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Effects of hydrogen peroxide addition on combustion characteristics of *n*-decane/air mixtures

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ABSTRACT

To curb the carbon footprint from the combustion of fossil fuels, hydrogen-enriched fuels have received much research attention in recent years. Hydrogen peroxide (H_2O_2) has unique combustion characteristics, as it can be used as a fuel or serve as an oxidizer when reacting with other fuels. Considering the dual nature of H_2O_2 and exploring its potential benefits in clean combustion technology, a numerical study is carried out to systematically investigate the effects of H_2O_2 addition on combustion properties of *n*-decane/air mixtures, including ignition delay times, laminar flame speeds, extinction residence times, and emissions of CO and NO_x. The results show that H_2O_2 addition can greatly enhance the premixed combustion with shortened ignition delay times, increased laminar flame speeds, and extended extinction limits. While CO emissions increase with increasing H_2O_2 addition for stoichiometric and lean *n*-decane/air mixtures, NO_x emissions first increase with increasing H_2O_2 addition and then decrease as air is completely replaced by H_2O_2. Sensitivity and reaction pathway analyzes are further conducted to identify the changes in controlling chemistry as a result of H_2O_2 addition. It is found that the production of OH radicals are greatly enhanced by H_2O_2 decomposition, and OH radicals play a dominant role in fuel oxidation process. The current simulation results suggest that reduced NO_x emissions can be achieved with H_2O_2 addition at leaner combustion conditions without compromising the static combustion stability.

1. Introduction

About 80 percent of world energy comes from the combustion of fossil fuels [1], which has posed a great threat to global climate and public health due to the emissions of greenhouse and pollutant gases. The ever-increasing energy demand and the growing environmental concerns have driven the engine and power manufacturers to develop advanced combustion systems of high efficiency and low emissions along with the use of viable alternative fuels. In the transportation sector, fuel requirements, such as energy density, onboard storage, handling, and safety, determine that liquid fuels will still dominate in the near and medium-term future. While most research attention on alternative fuels has focused on the development of bio-derived fuels to reduce the life-cycle carbon emissions [2], a more direct approach for decarbonizing the fuel source is to use hydrogen-enriched fuels.

Among the hydrogen-enriched fuels, hydrogen (H_2) has already received much attention in the past decades [3,4]. However, the issues of high production cost, handling/storage, and safety have prevented the wide applications of H_2 fuel. Unlike H_2, hydrogen peroxide (H_2O_2) has two hydrogen atoms and two oxygen atoms, H_2O_2 can decompose rapidly to H_2O and O_2 with an energy release of 98.2 kJ/mol. In the case of high-concentration solution of H_2O_2 (85–98 percent), it is often referred to as “high-test peroxide” (HTP) [5], through which much of the energy release can be converted to a thrust to power aircrafts and vehicles. Due to the extra oxygen atom in its molecule, H_2O_2 can also be used in bipropellant when combined with other fuels [6,7]. In such cases, H_2O_2 acts as an oxidizer and its presence can greatly facilitate the oxidation process of other fuels [8,9]. In addition to its high reactivity and oxidizing ability, H_2O_2 exists in liquid form at normal conditions, and can be easily handled and transported, thus it does not require an overhaul of existing fuel storage and distribution infrastructure. Regarding its production, H_2O_2 is manufactured almost exclusively through the conventional anthraquinone process. Recent advances in electrochemistry have demonstrated the feasibility of a more economic and efficient H_2O_2 production through electrochemical reaction of oxygen and hydrogen in a fuel cell [10]. The strong reactivity, easy handleability/storage, and reduced production cost make H_2O_2 a very promising clean fuel option for future transportation.

H_2O_2 has proven to be a good combustion enhancer [11], it has great potential in improving combustion efficiency as well as reducing

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Nomenclature

C_F	molar fraction of *n*-decane
C_{HP}	molar fraction of H_2O_2
C_{O_2}	molar fraction of O_2
EICO	CO emission index
EINO	NO emission index
f^0	laminar burning flux
k_i	*i*th reaction rate constant
P_0	initial pressure
R_{HP}	addition ratio
S_{k_i}	Normalized sensitivity coefficient for ignition
$S_{k_i,f}$	Normalized sensitivity coefficient for laminar burning flux
S_u^0	laminar flame speed
T_0	initial temperature
T_{ad}	adiabatic flame temperature
T_{in}	inlet temperature
T_u	unburned mixture temperature
t	ignition delay time
ρ_u	unburned mixture density
τ	residence time
τ_{ext}	extinction residence time
ϕ	equivalence ratio
$\Delta S_{u,chem}^0$	normalized laminar flame speed difference

emissions through lean premixed (LPM) combustion technology. However, despite research attention that H_2O_2 has garnered, studies exploring the effects of H_2O_2 addition on fundamental combustion properties of large hydrocarbon fuels at engine-relevant conditions are meager. Given the distinct combustion characteristics of H_2O_2, it is of fundamental and practical interest to achieve a comprehensive understanding of the effects of H_2O_2 addition on the combustion characteristics of large hydrocarbons representative of transportation fuels.

The early application of H_2O_2 for power systems can be traced back to World War II, when it was used as a fuel to power underwater torpedoes. H_2O_2 was later widely adopted as a monopropellant in rocket applications; however, it was eventually replaced by hydrazine (toxic) to increase the specific impulse. The environmental benefits of using H_2O_2 have revitalized a number of studies in the past decades. Born and Peters [12] studied the injection of H_2O_2 into the combustion chamber of a diesel engine, and found that the soot emissions can be significantly reduced due to the enhanced soot oxidation by OH radicals produced from H_2O_2 decomposition. Cong et al. [13] evaluated the performances of kerosene with H_2O_2 for hypergolic application, showing that the bipropellant of kerosene/H_2O_2 has fast acceleration, reliable startup, and stable combustion performance along with good storage stability. Prongidis et al. [14] studied the lean ignition limits of Jet A in a Rolls-Royce Olympus combustion chamber, and notable ignition improvements were observed with the addition of H_2O_2. To further understand the effects of H_2O_2 addition on fundamental combustion characteristics of hydrocarbon fuels, Golovitchev et al. [15] numerically investigated the ignition delay times of $CH_4/O_2/Ar/N_2$ mixtures with H_2O_2 addition, and showed that replacing 5–10% (by volume) of CH_4 by H_2O_2 can shorten the ignition delay time by over one order of magnitude for all the conditions studied. In a subsequent study, Golovitchev and Chomiak [16] revealed that the acceleration of CH_4 autoignition by H_2O_2 addition is attributed to the dominant roles of O and OH radicals generated by the rapid decomposition of H_2O_2. Ting and Reader [17] simulated the laminar premixed combustion of CH_4/air mixtures with H_2O_2 addition, and found that H_2O_2 addition can significantly increase the laminar burning velocity, while the CO and NO_x formations also increase due to the increased oxygen concentration in the unreacted mixture. Recently, Chen et al. [18,19] numerically studied the premixed CH_4/air flames with H_2O_2 addition as an oxidizer substituent of air, showing that H_2O_2 enhances the combustion by promoting OH and HO_2 radicals, which in turn accelerate progressive reaction of CH_3 to form CH_3O and then CH_2O. Manias et al. [20] studied the mechanism by which CH_2O and H_2O_2 additives affect the autoignition of CH_4/air mixture, and found that small quantities of H_2O_2 can significantly decrease the ignition delay times. In light of the above-mentioned literature studies, fundamental combustion studies of H_2O_2 addition effects are only limited to H_2O_2 blending to small hydrocarbons (i.e., CH_4). Considering more studies on the combustion characteristics of large transportation-relevant hydrocarbons with H_2O_2 addition over a wide range of engine-like conditions (especially high pressures) are needed, a systematic numerical investigation using a well-validated chemical kinetic model has been conducted.

In the present study, *n*-decane ($C_{10}H_{22}$) is chosen as the representative hydrocarbon fuel because it is a major component in practical transportation fuels and their surrogates [21,22], and also the high temperature chemical kinetics of *n*-decane has been well studied [23,24]. By extending previous studies on H_2O_2 addition to large hydrocarbon, namely *n*-decane, the objective of the present study is to numerically investigate the combustion characteristics of *n*-decane/air/H_2O_2 mixtures, including autoignition, flame propagation, flame extinction, and pollutant emissions, under engine-relevant conditions with a special emphasis on the pressure effect associated with H_2O_2 addition.

2. Computational methods

2.1. Chemical kinetic model

The chemical kinetic model used in the simulations is taken from Naik et al. [22]. This detailed kinetic model was developed to predict the high temperature combustion properties for an alternative jet fuel surrogate composed of *n*-decane, *n*-dodecane, and *iso*-octane. The model consists of 597 species and 3854 reactions, and was assembled based on the *n*-alkane mechanism of Westbrook et al. [23] and the *iso*-octane mechanism of Curran et al. [25]. The H_2/O_2 subset in the *n*-alkane mechanism was taken from O'Conaire et al. [26]. In addition, the NO_x sub-mechanism was based on multiple mechanisms including GRI-Mech 3.0 [27], HCN chemistry from Dagaut et al. [28], and NO_x-hydrocarbon chemistry from Rasmussen et al. [29]. The detailed kinetic model of Naik et al. [22] has been validated with a variety of fundamental experimental data for the three individual surrogate components, including ignition delay time, ignition temperature, laminar flame speed, extinction strain rate, and NO_x emissions, over a broad range of temperatures above 1000 K and pressures up to 50 atm. The model predictions are in good agreement with the experimental data as demonstrated in [22,30].

2.2. Numerical models

The ignition delay times are calculated using the transient zero-dimensional closed homogeneous reactor provided in CHEMKIN-PRO [31]. Constant volume and adiabatic simulation is conducted for a given premixed combustible mixture at the specified initial temperature and pressure. The ignition delay time leading to the subsequent thermal runway is defined as the time interval from the starting point to the point when the gas temperature is 400 K above the initial temperature.

The laminar flame speeds are calculated using the one-dimensional freely propagating flame model provided in CHEMIKN-PRO [31]. The adiabatic stretch-free flame speed of a given fuel/oxidizer mixture at specified pressure and unburned gas temperature is simulated with