COMPARISON OF FLAMMABILITY AND OXIDIZING POWER OF GAS MIXTURES USING THE ISO 10156 WITH MEASURED FLAMMABILITY DATA

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Outline

- Introduction, GHS, ISO 10156
- Test methods of flammability and oxidizing power
- Calculation method of flammability
  - Examples: comparison with experimental values
- Calculation of oxidizing power of gases
  - Examples: comparison with experimental values
- Summary
Introduction

- The Globally Harmonized System of Classification and Labelling of Chemicals (GHS) is a worldwide initiative of the United Nations to promote standard criteria for classifying chemicals.

- From 16 physical hazard classes of GHS are two hazard classes - flammable gases and oxidizing gases - which classifications are based on the international standard ISO 10156. This standard contains test methods and calculation methods for classification on flammability and oxidizing power of gas mixtures.
Determination of flammability

EN 1839-Tube method  ASTM E 681-04
Description of the test vessels

<table>
<thead>
<tr>
<th>EN 1839-Tube</th>
<th>ASTM E 681-04</th>
</tr>
</thead>
<tbody>
<tr>
<td>Open vessel: tube (Ø 80 mm, minimum length 300 mm)</td>
<td>Open vessel: Glass flask, volume = 5 dm³</td>
</tr>
</tbody>
</table>

Both methods can be used to determination of explosion regions of flammable gas/inert gas/air mixtures
Explosion diagram with threshold values

- MOC (LOC)
- MXC (Tc_i)

Measures:
- Measured data + expl. curve
- MOC line
- ICR line
- IAR line
- SCO line

Flammable gas (mol %)
Inert gas (mol %)
Oxygen (mol %)
### Threshold values of flammable mixture

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>LEL</td>
<td>lower explosion limits (mol%)</td>
</tr>
<tr>
<td>UEL</td>
<td>upper explosion limits (mol%)</td>
</tr>
<tr>
<td>MAI</td>
<td>minimum required amount of inert gas in inert gas/oxidizer mixtures (mol%)</td>
</tr>
<tr>
<td>MXC</td>
<td>maximum permissible amount of flammable gas in inert gas-flammable gas mixture in mol% (if inert gas is nitrogen and oxidizing gas air then it is the $Tci$ value)</td>
</tr>
<tr>
<td>MOC</td>
<td>maximum (permissible) oxidizing gas content in mol% (if air then LOC)</td>
</tr>
<tr>
<td>SCO</td>
<td>stoichiometric concentration for the oxidizing reaction (mol%)</td>
</tr>
<tr>
<td>ICR</td>
<td>minimum inert gas-combustible ratio (-)</td>
</tr>
<tr>
<td>IAR</td>
<td>minimum inert gas/oxidizer (air) ratio (-)</td>
</tr>
</tbody>
</table>
By help of this specific $Tci$ values, it is possible to calculate the flammability of gas mixtures consisting of one or more flammable gases and one or more inert gases.

Basis for this relatively simple calculation method is Le Chatelier’s law for flammable gases and the different molar heat capacities of the inert gases, expressed as $K$ value.
Calculation method of flammability

If this condition is NOT fulfilled – the mixture is classified as flammable
### Tci values from ISO 10156 editions in %

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>40.1</td>
<td>----</td>
</tr>
<tr>
<td>Bromomethane</td>
<td>13.9</td>
<td>16.0</td>
</tr>
<tr>
<td>$n$-Butane</td>
<td>3.6</td>
<td>5.7</td>
</tr>
<tr>
<td>1-Butene</td>
<td>3.3</td>
<td>5.5</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>15.2</td>
<td>20.0</td>
</tr>
<tr>
<td>Ethane</td>
<td>4.5</td>
<td>7.6</td>
</tr>
<tr>
<td>Ethylene</td>
<td>4.1</td>
<td>6.0</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>5.5</td>
<td>5.7</td>
</tr>
<tr>
<td><strong>Methane</strong></td>
<td><strong>8.7</strong></td>
<td><strong>14.7</strong></td>
</tr>
<tr>
<td><strong>Propane</strong></td>
<td><strong>3.7</strong></td>
<td><strong>6.0</strong></td>
</tr>
</tbody>
</table>
### Coefficients of equivalency for inert gases relative to $\text{N}_2$ (ISO 10156:2010)

<table>
<thead>
<tr>
<th>Gas</th>
<th>$K_k$ value</th>
<th>Gas</th>
<th>$K_k$ value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{N}_2$</td>
<td>1</td>
<td>$\text{SO}_2$</td>
<td>1.5</td>
</tr>
<tr>
<td>$\text{CO}_2$</td>
<td>1.5</td>
<td>$\text{SF}_6$</td>
<td>4 (1.5)</td>
</tr>
<tr>
<td>$\text{He}$</td>
<td>0.9 (0.5)</td>
<td>$\text{CF}_4$</td>
<td>2 (1.5)</td>
</tr>
<tr>
<td>$\text{Ar}$</td>
<td>0.55 (0.5)</td>
<td>$\text{C}_3\text{F}_8$</td>
<td>1.5</td>
</tr>
<tr>
<td>$\text{Ne}$</td>
<td>0.7 (0.5)</td>
<td>$K_k$ values in ( ) cited from ISO 10156:1996</td>
<td></td>
</tr>
<tr>
<td>$\text{Kr}$</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Xe}$</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Determination of $T_{ci}$ from x-y diagram

Explosion range, methane/nitrogen/air measurement by Schulz BAM Lab. II.22 (1996)

**ISO 10156 (1996)** $T_{ci}$ value for methane was 14.3 mol in %
What does a lower $Tci$ value mean?

- Will the classification of a mixture of flammable gases be changed or not, if we use the new edition of ISO 10156:2010?

- See an example of a mixture with methane and propane
Example: two flammable gases with additional nitrogen in air

Explosion diagram of the mixture methane/propane (20:80 mol%) in air with additional nitrogen as inert gas.

Source: Fuman Zhao

MXC=5.6 mol%
Consider a gas mixture containing:
Flammable gas mixture: Methane/propane (20:80 mol%) altogether 5.6 mol%,
Nitrogen = 94.4 mol%

\[
\sum_{i=1}^{n} A_i \left( \frac{100}{T_{ci}} - 1 \right) \leq \sum_{k=1}^{p} B_k K_k
\]

\[
5.6 \times 0.2 \times (100/8.7-1) + 5.6 \times 0.8 \times (100/3.7-1) = 128.35 \quad > \quad 94.4 \times 1
\]

\(T_{ci}\) methane 8.7 mol%, \(T_{ci}\) propane = 3.7 mol%. \(K_k\) nitrogen = 1.

\(B_k\) nitrogen = = 100-5.6 = 94.4 mol%

\(A\) methane= 0.2 * 5.6 = 1.12; \(A\) propane= 0.8*5.6 = 4.48

\[
128.35 \leq 94.4
\]

the condition is not fulfilled, consequently the mixture is classified as **FLAMMABLE**.
Example with $T_{ci}$ values from ISO 10156:1996

Consider a gas mixture containing:

- Flammable gas mixture: Methane/propane (20:80 mol%) altogether 5.6 mol%
- Nitrogen = 100 - 5.6 = 94.4 mol%

\[ \sum_{i=1}^{n} A_i \left( \frac{100}{T_{ci}} - 1 \right) \leq \sum_{k=1}^{p} B_k K_k \]

$T_{ci}$ methane 14.7 mol%, $T_{ci}$ propane = 6 mol%. $K_k$ nitrogen = 1.

$B_k$ nitrogen = 94.4 mol%

$A_i$ methane = 0.2 * 5.6 = 1.12; $A_i$ propane = 0.8 * 5.6 = 4.48

76.7 \leq 94.4

the condition is fulfilled, consequently the mixture will NOT be classified as FLAMMABLE.
Example with the calculation method for flammability (ISO 10156:2010)

Consider a gas mixture containing:
- Flammable gas mixture: Methane/propane (20:80 mol%) altogether 4.1 mol%
- Nitrogen = 100 - 4.1 = 95.9 mol%

\[
\sum_{i=1}^{n} A_i \left( \frac{100}{T_{c_i}} - 1 \right) \leq \sum_{k=1}^{p} B_k K_k
\]

- \( T_{c_i} \) methane 8.7 mol%, \( T_{c_i} \) propane = 3.7 mol%. \( K_k \) nitrogen = 1.
- \( B_k \) nitrogen = 95.9 mol%
- \( A \) methane = 0.2 * 4.1 = 0.82; \( A \) propane = 0.8 * 4.1 = 3.28

\[93.97 \leq 95.9\]

the condition is fulfilled, consequently the mixture is **NOT** classified as FLAMMABLE.
Example with Tci values from ISO 10156:1996

Consider a gas mixture containing:

- Flammable gas mixture: Methane/propane (20:80 mol%) altogether 4.1 mol%
- Nitrogen = 100 - 4.1 = 95.9 mol%

\[ \sum_{i=1}^{n} A_i \left( \frac{100}{T_{ci}} - 1 \right) \leq \sum_{k=1}^{p} B_k K_k \]

- \( T_{ci} \) methane = 14.7 mol%, \( T_{ci} \) propane = 6 mol%. \( K_k \) nitrogen = 1.
- \( B_k \) nitrogen = 95.9 mol%
- \( A \) methane = 0.2 * 4.1 = 0.82; \( A \) propane = 0.8 * 4.1 = 3.28

56.3 ≤ 95.9

the condition is not fulfilled, consequently the mixture is **NOT** classified as FLAMMABLE.

- Will the classification of a mixture of a flammable gas with two inert gases be changed or not?

- See an example of a mixture from methane and two inert gases
Explosion diagram: Methane/CO\textsubscript{2} : N\textsubscript{2} (70:30 mol\%) mixture in air


MXC (exp) = 16.4\%
Using the $Tci$ value for methane 14.3 mol% from ISO 10156:1996

Consider a gas mixture containing:

- Flammable gas: Methane 18.3 mol%
- Inert gas mixture: Carbon dioxide /nitrogen (70:30) = 100 - 18.3 = 81.7 mol% 
- The calculated result is $109.67 \leq 110.27$ NOT flammable => Very dangerous, not safe result! This mixture ratio crosses the explosion region!
Using the $Tci$ value for methane 8.7 mol% from ISO 10156:2010

Consider a gas mixture containing:
- **Flammable gas:** Methane 18.3 mol%
- **Inert gas mixture:** Carbon dioxide /nitrogen (70:30) = 100 - 18.3 = 81.7 mol%
- The calculated result is $192.04 \leq 110.27 \Rightarrow \text{Flammable}$

Which is a safe classification?
Oxidizing potential

- will be experimentally determined or
- will be calculated by the calculation method of ISO 10156:2010

Which can be used for classifying a gas mixture according to GHS?
Explosion region of ethane/N\textsubscript{2} with different oxidizing gases

![Diagram of explosion region]

- Ethane
- Oxidizer
- Chlorine
- Nitrous oxide
- Nitric oxide
- Air
- Nitrogen trifluoride (70 mol%)

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Experimental determination of oxidizing potential and $C_i$ coefficients

**EN 1839 –B Bomb method**
- closed vessel
- spherical or cylindrical
- internal volume of at least 5 dm³
- spark or fusing wire igniter
Determination of the limiting oxidizer fraction of an ethane/nitrogen/air mixture

Explosion range
Ethane/Nitrogen/Air

apparatus: acc. to ISO 10156
temperature: 20 °C
pressure: 101 kPa

limiting ratio
43.4 mol% Air
56.6 mol% Nitrogen

Ethane in mol%

Nitrogen in mol%

Air in mol%

Limiting oxidizer fraction
LOF = 43.4 mol% Air
Calculation of $C_i$ from the LOF of an ethane/nitrogen/oxidizing gas mixture

\[ C_i = F \cdot \frac{1}{LOF} \]

where

- $F =$ constant mathematical factor
- LOF = limiting oxidizer fraction

\[ F = C_i \cdot LOF(O_2) = 1 \cdot 43.4 \cdot 0.209 = 9.07 \]

The factor $F$ can be deduced from the $LOF_{\text{air}} = 43.4$ mol\% by using the definition $C_i = 1$ for oxygen. Taking the 0.209 molecular fraction $O_2$ in air.
Calculation of the oxidizing potential (OP) of a gas mixture

\[ \sum_i x_i C_i > 23.5 \text{ mol}\% \ (21 \text{ mol}\% \text{ in ISO 10156-2:2005}) \]

A mixture is considered to be more oxidizing than air if the condition: \( \text{OP} > 23.5 \text{ mol}\% \) is satisfied.

In the presence of inert gases in the mixture:

\[
\text{OP} = \frac{\sum_{i=1}^{n} x_i C_i}{\sum_{i=1}^{n} x_i + \sum_{k=1}^{p} K_k B_k}
\]

- \( x_i \): content of the oxidizing component (mol\%)
- \( C_i \): coefficient of oxygen equivalency
- \( n \): number of oxidizing components
- \( B_k \): mole fraction of the inert component \( k \) in the mixture in mol\%
- \( p \): number of inert components
- \( K_k \): nitrogen equivalence coefficient of the inert component
Ethane/nitrous oxide – oxygen (50/50 mol%) / nitrogen
Explosion region of ethane/N₂O - O₂ (50/50) / N₂ mixture - threshold values

Calculated by the Triangle program (BAM)

- LFL: Lower flammability limit 2.5 mol%
- UFL: Upper flammability limit 48.4 mol%
- MOC: Maximum oxidizing gas concentration 11.9 mol%
- MAI: Minimum required inert gas concentration 87.7 mol%
- IAR: Minimal inert/oxidizing gas ratio 7.14 -
- MXC: Maximum flammable gas concentration 2.9 mol%
- ICR: Minimal inert/flammable gas ratio 33.76 -
Explosion region of ethane/N₂O - O₂ (50/50) / N₂ mixture - threshold values

Minimum required inert gas concentration (MAI) = 87.7 mol%
LOF = 100-MAI= 100 - 87.7=12.3 mol%

\[ C_{\text{mixture}}(\text{exp}) = 9.07 \times \frac{1}{12.3} = 0.74 \]

\[ \text{OP}(\text{exp}) = 74 \text{ mol}\% > 23.\% \text{ mol}\% \]

\[ \text{OP}(\text{calc}) = 0.5 \times 1 + 0.5 \times 0.6 = 0.8 = 80 \text{ mol}\% \]

which is more than 23.5 mol%, so this mixture is “more oxidizing than air”.
Changes in the classification of gas mixtures due to ISO 10156:2010

- NO changes to the classification of pure gases
- Changes which may effect the classifications of various mixtures

\( T_{ci} \) is defined as the maximum content of a flammable gas which, when mixed with nitrogen, is not flammable in air. \( T_{ci} \) is also used as a reference parameter in any kind of mixture that contains a flammable component.

- The new standard includes changes to these values for a number of gases. New \( T_{ci} \) values will influence the assignment of many existing mixtures. Depending on the mixture:
  - the \( T_{ci} \)-s may be higher (less restrictive situation) or
  - lower (more restrictive situation) than as defined in the previous edition of the standard.

Cited from Linde AG
Direct implication

• A **new transportation identification label**

• In some countries, a **new cylinder shoulder color** may be required to indicate the change from either a non flammable to a flammable mixture, or from a flammable to a non flammable mixture.

• The **Safety Data Sheet** (SDS) will need to be updated to include the updated changes for cylinder safety and transportation.

• In some countries, a **different cylinder valve outlet** may be required.

Cited from Linde AG
Indirect implication for the user

• Storage conditions may need to be reviewed (including permits for storage of dangerous substances).

• Transport conditions will need to be reviewed.

• Risk assessment to be reviewed, with operational procedures updated according to the new risk assessment outcome.

• Gas control equipment and supply system compatibility may need to be checked, as changes may be required for both cylinder connections and supply line labeling.

Cited from Linde AG
Mixture data are rare and the determination of flammability and oxidizing potential by test is very complex.

The ISO 10156:2010 deliver useful calculation methods for selection of cylinder valves (originally), but these methods can be use for classification (GHS) of gas mixtures.

Furthermore it is not allowed to apply these methods to gas mixtures under non atmospheric conditions.
Acknowledgement

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BAM Test Site Technical Safety

Thank you for your attention!

Questions?