Proper determination of the upper flammability limit at elevated conditions (high temperature and high pressure)

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### SOCIETAL NEED – industrial processes
Partial oxidation processes and their conditions in chemical industry

<table>
<thead>
<tr>
<th>Final product</th>
<th>Annual world production (10^6 tonnes/year)</th>
<th>Temp. (°C)</th>
<th>Pressure (bars)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Acetic acid</strong></td>
<td>6.0 (1994)</td>
<td>50 ÷ 200</td>
<td>15 ÷ 80</td>
</tr>
<tr>
<td>From: acetaldehyde, alkanes,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>alkenes, light gasoline, methanol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Acetaldehyde</strong></td>
<td>2.4 (1993)</td>
<td>100 ÷ 460</td>
<td>3 ÷ 20</td>
</tr>
<tr>
<td>From: ethylene, ethanol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Ethylene oxide</strong></td>
<td>11.2 (1995)</td>
<td>200 ÷ 300</td>
<td>10 ÷ 30</td>
</tr>
<tr>
<td>From ethylene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Propylene oxide</strong></td>
<td>4.0 (1993)</td>
<td>90 ÷ 140</td>
<td>15 ÷ 65</td>
</tr>
<tr>
<td>From propylene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Maleic anhydride</strong></td>
<td>0.87 (1995)</td>
<td>350 ÷ 500</td>
<td>2 ÷ 5</td>
</tr>
<tr>
<td>From: benzene, butene, butane</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Phtalic anhydride</strong></td>
<td>2.9 (1995)</td>
<td>150 ÷ 550</td>
<td>1 ÷ 3</td>
</tr>
<tr>
<td>From naphtalene, o-xylene, butane</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
Precise determination of the upper explosion limits enables:

- Safe operation (most desired outside the flammable range)
- Process optimisation (reduction of unnecessary error margin)
- Productivity increase
International standards on flammability limits

At elevated temperature and atmospheric pressure

- ASTM E 681-01; up to 150 °C
  ignition criterion: flame detachment
- DIN 51 649, part 1; up to 200 °C
  ignition criterion: flame detachment
- prEN 1839 (T-tube) and (B-bomb); up to 200 °C
  ignition criterion (T): flame detachment
  ignition criterion (B): \( \frac{P_{\text{exp}}}{P_{\text{init}}} > 5\% \)

At elevated temperature and elevated pressure

- ASTM E918-83 (1999); up to 200 °C and 138 bara
  ignition criterion (B): \( \frac{P_{\text{exp}}}{P_{\text{init}}} > 7\% \)
Cool flames

Cool flames are observed for most hydrocarbons

- Present in fuel rich mixtures, at elevated conditions
- Higher pressure enhances its occurrence
## Comparison between cool flames and hot flames

<table>
<thead>
<tr>
<th></th>
<th>Cool Flames</th>
<th>Normal flames</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flammability range</td>
<td>Wide</td>
<td>Narrow</td>
</tr>
<tr>
<td>Heat liberation</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>$\Delta T$ [deg] (in air)</td>
<td>10-150 (400)</td>
<td>1600-2800</td>
</tr>
<tr>
<td>Temperature coefficient</td>
<td>Negative</td>
<td>Positive</td>
</tr>
<tr>
<td>$P_f/P_0$ (in confined spaces)</td>
<td>Below 2 (low)</td>
<td>6-10 (high)</td>
</tr>
<tr>
<td>Flame velocity [cm/s]</td>
<td>3-5</td>
<td>30-325</td>
</tr>
<tr>
<td>Degree of conversion</td>
<td>Low</td>
<td>Completely</td>
</tr>
<tr>
<td>Products</td>
<td>HCHO, CO</td>
<td>H$_2$O, CO$_2$</td>
</tr>
</tbody>
</table>
Problem Formulation

1. How to distinguish between the UEL and the LCFL at elevated conditions in a closed volume?

2. What kind of flame is propagating at very fuel rich compositions?
$T_{\text{max}} = 300^\circ \text{C}, \ P_{\text{max}} = 275 \text{ bar}$

Flame emission spectroscopy was applied
Experimental programme

n-butane/oxygen mixture
  Tinit = 225 °C, Pinit = 2 bara, varying O₂ concentration
  Tinit = 225 °C, Pinit = 4 bara, varying O₂ concentration

CH₄/C₂H₄/O₂ mixture
  Tinit = 225 °C, Pinit = 16 bara
A typical experimental run

O₂ = 27.06 %, C₄H₁₀ = rest, P_{init} = 4 bara, T_{ini} = 228°C

- P₂
- ign
- T₁
- T₂
- T₃
- T₄
- T₅
- T₆

Pressure [bar abs] vs. time [s]

Temperature [°C]
CCD camera image record

Exposure time = 5 seconds, max gain, slot 1 mm
Flame emission
N-butane/O$_2$ mixture at 4 bara

N-Butane/oxygen flame (XO2 = 27.06%)

Intensity coming from chemically excited HCHO (highest 10) : 385.6 (9) 396.0 (10), 405.3 (5) and 412.9 (8)
CH$_4$/C$_2$H$_4$/O$_2$ mixture at 16 bara  
Methane/ethylene flame, experiment 20 (T16-17)

Up going flame

Returned flame (down going) ONLY

Subtraction of up-going flame from up and down spectra
Propagating flame in the sphere, initiated by a fused wire, forms excited formaldehyde.

At fuel rich concentrations at elevated conditions artificial ignition source (fused wire) initiates propagation of cool flame.

Based on the current international standards one may determine upper cool flame limit instead of the upper flammability limit.
Any questions are welcome
Cool flames appearance

Pressure records in a closed volume:

a – one cool flame,
b – two cool flames,
c – two-stage ignition with intermediate temperature decrease,
d – two-stage ignition without intermediate temperature decrease,
e – one-stage ignition (hot ignition)