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Prediction of flammability limits of fuel-air and fuel-air-inert mixtures from explosivity parameters in closed vessels

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ABSTRACT

Flammability limits of fuel-air and fuel-air-inert gaseous mixtures, especially at non-atmospheric conditions, are essential properties required for establishing safety operating conditions for handling and processing flammable gases. For pure fuels, an important data pool exists, formed by the flammability limits of fuel-air and fuel-air-inert gaseous mixtures at ambient initial conditions measured by standard methods. Such methods can be used for experimental determination of flammability limits for multi-fuels mixed with air, with or without additives, under non-atmospheric conditions. Their use is however a time- and material-consuming process; in addition, the flammability limits obtained by various standard methods may be scattered as a result of different choices in the operating parameters, for each standard method. It appears that a preliminary estimation of the flammability limits for fuel-air and fuel-air-inert gaseous mixtures can minimize the effort of measuring them in specific initial conditions.

The present paper describes a new method for estimating the flammability range of fuel-oxidizer gaseous mixtures based on measurements of explosivity properties e.g. the peak explosion pressure and maximum rate of pressure rise recorded during closed vessel laminar explosions of fuel-oxidizer mixtures far from limits. Data obtained for several hydrocarbon-air gaseous mixtures with or without inert gas addition are used to examine the accuracy of estimated flammability limits (LFL – the lower and UFL – the upper flammability limit) as well as of the Limiting Oxygen Concentration (LOC) and the Minimum Inert Concentration (MIC). The predictive ability of the proposed method is examined against the predictive ability of other recently described methods.

1. Introduction

Knowledge of safety properties for various materials is essential during handling and processing of flammable gases. It is well known that to produce a fire or an explosion, three elements must be present: a fuel, an oxidizer, and an ignition source. The removal of the ignition source to suppress fires and explosions is not always possible; an alternative method to prevent the explosion is the progressive addition of an inert gas to fuel-oxidizer gaseous mixture until its ignition is no longer possible. This method removes the fuel-oxidizer mixture out of its flammability range.

The flammability range of any fuel-oxidizer gaseous mixture is delimited by LFL – the lower flammability limit and UFL – the upper flammability limit. LFL and UFL are the limiting values of fuel content at which an explosive process no longer propagates autonomously in this mixture (Hattwig and Steen, 2004): LFL is the lowest concentration of fuel in air that will support flame propagation, whereas UFL is the maximum fuel concentration that can burn in air. Addition of an inert gas to a flammable mixture results in the increase of LFL and the decrease of UFL until the two limits merge and the mixture becomes not flammable. This "critical" composition is characterized by LOC – the limiting oxygen concentration, i.e. the maximum allowed oxygen concentration of the fuel-air-inert mixture in which an explosion will not occur and MIC – the minimum inert concentration required for suppressing an explosion, whatever amount of flammable gas is added.

The flammability limits as well as LOC and MIC can be determined by various experimental methods; among them, the most important are:

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- the USBM method (Coward and Jones, 1952) where the ignition source is an electric spark or a pilot flame passed by at the open lower end of the explosion vessel (a cylindrical vertical glass tube with an inner diameter of 50 mm and a length of 1500 mm);
- the ASTM E 681-98 standard (ASTM, 1998) where the ignition source is an high-voltage electric spark centrally positioned in the explosion vessel, which is a 5 dm^3 spherical glass bulb;
- the European standard EN 1127 (European Standard, 1997) based on the German standard method (DIN 51 649, 1987) where the explosion vessel is a cylindrical vertical glass tube with an inner diameter of 60 mm and a length of 300 mm and the ignition of the mixture is made by a high-voltage (15 kV) electric spark produced 60 mm above the tube bottom;
- the standard method issued by the Expert Commission for Safety in the Swiss Chemical Industry, ESCIS (Hoppe and Jaeger, 2005) where the ignition source is an high-voltage (15 kV) electric spark and the explosion vessel is a 20 L stainless steel sphere.

The limits of flammability should be independent of the ignition source strength. The experimentally measured flammability limits are however quite dependent on the apparatus and methodology used. The most recent regulations require large vessels, up to a 20 L volume, and a high energy of the ignition source, up to 10–15 kJ. Only in such conditions one can observe ignition of near-limit mixtures and observe the flammability criterion: the autonomous flame propagation over a settled length. The use of metallic vessels enables measurements of the flammability range at pressures and/or temperatures higher than ambient.

Data collections such as: the Bulletin nr. 627 of the U.S. Bureau of Mines (Zabetakis, 1965), the CHEMSAFE Database from Germany (Brandes and Mőller, 2003; Molnarne et al., 2003; CHEMSAFE, 2009) or the publications issued by the NFPA (National Fire Protection Association) from USA (NFPA, 2008) contain measured LFL, UFL, LOC and MIC for a large number of fuel-air and fuel-air-inert gaseous mixtures, mostly at ambient initial conditions. Unfortunately, the mapping of the flammability range by measurements of the flammability limits and of LOC and MIC is a time- and material-consuming process, especially at non-atmospheric conditions. It requires expensive equipment, e.g. high-voltage sources, measuring devices for determining the energy of capacitive electric sparks and fast-speed cameras for recording the flame appearance and propagation. Therefore, the prediction of the flammability range for fuel-air and fuel-air-inert gaseous mixtures is a task of great interest for safety recommendations in all domains of activity where flammable mixtures can be formed (Molnarne and Schröder, 2011).

Reliable, but conservative estimates of both the lower flammable concentration and limiting oxygen concentration for many fuels have been made using the limit heat of combustion of fuel-air mixtures (Britton, 2002). Most frequently, the prediction of the flammability limits of a gaseous mixture with or without inert addition was based on the assumption of a constant adiabatic flame temperature in the limit mixtures (Shebeko et al., 1982; Melhem, 1997; Mashuga and Crowl, 1999; Vidal et al., 2006; Hansen and Crowl, 2010; Liaw et al., 2012; Zlochower, 2012; Ma and Larranaga, 2014). Melhem (1997) developed a method for estimating the flammability limits of fuel-air and fuel-air-inert mixtures assuming that the chemical equilibrium is reached in the burned gas and the limit mixtures have a constant flame temperature. Using various threshold flame temperatures, he predicted the flammability ranges for mixtures of fuels and for gaseous mixtures where the initial temperature and pressure are different from ambient conditions, especially at high pressure. In a similar way, Vidal et al. (Vidal et al., 2006) used threshold values of adiabatic flame temperature for estimating LFL of several fuel-air mixtures. Ma and Larranaga (2014) acknowledged that the theoretical LFLs are generally lower than the experimental LFLs due to the assumption on constant flame temperature. So, the prediction is usually conservative, which is good for estimation purposes. The approaches based on the assumption of a constant adiabatic flame temperature (AFT) in limit mixtures differ by the method of computing the equilibrium conditions and the corresponding flame temperature. Other characteristic flammability properties, such as the normal burning velocity, have been used to provide threshold values for evaluating the composition of limit mixtures (Shebeko et al., 2002), based on the remark that an abrupt reduction in the heat release rate appears at these critical compositions.

For flammable mixtures of hydrocarbons, an interesting correlation was found by Chen et al. between the reciprocal of the upper/lower flammability limits and the reciprocal of the molar fraction of hydrocarbon in the hydrocarbon/inert gas mixture (Chen et al., 2009a; Chen et al., 2009b). The correlation was validated for hydrocarbon-air mixtures diluted with N_2 or with CO_2; the authors expected to extend it to non-hydrocarbon flammable compounds.

In other recent contribution, Di Benedetto (2013) proposed a method to determine the adiabatic lower and upper flammability limits, under zero losses of heat. The limiting concentration of fuel, at both lean and rich conditions, is assumed to be the concentration at which the heat produced by reaction allows the preheating of the unburnt mixture up to the ignition temperature, thus sustaining the flame propagation. In addition, the ignition temperature was assumed identical to the adiabatic flame temperature. The adiabatic flammability limits are intrinsic properties of the flammable mixtures that do not depend on the experimental conditions used and the adiabatic flammability range is much wider than that obtained by experiments.

A critical review of predictive methods for flammability envelopes has been recently made by Giurcan et al. (2013) who discussed their abilities and drawbacks. The thorough analysis of existing data on AFT of limit fuel-air and fuel-air-inert mixtures (Razus et al., 2004; Razus et al., 2006a) has shown that a considerable scatter of these AFT exists; therefore, the mapping of the flammability range by using threshold values of AFT is a rather rough approximation. The alternative procedure proposed in these contributions is based on the idea of proportionality between AFT^{LFL} (AFT of the fuel-air mixture at LFL) and AFT^{LOC} (AFT of the fuel-air-inert mixture at the extreme point of the flammability range, where LOC and MIC are defined) for each fuel and each inert gas. Therefore, knowing the LFL (and its characteristic flame temperature) one can easily find the composition of the fuel-air-inert mixture at its extreme point of flammability.

The purpose of the present work is to examine other properties of flammable mixtures, dependent on the available thermal energy supplied by combustion and on its release rate, such as the peak explosion pressure and the maximum rate of pressure rise reached in closed-vessel explosions, in order to find their threshold values at limit concentrations. Such threshold values might be used to estimate the flammability zone boundaries in fuel-air (or multiple fuels-air) and fuel-air-inert gaseous mixtures in order to reduce the amount of experimental work required to measure the flammability zone boundaries. This evaluation is based on new measurements of pressure evolution during closed vessel explosions of fuel-air and fuel-air-inert mixtures, using various hydrocarbons as test fuels at ambient initial pressure and temperature, completed by p_{max} and $(dp/dt)_{max}$ extracted from our previous publications or from other authors' publications.