



## Flammability parameters of liquified natural gas

Gianmaria Pio, Ernesto Salzano\*

Dipartimento di Ingegneria Civile, Chimica, Ambientale e dei Materiali, Università di Bologna, via Terracini 28, 40131, Bologna, Italy



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### ABSTRACT

The use of liquefied natural gas (LNG) is constantly growing. However, safety issues regarding cryogenic storage and transportation systems are still to be fully resolved. In particular, the evaluation of the efficiency of inerting systems for low-temperature LNG vapour is essential. In this work, the variation of the flammability range (in terms of lower and upper flammability limits and minimum oxygen concentration) obtained by adding nitrogen to pure air for some representative LNG mixtures has been evaluated at ambient temperature and at temperatures below 0 °C by using a detailed kinetic model entitled KIBO, which has been proved to be reliable for the description of C<sub>0</sub>–C<sub>4</sub> reactions in oxidative conditions, and by the limiting burning velocity theory.

Strong differences are reported among pure methane and natural gas mixtures for all the investigated temperatures. The effect of composition is therefore relevant. Furthermore, the obtained results suggest that the lower flammability limit is determined by thermal aspects at high temperature only, whereas at low temperature, kinetic limitations are more relevant.

### 1. Introduction

In recent years, the utilisation of natural gas or biogas for industrial and civil applications has considerably grown due to increased availability, reduced costs and low environmental impacts. However, the storage, handling and transportation processes of these fuels present several issues, particularly for cryogenic or cryo-compress technology, due to the possible inefficacy of the standard prevention and mitigation strategies, which may be adopted in the case of releasing of large amount of these gases from containment systems at temperatures consistently lower than ambient (Razus et al., 2006).

The aim of this work is to evaluate the efficiency of the inertisation of the vapours produced by liquefied natural gas (LNG) by nitrogen, taking into account the low temperature and the effect of actual composition of natural gas with respect to the standard assumption of pure methane.

For these purposes, the functional dependency of the lower and upper flammability limits (FLs) and the minimum oxygen concentration with temperature is needed. Clearly, standard empirical models have been first tested (see Li et al., 2017 for a complete review). These methods are, however, validated only for ambient (or more elevated) temperatures and may be completely inadequate at lower temperatures, due to the expected strong non-ideality of the physical properties affected by the proximity of the vapour temperature to the boiling temperature. As a consequence, the limiting burning velocity theory

(Hertzberg, 1984) based on a detailed kinetic model has been adopted. Moreover, a detailed kinetic model, entitled KIBO, which has been produced by the current authors based on the models developed by the University of California at San Diego (Combustion Research, 2018) for < C<sub>3</sub> compounds and the Lawrence Livermore National Laboratory (Curran et al., 1998) for C<sub>4</sub> proven as the optimized mechanism for the prediction of C<sub>0</sub>–C<sub>4</sub> oxidative reactions, in terms of both limited reaction number considered and accuracy with respect to experimental data (Pio et al., 2018), has been used.

### 2. Methodology

In order to evaluate the FLs and minimum oxygen concentration (MOC) for both pure fuels and mixtures, simple equations based on the mixture properties have been developed by using heat balance-based approaches (Eq. (1)). The main assumption regarding these methods is the hypothesis of constant adiabatic flame temperature (T<sub>F</sub>) in air for given operative conditions, i.e., FLs were calculated as a function of the effective heat of combustion (ΔH<sub>c</sub>) of the fuel mixture (e.g. Hanley's rule as reported in Hanley, 1998). For this reason, these methods are often regarded as adiabatic flame temperature methods.

$$FL = \Delta H_f / (\Delta H_c \cdot \dot{m}_U) \quad (1)$$

where ΔH<sub>f</sub> is the enthalpy variation from an unburned to a burned mixture and  $\dot{m}_U$  is the mass flowrate of the unburned mixture. To take

\* Corresponding author.

E-mail address: [ernesto.salzano@unibo.it](mailto:ernesto.salzano@unibo.it) (E. Salzano).

into account the variation in the mixture heat capacity due to product formation, reactant consumption and the increase in the mixture temperature occurring during the combustion phenomena, several numerical tools were developed to determine the critical adiabatic flame temperature (CAFT) (Razus et al., 2006). Alternative correlations have been proposed on the base stoichiometric equations, assuming the ratio of the FLs to oxygen required for the theoretical combustion constant, i.e., by using this approach, FLs were correlated with a stoichiometric concentration by using an empirical constant (e.g. Lloyd's rule as reported by Zabetakis, 1965, Eq. (2)).

$$FL = K \cdot x_{st} \quad (2)$$

where  $x_{st}$  is the oxygen molar fraction at stoichiometric conditions and  $K$  represents a universal constant equal to 0.55 for LFL and 3.5 for UFL. Clearly, the latter category directly derives from the assumptions made for the first group because of the oxygen calorimetry. Indeed, the constancy of heat released per unit mass of oxygen consumed during the combustion of commonly used organic materials ( $\Delta H_{ox}$ ) is also known as Thornton's rule, which has been widely used for decades.  $\Delta H_{ox}$  could be calculated by means of suitable software, based on chemical equilibrium calculations and a comprehensive database of thermodynamic properties. However, this value is widely assumed constant and is equal to 13.1 MJ/kg<sub>oxygen</sub> (Britton and Harrison, 2014). Furthermore, a stoichiometric-based methodology is usually preferred in the preliminary studies, since stoichiometric coefficients are theoretical values always available and easy to calculate, while the heat of combustion requires experimental determination and has some uncertainties.

Starting from these preliminary analysis, the effect of temperature on FLs can be estimated by using the classical Burgess and Wheeler correlation, modified by Zabetakis (1965) (Eq. (3)).

$$LFL(T) = LFL(T_0) + \frac{c_{p,u}}{(-\Delta H_c)} \cdot (T - T_0)$$

$$UFL(T) = UFL(T_0) - \frac{c_{p,u}}{(-\Delta H_c)} \cdot (T - T_0)$$

Where  $c_{p,u}$  is the heat capacity of the unburned mixture,  $T_0$  is the reference temperature and  $(-\Delta H_c)$  is the heat of reaction (heat of combustion) of the fuel. These correlations have large uncertainties, particularly when complex mixtures are adopted, and are not suitable at low temperatures.

In recent years, the availability of a fully validated detailed kinetic model and optimized numerical codes for the estimation of system reactivity for a wide range of conditions and compositions have pushed the development of more fundamental methodology, such as the limiting laminar burning velocity theory (Hertzberg, 1984), based on the detailed kinetic model, where the flammable zone is identified assuming the flammable limits as the condition at which the laminar burning velocity ( $S_u$ ) is equal to the threshold value ( $S_{u,lim}$ ) (Eq. (4)). The main advantage of this approach is represented by the possibility of estimating the coupled effect of initial temperature and composition at the same time.

$$S_{u,lim} = \sqrt[3]{2\alpha g \frac{\rho_b}{\rho_u}} \quad (4)$$

where  $\rho_u$  and  $\rho_b$  are the unburned and burned gas density, respectively,  $g$  is the gravitational acceleration and  $\alpha$  is the effective thermal diffusivity. This procedure is suitable for the estimation of light hydrocarbons safety parameters at low temperature (Pio and Salzano, 2018a). The adopted methodology can be schematized as in the Fig. 1.

In this work, the estimations of  $S_u$  and the other parameters given in Eq. (4) have been performed assuming one-dimensional, adiabatic flames by means of the KIBO model and the open-source code Cantera (Goodwin, 2003). KIBO is a detailed kinetic mechanism composed by 581 reactions and 128 species containing up to 4 carbon atoms,

including radicals. This model was already validated against experimental data of methane  $S_u$  at the investigated initial temperature (Pio and Salzano, 2018b) and light alkanes at room temperature (Salzano et al., 2018).

For the one-dimensional analysis, the setting slope was set to 0.07, the curve equal to 0.14 as grid parameters, the relative error criteria (RTol) and absolute error criteria (ATol) were equal to  $1.0 \cdot 10^{-9}$  and  $1.0 \cdot 10^{-14}$  for the steady-state problem and  $1.0 \cdot 10^{-5}$  and  $1.0 \cdot 10^{-14}$  for time stepping problem, respectively. See elsewhere for further details (Pio et al., 2018).

The analysed mixtures were unequivocally expressed by specifying the equivalence ratio ( $\varphi$ ), as defined in Eq. (5), and the molar fraction of diluent added and the fuel:

$$\varphi = \sum \frac{\left(\frac{Fuel}{Oxidant}\right)}{\left(\frac{Fuel}{Oxidant}\right)_{st}} \quad (5)$$

where the fuel and oxidant are molar fractions and the subscript  $st$  stands for stoichiometric conditions, calculated by the stoichiometric coefficient of the complete oxidation reaction of the corresponding fuel.

Considering the boundary conditions analysed, the large availability of inert gases needed for LNG application and the common practices for the inerting of LNG cargo tanks, the analysis of the diluent agent was restricted to nitrogen only (Siu et al., 1999). The MOC, as defined in the international standards (ASTM E – 681:2015; BS EN, 1839:2017), was estimated at the intersection point of the LFL and UFL curves with respect to diluent concentration, assuming 21%v/v as the oxygen content in air.

In order to analyse the effect of fuel composition, typical values for the concentrations of components in natural gas were considered as reported in the international standards (ISO 13686:2013; ISO 15403:2008). More specifically, binary and ternary mixtures of methane, ethane and propane containing up to 10%v/v of ethane and/or 5%v/v of propane in pure methane were investigated (Table 1).

Further information on the effect of temperature and composition on the chemical aspects were obtained by means of sensitivity analysis at lean ( $\phi = 0.5$ ) and rich ( $\phi = 2.0$ ) conditions for all the investigated mixtures, calculating the normalised sensitivity coefficient (NSC) as in the following equation.

$$NSC_i = (k_i/S_u) \cdot \frac{\partial S_u}{\partial k_i} \quad (6)$$

where  $k$  is the reaction rate coefficient and the subscript  $i$  represents the  $i$ -th reaction.

The reactions were sorted by decreasing absolute value of NSC to highlight the most relevant in the studied conditions and evaluate the effect of initial temperature and composition on the reaction paths.

### 3. Results and discussion

In this section, the flammability limits of natural gas mixtures in air obtained by the detailed kinetic model KIBO and using the limiting burning theory are first reported (Table 1). Data for pure light alkanes (i.e. methane, ethane and propane) were added to facilitate further comparisons and discussions. It should be noted that the results at 200 K for the mixture containing propane were not reported, since it was liquid at that temperature and the corresponding equilibrium composition in the vapour mixture is negligible. The numerical results were compared with the experimental data (Table 2) reported by Cui et al. (2016) and Li et al. (2011) for low temperature methane, by Liao et al. (2005) for natural gas at room temperature, by Shen et al. (2017) for methane/ethane mixtures and by Woodward and Pitblado (2010) for mixtures containing propane and ethane.

The magnitude of the experimental data range for the FLs underlines the variability of the experimental data, which may be attributed

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