Method for predicting hypergolic mixture flammability limits: Application for non-ionic liquid based systems

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ABSTRACT

A numerical method is demonstrated in which a simple flame temperature criterion of 2700 K is used to map out flammability diagrams as a function of total mixture pressure and equivalence ratio in the hypergolic system, MMH/NTO/He. The computed results are in good agreement with experimentally determined ignition diagrams for MMH/NTO/He. The method is used to predict the lower and upper hypergolicity limits of other mixtures known to be hypergolic at 298 K and 1 atm. Comparisons between available experimental data (mixing ratios) and calculated limits lead to the conclusion that the present numerical method may allow the screening of other fuel/oxidant systems potentially of interest for spacecraft propulsion as well as for the determination of the range of mixing ratios able to ensure auto-ignitibility (hypergolicity) in combustion devices. In the safety field, the same method allows for the rapid assessment of hazards in terms of hypergolicity.

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1. Introduction

The concept of limits was first formulated over 200 years ago by Humboldt and Gay-Lussac. Mixtures of combustible materials (such as gaseous or vaporized fuels and also particles) and air will only burn if the fuel concentration lies within the well-defined bounds of lower limit and upper limit, which are determined experimentally, and often referred to as flammability or explosion or ignition limits. LFL (lower flammability limit) is the lowest concentration of a gas or a vapor in air capable of sustaining a flame in the presence of an ignition source (such as an arc or flame). Concentrations lower than LFL are too lean (in fuel) to burn. UFL (upper flammability limit) is the highest concentration of a gas or a vapor in air capable of sustaining a flame in the presence of the ignition source. Concentrations higher than UFL are too rich (in fuel) to burn. These limits are generally expressed in terms of volume percentage at a given condition of temperature and pressure. It is also possible to ignite a mixture, without the presence of an ignition source, by heating the mixture up to the auto ignition temperature (AIT). In that case it is also possible to define and measure lower and upper limits. In this study, we are interested in hypergolic ignition, which is another type of ignition that requires neither an ignition source nor heating.

In most cases, liquids or gases once mixed do not react violently at room temperature. The resulting mixtures often are comprised of no reactions at all or of ones with slow-rate reactions. However, some combinations, termed hypergolic, are known to react rapidly and under appropriate mixing ratios can lead to violent explosions. In that case, lower and upper limits can also be defined, which we will refer hereafter as LHL (lower hypergolicity limit) and UHL (upper hypergolicity limit). Quantitative knowledge of these hypergolicity limits is relevant to the optimization of fuel oxidation in a combustion engine.

One such combination is that of monomethylhydrazine (MMH) and nitrogen tetroxide (NTO), which for many years has been the preferred choice for creating propulsive thrust in numerous spacecraft applications [1]. This energetic mixture affords a great advantage for the propulsion ignition system since the mixture can be auto-igniting at low temperatures and low pressures, thereby circumventing the need for an external ignition source, but its components also possess drawbacks. MMH and NTO are toxic and carcinogenic compounds, and pure MMH vapor is flammable (it can act as a monopropellant). One of the alternatives proposed to replace MMH is ionic liquids. Ionic liquids exhibit physico-chemical properties (of low vapor pressure, thermal stability, etc.) which make them ideal for replacing MMH and some of these ionic liquids are also hypergolic with common oxidants (like nitric acid and

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NTO) [2,3]. However, due to the vast number of possible ionic liquids (10^{18}) [4]. it is crucial to be able to *a priori* predict the autoignition behavior that may arise from the mixing of two or more liquids. Such information would be valuable in the development of new chemical rocket propulsion technologies or for the purpose of mitigating the explosion risks [5] associated with the transportation and management of these rocket fuels.

An extensive search in the open literature has shown that there are no computational chemical kinetics methods or thermochemical methods currently available to address these tasks. The objective of this work, in the propulsion field, is to present a numerical procedure to predict mixture hypergolicity limits (LHL and UHL) to model ignition conditions. Here we restrict our analysis to the MMH/NTO system since the procedure presented herein can be validated against previous experimental data [6]. We then make predictions for other hypergolic systems for which limited or no experimental flammability limit data is available. Another objective of this study is relevant to the safety field: it is to allow the screening of numerous systems to determine if these systems are potentially hypergolically hazardous.

2. Flame temperature criterion

2.1. Proof-of-concept procedure

Traditionally, flammability limits for a given fuel/oxidizer system are determined by pass-or-fail flame-test results for known compositions of experimentally prepared pre-mixtures of the nonreactive gaseous components that are subjected to a standardized external ignition source [7]. For a given initial condition of temperature and pressure, the region between the lower and upper flammability limit defines the envelope of chemical compositions, which when ignited will support the propagation of a flame. Chemical equilibrium calculations can be used to estimate flammability envelopes where the use of a theoretical flame temperature threshold is applied as a criterion to estimate lower and upper flammability limits. By following the works of Egerton [8], White [9] and both Zabetakis et al. [10] and Burgess and Wheeler [11] have shown that the adiabatic flame temperature, at the lower and upper flammability limit, remains approximately constant in hydrocarbon/air mixtures, and that the reported experimental flammability limits correspond to fuel/oxidizer ratios for which in general, the adiabatic flame temperature is in the 1000–1500 K range. Melhem and Shanley [12] have found a flame temperature of 1400 K in the flammability limits determination for hydrocarbons (e.g., ethane/air mixture). However, a flame temperature equal to 1200 K was recommended by the authors for safety issues. In 1999 and 2000, Mashuga and Crowl [13] also proposed a flame temperature criterion of 1200 K in order to determine flammability limits of hydrocarbon–air mixtures. In 2003, Hshieh et al. [14] proposed a different set of correlations for flammability limits via the measurement of gross (or net) heat of combustion of the compound. Heats of combustion and flame temperatures are related properties and therefore this latter idea is not fundamentally different from that of previous studies. Further works are available in this field, which are all based on the same premise [15–21]. Occasionally, a higher critical flame temperature has been proposed such as 1600 K. Correlation methods are also available and reviewed in the literature to predict flammability limits [22–26].

The assumption that the limits of hypergolic mixtures can be similarly rationalized with a simple thermochemical criterion is examined and validated in Section 2.2 and extended to other combinations in Section 2.3.
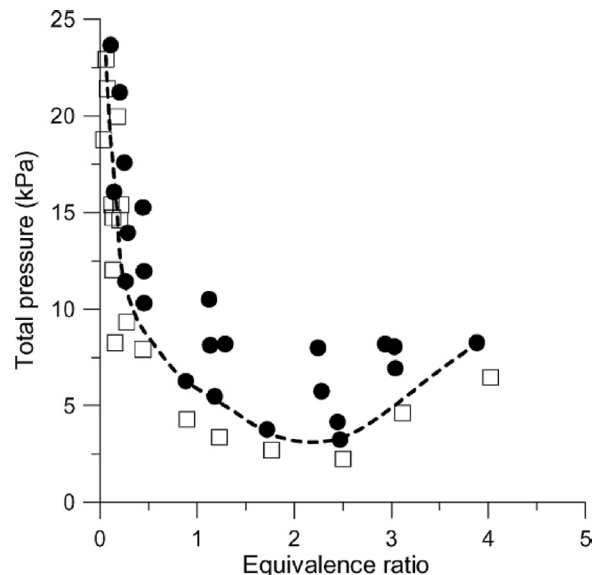

Fig. 1. MMH/NTO/He (with 53 mol% of He) hypergolicity diagram as a function of total mixture pressure and equivalence ratio obtained by assuming rapid mixing. □: no ignition; ●: ignition.
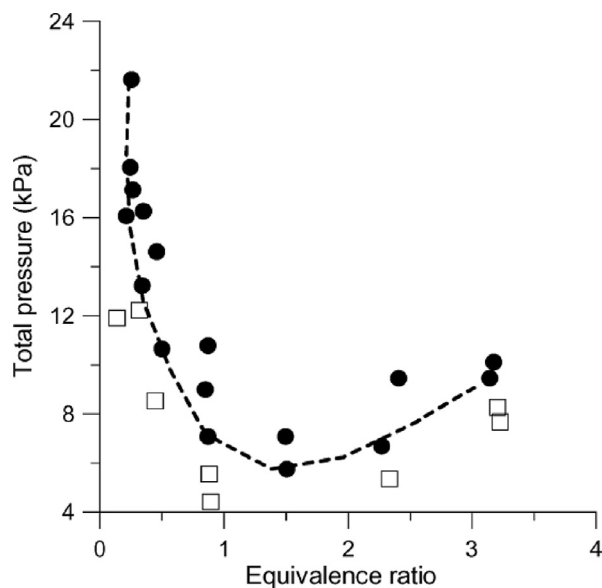

Fig. 2. MMH/NTO/He (with 60 mol% of He) hypergolicity diagram as a function of total mixture pressure and equivalence ratio obtained by assuming rapid mixing. □: no ignition; ●: ignition.

2.2. Approach

One difficulty in determining a threshold flame temperature for hypergolic systems is due to the sparsity of experimental data. Previously, we have reported experimental hypergolicity diagrams at room temperature in the gas phase combination of NTO and MMH in helium. Because premixed mixtures were not feasible, the assumption of rapid adiabatic mixing was applied to obtain hypergolicity envelopes from the experimental data reported by Catoire et al. [6]. Figures 1–5 summarize these results for hypergolic-ignition and non-ignition as a function of total pressure and equivalence ratio at different mol% of the helium diluent. Here we define equivalence ratio to be (fuel/oxidant)/stoichiometry ratio. By