL}_i}} = \frac{1}{\frac{0.24}{7.5} + \frac{0.61}{15} + \frac{0.15}{32.0}}$$

$= 12.9\%$ by volume total combustibles.

Because the mixture contains 3.3% total combustibles, it is flammable.

Flammability Limit Dependence on Temperature

- As temperature increases:
  - UFL increases.
  - LFL decreases.
  - Flammability range increases.

$$LFL_T = LFL_{25} - \frac{0.75}{\Delta H_c}(T-25) = LFL_{25} - \frac{100 C_P}{\Delta H_c}(T-25)$$

$$UFL_T = UFL_{25} + \frac{0.75}{\Delta H_c}(T-25)$$

$T: ^{o}C$

Approx. for many hydrocarbons

ΔH_c : kcal/mole, heat of combustion

Flammability Limit Dependence on Pressure

- As pressure increases:
  - UFL increases.
  - LFL mostly unaffected.
  - Broadening the flammability range

$$UFL_P = UFL + 20.6 * (\log P + 1)$$

P is pressure in mega-Pascals, absolute

No theoretical basis for this yet!

Example 6-3

If the UFL for a substance is 11.0% by volume at 0.0 MPa gauge, what is the UFL at 6.2 MPa gauge?

Solution

The absolute pressure is $P = 6.2 + 0.101 = 6.301$ MPa. The UFL is determined using Equation 6-6:

$$\begin{aligned} UFL_P &= UFL + 20.6(\log P + 1) \\ &= 11.0 + 20.6(\log 6.301 + 1) \\ &= 48 \text{ vol. \% fuel in air.} \end{aligned}$$

In Class Problem

What is the UFL of a gas mixture composed of 1% methane, 2% ethane and 3% propane by volume at 50°C and 2 atmospheres:

Data:

Component	MW	Heat of Combustion (kcal/mol)
Methane	16.04	212.79
Ethane	30.07	372.81
Propane	44.09	526.74

Solution Procedure:

1. **Correct for temperature**
2. **Correct for pressure (only for UFL)**
3. **Find for mixture.**

Correction for Temperature : UFL from Table 6-1

$$\text{Eq. 6-4} \rightarrow \; UFL_T = UFL_{25}\left(1 + 0.75(T-25)/\Delta H_c\right)$$

$$\text{Methane } UFL_{50} = 15\left(1+0.75(25)/212.79\right) = 16.32$$

$$\text{Ethane } UFL_{50} = 12.5\left(1+0.75(25)/372.81\right) = 13.13$$

$$\text{Propane } UFL_{50} = 9.5\left(1+0.75(25)/526.74\right) = 9.84$$

Correction for Pressure (UFL only)

$$\text{Eq. 6-5} \rightarrow UFL_P = UFL + 20.6(\log_{10} P + 1)$$

$$P = (2atm)\left(\frac{101kPa}{atm}\right)\left(\frac{MPa}{1000kPa}\right) = 0.202\,MPa$$

$$UFL_{2atm} = UFL_{1atm} + 20.6(\log_{10}(0.202\,MPa) + 1)$$

$$UFL_{2atm} = UFL_{1atm} + 6.290$$

$$UFL_{Methane} = 22.61$$

$$UFL_{Ethane} = 19.40$$

$$UFL_{\text{Propane}} = 16.13$$

Mixture calculation

Mixture	Vol%	Mol frac
Methane	1	0.1667
Ethane	2	0.3333
Propane	3	0.5000
Combustibles	6	

Equation 6-2 for mixtures

$$\mathrm{UFL}_{\mathrm{mix}} = \frac{1}{\sum_{i=1}^{n} \frac{y_i}{\mathrm{UFL}_i}} = \frac{1}{\frac{0.1667}{22.61} + \frac{0.3333}{19.40} + \frac{0.5}{16.13}} = 18.0\,\mathrm{vol\%}$$

Since total combustibles in air 1+2+3=6 < 18 then the system is in the combustible range (below UFL)

Estimating Flammability Limits

- For many hydrocarbon vapors the LFL and the UFL are a function of the stoichiometric concentration (C_{st}) of fuel.

$$LFL = 0.55 \cdot C_{st}$$

$$UFL = 3.5 \cdot C_{st}$$

C_{st} **stoichiometric conc. [vol%]**

Very approximate!
Not always conservative!

General combustion reaction:

$$C_mH_xO_y + zO_2 \rightarrow mCO_2 + \frac{x}{2}H_2O$$

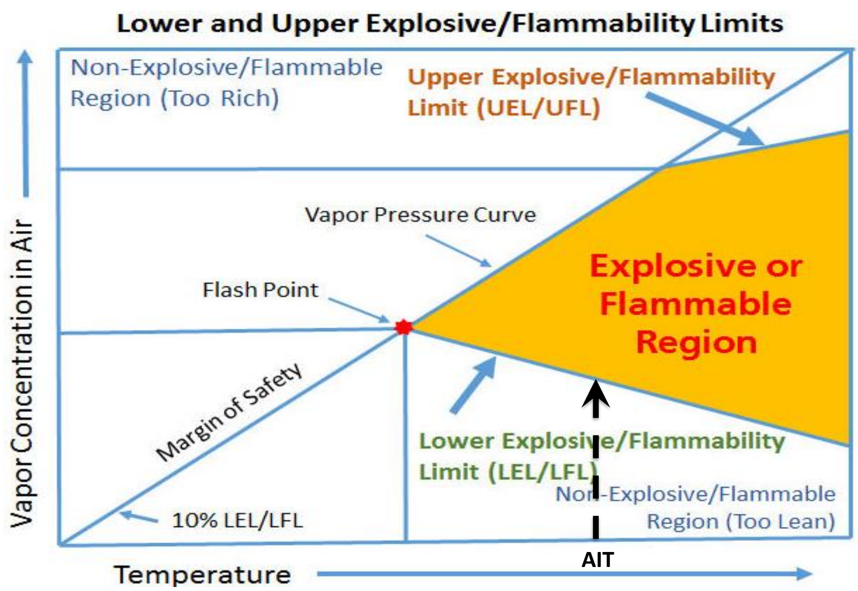
$$z = m + \tfrac{1}{4}x - \tfrac{1}{2}y$$

$$C_{st} = \frac{21\%}{0.21 + z}$$

$$\mathrm{LFL} = \frac{0.55(100)}{4.76m + 1.19x - 2.38y + 1},$$

$$\mathrm{UFL} = \frac{3.50(100)}{4.76m + 1.19x - 2.38y + 1}.$$

Flammability Relationships



Example 6-4

Estimate the LFL and the UFL for hexane, and compare the calculated limits to the actual values determined experimentally.

Solution

The stoichiometry is

$$C_6H_{14} + zO_2 \rightarrow mCO_2 + \frac{x}{2}H_2O,$$

and z, m, x, and y are found by balancing this chemical reaction using the definitions in Equation 6-9:

$m = 6,$
$x = 14,$
$y = 0,$

The LFL and the UFL are determined by using Equations 6-10 and 6-11:

$$\begin{aligned} \text{LFL} &= 0.55(100)/[4.76(6) + 1.19(14) + 1] \\ &= 1.19 \text{ vol. \% versus } 1.2 \text{ vol. \% actual,} \\ \text{UFL} &= 3.5(100)/[4.76(6) + 1.19(14) + 1] \\ &= 7.57 \text{ vol. \% versus } 7.5 \text{ vol. \% actual.} \end{aligned}$$

Estimating LOC

$$\text{LOC} = \left(\frac{\text{moles fuel}}{\text{total moles}}\right)\left(\frac{\text{moles } O_2}{\text{moles fuel}}\right) = \text{LFL}\left(\frac{\text{moles } O_2}{\text{moles fuel}}\right).$$

LOC limiting oxygen conc. [vol% O_2]

(1)Fuel + (z) Oxygen --> Products

$$LOC \cong z \cdot LFL$$

Typically 8 - 10%

Very approximate!

Not always conservative!

Example 6-5

Estimate the LOC for butane (C_4H_{10}).

Solution

The stoichiometry for this reaction is

$$C_4H_{10} + 6.5O_2 \rightarrow 4CO_2 + 5H_2O.$$

The LFL for butane (from appendix B) is 1.9% by volume. From the stoichiometry

$$\text{LOC} = \left(\frac{\text{moles fuel}}{\text{total moles}}\right)\left(\frac{\text{moles } O_2}{\text{moles fuel}}\right) = \text{LFL}\left(\frac{\text{moles } O_2}{\text{moles fuel}}\right).$$

By substitution, we obtain

$$\text{LOC} = \left(1.9\frac{\text{moles fuel}}{\text{total moles}}\right)\left(\frac{6.5 \text{ moles } O_2}{1.0 \text{ moles fuel}}\right)$$

$$= 12.4 \text{ vol. \% } O_2.$$

The combustion of butane is preventable by adding nitrogen, carbon dioxide, or even water vapor until the oxygen concentration is below 12.4%. The addition of water, however, is not recommended because any condition that condenses water would move the oxygen concentration back into the flammable region.

شكرا لحسن ألاستماع

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