



Effects of buffer gas composition on autoignition



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ABSTRACT

This work quantifies the chemical kinetic and thermal effects of buffer gas composition on autoignition of three fuels at conditions relevant to engines, combustors, and experimental facilities used to study ignition kinetics. Computational simulations of autoignition of *iso*-octane, *n*-heptane, and of *n*-butanol were used to characterize the effects of buffer gas composition on ignition delay time and heat release rate. Stoichiometric mixtures, $\phi = 1.0$, and a temperature range of 600–1100 K were considered. *iso*-octane and *n*-heptane were studied at initial pressures of 9.0 atm and 60.0 atm, and *n*-butanol was studied at initial pressures of 3.2 atm and 60.0 atm. Two dilution levels of buffer gas to O₂ of 3.76:1 (mole basis) and 5.64:1 were considered ($\sim 21\%$ and $\sim 15\%$ O₂ respectively, mole basis). The fuels and simulation conditions were selected based on the relevance to engine operating conditions and previously published ignition studies. The buffer gases considered were argon, nitrogen, water, and carbon dioxide. Simulation results predicted changes of greater than a factor of 2 in ignition delay time and heat release rate as a function of buffer gas composition in the negative temperature coefficient (NTC) region for *n*-heptane and *iso*-octane. Outside the NTC region, the predicted effects of changes in buffer gas composition were small (<20%); however, experimental data for *n*-heptane indicate larger effects of buffer gas composition on ignition delay time at higher temperatures (>a factor of 2). The heat release rates were also sensitive to buffer gas composition, with carbon dioxide exhibiting relatively high levels of early and late heat release relative to the other buffer gases. Sensitivity analysis of the third-body collision efficiencies for the buffer gases showed the effects of uncertainties in the third body collision efficiencies on ignition delay time and heat release rate. The results highlight the significance of buffer gas composition on low-temperature combustion chemistry, particularly via H₂O₂ and HO₂ decomposition and recombination reactions.

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1. Introduction

Dilution strategies, such as exhaust gas recirculation (EGR), are important tools to achieve high efficiency, low pollutant emissions combustion. There are multiple mechanisms by which EGR can improve combustion performance, including direct cooling or heating, dilution, and potential chemical kinetic interactions through three-body reactions and through trace reactive components in the EGR gases, to name a few. The chemical kinetic and thermal effects of EGR are important as they play significant roles on reaction rates and thereby affect autoignition times and heat release rates. Moreover, thermal, dilution, and chemical kinetic effects are often convolved. For example, thermal effects of buffer gas composition include changes in the specific heat capacity of the fuel/air mixture which affect compression heating and heat transfer losses, and thereby impact chemical reaction rates. Dilution impacts reaction

rates (chemical kinetic effects) and heat transfer rates (thermal effects). Chemical kinetic effects also include the impact of third-body collision efficiencies. It is challenging to isolate the effects of EGR composition in internal combustion engine (ICE) studies due to the complexities of the combustion systems and the often limited access for engine diagnostics. Despite these challenges, there have been valuable experimental and computational ICE studies that have investigated some of the thermal and chemical kinetic effects of buffer gases on autoignition, or combustion phasing, and exhaust gas emissions [1–5].

Ladommatos et al. [1] investigated EGR effects which they categorized as thermal (due to changes in the specific heat capacity of the mixture), dilution (due to changing the oxygen concentration of the mixture), and chemical kinetic effects (associated with dissociation of CO₂) on ignition delay times and exhaust emissions using CO₂ as an EGR substitute in a single cylinder, direct injection diesel engine. The authors found that the magnitudes of the three effects on ignition delay times and exhaust emissions ranked dilution effects as most important, chemical kinetic effects second, and thermal effects as the least important at the conditions studied.

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With increased EGR (i.e., CO₂) Ladommatos et al. [1] reported decreased NO_x emissions and increased ignition delay times, unburnt hydrocarbons, and particulate emissions. A single-cylinder engine operated in homogeneous charge compression ignition (HCCI) mode was used by Sjöberg et al. [2] to study EGR effects via simulated complete stoichiometric products (i.e., N₂, CO₂, and H₂O) and real EGR on autoignition behavior of gasoline and gasoline surrogates (including *iso*-octane and primary reference fuel, PRF, blends of *iso*-octane and *n*-heptane). The authors reported enhanced EGR dilution effects (due to changing the oxygen concentration of the mixture) in fuels with two-stage heat release compared to fuels with single stage heat release, stronger acceleration of autoignition by water (considered a chemical effect, where the authors stated that early reactions were enhanced by the presence of H₂O) for two-stage fuels relative to single stage fuels, and a higher sensitivity to the specific heat capacity of the mixture for single stage fuels. In the work by Machrafi et al. [3], the authors used simulated EGR gases during HCCI operation of a single cylinder engine. They considered the chemical kinetic effects of trace reactive species found in real EGR (the authors added small quantities of CO, NO, and CH₂O to the simulated EGR mixtures), dilution effects (specifically the oxygen concentration of the mixture), and the thermal effects of the specific heat capacity of the EGR gases. Machrafi et al. [3] proposed the formation and consumption rates of OH were critical to the effects of the EGR gases on autoignition. In the work by Al-Qurashi et al. [4], the authors spent considerable effort to isolate and quantify the thermal (specific heat capacity of the mixture), dilution (oxygen concentration of the mixture), and chemical kinetic (dissociation of CO₂) effects of CO₂ on the reactivity of soot produced in co-flow flames and compared the results with soot produced in diesel engines using CO₂ with simulated and actual EGR. The authors found the thermal effects were the most important (45%) on the soot oxidation rate compared to the dilution (35%) and chemical kinetic effects (20%). Sjöberg and Dec [5] studied EGR effects on autoignition of ethanol in an HCCI operated engine and compared results to their previous study of gasoline and PRF blends [2]. The authors found that ethanol was less sensitive to EGR effects. Sjöberg and Dec attributed the difference in sensitivity to the shorter chain length of ethanol and generally lower intermediate temperature heat release rates. The authors also noted that water decreased ignition delay times for ethanol, but less than was observed for gasoline and PRF blends.

In other devices, buffer gas composition is used to control state conditions in combustion chemistry studies using shock tube (ST) and rapid compression machine (RCM) facilities. These facilities, which provide important experimental knowledge of chemical kinetics, rely on buffer gases ranging from monatomics (typically Ar and He) and diatomics (typically N₂) to polyatomics (typically CO₂) to control shock wave characteristics and thermodynamic conditions. The composition of the buffer gases affects the specific heat capacity of the test gas mixtures, the three-body collision reactions, and the heat transfer rates of the test gas mixtures. Few studies have focused on these important and interrelated mechanisms; however, some researchers have identified concerns particularly with autoignition studies. Davidson and Hanson compared predictions for autoignition times for *iso*-octane using two reaction mechanisms and conditions of $\phi = 1.0$, 2% O₂, and $P = 2$ atm [6]. They considered argon and nitrogen as buffer gases and found the change in specific heat capacity significantly affected the autoignition time (~50%) for one reaction mechanism, but not the other, at 1400 K. At NUI-Galway, Würmel et al. [7] conducted an experimental and computational study of buffer gas composition (Ar, Xe, He, N₂) effects in an RCM for 2,3-dimethylpentane ($\phi = 1.0$, 15 atm, and 650–950 K) [7], and a computational study of *iso*-octane ($\phi = 1.0$, 2.0 atm) and methane ($\phi = 0.5$, 1.8 atm) each with Ar and N₂ buffer gases at time scales relevant

to shock tubes. Würmel et al. [8] also conducted a separate computational study of their RCM [8] which focused on the effects of buffer gas composition as related to piston head design and heat transfer. Würmel et al. concluded that argon tends to increase autoignition times in their RCM [7,8] and decrease autoignition times in their ST [7], with different physical phenomena dominating the behavior over the wide time scales relevant to the RCM and ST facilities. Shen et al. [9] conducted experimental shock tube studies of *iso*-octane over a range of equivalence ratios, pressures, and temperatures with argon and nitrogen as buffer gases, and made comparisons with three chemical kinetic mechanisms. Shen et al. [9] determined that argon autoignition times were 20% shorter than autoignition times of nitrogen buffer gas experiments, primarily due to the lower specific heat capacity of argon, and that the mechanisms accurately captured the trend but generally failed to accurately predict autoignition times.

In summary, previous studies have highlighted the value of identifying conditions that are most and least sensitive to buffer gas composition and the mechanisms causing such sensitivity. Isolating, in as much as possible, the chemical kinetic and thermal effects of buffer gas composition on fuel ignition characteristics will help interpret previous results as well as guide future efforts to leverage buffer gas composition as a combustion design tool. The objective of this study was to quantify specific chemical kinetic and thermal effects of buffer gas composition using reaction mechanisms that have been well validated and are widely accepted for representing the autoignition chemistry of three important fuels. The computational simulations of autoignition of test gas mixtures were used to identify conditions where buffer gas composition has the highest impact on ignition delay times and heat release rates, and to quantify the effects of uncertainties in the species-specific collision efficiencies used in three-body reactions.

The computational methods were applied across a range of thermodynamic conditions for *iso*-octane, *n*-heptane, and *n*-butanol. The autoignition characteristics of each of the fuels have been previously studied by several research groups, providing a range of data for comparison, and the experiments provide the basis for the conditions simulated in this study. *Iso*-octane and *n*-heptane, as primary reference fuels, have been extensively studied using rapid compression machines (*i*-C₈H₁₈ [10–16], *n*-C₇H₁₆ [10,16–19]) and shock tubes (*i*-C₈H₁₈ [9,20–24], *n*-C₇H₁₆ [20,25–30]) encompassing a wide range of conditions. Studies of *n*-butanol have occurred with greater frequency over the last 5 years, and autoignition data are available from rapid compression machines [31,32] and shock tubes [33–39].

2. Computational methods

Computational simulations were carried out using the CHEMKIN suite of software (version 10113, x64) [40] and assuming a closed 0-D homogeneous batch reactor at adiabatic, constant volume conditions. Default values from CHEMKIN were used for the solver tolerances and solver time-steps. Detailed chemical kinetic mechanisms were used for each of the fuels, and extensive information on the mechanisms can be found in the literature for *iso*-octane [41], *n*-heptane [19], and *n*-butanol [34]. Brief summaries of the development and validation of each reaction mechanism used in this study are provided below. The reaction mechanisms were selected due to the maturity and extensive validation that has been previously completed on the reaction chemistry. No modifications to reaction rates were made to the mechanisms considered in this study. The mechanisms do not consider NO_x chemistry. Table 1 provides a brief summary of the characteristics of the reaction mechanisms, including the range of conditions for which the mechanisms have been developed and validated. The

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