A Numerical Approach to Determining Flammability Limits of Hydrocarbon Process Fluids

Peter S. Veloo[a], Okjoo Park[b], Fokion N. Egolfopoulos[c]

[a]Exponent, Failure Analysis Associates, Los Angeles, CA 90066, USA
[b]Department of Aerospace Engineering and Engineering Mechanics
University of Texas at Austin, TX 78712-1221, USA
[c]Department of Aerospace and Mechanical Engineering
University of Southern California, Los Angeles, CA 90089-1453, USA
pveloo@exponent.com

Abstract

Intrinsic to the computer modeling of explosions and fires is the concept of flammability limits. Conventionally, the term "flammability limit" is defined loosely as the concentration limits beyond which flame propagation is no longer possible. More formally, a fundamental flammability limit is defined as the mixture concentration at which a steady, laminar, one-dimensional, planar, and adiabatic flame fails to propagate. Fundamental flammability limits are reached when the heat release from chemical reactions becomes comparable to the radiative heat loss from the flame. The difficulty in predicting these fundamental limits, a priori, for a given combustible mixture is the dependence of the flammability limit on chemical kinetics. In this study we present a computational methodology for the determination of a mixture's fuel lean and fuel rich flammability limits. Numerical calculations were performed using a modified version of the CHEMKIN PREMIX flame code. This code has been modified to allow for the capturing of the singular behavior around the turning point and allowing, thus, the accurate determination of a mixture's flammability limits. The present methodology has been extensively validated to determine the flammability limits of single component and binary fuel mixtures. These validations are presented. Real hydrocarbon process fluids are complex mixtures that consist of hundreds of species spanning a wide range of molecular weights and chemical classes. The surrogate fuel approach, whereby the kinetics of the complex mixture is modeled using a few individual components, is now applied to determine the flammability limits of real hydrocarbons.

Introduction

Process hazard and consequence analysis at petroleum refining and downstream chemical product facilities are complicated by the diverse set of process streams present at these facilities operating in tandem. Refinery streams can include LPG, butanes, butenes, automotive gasolines, diesels, bunker fuels, and jet fuels. Hydroprocessing units (e.g. hydrocracking, hydrodesulfurization (Fig. 1), and hydrodenitrogenation) contain process streams blended with H_2. Petrochemical facilities can include process streams containing ethylene, propylene, and alcohols. A single stream can be a complex chemical mixture of hundreds of chemical species or a single compound. These compounds span a wide range of molecular weights and chemical classes.

Complicating matters further, the temperature and composition of process streams can vary significantly throughout any given plant resulting in varying degrees of the probability and severity potential loss of containment (LOC) events. Understanding how process stream chemical composition and temperature impact the flammability limits of a process fluid can help better inform computational fluid dynamic simulations of industrial fires and explosions. Additionally, the quantification of FLs affects the numerical assessment of the effectiveness of installed fire suppression methodologies.

Figure 1: Schematic diagram of a typical Hydrodesulfurization (HDS) unit in a petroleum refinery [1]

The flammability limit (FL) of a combustible fluid is typically loosely used to describe the fuel/oxidizer concentration limits (upper and lower) beyond which flame propagation is no longer possible [2]. The difficulty of assigning FLs is the lack of readily available, reproducible, experimental data with well quantified uncertainties. Standard test methods, for example ASTM E681 [3], for fluid FLs are costly and pose an intractable challenge in numerically modeling, accurately. Additionally, the prolonged and sustained heating needed to vaporize heavy hydrocarbon process fluids can result in the cracking of the large molecular weight compounds resulting in a quantification of the FLs of an unknown mixture of cracked compounds, not the parent fuel molecules.

A more formal definition of a mixture's FL involves the failure of the propagation of the ideal, one-dimensional, steady, planar, nearly adiabatic flame; otherwise referred to as the Ideal One-Dimensional Flame (IODF) [2],[4]. Experimentally, FLs have been determined through the use of the standard flame tube or spherical bomb. Modeling such devices poses a lot of uncertainty due to heat and radical losses, unsteadiness, and quantifying strain rates and ignition energy. Stagnation type flames have also been utilized to determine mixture FLs [5]. There has been a significant amount of effort within the combustion community to quantify, both experimentally and through numerical calculations, flammability limits (e.g., [7]-[14]). It was demonstrated that by simulating the IODF using detailed descriptions of chemical kinetics and thermal radiation, failure of flame propagation could be identified at both upper and lower concentration limits allowing for the quantitative determination of FLs [2].

The large number of individual species that are potentially present in hydrocarbon process fluids leads to the notion of developing surrogate mixtures of a small number of known components that would suitably emulate the behavior of real fuels. These approaches have been utilized within combustion research to model aviation and automotive fuels in computational fluid dynamic simulations of combustors. Recent research, focused on emulating fully vaporized real fuel combustion chemistry, has demonstrated the importance of replicating only the important functional groups over the molecular class structure composition ([15],[16]). Surrogate mixtures designed using such a methodology are able to reproduce real fuel global combustion properties including auto-ignition, flammability limits, burning rate, strained premixed and non-premixed flame extinction.

The purpose of this paper is to demonstrate the feasibility of employing detailed chemical kinetics to determine, a-priori, the flammability limits of complex hydrocarbon mixtures. In the proceeding sections, the numerical methodology employed will be outlined and developed. Following which set of validation targets have been selected to demonstrate the repeatability of present results. Using methane and propane as examples, the effect of mixture temperature on FLs is shown. Finally, using the surrogate fuel methodology, the FLs of gasoline at ambient and elevated temperatures is calculated.

Numerical Approach

Freely propagating flames were computed using the PREMIX code [17] that was modified with modifications discussed in depth in previous publications by these authors ([2],[6]). The effect of thermal radiation from CO_2, H_2O, CO, and CH_4 at the optically thin limit was incorporated, similarly to previous studies [18]. The code was also modified to allow for capturing the singular behavior around the turning point and allowing, thus, the accurate determination of the FLs. Similar to previous studies of stagnation-type flames ([19],[20]), a one-point continuation approach was implemented by imposing a predetermined temperature or mass fraction of a specific species, at one point in the flow field. Thus, the fuel concentration in the unburned mixture is solved for, rather than imposed as a boundary condition. The code was integrated with the CHEMKIN [21] and Sandia Transport [22] subroutine libraries.

A modified version of the Jet Surrogate Fuel (JetSurF) 1.0 mechanism [23] was used in all simulations. The original model consists of 194 species and 1459 reactions, and it has been developed for high-temperature oxidation of n-alkanes up to n-$C_{12}H_{26}$. It uses USC-Mech II [24], a $H_2/CO/C_1$-C_4 model, as its foundation, and additional detailed description of the kinetics of pyrolysis and oxidation of n-alkanes with $C_\# \geq 5$. The mechanism has been validated against experimental data such as flame speeds, ignition delay times behind reflected shock waves, and detailed species profiles for fuel pyrolysis in flow and jet-stirred reactors. The model was supplemented with the high temperature flame chemistry for *iso*-octane developed by Westbrook and co-workers [23]. The final combined model consists of 220 species and 1520 reactions. This model is readily available upon request to the authors.

Results and discussion

As part of the validation process for the present numerical approach to calculating flammability limits, the lower flammability limit (LFL) of a series of n-alkanes with well-established literature flammability data was computed. The LFL for C_1-C_7 (methane to n-heptane) n-alkanes were computed and these results are depicted below in Fig. 2. Methane has the highest LFL, approximately 5% (volume fuel in air), and with increasing carbon chain length the FLs decrease monotonically. The rate of change of the LFL with increasing carbon chain length decreases with larger molecular n-alkanes and these values tend to asymptote around 1%. Present numerical calculations are in good agreement with literature results. For ethane, and to a lesser degree for the larger n-alkanes considered, the numerical calculations are underpredicting the reported LFL. It should be noted that there is little quantification of the uncertainties in these literature values commonly reported and more work needs to be done to systematically quantify these experimental uncertainties.
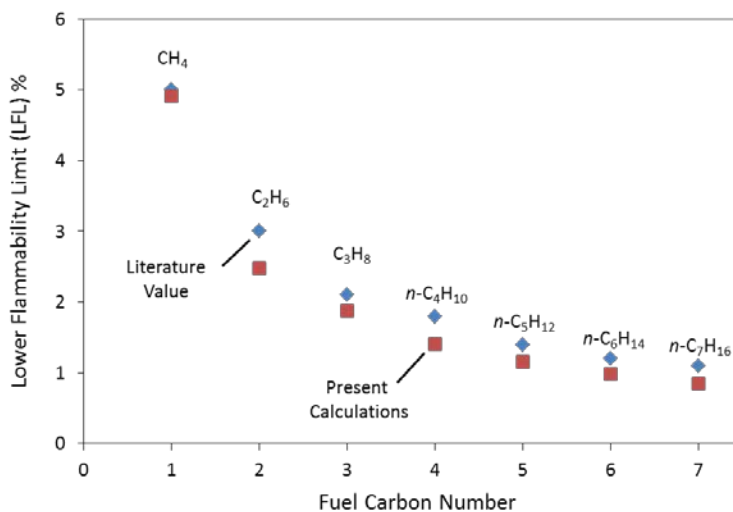

Figure 2: Literature and computed lower flammability results for *n*-alkanes from CH₄ to *n*-C₇H₁₆

Given the temperature variability of process fluids within any petrochemical facility, it is relevant to provide insight into the temperature dependence of these FLs. Figures 3 and 4 below depict the temperature dependence of the LFLs for methane/air and propane/air flames. The

mixture temperatures have been varied between 25-800°C (77-1472°F) and the LFL of the mixture calculated using the present numerical methodology. From Figs. 3 and 4, we can observe that this relationship is strongly linear as expected from literature results.
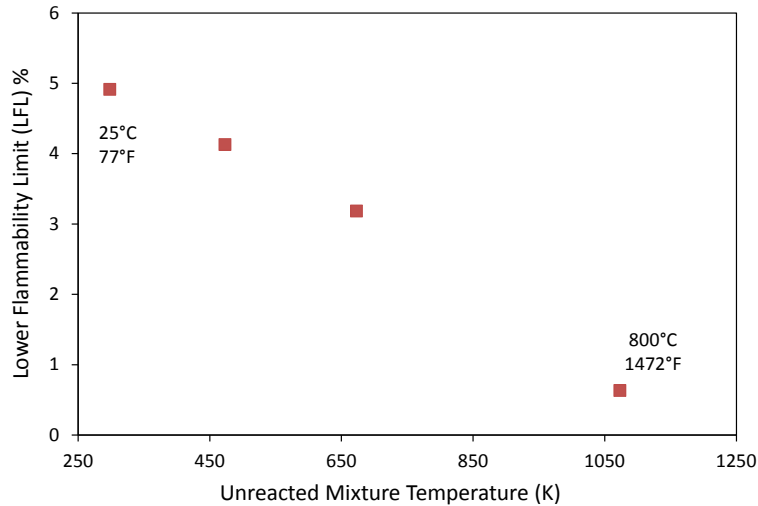

Figure 3: Calculated temperature dependence of the lower flammability limit of methane/air flames
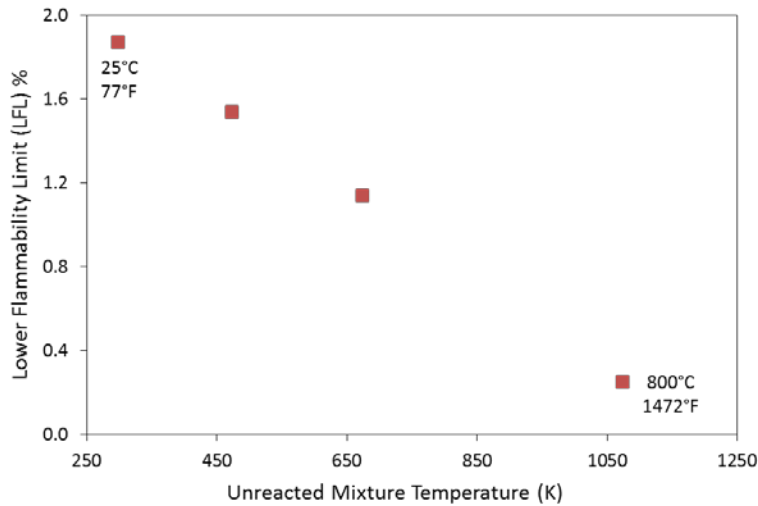

Figure 4: Calculated temperature dependence of the lower flammability limit of propane/air flames

Figure 5 below compares the trend lines for the numerical calculations for methane/air and propane air. Comparing the effect of temperature on the LFL for these two fuels, it can clearly be observed that methane/air flames have a much stronger dependence of temperature on the mixture LFL compared to propane/air flames.
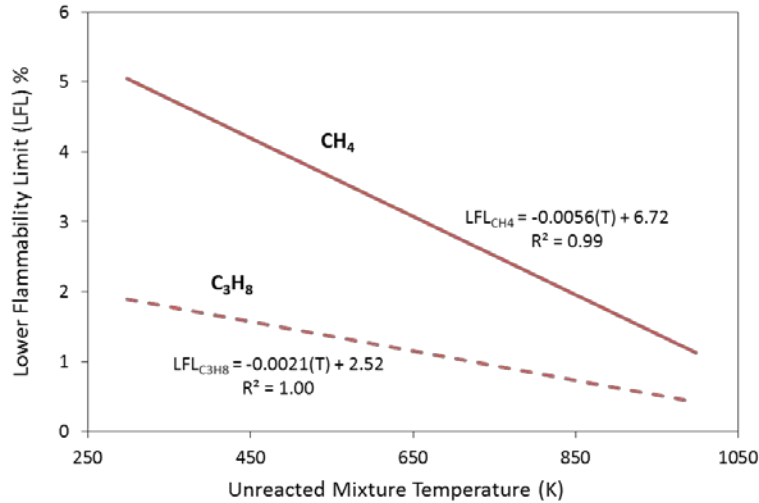
Figure 5: Temperature dependence of the lower flammability limit of methane/air and propane/air flames

As discussed in the introduction, process fluids, such as gasoline, diesel, and aviation fuels, contain hundreds of individual species spanning a range of molecular weights and chemical classes. The surrogate fuel methodology utilizes a select subset of chemical classes and a handful of species to represent the combustion behavior of a real fuel. Gauthier et al. [26] demonstrated the viability of a gasoline surrogate comprised of 50% *iso*-octane, 20% *n*-heptane, and 30% toluene (mole fraction basis) in reproducing the combustion characteristics of gasoline. Figure 6 depicts numerical calculations of the LFLs of this mixture at ambient and elevated mixture temperatures. At ambient conditions, the model is currently underpredicting literature results, there is some spread in recorded values, but present calculations are still notably lower. There have been a large set of gasoline surrogates proposed and formulated and as part of our ongoing work, we are assessing the suitability of these surrogates in reproducing, more accurately, the literature FLs of gasoline.
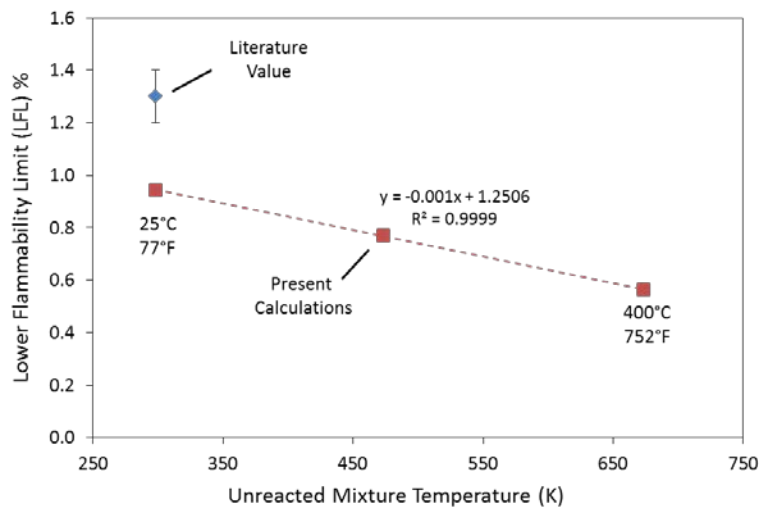

Figure 6: Temperature dependence of the lower flammability limit of gasoline surrogate / air flames

Concluding Remarks

A numerical approach to the assessment of flammability limits has been outlined in this paper. As a first step a number of validation studies were performed using the present methodology. The flammability limits of a large set of *n*-alkanes were calculated using the present methodology and these calculations compared favorably against literature results. Next, the effect of temperature of the unburned mixture on flammability limits was investigated using methane/air and propane/air flames. It was found that there was a strongly linear relationship, over the range of temperatures considered, between a mixture's flammability limit and its initial temperature. Between methane and propane, methane/air flames have a stronger dependence on initial mixture temperature relative to propane. Finally the surrogate fuel approach was utilized to model the flammability limits of gasoline air flames at ambient and elevated temperatures. The surrogate fuel was comprised of *iso*-octane, *n*-heptane, and toluene in the ratio 50/20/30. This mixture underpredicted the lower flammability limit of gasoline and further refinement of the surrogate mixture is being performed.

References
[1]. "HDS Flow". Licensed under GFDL via Commons – (accessed 08/30/2015) https://commons.wikimedia.org/wiki/File:HDS_Flow.png#/media/File:HDS_Flow.png
[2]. F.N. Egolfopoulos, A.T. Holley, C.K. Law, Proc. Combust. Inst. 31 (2007) 3015–3022.
[3]. ASTM E681 - Standard Test Method for Concentration Limits of Flammability of Chemicals (Vapors and Gases)
[4]. F.A. Williams, Combustion Theory, second ed., Benjamin Cummins, Menlo Park, 1985.
[5]. C.K. Law, D.L. Zhu, G. Yu, Proc. Combust. Inst. 21 (1986) 1419–1426.
[6]. C.K. Law, F.N. Egolfopoulos, Proc. Combust. Inst. 23 (1990) 413–421.
[7]. K.N. Lakshmisha, P.J. Paul, H.S. Mukunda, Proc. Combust. Inst. 23 (1990) 433–440.
[8]. C.K. Law, F.N. Egolfopoulos, Proc. Combust. Inst. 24 (1992) 137–144.
[9]. G. Dixon-Lewis, Proc. Combust. Inst. 25 (1994) 1325–1332.
[10]. F.N. Egolfopoulos, Proc. Combust. Inst. 25 (1994) 1375–1381.
[11]. K. Maruta, M. Yoshida, Y. Ju, T. Niioka, Proc. Combust. Inst. 26 (1996) 1283–1289.
[12]. C.J. Sung, C.K. Law, Proc. Combust. Inst. 26 (1996) 865–873.
[13]. H. Guo, Y. Ju, K. Maruta, T. Niioka, F. Liu, Combust. Flame 109 (1997) 639–651.
[14]. H. Zhang, F.N. Egolfopoulos, Proc. Combust. Inst. 28 (2000) 1875–1882.
[15]. S. Dooley, S.H. Won, M. Chaos, J. Heyne, Y. Ju, F.L. Dryer, K. Kumar, C.J. Sung, H. Wang, M.A. Oehlschlaeger, R.J. Santoro, T.A. Litzinger, Combust. Flame 157 (2010) 2333–2339.
[16]. S. Dooley, S.H. Won, J. Heyne, T.I. Farouk, Y. Ju, F.L. Dryer, K. Kumar, X. Hui, C.J. Sung, H. Wang, M.A. Oehlschlaeger, V. Iyer, S. Iyer, T.A. Litzinger, R.J. Santoro, T. Malewicki, K. Brezinsky, Combust. Flame 159 (2012) 1444–1466

[17].   R.J. Kee, J.F. Grcar, M.D. Smooke, J.A. Miller, A FORTRAN Program for Modeling Steady Laminar One-Dimensional Premixed Flames, Sandia Report.SAND85-8240, Sandia National Laboratories, 1985.

[18].   F.N. Egolfopoulos, Proc. Comb. Inst. 25 (1994) 1375-1381.

[19].   F.N. Egolfopoulos, P.E. Dimotakis, Proc. Combust. Inst. 27 (1998) 641–648.

[20].   M. Nishioka, C.K. Law, T. Takeno, Combust. Flame 104 (1996) 328–342.

[21].   R.J. Kee, F.M. Rupley, J.A. Miller, Chemkin-II: A Fortran Chemical Kinetics Package for the Analysis of Gas-Phase Chemical Kinetics, Sandia Report SAND89-8009, Sandia National Laboratories, 1989.

[22].   R.J. Kee, J. Warnatz, J.A. Miller, A FORTRAN Computer Code Package for the Evaluation of Gas-Phase Viscosities, Conductivities, and Diffusion Coefficients, Sandia Report SAND83-8209, Sandia National Laboratories, 1983.

[23].   B. Sirjean, E. Dames, D. A. Sheen, X.-Q. You, C. Sung, A. T. Holley, F. N. Egolfopoulos, H. Wang, S.S. Vasu, D. F. Davidson, R. K. Hanson, C. T. Bowman, A. Kelley, C. K. Law, W. Tsang, N. P. Cernansky, D. L. Miller, A. Violi, R. P. Lindstedt, A high-temperature chemical kinetic model of n-alkane oxidation, JetSurF version 1.0, September 15, 2009, (http://melchior.usc.edu/JetSurF1.0).

[24].   H. Wang, X. You, A.V. Joshi, S.G. Davis, A. Laskin, F.N. Egolfopoulos, C.K. Law, USC Mech Version II. High-Temperature Combustion Reaction Model of H2/CO/C1-C4 Compounds. http://ignis.usc.edu/USC_Mech_II.htm, May 2007.

[25].   H. J. Curran, P. Gaffuri, W. J. Pitz and C. K. Westbrook, "A Comprehensive Modeling Study of iso-Octane Oxidation," Combust. Flame 129 (2002) 253-280.

[26].   B.M. Gauthier, D.F. Davidson, R.K. Hanson, Combust. Flame 139 (2004) 300–311.