



The effect of ultra-low temperature on the flammability limits of a methane/air/diluent mixtures

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ABSTRACT

Natural gas represents an attractive fuel for industrialized and developing countries seeking an alternative to petroleum. Due to economic and safety considerations, liquefied natural gas (LNG) at cryogenic conditions is preferred for storage and transportation. The main drawback is the poor understanding of the physical and chemical phenomena that occur at the storage conditions of liquid methane, i.e. at ultra-low temperatures around 110 K and, if released, at temperatures below ambient. In this work, a procedure to evaluate the laminar burning velocity, the flammability limit (FL) and the limiting oxygen concentration (LOC) of methane-air-diluent mixtures based on detailed kinetic mechanism at ultra-low temperatures is proposed. The estimation of the FL was obtained with the limiting burning velocity theory. The effects of inert content (extinguishing) and agent (N_2 , H_2O and CO_2) on FL were evaluated and compared with data retrieved from the literature. The agreement between experimental observation and model results from 200 K–300 K incentivizes the adoption of the new procedure for further studies of fuel reactivity and safety parameters. Moreover, the proposed procedure may be suitable for the estimation of the safety parameters of complex fuel mixtures whose composition is closer to the actual values of LNG.

1. Introduction

In the recent years, researchers have focused on developing methods and technologies that allow the extensive use of liquefied natural gas (LNG) as a convenient fuel supply [1]. Natural gas shows a larger energy-to-volume ratio and lower levels of CO_2 , SO_x and NO_x production in combustion processes with respect to conventional fuels. This attribute makes it particularly suitable for marine propulsion due to more stringent SO_x emission limitations required by law in the near future [2]. Indeed, natural gas undergoes several purification processes. The liquefaction can take place only when the treated stream is mainly composed of methane and a small amount of light hydrocarbons [3]. In order to promote the use of LNG worldwide, deep knowledge of the safety hazards is required to develop suitable storage and transportation systems. In this regard, qualitative risk assessment (QRA) represents a powerful feature to indicate process critical points, improve the design and handling procedures and evaluate accidental scenario consequences. A comprehensive study on the identification of initiating events, definition of event trees and safety barriers, evaluation of accidental scenarios and case histories of LNG incidents was reported by Siu et al. (1999) [4]. They concluded that quantitative investigations are required and recommended additional studies regarding key

phenomenology during LNG accidents. Recently, particular attention has been paid to the study of the consequences of LNG spills close to seawater because of the transportation system commonly used for this fuel [5]. Indeed, under certain conditions, cryogenic liquid release can generate an intense heat transfer with other fluids (i.e. seawater) and give rise to rapid and large-scale evaporation of LNG. This phenomenon is called rapid phase transition (RPT) [2]. The event tree for an LNG spill is shown in Fig. 1, where rapid phase transition (RPT), cloud dispersion (CD), flash fire (FF) and pool fire (PF) are considered as final events.

Vandebroek and Berghmans (2012) [2] concluded that the main hazard connected to LNG storage is its vapor dispersion. Indeed, flammable vapour can diffuse for kilometres or be ignited and cause large-scale fires or even explosions in the case of elevated confinement [6]. Moreover, if instantaneous ignition occurs, a large-scale LNG pool fire may follow. Although effort has been made to develop accurate empirical and theoretical models suitable for the description of a pool fire [6,7] and vapour dispersion [8,9] of cryogenic fuels, the lack of experimental data on LNG fires results in the lack of validation of the mathematical models. That represents a serious limitation, in particular for the gas cloud formation, its spread and the time of ignition [10].

The data reported by Cui et al. (2016) [11] and Li et al. (2011) [12],

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Nomenclature

α	Thermal diffusivity
ρ	Gaseous density
ΔH_c	Heat of combustion
ATol	Absolute error criteria
CD	Cloud dispersion
c_p	Heat capacity
Exp	Experimental data
FB	Fractional bias
FIP	Fuel inertization point
FF	Flash fire
FL	Flammability limit
g	Gravitational acceleration
LFL	Lower flammability limit
LOC	Limiting oxygen concentration
N	Number of observations
NMSE	Normalized mean square error

Num	Numerical data
PF	Pool fire
RPT	Rapid phase transition
Rtol	Relative error criteria
S_u	Laminar burning velocity
$S_{u,lim}$	Limiting burning velocity
T_0	Reference temperature
UFL	Upper flammability limit

Subscripts

av	Averaged value
b	Burned conditions
H ₂ O	Water as diluent
CO ₂	Carbon dioxide as diluent
i	i-th observation
N ₂	Nitrogen as diluent
u	Unburned conditions

obtained by means of an explosion vessel, represent rare cases of experimentally determined methane flammability limits (FLs) at ultra-low and low temperatures. On the other hand, several numerical correlations for FL estimation exist. The comparative analysis among estimation methods carried out by Van den Schoor et al. (2008) [13] indicated that limiting burning velocity theory has the best potential for FL estimation because it considers both chemical aspects and natural convection, although approximately. The application of a suitable correlation to estimate the effect of initial temperature on FLs could be useful to remove the commonly used conservative assumption of constant FLs equal to the one at room temperature because this leads to large errors [11]. Moreover, additional information concerning the effect of dilution on system reactivity should be beneficial. In this regard, De Persis et al. (2013) [14] and Chan et al. (2015) [15] reported an S_u of CH₄/O₂/N₂/CO₂ mixtures measured by means of a spherical combustion chamber and flat burner, respectively. Numerical methods, such as critical adiabatic flame temperature [16] at the FL and the extended Le Chatelier's mixing rule [17], are applied to estimate safety parameters of hydrocarbons/air/diluent mixtures.

Dry chemical powders (e.g. bicarbonate salts), high-expanding foams, H₂O, inert gases and CO₂ inertization are considered to be the main extinguishing agents for dealing with liquefied gas fires [18]. In this sense, McGuire and White (2008) [18] carried out a detailed analysis and concluded that the main drawbacks of dry chemicals are the negligible cooling effect that leads to reignition hazards and the inactivity in combination with H₂O. Moreover, high-expanding foams should be applied exclusively from a relevant distance with respect to the fire source, which makes them ineffective for fire-fighting on LNG

ships. Water should not be present close to a burning LNG pool because it could represent a heat source that increases the vaporization rate, whereas water spray can be used to provide radiation protection for personnel. CO₂ is preferred to N₂ for fast inertization in cargo-related spaces because of larger flow rate. However, this procedure requires the evacuation of all personnel because CO₂ suppresses combustion displacing O₂ in the atmosphere.

In light of these considerations, the aim of this work was to develop and validate an effective tool and procedure for the evaluation of safety parameters at low temperatures, starting from a detailed kinetic mechanism. In particular, the effect of temperature and several diluents (e.g. N₂, H₂O and CO₂) were evaluated by considering LNG as pure methane because of its abundance. The proposed procedure could be applied to complex mixtures in order to evaluate the effect of fuel composition as well.

2. Methodology

In this work, the S_u , the thermodynamic properties and the transport coefficients of a methane-air mixture were calculated by means of the Cantera code [19] and the detailed kinetic model developed by the University of Bologna (KIBO) that combined the mechanism developed by the University of California at San Diego (UCSD) [20] and Lawrence Livermore National Laboratory [21]. This approach was used because previous studies indicated this to be a suitable model for the estimation of light hydrocarbon oxidation at atmospheric pressure [22] and methane at low temperature [23,24] for a wide range of compositions. A grid sensitivity analysis was performed to obtain the optimized numerical parameters in terms of result accuracy and computational time required for the simulation. To this aim, the slope and curve parameters were considered, representing the maximum fractional change in the value and in the derivative of each adjacent cell solution, respectively [19]. The S_u of the stoichiometric methane/air mixture at 300 K was selected as the base condition because of the elevated reactivity with respect to the other conditions. This was estimated by changing the curve values and keeping the slope constant, at first. Once the optimized curve value was found, the slope was varied. The slope value that was chosen was 0.07, being the default value adopted for a similar simulation in the utilized code [19]. The ranges within the slope and curve were 0.01–1, since the lower limitation related to the maximum grid number allowed ($= 1000$) and upper limitation related to the achievement of constant S_u exist. The obtained results are reported in Fig. 2.

It is worth noting that the differences between the obtained results are within the 3% of the final value for all the investigated conditions,

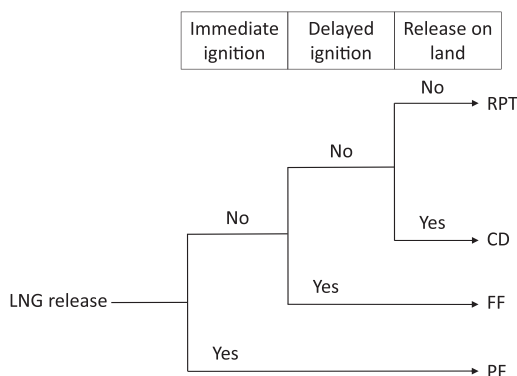


Fig. 1. Event tree for LNG release where RPT = rapid phase transition, CD = cloud dispersion, FF = flash fire and PF = pool fire.

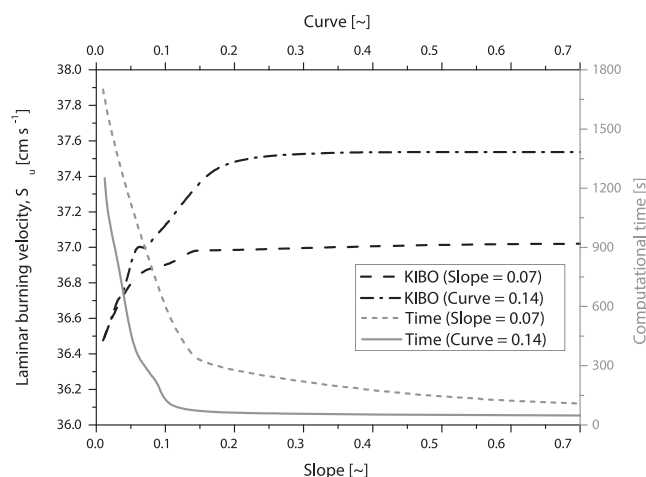


Fig. 2. Grid sensitivity for methane/air at 300 K.

whereas the computational time strongly decreases with the increase of grid parameters. Hence, the grid parameters can be optimized, considering both the variation in the obtained estimation and the required computational time, by adopting the grid values giving the average value of the laminar burning velocity. The main parameters and corresponding values used in this work were determined to be: slope equal to 0.07 and curve equal to 0.14 as grid parameters, relative error criteria (RTol) and absolute error criteria (ATol) 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.

The FLs were estimated by applying the limiting burning velocity theory [25], since previous studies have indicated this approach suitable for the estimation of the safety parameters of light hydrocarbons at low temperature [26], i.e. the FLs were assumed equal to the fuel mole fraction such that the $S_{u,lim}$ results were equal to a threshold value regarded as the limiting burning velocity ($S_{u,lim}$). This was calculated by using the correlation reported by Hertzberg (1984) [25] (Equation 1).

$$S_{u,lim} = \sqrt[3]{2\alpha g \frac{\rho_b}{\rho_u}} \quad (1)$$

where ρ_u and ρ_b are the unburned and burned gas density, respectively, α the thermal diffusivity of gaseous mixture and g the gravitational acceleration.

The same methodology was applied to estimate the S_u for the methane-air-inert mixture, where the inert was N_2 , H_2O or CO_2 in the range of 150 K–300 K, since the phase transition and strong non-ideality make the use of diluents disadvantageous. The obtained results were used to predict the effect of the initial temperature, diluent species and concentration of the FL of methane at room and low temperature. The limiting oxygen concentrations (LOC) were also calculated. This parameter is defined as the maximum concentration of oxygen in such a fuel-oxygen-inert mixture at which an explosion cannot occur as stated by European Standard EN 14756:2003 [27]. This value is mainly affected by the experimental rig, temperature, diluent concentration, turbulence, thermal and chemical properties.

The estimation quality with respect to the experimental data available in the literature was evaluated numerically by applying a statistical approach to unify data obtained at different conditions in two parameters (Eq. (2)). More specifically, the fractional bias (FB) and normalized mean square error (NMSE) were calculated to evaluate the overall accuracy of the model in terms of average value and random scatter of data, respectively.

$$FB = 2 \cdot \sum_i (Exp_i - Num_i) / \sum_i (Exp_i + Num_i)$$

$$NMSE = \sum_i (Exp_i - Num_i)^2 / (N \cdot Exp_{av} \cdot Num_{av}) \quad (2)$$

where Exp and Num stand for the generic experimental and numerical value, respectively. The subscripts i and av are the observation and the average value, respectively, and N is the observation number. These parameters were already adopted for the sake of the LNG vapour dispersion model evaluation [28]. Models are commonly accepted if the absolute value of the FB is smaller than 0.3 and the NMSE is smaller than 0.5 [29].

3. Results and discussion

In this section, the effects of ultra-low temperature, diluent species and concentration on safety parameters are shown and discussed. The model results are also compared with experimental data retrieved from the literature, where available.

3.1. Temperature effect on FLs

In this section, the lower flammability limit (LFL) and upper flammability limit (UFL) were estimated. The calculated $S_{u,lim}$ at lean and rich conditions were equal to 4.33 cm s^{-1} and 4.15 cm s^{-1} , respectively, in accordance with the methane upper limit of 5 cm s^{-1} observed by Ronney et al. (1985) [30]. These values were first used to predict the FLs at room temperature and pressure for the sake of validation. The results were compared with data reported by Coward and Jones (1952) [31], Chen et al. (2009) [16] and Li et al. (2011) [12] (Table 1).

The scattered UFL data did not allow an effective model evaluation, whereas the LFL predicted and reported data fit well together. However, it should be noted that all reported experimental values were slightly lower than the UFL model prediction, suggesting the presence of conservative assumptions on the safe side.

Once validated, the methodology was applied to the evaluation of the same parameters at a lower temperature. The $S_{u,lim}$ values are reported as a function of temperature and composition in the Table 2.

It is noteworthy that the reported values of $S_{u,lim}$ are weakly dependent on the gaseous composition and mostly affected by the initial temperature. The results indicate that the reason for this phenomenon is the negligible variation in both density ratio and effective diffusivity at different compositions. This trend should be attributed to the similar adiabatic flame temperature, burned mixtures properties and composition (mostly represented by N_2). Starting from these considerations, further analysis to evaluate the truthfulness of the commonly used hypothesis of constant adiabatic flame temperature at the composition for the FL was carried out. In this regard, the simplified correlations (Eq. (3)) developed by Zabetakis and co-workers [32] from the Burgess-Wheeler law were considered because they have been viewed as a benchmark in the evaluation of predictive correlations for the temperature effect on the FLs estimation by Mendiburu et al. (2017) [33].

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

$$UFL(T) = UFL(T_0) - \frac{c_{p,u}}{(-\Delta H_c)} \cdot (T - T_0) \quad (3)$$

Table 1

FLs for methane-air mixture at atmospheric pressure and room temperature.

	LFL [% v/v]	UFL [% v/v]
Li et al. (2011) [12]	4.97	15.70
Chen et al. (2009) [16]	4.98	14.95
Coward and Jones (1952) [31]	5.00	15.00
KIBO	4.99	15.89

Table 2

$S_{u,lim}$ for methane-air mixture at atmospheric pressure with respect to initial temperature.

T [K]	$S_{u,lim}$ (Lean) [cm s^{-1}]	$S_{u,lim}$ (Rich) [cm s^{-1}]
300	4.33	4.15
250	3.66	3.68
200	2.98	3.00
150	2.27	2.28

where $c_{p,u}$ represents the average heat capacity of unburned mixture at constant pressure, T_0 a reference temperature and $(-\Delta H_c)$ the specific heat of reaction of methane complete oxidation.

A comparison between the numerical predictions and experimental data reported by Cui et al. (2016) [11], Li et al. (2011) [12] and Siu et al. (1998) [4] for FLs as a function of initial temperature is reported, as shown in Fig. 3.

As expected, upon decreasing the initial temperature, the LFL increases and the UFL decreases, which makes the flammability zone narrower. It is noteworthy that the UFL was more affected by the change in initial temperature with respect to the LFL, which shows a nearly linear trend. This confirms the greater relevance of chemical aspects on the UFL with respect to the LFL. Hence, the commonly used assumption of constant FLs equal to the one observed at room temperature, i.e. 5% v/v and 15% v/v, leads to systematic errors up to 30%.

The increasing complexity of phenomena occurring at low temperature and rich conditions generates discrepancies among the linear trend expressed by the Zabetakis correlation and experimental observations reported in this work. Remarkably, the kinetic model estimation of the LFL and UFL is close to the experimental data at all investigated conditions, demonstrating the suitability of this model and procedure even at temperatures close to methane boiling point, where strong non-idealities were expected. This appears to be the first time that an effective procedure for FL evaluation through S_u simulations was successfully employed for methane at ultra-low temperature (120 K–300 K).

3.2. Dilution effect on FLs

The dilution effect of N_2 , H_2O and CO_2 on FLs for methane-air mixtures was evaluated at atmospheric pressure and 300 K. The model results were compared with experimental data and a simplified correlation retrieved from current literature (Fig. 4). More specifically, experimental data for N_2 dilution by means of an explosion vessel obtained by Li et al. (2011) [12] and Kondo et al. (2006) [17] and a numerical estimation carried out by using the extended Le Chatelier's rule for inert dilution reported by Chen et al. (2009) [16] were considered.

Unlike the UFL, the LFL was weakly affected by N_2 dilution and is almost constant at several diluent concentrations. On the other hand, the H_2O and CO_2 dilution strongly affect both FLs. This well-known behaviour can be explained considering that the presence of H_2O and CO_2 hinders complete methane oxidation by a thermodynamic point of view. This occurs because these compounds represent the reaction products and increase the effectiveness of the thermal dilution effect respect to N_2 . In addition, they decrease the fuel and oxygen concentrations in the unburned gas mixture, as expected for all diluents, and lead to a smaller flammability zone. Both the experiments and model indicate CO_2 as the most effective among the studied diluents, probably because of its peculiar physical properties that allow quick penetration through the flammable gaseous mixture [34]. In addition, results showed that the inert ability follows the same order of the mean molar heat capacities calculated between the initial and adiabatic flame temperatures ($CO_2 > H_2O > N_2$). Results are in accordance with observations reported by Thyer et al. (2009) [34]. The proposed

methodology has the potential to create an easier procedure for the classification and identification of extinguishing agent properties affecting inertization ability, which represents a crucial step for hazard mitigation material development and preparation.

Supplementary relevant information deducible from flammability diagrams could be the fuel inertization point (FIP) that corresponds to the maximum ratio of fuel to diluent that can give a flammable mixture whatever air is added or subtracted and represented by the envelope point of LFL and UFL curves. The LOC could be also expressed as the oxygen concentration at the FIP. In this work, LOCs were estimated assuming 21% v/v of oxygen in air mole fraction, calculated as a complementary compound of fuel and added diluent at the condition represented by FIP. Results showed in Table 3 confirm the aforementioned considerations on the inert ability of the studied gas, since a lesser amount of oxygen was required to create a flammable mixture for the case of N_2 with respect to H_2O and CO_2 .

In the following section, the authors will analyse and discuss the effect of N_2 dilution at low temperature on the methane/air mixture exclusively. The N_2 represents the worst diluent and the only one that did not undergo a phase transition in the investigated temperature range. Moreover, in some cases, cryogenic N_2 is already produced on LNG ships and used to prevent the formation of flammable mixtures [18]. Fig. 5 shows the effect of temperature and diluent concentration on FLs of methane-air- N_2 mixtures and compares numerical estimations with experimental data at 150 K, 200 K, 250 K and 300 K.

It should be highlighted that the calculated flammability diagrams at cryogenic temperatures are slightly narrower than experimental data. This suggest the need for further refinement in the kinetic model and procedure to be more suitable for FLs prediction of N_2 diluted gas at ultra-low temperatures. The observed discrepancies between the experimental data and the corresponding numerical results can be partially related to the database that was adopted for the estimation of the mixture thermal properties, which was limited in terms of range of applicability with respect to the temperature. Indeed, the data were extrapolated for ultra-low temperatures.

The values of the LOCs were calculated by using the same procedure and assumptions previously described for the study of the room temperature case. The obtained results are shown in Table 4.

As a consequence of the model underestimation, the calculated LOC values are higher than the literature data. In both cases, the discrepancies among the experiments and model are conservative and could be attributed to the assumption of perfectly adiabatic conditions and one-dimensional flames. However, the adopted procedure and model could be considered as an effective and easy method for safety

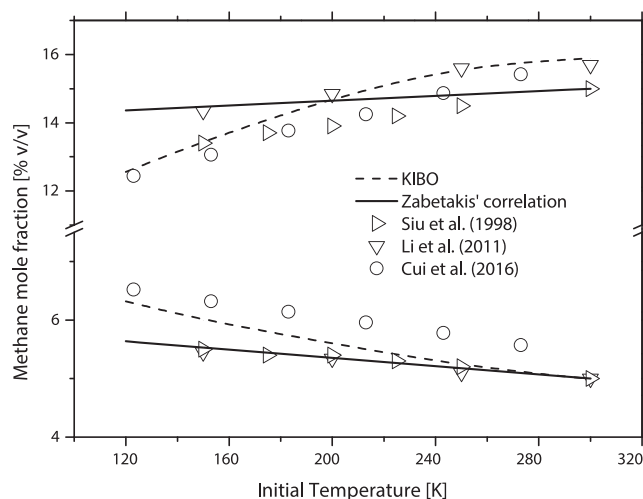


Fig. 3. Experimental (symbols) and calculated (lines) LFL and UFL at atmospheric pressure with respect to initial temperature.

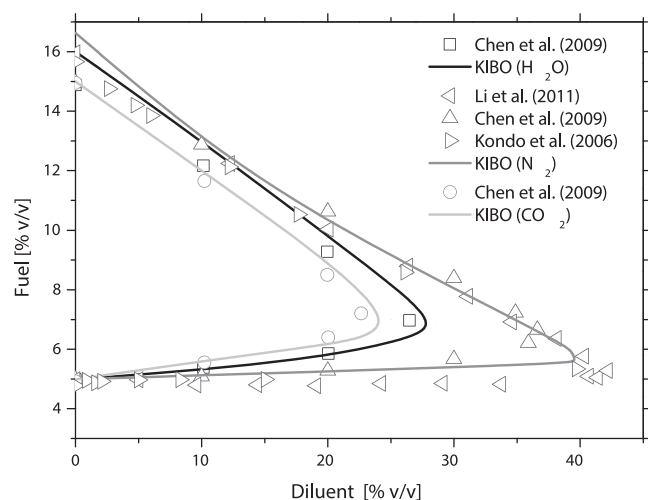


Fig. 4. Experimental (symbols) and calculated (lines) LFL and UFL for diluted methane-air mixtures at atmospheric pressure with respect to diluent concentration and used diluent. Note that the squares represent H₂O, triangles N₂ and circles CO₂ dilution.

Table 3
Diluent effect on methane LOC at room temperature and atmospheric pressure.

	LOC _{N2} [% v/v]	LOC _{H2O} [% v/v]	LOC _{CO2} [% v/v]
Li et al. (2011) [12]	11.03	–	–
Chen et al. (2009) [10]	11.92	13.98	14.73
KIBO	11.50	13.57	14.28

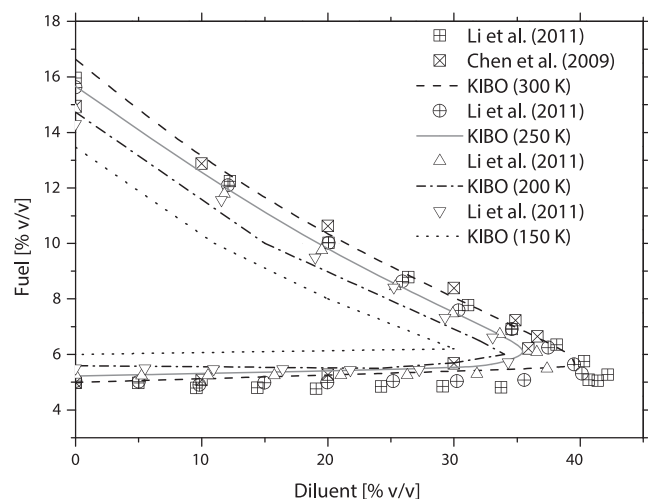


Fig. 5. Experimental (symbols) and calculated (lines) LFL and UFL for diluted methane-air mixtures at atmospheric pressure with respect to diluent concentration and initial temperature.

Table 4
Temperature effect on methane LOC_{N2} at atmospheric pressure.

T [K]	LOC _{N2} (Num) [% v/v]	LOC _{N2} (Exp) [% v/v]
150	13.40	12.60
200	12.60	12.00
250	12.18	11.46
300	11.50	11.03

parameter estimation.

To evaluate the prediction quality of the proposed technique with respect to experimental data, suitable indexes were calculated. The results of the overall statistical analysis are reported in Table 5 in terms of FB and NMSE as a function of the analysed safety parameters.

It should be noted that the aforementioned acceptance criteria for the estimation quality were respected for all the investigated conditions; thus, the applied approach can be considered as suitable for the estimation of safety parameters of methane at cryogenic conditions. Moreover, a slight improvement in the accuracy of the effect of low temperature on FLs is reported with respect to Zabetakis rule. The FB and NMSE are equal to $-3.91 \cdot 10^{-2}$ and $1.51 \cdot 10^{-3}$, respectively; thus, both the absolute values are greater than the corresponding values reported in Table 5.

4. Conclusions

The effect of the initial temperature, diluent and gaseous composition on the methane-air-diluent system reactivity and flammability at atmospheric pressure was studied. A procedure for FLs and LOC estimation from $S_{u,lim}$ data was applied by using the limiting burning velocity theory reported by Hertzberg (1984) [25] and a detailed kinetic mechanism. Comparing $S_{u,lim}$ calculated as function of temperature and composition (rich and lean conditions), it could be concluded that a change in the initial temperature had more relevance with respect to gaseous composition on $S_{u,lim}$.

Model predictions were found to be in accordance with experimental data retrieved from the literature, claiming the applicability of the described procedure for the evaluation of safety parameters at low temperature considered in this work. As expected, both increased diluent concentration and decreased initial temperature led to a narrower flammability zone due to the higher LFL and smaller UFL values.

In particular, it was found that the UFL was more affected by these conditions with respect to the LFL. The authors suggest the higher relevance of radical aspects with respect to heat transfer phenomenon in rich mixture cases as a possible explanation for reported behaviour. Such trends have already been reported in the literature and confirmed by the fact that the proposed methodology is more suitable for UFL prediction with respect to simplified correlations proposed in the literature (e.g. Zabetakis correlation and extended Le Chatelier's rule), developed by thermal based hypothesis. The N₂, H₂O and CO₂ diluent agent's ability was evaluated by computing the LFL and UFL at several dilution concentrations at room temperature and atmospheric pressure. The LOCs were evaluated in these conditions by estimating the flammability diagrams following the procedure described by the European Standards EN 14,756:2003 [27]. The obtained results were in agreement with experimental data retrieved from the literature. It could be concluded that the more the mean molar heat capacity between the initial and adiabatic flame temperatures, the higher inert ability.

Further analysis was carried out to determine the flammability diagrams at different initial temperatures in the range of 150 K–300 K. The discrepancies among the model results and experimental data of LOCs and FLs for diluted mixtures could be due to the assumption of perfectly adiabatic conditions and one-dimensional flames used for the S_u predictions and the limited availability of thermal properties at ultra-low temperatures. Their assumptions may not fully represent the experiments. Overall, statistical analysis indicated that the proposed approach is suitable for the evaluation of the safety parameters of methane at cryogenic temperatures and in the presence of common inert agents because the acceptance criteria were respected in all the investigated conditions. Moreover, the application of a kinetic-based methodology allowed for the estimation of fuel composition on LNG safety parameters. In this case, there would be the potential to assess the validity of the simplification to pure methane, which is commonly adopted in computational fluid dynamics (CFD) to model accidental scenarios involving LNG release.

Table 5

FB and NMSE with respect to the estimated parameter.

	FLs	LOC _{CO2}	LOC _{H2O}	LOC _{N2} at 300 K	LOC _{N2} at 250 K	LOC _{N2} at 200 K	LOC _{N2} at 150 K
FB	-2.31×10^{-2}	-9.57×10^{-3}	-3.69×10^{-2}	7.87×10^{-2}	1.18×10^{-2}	2.04×10^{-2}	-3.92×10^{-2}
NMSE	1.41×10^{-3}	4.49×10^{-4}	2.00×10^{-3}	1.04×10^{-2}	6.78×10^{-3}	5.65×10^{-4}	2.94×10^{-3}

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