The thermal/thermodynamic theory of flammability: The adiabatic flammability limits

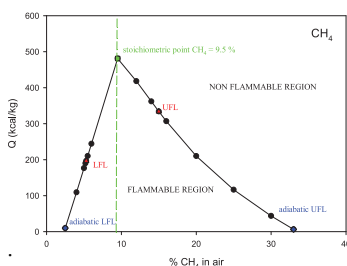CrossMark

Almerinda Di Benedetto *

Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università di Napoli Federico II, P.le Tecchio 80, 80125 Napoli, Italy

GRAPHICAL ABSTRACT

The overall region of methane concentration as a function of heat losses is shown. Also the adiabatic flammability limits are derived

ABSTRACT

A thermal/thermodynamic theory for the calculation of flammable fuel concentrations is derived here. It is based on the coupling between the heat balance equation across the flame, taking into account heat losses toward the environment, and the equilibrium composition equations.

From this theory, the flammable region for several hydrocarbons (paraffins, olfeins, aromatics) have been computed at varying fuel concentrations and heat losses.

A new concept of flammability limits is also given as the upper and lower fuel concentrations capable to propagate a flame in the absence of heat losses: the adiabatic flammability limits.

In this work, the use of these limits rather than the experimental classical limits is strongly suggested for designing measures of prevention and mitigation.

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1. Introduction

In industrial chemical processes involving flammable substances, safety reliable data are required for designing measures of prevention and mitigation.

When dealing with gases or vapors, the most important physicochemical parameters for assessing safety issues are flammability limits.

The lower (LFL) and upper (UFL) flammability limits identify the range of fuel concentration in which a fuel/air mixture is flammable, i.e. if an ignition source is applied, a combustion reaction self-sustains. The concept of flammability limits was first formulated in Humboldt and Gay Lussac (1805). Later, the theory of flames was gradually developed by Mallard and Le Chatelier (1881), Jouguet (1913), Daniell (1930), Lewis and Elbe (1934), Zel'dovich (1944) gave an outstanding contribution to the knowledge of flame propagation limits, concluding that flammability limits are concentration limits, owing to flame cooling by radiative heat losses from the flame and the adjacent hot combustion gases. He showed that, at the concentration limits, the laminar burning

velocity cannot be zero, but it has to take a finite value. He also determined the relationship between this velocity and the lowering of the temperature below the adiabatic value at the limit. Later, Spalding (1957) arrived at similar conclusions.

Notwithstanding, a theory which allows the quantitative evaluation of the flammability limits is not available.

Several methods for the prediction of the flammability limits have been proposed. Three main classes of correlations may be found in the literature: empirical correlations, group contribution models, and the quantitative structure–properties relationship (QSPR) models (Albahri, 2003; Vidal et al., 2004; Yong Pan et al., 2010).

All these methods do not rely on the theory of flammability limits, but rather are the best models trying to correlate the molecular structure of the fuels to the flammability properties. They are not based on a theory of the flammability limits, but are mainly empirical formula obtained by fitting the experimental results.

On the experimental side, flammability limits have been widely measured in many laboratories, in vessels of various shapes. Hence, it was not a surprise that the obtained flammability limits were apparatus-dependent. Coward and Jones (1952) gave a summary of empirical knowledge on this issue and proposed a new standard apparatus for determining flammability limits. This was a vertical tube, 51 mm in diameter and 1.8 m long, closed at the upper end and open to the atmosphere at the bottom. Nowadays, a standard procedure, ASTM standard E681, for the determination of the flammability limits has been identified in which the apparatus and the conditions are specified and widely accepted as standard.

The existence of a standard procedure for the evaluation of the flammability limits does not ensure about the reliability of these measured flammability limits as tools for prevention and mitigation of hazards coming from the use of flammable substances. Unique and universal parameters for the evaluation of the flammability of substances should be identified and used.

In the present work a thermal-thermodynamic theory for the evaluation of the flammability limits is proposed. According to this theory two new flammability parameters are derived: the adiabatic flammability limits, which are not dependent on the procedure and experimental apparatus and are uniquely determined.

2. Theory and model

A thermal/thermodynamic theory for the flammability limits is proposed here and from this we derive new flammability parameters (adiabatic lower and upper flammability limits) which are uniquely identified and allow conservative determination of the flammable properties of substances.

At the lower flammability limit, the flame propagation does not occur. According to the thermal theory of Zledovich, this is related to the fact that the heat generated by reaction is not enough to counter-balance the heat losses from the flame due to radiation and convection toward the surrounding gases. According to the Mallard–Le Chatelier theory, the flame structure is composed of a thermal zone ($\square_h$), where pre-heating of the unburnt gases occurs, and a reaction zone ($\square_R$), where combustion proceeds (Fig. 1). Flame propagation is allowed by the pre-heating of the unburnt gases from the ambient temperature (T°) up to the ignition temperature (T_i).

Williams (1985) developed a model based on the energy balance equation across the flame showing the critical role of heat losses (Q) on the flammability limits. However, the sole energy balance equation is not sufficient for evaluating both lower (LFL) and upper (UFL) flammability limit.
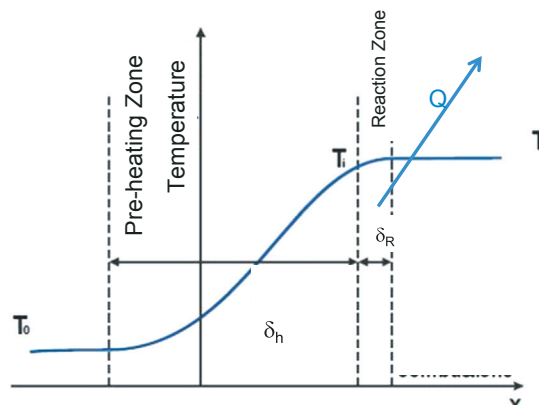

Fig. 1. Flame structure and temperature profile.

In particular, in the case of the rich condition (UFL) it is well known that the product distribution is very wide since not only CO_2 and H_2O are formed, but partial oxidation reactions and decomposition reactions have to be taken into account leading to CO, H_2, CH_4, C_2H_4, C_2H_2 species.

Due to the very high combustion rate, we may assume that the product composition is at equilibrium and then the energy balance equation should be coupled to the equilibrium equations.

In the following the approach for the calculation of the flammable region of hydrocarbons is described.

2.1. Model equations

To compute the flammable region of each fuel, we evaluated the limiting concentration of fuel, at both lean and rich conditions, at which the heat produced by reaction allows preheating of the unburnt mixture up to the ignition temperature (T_i), thus sustaining the flame propagation.

To this end, we solved the energy balance equation across the flame (sketched in Fig. 1) coupled to the thermodynamic constants for the evaluation of the product distributions.

The energy balance equation reads as follows:

$$n_u \int_{Tu}^{Ti} Cp_u \, dT + n_b \int_{Ti}^{Tf} Cp_b \, dT = n_f |\Delta H_R| - Q' \tag{1}$$

where n_u and n_b are the moles of the unburnt and burnt species respectively, Cp_u and Cp_b are the thermal capacity of the unburnt and burnt mixture, respectively and they have been assumed as variables with temperature through a polynomial formula. T_i is the ignition temperature, T_u is the temperature of the unburnt mixture, n_f are the moles of the fuel and ΔH_R is the heat of reaction. T_f is temperature of the burnt mixture. Q is the heat losses by radiation, convection and conduction toward the surrounding. Q depends on the experimental conditions and, in particular, on the shape and size of the experimental apparatus. At limiting conditions (flammable), we have that the burnt gases reach the minimum temperature to allow ignition, all the surplus heat being lost. As a consequence, in Eq. (1) we assume $T_f = T_i$.

Eq. (1) was solved as coupled to the thermodynamic Eq. (2)

$$dG = 0 \tag{2}$$

where G is the Gibbs function. In particular, for each fuel, in the burnt mixture the following species are computed at equilibrium: CH_4, C_2H_4, C_2H_2, H_2, CO, H_2O and CO_2 (and O_2 at rich conditions).

The equilibrium equations are the following:

$$CH_4 + 1/2O_2 \leftrightarrow CO + 2H_2 \tag{3}$$

$$2CH_4 \leftrightarrow C_2H_2 + 3H_2 \tag{4}$$