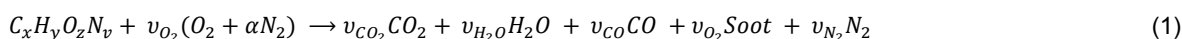# Numerical Simulation of Multi-Component LNG Pool Fire

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The release of large amount of liquefied natural gas from fixed or mobile equipment may induce to pool fire when immediate ignited. The prediction and simulation of this phenomenon is very complex because several premixed, convective and diffusive burning phenomena, and rapid phase evaporation, are involved simultaneously. Nevertheless, the use of Reynolds-averaged Navier-Stokes (RANS) equations with k-ε model for turbulence and classical models are still adopted, although strong uncertainties and over-simplifications with respect to the real scenario. More recently large-eddy simulation (LES) modeling, as adopted in some codes as FLUENT or FDS, has been adopted. LES methodology is able to introduce more detailed information on the chemical kinetic of the oxidation reactions. Again, however, poor kinetic combustion mechanisms suitable for the implementation in computational fluid dynamic (CFD) codes, and simplified composition for the LNG - often treated as pure methane - are typically adopted. In this work, the simulation of a LNG pool fire was performed by detailed (reduced) kinetic model validated for multi-component LNG compositions by using FDS. Results were compared with both experimental and numerical analyses retrieved from literature. This approach has the potential to correctly estimate the heat radiation and the production rates of the main reaction products, including soot.

1. Introduction

Pool fires are typically represented as an inclined cylindrical flame over the fuel liquid surface, thermal radiation is estimated by surface emitter model, considering its magnitude proportional to the flame temperature and emissivity, as described by the Boltzmann law (Bubbico et al., 2016). Several empirical and semi-empirical correlations to estimate the geometrical dimensions of the pool fire (height, diameter, tilt angle in the wind direction), thermal radiation and burning rate are presented in the current literature (Babrauskas, 1983)(Drysdale, 2011). Computational fluid dynamics (CFD) is often applied to assess the evolution and the thermal effects of the pool fire. To this aim, large eddy simulation (LES) are currently considered an optimized tool from the technical and economical point of view. In this study, fire dynamic simulator (FDS) was adopted, because utilized models have been extensively validated and commonly used for the pool fire scenarios (McGrattan et al., 2017). However, the use of simplified kinetic model represents a strong limitation in case of non-standardized conditions. Indeed, single-step, mixing controlled combustion model (Eq. 1) needs the definition of product yields for the studied species as input data. However, comprehensive database or empirical-based correlations to consider the composition and ambient conditions including ventilation does not exist.

$$C_xH_yO_zN_v + v_{O_2}(O_2 + \alpha N_2) \longrightarrow v_{CO_2}CO_2 + v_{H_2O}H_2O + v_{CO}CO + v_{O_2}Soot + v_{N_2}N_2 \qquad (1)$$

v represents the stoichiometric coefficient of the corresponding chemical species in the overall reaction, and soot is commonly considered as a pure substance having the ration C/H = 10. On the other hand, the LES methodology has the potential to include kinetic models suitable for the description of the chemistry occurring in the presence of flame. On this regard, several detailed kinetic models suitable for a wide range of conditions in terms of temperature, pressure and composition are available in the current literature. However, the number of reactions and species considered in these mechanisms, although in the reduced or skeletal versions, limits the implementation in CFD codes when describing realistic and complex scenarios (Lu and Law, 2009).

Several tools, such as the sensitivity analysis, were commonly adopted to individuate the main reactions involved in the studied conditions. As well-known, the production of soot particles produced in non-negligible quantity by diffusion flames affects the human health and environment, summoning the researcher's attention for the development of accurate models to estimate and reduce the production (Schulz et al., 2018). However, understanding the soot formation process requires suitable gas-phase kinetic models for fuel rich chemistry and physical models for the description of particle formation, heterogeneous growth and agglomeration. This process is commonly divided in four different phases: the formation of soot precursors, also referred as soot particle inception, the particles aggregation, the surface growth and the oxidation of produced particles. The commonly adopted approach to model the first step is the estimation of the production rate of polycyclic aromatic hydrocarbons (PAHs), assumed as precursors of soot particles in the gaseous mixture (Sánchez et al., 2012). Quite clearly, the PAH production rate is sensible to the fuel composition. However, the particle size distribution is qualitatively similar for light hydrocarbons flames (Lin et al., 2018), thus the chemical aspects have significant effect on the precursors formation only. Another important issue concerning the modelling of pool fire is the accurate prediction of the evaporation rate as a function of atmospheric conditions, release conditions and scale. Several empirical models have been developed and are available in the current literature. However, a limited number of these models can be successful applied to the cryogenic scenarios, where the peculiarity of the studied conditions required tailor made experiments to validate and enlarge the validity of these correlations. Indeed, complex physics like LNG flashing could not be evaluated by means of phenomenological models, whereas the application of integral models (e.g. PHAST) fail when the assumption of uniform pool thickness cannot be applied or in case of scenarios involving obstacles (Gopalaswami et al., 2017). In contrast with the case where pure methane was adopted it should be also considered that the evaluation of realistic compositions for LNG affects the evaporation rate, because the remaining liquid composition is dependent on the time, resulting in variations of the boiling temperature and the heat of vaporization; as well as vapour composition, affecting the heat transfer coefficient, and the boiling regime at the later stages. These observations result in significant discrepancies among pure methane and LNG vaporization rate, especially at the later stage of the spill (Conrado and Vesovic, 2000).

2. Methods

Three different compositions of LNG were investigated to assess the effect of the addition of light alkanes (i.e. ethane and propane) to methane combustion at cryogenic conditions. The compositions were individuated assuming the maximum allowed content of ethane and propane, as indicated in the ASTM E-681: 2015. More specifically, binary fuel mixture containing 10 % v/v of ethane in methane (Mix 2) and ternary fuel mixture consisting of 10 % v/v of propane, 10 % v/v of ethane in methane (Mix 3) were analyzed (Table 1).

Table 1 Summary of the mixture composition analysed in this work.

Mixture	CH_4 [% v/v]	C_2H_6 [% v/v]	C_3H_8 [% v/v]
Mix 1	100	0	0
Mix 2	90	10	0
Mix 3	80	10	10

A detailed kinetic model, entitled KIBO, has been recently produced by the current authors (Pio et al., 2018), proven as the optimized mechanism for the prediction of C_0–C_4 oxidative reactions at the investigated conditions (Pio and Salzano, 2018a) and validated for the evaluation of safety parameters and system reactivity for methane-based fuels (Salzano et al., 2018)(Pio and Salzano, 2019). In order to reduce the number of reactions and compounds considered without relevant reduction in the estimation quality of kinetic model and main combustion products distribution (e.g. CO_2, H_2O, CO and soot), a sensitivity analysis and reaction path analysis were performed at different temperatures and equivalence ratio by using the open source code Cantera (Goodwin, 2003). The main combustion products and the resulting reactions were sorted according to their relevance in the reaction system, expressed in terms of normalized sensitivity coefficients (NSCs); i.e. the absolute value of the NSC of each reaction was calculated and adopted as sorting criteria for each studied condition. Then, values corresponding to the obtained ranking were attributed, summed and utilized to sort the reactions. Further information on the adopted procedure can be found elsewhere (Pio and Salzano, 2018b). The evaporation rate for cryogenic liquid was modeled assuming that it was governed by Stefan diffusion, as described in the Equation 2

$$\dot{m}'' = h_m \left(\frac{P \cdot W_f}{R \cdot T_g} \right) ln \left(\frac{x_{f,g} - 1}{x_{f,l} - 1} \right) \qquad (2)$$

where P stands for pressure, T_g for gas temperature, $x_{f,g}$ for the fuel vapor volume fraction in the grid cell adjacent to the pool surface, $x_{f,l}$ for the fuel volume fraction in the liquid mixture, W_f for the molecular weight of the fuel gas, R for the ideal gas constant and h_m is the convective mass transfer coefficient calculated by using the correlation (Equation 3) expressed in terms of the dimensionless number Sherwood (Sh), Schmidt (Sc) and Reynolds (Re),

$$Sh = \frac{h_m L}{D_{l,g}} = 0.037 \cdot Sc^{1/3} \cdot Re^{4/5}$$
(3)

where L is the length scale and $D_{l,g}$ the mass diffusivity. Physical properties of the analyzed species (i.e. methane, ethane, propane, carbon monoxide, carbon dioxide, nitrogen, oxygen, water and soot) and their dependence on the temperature were estimated by using the thermodynamic and transport coefficient databases included in the KIBO mechanism, for LNG compounds, and default values included in the FDS package for the other species, since negligible discrepancies were observed among these data at temperature above the room temperature. Further information regarding the adopted models for the dispersion of the LNG vapor can be found elsewhere (McGrattan et al., 2017). By combining these approaches, the LNG pool fire scenario was evaluated for the aforementioned fuel compositions, at homogeneous initial room temperature of 20 °C. A pool of 1 m x 1 m x 0.01 m was modelled to evaluate the small-scale case, assuming open field, absence of obstacles and wind. For the sake of computational time reduction, a symmetry plane was considered, so that the system was simplified to a 2-dimensional domain. Suitable devices were placed at several distances from the pool to evaluate the distribution of temperature, reactants and main combustion products (i.e. CO, CO_2 and H_2O) volume fraction and heat radiation with respect to the position and time. Finally, the floor was modelled as concrete having thermal conductivity of 1.65 W/(mK), as reported in the international standard EN-ISO 10456:2007. To perform quantitative comparison of the soot formation between the investigated mixture, the total mass of produced soot (Δm_s) was estimated and utilized to calculate the soot yield (Y_s) by dividing for the total mass of fuel consumed ($\sum \Delta m_f$) as defined in the Equation 4.

$$Y_s = \frac{\Delta m_s}{\sum \Delta m_f}$$
(4)

2.1 Kinetic model reduction

For the sake of clarity, the sensitivity analysis results were reported for 20 reactions only, selected by considering the NSC and the sorting procedure described in the previous paragraph. Moreover, stoichiometric composition in air at 298 K were reported, since no significant variations were observed at lower temperatures, with except of the obvious reduction of reactivity expressed in terms NSC for all the investigated reactions (Figure 1).
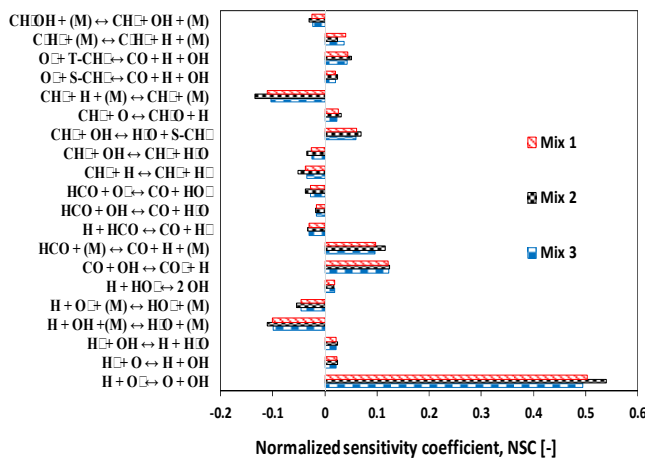

Figure 1: Sensitivity analysis for stoichiometric mixture of LNG/air for different fuel composition.

It is worth noting that the coexistence of propane and ethane (Mix 3) reduces the effect of ethane (Mix 2) on the system, as indicated by the similar NSC of Mix 1 and Mix 3 for all the reactions included in the model, but different from the corresponding NSC of Mix 2. In particular, the reaction $H + O_2 \leftrightarrow O + OH$, commonly considered as the ruling radical reaction for the characterization of reactivity of hydrocarbons in oxidant environment (Xu and Konnov, 2012), shows lower NSC for Mix 1 and Mix 3 with respect to Mix 2. These phenomena can be attributed to the combined effect of higher reactivity of ethane than methane and propane,

as demonstrated by the fundamental burning velocity of these alkanes in air of 42 cm/s, 38 cm/s and 39 cm/s, respectively (Dirrenberger et al., 2011), with the increased stability of the system related to the presence of substances with higher number of carbon atoms. The sensitivity analysis indicates as the first step of the methane oxidation the formation of the CH_3 by means of OH and H radicals, resulting, at the end, in the formation of CO and so CO_2. Thus the methane oxidation path can be simplified by considering CH_3O, CH_2O, HCO, CO, CO_2. Similarly the ethane and propane combustion could be reduced to three steps mechanisms as well, where the intermediate C_2H_5, C_2H_4 and CO for ethane and $N-C_3H_7$, C_3H_6 and CO for propane were formed. The production of C_3 species from ethane indicates the existence shared intermediate species with propane. This is a possible explanation for the aforementioned limited impact of ethane on Mix 3 chemistry. Fuel rich composition results indicate C_2H_2 and C_3H_3 as key soot precursors, in agreement with Agafonov et al. (2007) and Frassoldati et al. (2010) observations. The presence of both ethane and propane increases the production rate of soot precursors, as experimentally observed for methane/air non premixed flames doped with C_3 hydrocarbons(Mcenally and Pfefferle, 1998). Eventually, a skeletal reaction mechanism consisting in 18 species (i.e. N_2, H_2, CH_4, C_2H_6, C_3H_8, H, CH_3, C_2H_5, $N-C_3H_7$, O_2, CO, CO_2, H_2O, O, OH, C_2H_2, C_3H_3 and Soot) and 12 reactions was developed and implemented in the FDS (Figure 2).
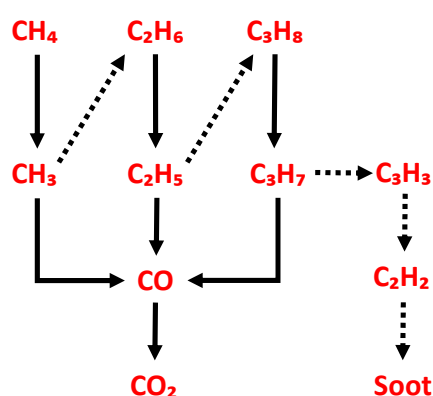

Figure 2: Schematic representation of the KIBO skeletal mechanism.

2.2 Pool fire scenario

The simple chemistry (SC) approach and kinetic model (KM) implementation in CFD code were compared in terms of temperature distribution and surface emitter power (SEP), for Mix 1 as first. It is worth noting that the differences between SC and KM average temperature at pseudo-steady state are reduced at higher distance from the pool, suggesting that the effect of detailed kinetic is limited to the reacting zone. Instantaneous hot spots showing temperature within the range 1600 – 1800 °C were reported in both cases. Small discrepancies in the SEP values were found, being equal to 52.2 and 51.8 kW/m^2, for KM and SC, respectively. This values are in line with CFD analysis performed for small scale LNG pool fire, where temperature range from 1527 and 1888 °C and SEP of 55 kW/m^2 were reported (Schalike et al., 2011). Thus, it should be concluded that negligible differences are expected for pure methane pool fire consequence analysis, as well. The limited impact on pool fire modelling observed for the applied procedures can be associated to the elevated efficiency and ideality of the methane/air combustion system, as confirmed by the negligible amount of produced soot, i.e. the overall soot yield obtained in this case was $6.64 \cdot 10^{-4}$. Similarly the soot yield was calculated for Mix 2 and Mix 3, resulting in $8.41 \cdot 10^{-4}$ in $1.11 \cdot 10^{-3}$, respectively. Considering that fuel pockets due to local non-homogeneous conditions are more frequent at elevated pool diameter, the effect of fuel composition should be more relevant for large scale scenarios (Raj, 2007). The effect of fuel composition on SEP is reported in Table 2. Noteworthy, the discrepancies of the two approaches are enlarged by the presence of ethane and reduced by the addition of propane, although negligible variations are reported in terms of flame temperature at steady state condition.

Table 2: Comparison of surface emitter power (SEP) with respect to fuel composition and applied approach.

	Mix 1	Mix 2	Mix 3
SC [kW/m^2]	51.80	86.63	78.33
KM [kW/m^2]	52.20	89.41	80.20
Δ [%]	0.72	3.20	2.39

This trend clearly indicates that the simplified chemistry should not be adopted for complex mixture evaluation, since it is unable to evaluate the interactions between the fuel combustion processes. To this regard, further considerations can be proposed by comparing the evolution of temperature at a given position as a function of time (Figure 3).

Figure 3: Temperature evolution with respect to simulation time as a function of fuel composition for KM approach at 0; 0; 2·D position.
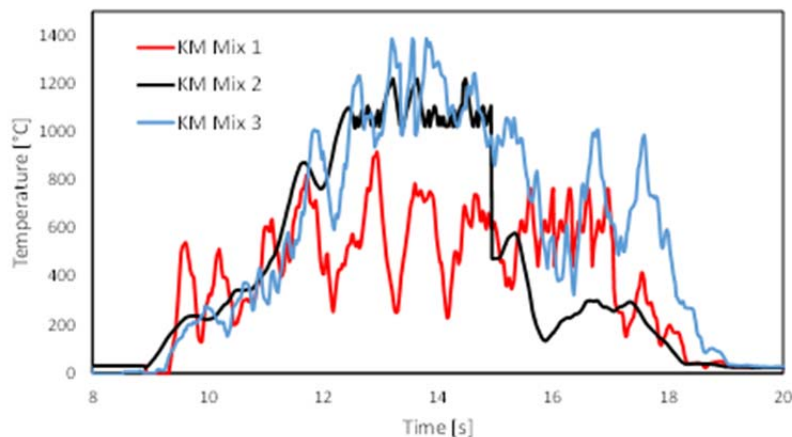
In accordance with the well-known theory and modelling for pool fire an initial step, where the temperature suddenly arises after a certain delay time, a pseudo steady state resulting in a fast decrease of temperature in case of complete consumption of the fuel, is observed for Mix 1, whereas multiple pseudo steady states are observed for Mix 2 and Mix 3 attributable to the difference in the vapor composition with respect to the time. Moreover, it should be considered that significant differences in terms of both duration and intensity were reported. Quite clearly the time shift reported for all the investigated mixtures for SC approach respect to KM indicates that the mixing controlled chemistry does not take into account of additional phenomena increasing the ignition delay time of cryogenic vapors. However, once the vapors are ignited reaction rate are comparable and equilibrium conditions are suddenly achieved within the flame core, thus the temporal evolution and the final value of temperature are comparable. Eventually, a kinetically-controlled ignition is followed by diffusion-controlled or instantaneous phenomena.

3. Conclusions

In this work, a detailed kinetic model developed by the University of Bologna, suitable for light hydrocarbons at cryogenic conditions and atmospheric pressure, has been reduced and validated against experimental and numerical data, for the sake of implementation in CFD codes suitable for the prediction of the LNG pool fire scenario. To this aim, sensitivity analysis and reaction path analysis were performed at different temperatures, fuel compositions and fuel air ratios, resulting in a skeletal mechanism consisting in 18 compounds and 12 reactions. The formation of chemical precursors for soot formation was included in this analysis. The reduced model was implemented in an open source CFD code, FDS, to evaluate the safety aspects involving the LNG pool fire scenarios at different fuel composition, in terms of methane, ethane and propane. The obtained data were compared against the results obtained by the default approach, commonly referred as simple chemistry, where the chemical phenomena are estimated by empirical rules. It was found that both approaches give similar results in terms of temperature and heat radiation at several distance with respect to the pool fire, being the heat release, the burning rate and heat of combustion inserted in the FDS database empirical-based values, already validated for cryogenic conditions, as well. However, it should be considered that the simple chemistry approach does not allow for the accurate evaluation of ignition delay time, CO and soot formation, since no sufficient data are available for the yield at investigated conditions. This is particularly relevant for the evaluation of fire in under-ventilated enclosures. On the other hand, the assumption of pure methane composition for LNG pool seems to be oversimplified, because the presence of ethane and propane clearly affects the pool fire in terms of SEP, especially at later stage from the ignition. Indeed, the heat release rate and flame temperature variate during the simulation, being the fuel vapor composition a function of the time. Negligible discrepancies between pure methane and LNG surrogate mixtures where found in the first stage only, where the fuel vapor are rich in light species, then the evaporation of ethane, at first, and propane, at later stage, leads to significant variation in fire duration and intensity with respect to the simulation time. This study highlights the significance of fuel composition on LNG pool fire scenario evaluation and proposes an

innovative approach to evaluate the plume composition, particularly relevant for confined scenarios and LNG bunkering vessel systems. The application of the proposed procedure should be extended to large scale scenario, where the application of phenomenological models, such as the reduced kinetic model, assumes additional relevance due to the non-ideal mixing locally observed. Indeed, the formation of fuel pockets and hotspots requires particular attention for the sake of accurate model results.

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