Combustion and Flame 161 (2014) 2242–2251

Contents lists available at ScienceDirect

Combustion and Flame

journal homepage: www.elsevier.com/locate/combustflame

High-pressure low-temperature ignition behavior of syngas mixtures

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ARTICLE INFO

Article history:
Received 11 September 2013
Received in revised form 28 December 2013
Accepted 1 March 2014
Available online 26 March 2014

Keywords:
Syngas
Hydrogen
Strong and weak ignition
Rapid compression facility

ABSTRACT

Ignition properties of simulated syngas mixtures were systematically investigated at high-pressure low-temperature conditions relevant to gas turbine combustor operation using the University of Michigan Rapid Compression Facility. Pressure time history measurements and high-speed imaging of the ignition process in this facility were used to determine auto-ignition delay times and observe and characterize ignition behaviors. The simulated syngas mixtures were composed of H_2 and CO with a molar ratio of 0.7, for equivalence ratios (φ) of 0.1 and 0.5, near air dilution (i.e. molar O_2 to inert gas ratio of 1:3.76), with N_2 as the primary diluent gas. The pressures and temperatures after compression ranged from 3–15 atm and 870–1150 K respectively. The comprehensive results of the present work combined with those from previous shocktube studies in the literature clearly illustrate the existence of both homogeneous and inhomogeneous auto-ignition behaviors at these conditions. Analysis of patterns in the ignition behaviors revealed a dependence on temperature, pressure, and equivalence ratio with distinct thermodynamic regions in which the ignition behavior is consistent and repeatable. Predicted locations of the strong ignition limit made using a criterion which compares laminar flame speed to a thermal gradient driven front propagation speed have excellent agreement with the experimental findings for each φ and an assumed gradient of 5 K/mm. Experimental validation of this unique and powerful criterion means that it can be used for *a priori* prediction of the strong ignition limit using basic computational simulations. The validity of this criterion is fundamentally important, quantitatively describing the roles of chemical kinetics, thermo-physical properties, and device dependent thermal characteristics in determining auto-ignition behavior. Additionally, a comparison of the measured auto-ignition delay times to predictions made using zero-dimensional homogeneous reactor modeling revealed that agreement was dependent on φ, with excellent agreement for $\varphi = 0.1$ and large discrepancies for $\varphi = 0.5$. These results indicate that while inhomogeneous ignition phenomena are not entirely avoidable by reducing equivalence ratio, the subsequent effects on the accuracy of typical auto-ignition delay time predictions may be reduced or eliminated.

1. Introduction

Synthesized gas, or syngas, is a mixture composed primarily of hydrogen and carbon monoxide, which can be produced via gasification of coal and combusted directly in a gas turbine as part of an Integrated Gasification Combined Cycle (IGCC) power plant. Compared to a pulverized coal system, an IGCC plant can achieve reductions in emissions of SO_x, NO_x, particulate matter, and heavy metals without a significant decrease in overall plant efficiency [1]. Currently the gas turbine portion of the IGCC system is in development, with a focus on the abatement of increased NO_x production resulting from the increased flame temperatures of this high-hydrogen-content fuel [2]. A modern method of temperature control is to utilize a lean pre-mixed combustion strategy, otherwise known as "Dry Low-NO_x", with a fuel-to-air equivalence ratio (φ) nearing 0.5 [3]. Given that the behavior of a pre-mixed combustion system is highly dependent on the chemical kinetics of fuel oxidation, it is imperative that both these kinetics and the chemically driven ignition behaviors (auto-ignition) be well understood at gas turbine post-compressor conditions ($P \sim 10$–30 atm, $T < 1000$ K) [4] for air–dilute mixtures over a range of equivalence ratios [5]. Adding to the complexity of such a combustion system is the high variability in syngas fuel composition, where, for example, relative molar fractions of H_2 to CO can range from ~0.4 to 1 for coal-derived syngas [6].

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http://dx.doi.org/10.1016/j.combustflame.2014.03.001
0010-2180/

While the kinetics of syngas and pure hydrogen oxidation have been well studied and modeled, see Chaos and Dryer [4] and the references contained therein, there have been only a few experimental investigations of auto-ignition behavior conducted at a small range of conditions (Voevodsky and Soloukhin [7] – undiluted H_2, Meyer and Oppenheim [8] – air–dilute H_2 $\varphi = 1.0$, Blumenthal et al. [9] – air–dilute H_2 $\varphi = 0.4$, Kalitan et al. [10] – air–dilute syngas $\varphi = 0.4$ and molar H_2:CO = 0.05–4.0, and Walton et al. [11] – air–dilute syngas $\varphi = 0.1$–0.4 and molar H_2:CO = 0.25–4.0). In these studies, optical techniques were employed during ignition measurements in a variety of experimental facilities, which revealed diverse auto-ignition behaviors at thermodynamic conditions relevant to gas turbine operation. The observed behaviors consisted of both homogeneous (spatially uniform emission or detonation wave) and inhomogeneous (localized reaction sites and deflagration) phenomena.

Voevodsky and Soloukhin [7] and Meyer and Oppenheim [8] observed a clear transition between inhomogeneous and homogeneous auto-ignition behavior at varying initial thermodynamic conditions, i.e. the *strong ignition limit*. These studies indicate ignition behaviors are generally repeatable and strongly related to the unburned condition. Voevodsky and Soloukhin [7] further illustrated that the strong ignition limit corresponds to the second explosion limit of hydrogen at low pressures, demonstrating the importance of dominant chemical kinetic pathways in determining ignition behavior. Meyer and Oppenheim [8] expanded on the work by Voevodsky and Soloukhin [7] at low pressures, discovering that a specific value of the temperature derivative of the auto-ignition delay time (which they defined as the *thermal sensitivity* of the system) was well correlated with the strong ignition limit – thus connecting auto-ignition behavior to the dominant chemical kinetic pathway and thermal non-uniformities in the unburned gas. This was an important indication that transitions in auto-ignition behavior can be understood and potentially predicted using thermal sensitivity.

The relationship between thermal non-uniformities and auto-ignition behavior was investigated computationally by Sankaran et al. [12] using high fidelity direct numerical simulations of air–dilute pure H_2 at $\varphi = 0.1$. These simulations revealed that indeed various auto-ignition behaviors could be caused by distributed thermal non-uniformities. A non-dimensional criterion was proposed which compared thermal gradient driven propagation speed and laminar flame speed to indicate the transition between inhomogeneous and homogeneous ignition behaviors. Since a propagation speed determined by a thermal gradient is directly related to thermal sensitivity, this criterion again highlights the importance of the value of the thermal sensitivity. While providing a potentially powerful tool in the prediction of auto-ignition behavior, this criterion had not been experimentally validated prior to the results of the current work.

The understanding and prediction of the occurrence of various auto-ignition behaviors are important, as is the relationship between auto-ignition behaviors and the accuracy of basic homogeneous ignition modeling. As highlighted in Chaos and Dryer [4], it is apparent that auto-ignition delay time measurements for experiments with inhomogeneous ignition behavior are up to several orders of magnitude less than typical model predictions; whereas measurements for experiments with homogeneous ignition behavior are generally in excellent agreement with these predictions. This highlights a potentially catastrophic tendency of syngas fuels to ignite at unexpected locations or times if inhomogeneous ignition behavior occurs. With this in mind, there is currently a lack of understanding as to whether the effects inhomogeneous ignition necessarily lead to inaccuracy in basic auto-ignition delay modeling.

The objectives of the current study were to comprehensively advance the understanding and prediction of the auto-ignition behaviors of air–dilute syngas for a broad range of conditions, and to evaluate the relationship of such behaviors to the predictive accuracy of basic auto-ignition delay time modeling. The objectives were accomplished in part through an experimental investigation of syngas auto-ignition behavior and ignition delay times at lean conditions, using the University of Michigan Rapid Compression Facility (UM-RCF). The results were then combined with those from the shocktube studies of Blumenthal et al. [9] and Kalitan et al. [10] to comprehensively map auto-ignition behavior as a function of initial thermodynamic state and equivalence ratio. On these maps, the strong ignition limit was identified and compared to the second explosion limits of hydrogen and values of thermal sensitivity. The locations of the experimentally determined strong ignition limits were also compared to predictions made using the criterion of Sankaran et al. [12], the first application of this tool to experimental data. Lastly, the auto-ignition delay time measurements were compared to predictions made using typical zero-dimensional homogeneous reactor ignition modeling and the formaldehyde oxidation mechanism of Li et al. [13] (Li 2007 mechanism).

2. Methods

2.1. Experimental

Ignition experiments were conducted for realistic but simple syngas mixtures for two values of equivalence ratio ($\varphi = 0.1$ and 0.5), designed to represent lean syngas mixtures used in the power industry [14]. Both mixtures contained only H_2 and CO as fuel, with a molar ratio of H_2:CO = 0.7, and were approximately air–dilute with N_2, i.e. molar O_2 to inert gas ratio of 1:3.76. In some cases small amounts of the N_2 diluent gas were replaced by Ar and/or CO_2 to modify the test temperature. Ignition experiments were conducted at approximately 3, 5, 10, and 15 atm for the broadest range of temperatures allowable in the UM-RCF for these mixtures (~950–1150 K, based on experimental test times). The composition of the gas mixture and the thermodynamic state corresponding to each auto-ignition delay time measurement are given in the Supplemental material section.

Regarding the experimental apparatus, the UM-RCF is uniquely designed to create uniform thermodynamic conditions through an isentropic compression process [15]. A detailed description of the UM-RCF and results of studies characterizing its performance can be found in Donovan et al. [15] and He et al. [16]. Briefly, the apparatus consists of a long cylinder, the Driven Section, in which a gas mixture is rapidly compressed by the motion of a free piston (Sabot). Prior to compression, the test volume is evacuated with a pump and then filled with a specific test gas mixture. Upon firing, the Sabot travels the length of the Driven Section compressing the test gas mixture into the Test Section – a small cylindrical volume located at the end of the Driven Section (~50 mm length and 50 mm diameter). As the Sabot reaches its final position near the Test Section, the Sabot achieves an annular interference fit, thereby sealing the test gas mixture in the Test Section. At this point, the Test Section is filled with a uniform and isentropically compressed test gas mixture at the desired initial thermodynamic condition. This is achieved in large part because cool boundary layer gases from the Driven Section are trapped in an external volume formed by the geometry of the Sabot [15,17].

For this study, the Test Section was instrumented with a piezoelectric transducer (6125B Kistler, Amherst, NY) and charge amplifier (5010 Kistler, Amherst, NY) for pressure measurements, and a transparent polycarbonate end-wall to permit high-speed imaging