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Committee of Experts on the Transport of Dangerous Goods and on the Globally Harmonized System of Classification and Labelling of Chemicals

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Issues relating to the Globally Harmonized System of Classification and Labelling of Chemicals: miscellaneous

**Sub-Committee of Experts on the Globally Harmonized System of Classification and Labelling of Chemicals** 

Twenty-eighth session

Geneva, 10–12 (a.m) December 2014 Item 2 (b) (i) of the provisional agenda Classification criteria and related hazard communication: work of the Sub-Committee of Experts on the Transport of Dangerous Goods (TDG): physical hazards

# **Classification of Flammable Gases**

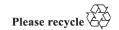
# **Transmitted by the European Chemical Industry Council (CEFIC)**

# Introduction

1. Following the proposal by Belgium in informal document INF.10 (46th session), informal document INF.5 (28th session) and the inclusion of an item in the programme of work on the view of the criteria for categorisation of flammable gases (ST/SG/AC.10/C.3/90, ST/SG/AC.10/C.4/54), the expert from CEFIC submits the attached study summary, "GHS Category 2 Flammable Gases: Review and Proposed Modification – Summary Version-" in support of the establishment of a TDG-GHS joint informal working group to study the classification of flammable gases.

# **Submission**

- 2. The study that is summarized has been carried out under the auspices of an industry sector group within CEFIC.
- 3. The full study, "GHS Category 2 Flammable Gases: Review and Proposed Modification" can be made available to both sub-committees as deemed appropriate.
- 4. CEFIC does not, by submission of this study, take a position on the issues covered. It is considered, however, that this study is valuable to the consideration of the issue and proposal by the expert from Belgium.





# GHS Category 2 Flammable Gases: Review and Proposed Modification

# - Summary Version -

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# 1. Executive Summary

This is a study on the flammability classification of gases. It appraises the current GHS (Global Harmonised Standard) classification for flammable gases and evaluates a proposed amendment to the current regulation. In light of the study, the authors concur that using Laminar Burning Velocity (LBV) may serve as an additional optional metric for the flammability classification of gases. It is proposed that a gas with a LBV less than 10 cm/s may be reclassified from a Category 1 Extremely Flammable Gas to a Category 2 Flammable Gas.

The rationale behind this proposal comes directly from the findings of this study:

- 2000 flammable gases were reviewed to determine which if any are eligible for
  Category 2 under the current GHS regulation. It was concluded that no gases could
  be definitively classed as Category 2 using the *lower flammability limit* (LFL) and
  flammability range criteria currently given. It would therefore mean that the current
  classification system is too coarse a method for categorising how dangerous
  (flammable) a particular gas is.
- It is therefore suggested that there is scope for the current classification scheme to be amended by way of adding an optional, complementary parameter to the existing LFL / flammable range criteria for Category 1.
- Currently, the usage of LFL and flammability range prioritises ignition probability only. However, LBV is related numerically to several other very important flammability and explosivity properties of gases. LBV would help to introduce the danger represented by combustion itself while not ignoring ignition probability. For example; LBV is correlated to the peak overpressure in a semi-confined explosion as well as the rate of pressure rise. This would suggest that if an explosion occurs, with other conditions being the same, the peak overpressure from a gas explosion with a low LBV would be less severe than one with high LBV. This is important, since the effects of overpressure (e.g. ejection of missiles, failure of structures and buildings) are the causes of injury and fatality. LBV is also related to the ignition sensitivity of a gas, e.g. via Minimum Ignition Energy (MIE) and Maximum Experimental Safe Gap (MESG). Low LBV gases are harder to ignite compared to high LBV gases.

This proposal would bring Category 2 into use to serve as a more fine-grained characterisation of gases. Such differentiation could even play an important safety role; enabling the most dangerous gases to be prioritised (for example by emergency responders), whilst making clear that Category 2 gases must continue to be treated with care.

The consequences from a regulatory perspective in adopting the proposal are as follows:

- For transportation purposes, the following regulations ADR, ADN, RID, US DOT, ICAO DGR and IMDG - do not distinguish between Category 1 and Category 2 gases, and so the proposal in this study will not have any immediate effect.
- In plants/facilities subject to SEVESO (legislation for managing major hazard process plants); both currently (SEVESO II) and the proposed update (SEVESO III) make no distinction between Category 1 and Category 2 gases. This means that plants already subject to SEVESO will remain being so, and those not subject to SEVESO will remain being so.

The term 'explosion' is used to refer to a release of energy generating overpressure and not necessarily a rapid violent chemical reaction.



2. Abbreviations

ADN European Agreement concerning the International Carriage of Dangerous

Goods by Inland Waterways

ADR European Agreement concerning the International Carriage of Dangerous

Goods by Road

AIChE American Institute of Chemical Engineers

ANSI American National Standards Institute

ATEX Atmosphères Explosibles (French)

BLEVE Boiling Liquid Expanding Vapour Explosion

BV Burning Velocity

CCPS Center for Chemical Process Safety, of the AIChE

CFD Computational Fluid Dynamics

CLP European Regulation on Classification, Labelling and Packaging of

Substances and Mixtures

DOT US Department of Transportation

Globally Harmonized System of Classification and Labelling of Chemicals

HoC Heat of Combustion

IATA International Air Transport Association

ICAO International Civil Aviation Organisation

IM(C)O International Maritime (formerly Consultative) Organization

IMDG International Maritime Dangerous Goods Code

LBV Laminar Burning Velocity

LFL Lower Flammability Limit

MEM Multi-Energy Method

MESG Maximum Experimental Safe Gap

MIE Minimum Ignition Energy

OSHA US Occupational Safety and Health Administration

PHA Process Hazard Analysis

PS Process Safety



RAGAGEP Recognised and Generally-Accepted Good Engineering Practice

RID Regulations Concerning the International Carriage of Dangerous Goods by

Rail

TDG Transportation of Dangerous Goods

**UFL** Upper Flammability Limit

UK United Kingdom

UNDG United Nations Recommendation on the Transport of Dangerous Goods

US United States

VCE Vapour Cloud Explosion



# 3. Glossary

A glossary of the most important terms for the purposes of this study is given below. The majority of the definitions are taken from Crowl (2003) [3] but some are from the authors.

Confined explosion: an explosion without any venting.

**Deflagration:** a reaction in which the speed of the reaction front propagates through the unreacted mass at a speed less than the speed of sound in the unreacted medium.

Deflagration Index (K<sub>G</sub>): the maximum rate of pressure rise normalised for volume.

Explosion: a release of energy that causes a rapid pressure rise.

**Fire:** a slow combustion that occurs without significant overpressure. Damage is mostly due to thermal or radiation energy release.

Flammability Range: the difference between the upper flammability limit (UFL) and the lower flammability limit (LFL).

Laminar Burning Velocity: velocity at which the flame propagates relative to the unburnt gas at laminar conditions.

Lower Flammability Limit (LFL): a fuel concentration below which combustion is not possible – the fuel concentration is too lean

Maximum Experimental Safe Gap (MESG): the maximum clearance between two parallel metal surfaces that has been found, under specified test conditions, to prevent an explosion in a test chamber from being propagated to a secondary chamber containing the same gas or vapour at the same concentration.

Minimum Ignition Energy (MIE): the minimum amount of thermal energy released at a point in a combustible mixture that will cause indefinite flame propagation away from that point, under specified test conditions.

Overpressure: the pressure above ambient that results from an explosion.

Semi-confined Explosion: an explosion where there is venting. The venting can be intended like a burst panel for an explosion inside a vessel, or, it can be unintended like a window for an explosion inside a room.

Upper Flammability Limit (UFL): a fuel concentration above which combustion is not possible – the mixture is too rich in fuel.



# 4. Introduction

Chilworth Technology Ltd ('Chilworth') has been engaged to undertake a review of the GHS classification scheme for flammable gases and examine whether Laminar Burning Velocity (LBV) is a good metric for determining the flammability hazards of gases.

The current GHS regulation categorises flammable gases into one of two categories; Category 1 ("Extremely Flammable Gas") and Category 2 ("Flammable Gas"). This study gave particular interest to any gas which would fall under Category 2, and thus a survey of many gases was requested to be carried out.

This study also examines the merits of LBV as a metric in classifying the flammability hazards of gases. This looks at its relationship with many other flammability and explosivity parameters.

Consequence modelling was outside the scope of this phase of the study and is planned for the next phase.

The work contained within this report is based upon Chilworth quotation number 111455.



# 5. Proposal for Additional Metric

This section proposes laminar burning velocity (LBV) as a metric for determining the flammability hazards of a gas. It describes the relationship LBV has with many other important flammability and explosivity parameters, and thus why it would act as a good metric.

#### 5.1 Introduction

The current GHS classification for the flammability of gases is based solely upon LFL and flammability range. The main reason why LFL and flammability range has been selected is primarily related to its relation in describing the likelihood of a flammable gas mixture being formed, i.e. the release of a gas which has a wide flammability range and/or low LFL is more likely to produce a flammable atmosphere than a similar release of a gas possessing a narrow flammability range or a high LFL.

In addition, the literature contains a great deal of information regarding flammability limits for particular gases, the test methods by which they may be obtained, and their expected behaviour under different conditions.

However under this way of classification Category 2 is not used at all. Therefore, this study proposes using LBV as an optional additional metric for determining the flammability hazards of gases.

LBV is defined as the "velocity at which the flame propagates relative to the unburnt gas at laminar conditions" [34]. Laminar conditions are those when the streamlines of the fluid flow are in parallel to one another with no disruption/intersection between layers. This is a fundamental property of the mixture.

"The laminar burning velocity depends primarily upon the chemical reaction rate, the heat of combustion of the gas, and the thermal diffusivity  $\mathcal{N}\rho C_p$  of the unburnt gas, where  $\lambda$  is the thermal conductivity,  $\rho$  is the density and  $C_p$  is the specific heat at constant pressure of the unburnt gas" [35].

In a real combustion process, the overall flame speed is made up of the laminar burning velocity and the gas velocity. Once the mixture is ignited, due to expansion of the hot burnt gases behind the flame, the unburnt gas is pushed away outwards – this is known as the gas velocity. This is shown in Figure 1:

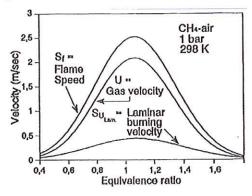


Figure 1: Burning velocity, gas velocity and flame speed for methane-air mixtures. [35].

The relationship between flame speed and burning velocity under ideal adiabatic conditions can be described by [35]:



$$S_f = S_u + S_g = S_u \frac{\rho_u}{\rho_b} = S_u \frac{n_b T_b p_u}{n_u T_u p_b}$$

Equation 1

#### Where:

- S<sub>f</sub> is the flame speed
- S<sub>u</sub> is the laminar burning velocity
- S<sub>q</sub> is the gas speed
- *n* is the number of moles
- T is the absolute temperature
- p is the pressure
- ρ is the density
- The subscripts u and b refer to the unburnt and burnt gases respectively

LBV has connection with many other important flammability and explosivity properties of a gas. The term 'explosion' in this context is used to refer to a release of energy generating overpressure and not necessarily a rapid violent chemical reaction. These relationships are:

- Peak overpressure generated in a semi-confined explosion. This is discussed in Section 5.2.
- 2. Rate of pressure rise in an explosion, i.e. dp/dt and thus it is directly related to the deflagration index (K<sub>G</sub>). This is discussed in Section 5.3.
- 3. Minimum Ignition Energy. This is discussed in Section 5.4.
- Quenching distance and thus MESG (maximum experimental safe gap) which is directly related to ignition sensitivity gas groups. This is an alternative way of looking at the ignition sensitivity of a material. This is discussed in Section 5.5.

It can be seen therefore that LBV is a proxy for determining both the explosion severity via explosion overpressure and  $K_{\rm G}$  as well as the likelihood of ignition via MIE and MESG. This is very important because risk is the product of likelihood and severity.



#### 5.2 Explosion Overpressure

#### **Theoretical Basis**

According to Schotte et al [35], the maximum explosion pressure is made of a static (no flow) and a dynamic part, i.e.

$$p_{max} = p_{static} + p_{dynamic}$$

Equation 2

For a deflagration (flame propagation at subsonic speeds) occurring in a closed vessel, the static part of the explosion pressure is a function of the initial pressure, change in moles and change in temperature. If the ideal gas behaviour is assumed, the maximum static explosion pressure is given by:

$$p_{static} = \frac{p_i n_f T_f}{n_i T_i}$$

Equation 3

#### Where:

- p<sub>i</sub> is the initial pressure
- n<sub>i</sub> is the initial number of moles of the gas
- n<sub>f</sub> is the final number of moles
- T<sub>i</sub> is the initial temperature
- T<sub>f</sub> is the adiabatic flame temperature at constant volume

"With explosions in air, the change in moles of gas is usually negligible ( $n_i/n_i = 1$ ), because of the large concentration of inerts (nitrogen) presents. Therefore, the static explosion pressure develops principally from an increase in temperature in the combustion process. The flame temperature (at constant volume) for most organic-air mixtures is optimal at a concentration slightly above stoichiometric and usually lies in the order of some 2000-3000K." [35]. The maximum static explosion pressure is roughly about eight times the initial pressure for typical hydrocarbons.

The dynamic part of the explosion pressure consists of a side-on pressure (a wave/flame moving along a surface) and of a reflected pressure (collision of wave/flame with a surface). The dynamic part of the explosion pressure is given using the well-known Bernoulli equation . [35]:

$$p_{dynamic} = \rho_{gas} v_{gas}^2$$

Equation 4

#### Where

- ρ is the density of the burnt gas
- v<sub>gas</sub> is the flame speed

The flame speed as previously defined in Equation 1 is the sum of the gas speed and the laminar burning velocity. Using Figure 1, it can be seen that the laminar burning velocity contributes to the overall gas velocity (about 25% in the example cited) and thus contributes to the overall overpressure.



#### Model

The GAME (Guidance for Application of Multi-energy Method) project [36] established that maximum explosion pressure may be related to laminar burning velocity (SL) to the power of 2.7. The other variables comprise volume blockage ratio and typical diameter of obstructions, and the flame path length – these are all environmental variables, not material properties. The equation given is:

$$P_0 = 0.84 \cdot \left( VBR \cdot \frac{L_P}{D} \right)^{2.75} \cdot S_L^{2.7} \cdot D^{0.7}$$

Equation 5

#### Where

- P<sub>o</sub> is the peak overpressure
- VBR is the volume blockage ratio
- L<sub>p</sub> is the flame path length
- D is the typical diameter of obstructions
- S<sub>L</sub> is the laminar burning velocity

Table 1 displays the results of this relationship for two examples from p76 of the reference, with varying laminar burning velocities:

Laminar Burning	Peak Explosion Overpressure (bar)		
Velocity (cm/s)	Example a)	Example d)	
10	0.01	0.06	
20	0.07	0.41	
40	0.43	2.7	
100	5.1	31.9	

Table 1: Peak explosion overpressure for varying laminar burning velocity

As it can be seen, peak overpressures from a low LBV gas will be less severe than a high LBV gas, given identical release and scenario conditions.

It should be noted that in many real life situations, the governing factor behind the overpressure generated is normally turbulence. Turbulence is mainly caused by obstacles in the flammable atmosphere; it forms a positive feedback loop in generating the overpressure. Turbulence can be generated in confined scenarios, semi-confined scenarios as well as unconfined scenarios.

In the next phase of this project, there will be a study examining the relationship between the laminar burning velocity and transition between laminar to turbulent flows. It is proposed that low laminar burning velocity gases will have a longer distance to transition from laminar flows to turbulent flows.



## 5.3 Rate of Pressure Rise

Schotte et al [35] also obtained a theoretical equation relating the average rate of pressure rise to laminar burning velocity:

$$\left(\frac{dp}{dt}\right)_{ava} \approx constant \frac{p_i S_u}{V^{1/3}}$$

Equation 6

Where the constant is a value about 55 and V is the volume of the vessel. "To obtain the maximum rate of pressure rise, the average value has to be multiplied by another factor, dependent of the form of the pressure-time curve (circa 5). It should be emphasised that this formula is only very rough due to the many highly simplifying assumptions made, but it can be used to illustrate the effects of the process conditions." [35]

Similar relationships connecting rate of pressure rise to laminar burning velocity have also been derived by various other researchers e.g. models by Zabetakis (1965) [37], Harris (1983) [38] and others.

This relationship can be graphically seen from the works of Senecal et al [39] where deflagration experiments were carried out in a 22 litre stainless steel vessel of different gases. However this work is only for a small number of gases (methane, propane, ethylene and hydrogen).

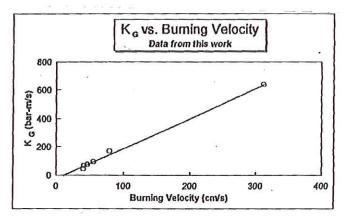


Figure 2: Correlation between K<sub>G</sub> and published value of burning velocity [39].

One consequence of lower  $K_G$  value is smaller vent sizes or suppression systems which do not need to act as fast compared to those with high  $K_G$ . Therefore it would be expected that processes handling gases exhibiting a low laminar burning velocity would easier to protect than those handling gases with high laminar burning velocity.



# 5.4 Minimum Ignition Energy

One of the most significant correlations that laminar burning velocity has with other flammability properties is the minimum ignition energy (MIE). This is quite unintuitive but has been demonstrated by different researchers to be the case. Kondo et al [19] have developed a theoretical relationship between the minimum ignition energy and burning velocity:

$$E_{min} = \pi d^2 \frac{\lambda_{av} (T_b - T_u)}{S_{av}}$$

Equation 7

#### Where:

- d is the diameter of minimal flame
- T<sub>u</sub> is the unburnt gas temperature
- T<sub>b</sub> is the burnt gas temperature
- $\lambda_{av}$  is the heat conductivity averaged for the temperature from  $T_u$  to  $T_b$
- S<sub>av</sub> is the burning velocity

The relationship does not have very good accuracy and the errors are "considerable" (in the words of its author) when compared with experimental results. However, Takizawa et al [33] have demonstrated that if the equation is calibrated with an experimentally obtained MIE (or  $E_{min}$ ), then the accuracy of the equation can be greatly improved, but this work was carried out with a limited number of gases. Nevertheless, this supports the principle behind the formula is sound.

In appraising the gases found as part of this study the inverse relationship given in Equation 7 is in alignment with experimental results, see Figure 3.

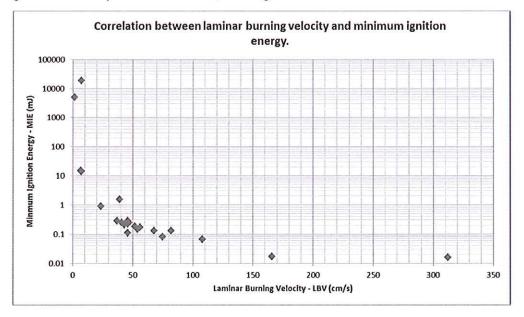


Figure 3: Correlation between laminar burning velocity and minimum ignition source.

Source: this literature research, refer to full version of report.

This trend is also confirmed by a formula developed by Ballal [40]. Ballal's method of obtaining the MIE is generic and applicable to dust clouds, vapours, gases and aerosols. The correlation



between MIE and LBV is through another term, called the Spalding mass transfer number *B*. The formula given by Ballal is:

$$E_{min} = \pi c_p \rho_a \Delta T d_q^3$$

Equation 8

#### Where:

- $c_p$  is the specific heat of the fuel
- $d_q$  is the quenching distance
- ΔT is the temperature difference
- $\rho_a$  is the density of air

With:

$$d_q = (8\alpha)^{0.5} \left\{ \left[ \frac{C_3^3 \rho_p D_{32}^2}{8C_1 f^2 \left(\frac{k}{c_p}\right) \phi \ln(1+B)} + \frac{12.5\alpha}{S_u^2} \right]^{-1} - \frac{9qC_1^2 \epsilon \sigma T_p^4}{c_p \rho_p C_3^3 f D_{32} \Delta T_{st}} \right\}$$

Equation 9

#### Where:

- c<sub>pg</sub> is the specific heat of the gas
- C<sub>1</sub> is the ratio of the surface mean area to the Sauter mean diameter
- C<sub>3</sub> is the ratio of the volume mean diameter to the Sauter mean diameter
- D<sub>32</sub> is the Sauter mean diameter
- f is the swelling factor of the fuel
- k is the thermal conductivity of the fuel
- S<sub>u</sub> is the laminar burning velocity
- α is the thermal diffusivity of the particle
- $\epsilon$  is the emissivity of the particle
- ρ is the density
- ΔT is the temperature difference
- σ is the Stefan Boltzmann constant
- φ is the equivalence ratio
- and subscript p denotes fuel

The Spalding mass transfer number B is given by:

$$B = \frac{q_{st}H + c_{pa}(T_g - T_b)}{L + c_p(T_b - T_s)}$$

Equation 10

#### Where:

- c<sub>p</sub> is the specific heat of the fuel
- c<sub>pa</sub> is the specific heat of air
- H is the heat of combustion
- L is the latent heat of vaporization



- q is the mass ratio of fuel to air
- and subscripts b, g, s and st denote the boiling point of the fuel, gas, the surface of the fuel and stoichiometric, respectively

Although the relationship between minimum ignition energy and burning velocity is difficult to see from the formula, the following two graphs (Figure 4 and Figure 5) produced using the formula demonstrate the relationship:

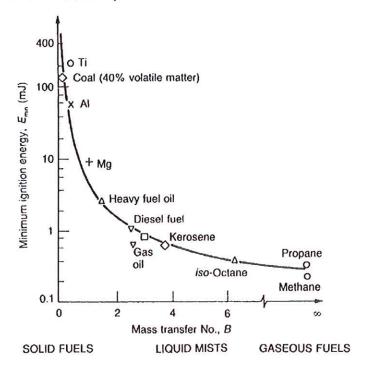


Figure 4: Relationship between Mass Transfer No. B and Minimum Ignition Energy.

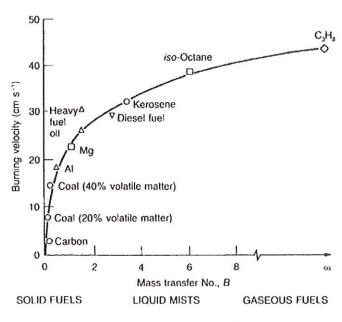


Figure 5: Relationship between Mass Transfer No. B and Burning Velocity.



Using the above two graphs (Figure 4 and Figure 5), high mass transfer corresponds to a low MIE and thus a high burning velocity. Therefore a gas with a high burning velocity would have a low MIE, where as one with a low burning velocity has a high MIE. This is consistent with the work of Kondo et al [19]. Note that this is a relationship holds across various states of matter; solids, liquid vapours, gases and liquid mists.



# 5.5 Quenching Distances

Much of the research involving LBV also examines its relationship with quenching distances. The quenching distance is the gap below which flame propagation is not possible, i.e. the flame is quenched by heat losses to the surrounding walls. There is significant research which concludes an inverse relationship between the laminar burning velocity and the quenching distance; this is cited by Lees [41].

Takizawa et al [42] expressed such an inverse relationship relating quenching distance and laminar burning velocity:

$$d_q = a \left( \frac{\lambda_{av}}{c_p \rho_0 S_u} \right)$$

Equation 11

#### Where:

- d<sub>q</sub> is the quenching distance
- a is a proportionality constant
- c<sub>p</sub> is the isobaric heat capacity
- S<sub>u</sub> is the laminar burning velocity,
- $\rho_0$  is the density of the unburned gas.

The work also compares the equation with experimental results and there is generally good agreement.

Quenching distances in this context have also been shown to be approximately twice the MESG (maximum experimental safe gap) [43]. MESG can be loosely used as a parameter for classifying the ignition sensitivity of gases and vapours, and this is used for selection of suitable equipment in flammable (ATEX zoned) atmospheres [3]. MESG categories are shown in Table 2.

Class	MESG Boundaries	Examples
I	Firedamp (CH4) only: MESG = 1.14mm	Methane
IIA	MESG ≥ 0.9mm	Acetaldehyde, Acetic Acid, Acetone, Benzene, Ethane, Propylene
IIB	0.9mm > MESG ≥ 0.5mm	Ethylene, Ethylene Oxide, Formaldehyde
IIC	MESG < 0.5mm	Acetylene, Carbon Disulphide, Hydrogen

Table 2: MESG categories for different types of gases.



#### 5.6 Summary

It has been shown that laminar burning velocity (LBV) has relationships with a number of other flammability and explosivity properties. These are:

- Peak overpressure generated in a semi-confined explosion; here it is expected that a
  gas of low LBV will generate lower peak overpressure than one of high LBV. Therefore
  the damages and injuries would be lower for a low LBV gas compared to a high LBV
  gas. It should also be noted that explosions are not simple and therefore do not
  depend solely on LBV or any other single parameter.
- Rate of pressure rise in an explosion, i.e. dp/dt and thus the deflagration index (K<sub>G</sub>).
   Lower LBV corresponds to lower pressure rise rate. It is therefore expected that
   processes handling gases of low LBV are easier to protect i.e. explosion venting or
   suppression systems will be less stringent for gases of low LBV compared to high LBV.
- Minimum Ignition Energy. Gases exhibiting high LBV are easier to ignite compared to those exhibiting low LBV. Therefore it can be said that generally gases exhibiting a low LBV would not be readily ignited by many forms of static electricity and mechanically generated sparks compared to those of high LBV.
- 4. Quenching distance and thus MESG (maximum experimental safe gap). This is an alternative way of looking at the ignition sensitivity of a vapour or gas. A gas with low LBV generally has a bigger quenching distance than one of high LBV. Therefore, low LBV gases would require the least stringent protection construction for equipment certified for operation in hazardous areas. These are equipment specifically built on the concept of MESG (i.e. flame proof).



# 6. Limiting Laminar Burning Velocity

The case for using laminar burning velocity (LBV) as an additional metric for GHS has been presented in Section 5. However before it can be included as part of the regulation, a useful and realistic limiting value must be determined.

The literature research showed that the majority of hydrocarbon gases have LBVs within the 35-60 cm/s range; there is a clear boundary between these gases and a small grouping that have LBVs below 10 cm/s. It has been shown that these latter gases tend to possess lower peak overpressure and rate of pressure rise, and higher MIEs and MESGs, all of which qualities are more conducive to safer handling and reduced consequences of ignition.

Two international standards already use LBV as a metric for categorising flammable gases: ASHRAE Standard 34-2013 in particular uses the value of 10 cm/s to introduce an optional 'Subclass 2L' for gases with a lower LBV, and it is understood that the recently ratified ISO 817 'Refrigerants – Designation System' also uses a value for LBV of 10 cm/s as a limiting value.

It is therefore proposed that the use of LBV within GHS also use the value of 10 cm/s, whereby gases with a lower LBV may be reclassified from Category 1 to Category 2.

It is noted that the use of specific values of LBV will require a specific and consistent test method i.e. ASHRAE Burning Velocity Test Evaluation for obtaining them, and that the resultant values be normalised in relation to a specific reference material, for example (R32 or R152a).



# 7. Conclusions

This study appraised the current classification methodology for the flammability hazards of gases. It also examined whether laminar burning velocity (LBV) would be a good metric to use for determining the flammability hazards of gases.

This study has found that GHS Category 2 Flammable Gas is essentially unused. Approximately 2000 gases were surveyed and not a single one could be definitively classed as a Category 2 Flammable Gas using the Lower Flammability Limit (LFL) and flammability range criteria.

If LBV is brought into use as an addition of a complementary, optional criterion to the GHS classification scheme, this could even aid the industry and emergency responders by providing a more fine-grained assessment of the flammability hazards and consequences.

The relationship of LBV to other flammability and consequence-related parameters were examined, and its suitability for serving as the additional criterion has been assessed. This report finds that LBV is related to a number of other very important flammability and explosivity properties. These are:

- Peak overpressure generated in a semi-confined explosion; here it is expected that a
  gas of low LBV will generate lower peak overpressure than one of high LBV. Therefore
  the damages and injuries would be lower for a low LBV gas compared to a high LBV
  gas.
- Rate of pressure rise in an explosion, i.e. dp/dt and thus the deflagration index (K<sub>G</sub>).
   Lower LBV corresponds to lower pressure rise rate. It is therefore expected that
   processes handling gases of low LBV are easier to protect i.e. explosion venting or
   suppression systems will be less stringent for gases of low LBV compared to high LBV.
- Minimum Ignition Energy. Gases exhibiting high LBV are easier to ignite compared to those exhibiting low LBV. Therefore it can be said that generally gases exhibiting a low LBV would not be readily ignited by many forms of static electricity and mechanically generated sparks compared to those of high LBV.
- 4. Quenching distance and thus MESG (maximum experimental safe gap). This is an alternative way of looking at the ignition sensitivity of a vapour or gas. A gas with low LBV generally has a bigger quenching distance than one of high LBV. Therefore, low LBV gases would require the least stringent protection construction for equipment certified for operation in hazardous areas. These are equipment specifically built on the concept of MESG (i.e. flame proof).

It can be seen therefore that LBV is a proxy for determining both the explosion severity via peak overpressure and  $K_G$ , as well as the likelihood of the ignition via MIE and MESG. This is very important since risk is the product of likelihood and severity. Therefore it would be expected that the risks of fires and explosions is lower for a low LBV gas compared to a high LBV gas in two identical scenarios. It is advised to carry out detailed consequence modelling for scenarios of interest (i.e. transportation and storage) to confirm these initial findings.

Were this proposal to be adopted, it is believed that the immediate regulatory consequences will be minimal; only gases that are currently in Category 1 and meet the new criterion could be reclassified to Category 2. Furthermore, the primary global transport and storage regulations (that have been examined as part of this study) do not distinguish between the Category 1 and Category 2 flammable gas and so will not be affected.



# 8. References

- United Nations. 2013. Globally Harmonized System of Classification and Labelling of Chemicals (GHS). Fifth revised edition,
- European Parliament. 2008. Directive 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006, commonly known as the CLP Regulation.
- Directive 1999/92/EC of the EU on minimum requirements for improving the safety and health protection of workers potentially at risk from explosive atmospheres. (15th individual Directive within the meaning of Article 16(1) of Directive 89/391/EEC)', commonly called the ATEX 137 Directive.
- 4. **Daniel A. Crowl. 2003**, *Understanding Explosion*, CCPS, Center for Chemical Process Safety of the American Institute of Chemical Engineers.
- 5. **Jones, G.W. 1928.** *The Flammability of Refrigerants.* Industrial and Engineering Chemistry, 20: pp 367 370.
- 6. Simmons, R.F. & Wolfhard, H.G. 1955. The Influence of Methyl Bromide on Flames. Trans. Faraday Soc., 51: pp. 1211 1217.
- 7. IEC. 2000. IEC 60079-20: Electrical Apparatus for Explosive Gas Atmospheres Data for flammable gases and vapours, relating to the use of electrical apparatus.
- Linteris, G.T. & Babushok, V. Marginally Flammable Materials: Burning Velocity of trans-Dichloroethylene. Scale Modelling 3<sup>rd</sup> International Symposium. Proceedings. ISSM3-C8. September 10-13 2000, Nagoya, Japan, pp 1-8.
- 9. **United Nations. 2013.** European Agreement Concerning the International Carriage of Dangerous Goods by Road (ADR).
- United Nations. 2013. European Agreement Concerning the International Carriage of Dangerous Goods by Inland Waterways (ADN).
- 11. Intergovernmental Organisation for International Carriage by Rail. 2013. Convention Concerning International Carriage by Rail (COTIF).
- 12. US Government. 2012. Code of Federal Regulations Title 49 (Transportation).
- 13. NFPA. 2013. NFPA 68: Standard on Explosion Protection by Deflagration Venting.
- 14. NFPA. 2000. NFPA 77: Recommended Practice on Static Electricity.
- NFPA. 1994. NFPA 325: Guide to Fire Hazard Properties of Flammable Liquids, Gases, and Volatile Solids.
- 16. IEC. 2000. IEC 60079-32-1: Explosive Atmospheres Electrostatic Hazards, Guidance
- Brandes, E. and Möller, W. 2003. Sicherheitstechnische Kenngrößen Band 1: Brennbare Flüssigkeiten und Gase [trans: Safety-Related Characteristic Quantities Vol. 1: Combustible Liquids and Gases].
- Britton, L. 1999. Avoiding Static Ignition Hazards in Chemical Operations. AIChE CCPS.



- 19. Kondo, S., A. Takahashi, and K. Tokuhashi. 2003. Calculation of minimum ignition energy. J. Hazardous Materials A103: 11-23.
- 20. DIPPR 801 Database
  - https://www.aiche.org/dippr/events-products/801-database
- 21. **Air Liquide.** Gas Encyclopedia [website] http://encyclopedia.airliquide.com/encyclopedia.asp
- 22. Daikin Industries Ltd. HFC-32 Safety Data Sheet. Revision 19-03-2012.
- 23. **Honeywell International Inc.** Solstice yf Refrigerant (R-1234yf) Safety Data Sheet. Revision 06-13-2013.
- 24. DNV GL Software. 2014. Phast 7.1. [Software product].
- 25. **Design Institute for Physical Properties. 2012.** *DIPPR Project 801.* http://www.aiche.org/dippr/products/801.aspx
- 26. International Association of Oil & Gas Producers. 2010. OGP Risk Assessment Data Directory Report 434 14.1: Vulnerability of Humans.
- 27. **TNO. 2005.** *Methods for the Calculation of Physical Effects*[...] 'Yellow Book' CPR 14E. [ed.] van den Bosch, C.J.H., Weterings, R.A.P.M.
- Eggen, J.B.M.M. 1998. GAME: development of guidance for the application of the multienergy method (HSE CRR 202/1998). TNO Prins Maurits Laboratory. HSE Books. Contract Research Report.
- 29. Chilworth Technology Ltd. 2014. J307651 Initial Progress Report: "Classification and Handling of Mildly Flammable Gases, having a Burning Velocity less than 10 cm/s" (140214djw-L01). Letter dated 14 February 2014.
- 30. The Japan Society of Refrigerating and Air Conditioning Engineers Risk Assessment of Mildly Flammable Refrigerants, 2012 Progress Report, April 2013.
- 31. Kutchta, J.M., (1985), Investigation of fire and explosion accidents in the chemical, mining and fuel related industries a manual, Bulletin 6980, US Bureau of Mines, Washington.
- 32. Kondo, S., A. Takahashi, and K. Tokuhashi. 2003. Calculation of minimum ignition energy. J. Hazardous Materials A103: 11-23.
- 33. The Japan Society of Refrigerating and Air Conditioning Engineers *Risk*Assessment of Mildly Flammable Refrigerants, 2012 Progress Report, April 2013.
- 34. Kutchta, J.M., (1985), Investigation of fire and explosion accidents in the chemical, mining and fuel related industries a manual, Bulletin 6980, US Bureau of Mines, Washington.
- 35. R.M. Schotte / dr ir S.M. Lemkowitz (May 1997), Explosion Indices Theory and Practice, TU Delft, Technische Universiteit Delft
- 36. Eggen, J.B.M.M. 1998. GAME: development of guidance for the application of the multienergy method (HSE CRR 202/1998). TNO Prins Maurits Laboratory. HSE Books. Contract Research Report.



- 37. **Zabetakis, M.G. (1965).** Fire and explosion hazards at temperature and pressure extremes. Am. Inst. Chem. Engrs-Instn Chem Engrs, Joint Mtg (London: Instn Chem. Engrs)
- 38. Harris, R.J. (1983). Investigation and Control of Gas Explosions in Buildings and Heating Plant (London: Spon)
- 39. **Joseph A. Senecal and Patricia A. Beaulieu (November 1996),** KG: New Data and Analysis, FENWAL Safety Systems, A Division of Kidde Technologies.
- 40. Ballal, D.R (1983). Further studies on the ignition and flame quenching of dust clouds. Proc. R. Soc., Ser. A., 385, 1
- 41. Frank P Lees (2001), Loss Prevention in the Process Industries; Hazard Identification, Assessment and Control, 2<sup>nd</sup> Edition, Butterworth-Heinemann.
- Kenji TAKIZAWA and Masanori TAMURA, Progress Report by Research Institute for Innovation in Sustainable Chemistry, AIST, Research Institute for Innovation in Sustainable Chemistry, National Institute of Advanced Industrial Science and Technology
- 43. Nicoleta-Gabriela MUŞAT (May 2009), Ignition and quenching of flammable n-butaneair mixture at various initial pressures. Critical Properties, ACADEMIA ROMÂNĂ, Rev. Roum. Chim., 2010, 55(2), 99-103
- 44. Technical Instructions for the Safe Transport of Dangerous Goods by Air, ICAO, 2013 Edition.
- 45. International Maritime Dangerous Goods Code 2012, IMDG.
- 46. Dag Bjerketvedt, Jan Roar Bakke, Kees van Wingerden Gas Explosion Handbook