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Impact of non-ideal behavior on ignition delay and chemical kinetics in high-pressure shock tube reactors

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ABSTRACT

Here, we study real gas effects on high-pressure combustion by comparing simulated and experimentally-measured shock tube ignition delay measurements for n-dodecane/O_2/N_2 mixtures. Experiments and simulations occur at conditions relevant to diesel engines: 40–80 atm, 774–1163 K, equivalence ratios of 1.0 and 2.0, and O_2 concentrations of 13–21%. At these conditions the fuel, oxidizer and intermediate species may exist in a supercritical state during combustion, requiring a real gas equation of state to incorporate non-ideal effects on thermodynamics, chemical kinetics, and the resulting ignition characteristics. A constant-volume, adiabatic reactor model is developed to simulate the reflected shock tube experiments, and simulations compare results for real and ideal gas equations of state, with different expressions for reacting species' activity concentrations. This paper focuses particularly on the cubic Redlich–Kwong equation of state and thermodynamically consistent chemical kinetic rate calculations based on it. Results demonstrate that the equation of state can have considerable influence on ignition delay times with increasing pressure, particularly in the negative temperature coefficient region. Additionally, the results establish important practices for incorporating real gas effects, namely that (i) the compressibilities of key species (i.e. those participating in rate-limiting reactions) are the appropriate way to screen for real gas effects, rather than the average mixture compressibility; and (ii) incorporating a real gas equation of state without also incorporating thermodynamically consistent chemical kinetics significantly underpredicts the magnitude of real gas effects.

1. Introduction

With the increasing relevance of high operating pressures for numerous combustion technologies, including diesel engines, jet propulsion, gas turbines and fuel injectors, understanding real gas effects on combustion performance becomes increasingly important. Simulation and analysis of high-pressure combustion (usually, more than 10 atm)—where major species experience transcritical and supercritical states—must incorporate non-idealities in thermodynamic and chemical kinetic properties, which are highly susceptible to even small fluctuations in pressure and temperature near the critical point. While real gas models have been common in the literature for many decades [1–3], their application to complex combustion simulations remains limited. As such, conventions for their adoption and use in the combustion field are not well defined, which can be the source of confusion, error, and inconsistency in their application.

The present paper focuses on real gas effects in reflected shock tube experiments at supercritical pressures. Achieving conditions found in internal combustion and gas turbine engines in controlled experimental reactors or flames is not trivial, and often kinetic models are not tested against target data at the conditions for which the models are eventually employed. Recent collaborative efforts within the Engine Combustion Network (ECN) [4] seek to exhaustively characterize canonical spray ignition and combustion experiments at realistic compression-ignition engine conditions and model those experiments using computational fluid dynamics. One such canonical experiment is the Sandia Spray A [4], where the baseline condition is n-dodecane injection into an ambient gas at a temperature of 900 K, density of 22.8 kg m^{-3} (ca. 60 atm), and containing 15% O_2. Perturbations in temperature, density/pressure, O_2 concentration, injection parameters, and fuel have been widely studied experimentally within the ECN in both the Spray A and other configurations [5–7]. Additionally, ignition delay studies

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for n-dodecane [8–11] have been carried out in shock tubes, but few studies approach the conditions found in the n-dodecane Spray A experiment. Lastly, autoignition experiments have been reported for n-decane in both shock tubes [10,12,13] and rapid compression machines [14], with two notable shock tube studies reporting ignition delay at high-pressure engine conditions. Pfahl et al. [12] measured ignition delay times (IDTs) for $\phi = 0.5$–2 n-decane/air mixtures at 13–50 atm and 700–1300 K, and Zhukov et al. [13] reported ignition delay for $\phi = 0.5$–1 n-decane/air mixtures at 10–80 atm and 800–1300 K.

Real gas effects in high-pressure combustion have been studied in individual efforts over the past several decades [15,16]. Li et al. [17] developed CHEMSHOCK, a shock tube modeling tool that includes facility dependent non-idealities such as incident-shock attenuation and boundary layer growth [15]. Sivaramakrishnan et al. [18], used non-Arrhenius rate parameters to incorporate real gas effects. Davidson and Hanson [19] modeled real gas shock wave equations using the Peng–Robinson [3] equation of state (EoS), and analyzed real gas effects in kinetics and reaction pathways. Schmitt et al.'s CHEMKIN REAL GAS package [20] extends CHEMKIN-II [21] with custom code to incorporate several cubic real gas EoS types, and has been used in subsequent studies to understand real gas effects on detonation properties of gases at high pressures [22]. Tang and Brezinsky [23] used CHEMKIN REAL GAS's Peng–Robinson [3] EoS to demonstrate the impacts of pressure and temperature variations, common assumptions about the quenching process, and non-ideality on the reaction conditions behind high pressure reflected shock waves. They present a set of equations to describe the impact of non-ideality on $p - v - T$ relationships, thermodynamic properties, and chemical kinetics, and consider the impact of non-ideality on the chemical rate coefficients themselves. Petersen et al. [24] use the Peng–Robinson EoS to extend the GRI-Mech 1.2 thermokinetic mechanism for high-pressure combustion of low-dilution methane-oxygen mixtures, validated against experimental IDT data. Despite the value of these studies, adoption of their insights and further study of real gas effects in high-pressure combustion has been limited. Experimental ignition delay studies to validate the kinetic models used in high-pressure combustion simulations are currently lacking, and in most cases the kinetic treatments of high-pressure reacting mixtures assume ideal gas behavior. Many models utilize commercial ANSYS CHEMKIN–PRO [25] software, which implements an ideal gas EoS [18,26,27].

In this paper, simulated high-pressure shock tube results are compared to experimental data to (i) estimate the magnitude of non-ideal effects and (ii) establish conventions for incorporating real gas effects in future studies. New shock tube ignition delay measurements are reported for n-dodecane at the conditions encompassing the very high pressures found in the Sandia Spray A experiment. The present condition space has been chosen to cover a parametric variation of pressure, temperature, and oxygen concentration considered within the spray experiments and provides data at fuel-rich conditions where local ignition within typical spray environments occurs. Of particular interest in this paper is negative temperature coefficient (NTC) behavior at intermediate temperatures, where observed IDTs increase with increasing temperature. IDT and NTC phenomena have been explored in low-pressure studies for applications such as diesel sprays [28] and oxy-methane combustion [29,30], but the effects of non-ideal behavior at high pressures have not been studied in detail.

Numerical simulations in this work follow an approach similar to Schmitt et al. [20], Tang and Brezinsky [23], and Petersen et al. [24], but employ the Redlich–Kwong (R–K) [1] EoS available in CANTERA [31], rather than the Peng–Robinson equation, to model real gas effects on shock tube ignition. The work by Tang and Brezinsky discusses, in considerable detail, real gas effects in the high pressure shock tube combustion of stoichiometric ethane/air, including endwall temperature measurement, species mole fraction profiles, and reaction pathway sensitivity. We extend this previous work to consider the real gas effects on IDTs for n-dodecane/air in the NTC region, and demonstrate the magnitude of common errors, such as neglecting the impact of real gas effects on $p - v - T$ behavior and chemical kinetics, as they relate to predicted IDT values. Another goal of the current study is to encourage greater adoption of non-ideal EoS by modelers and experimentalists alike. As such, we lay out a clear and unambiguous description of the relevant equations, which can readily be extended to other EoS, and concurrently make available a free, open-source version of the simulation tool used herein.

Simulated IDTs are compared to the experimental data and demonstrate the impact of a real gas EoS (i.e., ideal gas law versus a multi-component R–K formulation) and mass activity formulations (i.e., activity concentrations expressed as molar concentrations versus calculated via species activities). Results demonstrate that non-ideal behavior can affect predicted IDTs by as much as 50–100 μs in the NTC region, and that implementing a real gas thermodynamic model without also incorporating real gas chemical kinetic effects significantly under-predicts real gas effects. Results also demonstrate that the average compressibility of a mixture is an insufficient metric for determining real gas effects, which can be important even in cases where the average mixture behaves as an ideal gas (i.e. when the compressibility is very close to one). Rather than the mixture compressibility, the compressibility of key species—those participating in rate-limiting reaction steps—must be evaluated in order to predict the importance of real gas effects.

2. Methods

2.1. Shock tube reactor model

Following the example of Schmitt et al. [20], reflected shock tube experiments are modeled as a zero-dimensional, constant-volume, adiabatic reactor. The computational model is implemented in MATLAB,[1] and uses CANTERA—an open-source software tool for chemical kinetics, species transport, and thermodynamics calculations—to manage thermo-kinetic calculations [31]. CANTERA's object-oriented nature and the associated class inheritance characteristics make it easily extensible, such that real gas models can be incorporated efficiently while also preserving higher-level functionality common to multiple EoS formulations.

The applicable governing equations for energy and species conservation for a constant volume, adiabatic reactor, can be expressed as:

$$\frac{du}{dt} = 0 \tag{1}$$

and

$$\frac{d}{dt}[X_k] = \dot{\omega}_k. \tag{2}$$

In the above equations, $[X_k]$ is the molar concentration ($\text{mol}_k\ \text{m}^{-3}$), t is time, $\dot{\omega}_k$ is the net production rate of of kth species due to chemical reactions ($\text{mol}_k\ \text{m}^{-3}\ \text{s}^{-1}$), and u is the specific internal energy of the mixture, per unit mass (J kg^{-1}), calculated as:

$$u = \sum_k Y_k u_k, \tag{3}$$

where Y_k and u_k represent the mass fraction and specific internal energy (J kg_k^{-1}), respectively, of species k. These governing equations form a transient system of ordinary differential-algebraic

[1] The MathWorks, Inc; Natick, MA,USA; www.mathworks.com.