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Oxidation of *n*-hexane in the vicinity of the auto-ignition temperatureR. Mével^{a,b,*}, F. Rostand^{c,*}, D. Lemarié^c, L. Breyton^c, J.E. Shepherd^d^a Center for Combustion Energy, Tsinghua University, Beijing 100084, China^b Department of Automotive Engineering, Tsinghua University, Beijing 100084, China^c École Polytechnique Paris, 91128 Palaiseau Cedex, France^d Graduate Aerospace Laboratories, California Institute of Technology, 1200 E. California Blvd, Pasadena, CA 91125, USA

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ABSTRACT

The present study examines the possibility of inerting flammable mixtures (making the mixtures non-explosive/non-flammable) using a long duration thermal process close to but below the auto-ignition temperature. Experiments were performed in a stainless steel cell and a Pyrex cell. A Mid-IR FTIR spectrometer, a UV–vis spectrometer and several IR laser diodes were employed to monitor the gas-phase composition. Experiments were performed for *n*-hexane-air mixtures with $\Phi = 0.67$ – 1.35 . The temperature and pressure were $T = 420$ – 500 K and $P = 37$ – 147 kPa. Experiments were performed over period of up to 7200 s. At temperatures close to 420 K, the chemical activity is characterized by a slow and constant reaction rate. At temperatures close to 500 K, the reaction proceeds in two-phases: 1) rapid production of CO_2 , CO and carbonyls, identified as hydroperoxy-ketones, followed by 2) a period of slower production of CO_2 and H_2O and consumption of hydroperoxy-ketones. At the end of the thermal treatment, the possibility of igniting the mixtures using a large hot surface (representative of low-temperature ignition source) and a stationary concentrated hot surface (representative of high-temperature ignition source) was tested. The low-temperature flammability was verified by rapidly increasing the temperature of the test cell wall whereas the high-temperature flammability was verified by turning on a glow plug. The inerting strategy seems effective in preventing the low-temperature ignition but high-temperature ignition was always observed.

1. Introduction

Accidental combustion events in fuel tanks and flammable leakage zone is a major concern in aviation safety [1–4]. For example, the National Transport Safety Board investigation pointed out that the explosion of the center wing fuel tank resulting from the ignition of the flammable atmosphere in the tank as the probable cause of the flight TWA 800 accident in 1996 [5]. Possible ignition sources include electrical sparks [1,6–9], stationary hot surfaces [2–4] and moving hot particles [10–12]. In 2008, the Federal Aviation Administration published the Fuel Tank Flammability Reduction Rule [13] requiring the installation of a flammability reduction or ignition reduction means for the fuel tanks that are most at risk. A number of inerting strategies can potentially be employed to reduce or eliminate the risk of accidental explosion in the fuel tanks of aircraft [14–16]. In the framework of aircraft safety, the term “inert mixture/environment” designates a non-flammable or non-explosive mixture, not necessarily a mixture in which no reaction is taking place. One commonly-used strategy in military aircraft is explosion suppression with a polyurethane reticulated foam,

within the fuel tank. The applicability of this effective approach to commercial aircraft is limited due to the reduction of the volume available for fuel, an increased weight of the fuel tank, maintenance complication, and limited life-time. There are a number of other possible strategies, such as inerting with liquid nitrogen and inerting with halon, that have been examined [14–16] but the most practical one that is in use today is on-board inert gas generation system (OBIGGS). The OBIGGS is based on a hollow fiber membrane that exhibits selective permeability so that a nitrogen-enriched environment is created in the fuel tank [15]. The nitrogen-enriched stream may be employed to “wash” the fuel ullage to eliminate the gas-phase oxygen and/or to “scrub” the liquid fuel to eliminate the dissolved oxygen. Extensive studies have been carried out [15,17] to assess the effect of various parameters of the OBIGGS technique including the flow rate of the inert gas, the concentration of oxygen in the nitrogen-enriched stream, and the fuel mass loading of the tank.

Although effective, the OBIGGS strategy has limitations, such as the weight and the complexity of the system transporting bleed air. A potential alternative approach to OBIGGS is low-temperature oxidation:

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through a long duration thermal process close to but below the auto-ignition temperature, the flammable fuel-air mixture could be converted into an inert mixture. This mixture can then be re-injected in the fuel tank in order to reduce the oxygen concentration below the flammability limit. Recent results obtained at the Explosion Dynamics Laboratory [2,3] have demonstrated that under certain conditions of pressure, composition and heating rate, *n*-hexane-air mixtures can undergo a slow oxidation process in the vicinity of the auto-ignition temperature without explosion. Since the large majority of the studies on hydrocarbon fuel oxidation are performed for short residence times and over a range of temperature in which ignition is taking place [18,19], the chemical dynamics of hydrocarbons in the vicinity of the auto-ignition temperature and over long residence time is much less known.

The present study examines a long duration thermal process close to but below the auto-ignition temperature to create an inert mixture through slow oxidation for a range of *n*-hexane-air mixtures. The evolution of the gas-phase composition is monitored over tens of minutes using ultraviolet and infra-red spectroscopy and the flammability of the resulting mixture is verified using both low- and high-temperature ignition sources.

2. Materials and methods

2.1. Mixture preparation

For all the experiments, the mixtures were prepared in a separate evacuated stainless-steel mixing vessel using the partial pressure method. Liquid *n*-hexane with 99% purity was first injected in the mixing vessel to the appropriate pressure which depends on the equivalence ratio. The oxygen to *n*-hexane ratio was selected to give the desired equivalence ratio: the stoichiometric value is 9.5:1. Synthetic air (nitrogen to oxygen ratio 3.76) was added to the fuel and the mixture was actively mixed for an hour using an electrical fan inside the mixture vessel. The mixture was then transferred into a glass flask which was connected to the test cell. Introduction of the gas mixture into the test cell was performed after the cell was evacuated and had reached the desired temperature. The residual pressure following evacuation was less than 10 Pa. Based on the accuracy of the pressure sensors used to prepare the mixtures, the uncertainty of the component mole fractions was less than 2%.

2.2. Test cells

The experiments were performed using two test cells. The first cell was employed to study the evolution of the gas-phase composition and the high-temperature flammability (using the glow plug). The second cell was employed to test the low-temperature flammability (using the heated Pyrex vessel).

The first cell is a 1.14 L cylindrical cell made of stainless steel shown in Fig. 1. Two 5 cm in diameter, 5 mm thick ZnSe windows are located opposite to each other for optical access. The test vessel is equipped with pneumatic valves for rapid filling, gas sampling and evacuation. The temperature and pressure inside the cell are monitored using a shielded K-type thermocouple (uncertainty of 1%) and a pressure transducer (uncertainty of 3%) both from Omega. Mica foil or ceramic heaters and a heated magnetic stirrer plate are used along with temperature controllers to heat the vessel and maintain the temperature constant.

The second cell is the one used in Boettcher et al. [2]. Briefly, it is a closed 400 mL Pyrex cell equipped with two sapphire windows spaced 9 cm apart for optical access. The vessel was placed inside an aluminum shell which was heated by two band heaters with a maximum power of 800 W. The temperature inside the vessel was measured using a shielded K-type thermocouple while the pressure was monitored using a pressure transducer.

Signals from the thermocouple and the pressure transducer were recorded using acquisition cards and an in-house Labview program.

It is noted that, given the large size of the experimental matrix we investigated, only one experiment has been performed at each set of conditions.

2.3. Spectroscopic diagnostics

In a series of experiments, the composition of the gas-phase was monitored using a Frontier Perkin-Elmer Mid-IR FTIR (Fourier Transform InfraRed) spectrometer. Spectra were collected over a wide spectral range: from 1000 to 4000 cm^{-1} . The resolution used was 1 cm^{-1} at a sampling rate of 0.2 Hz. These experiments enabled monitoring absorption by CO, CO₂, H₂O, and by the C–H, C–O, and C=O bonds.

The FTIR results were complemented by experiments performed with a number of absorption based measurements to characterize the dynamics of carbonyls, hexane, oxygen and water vapor. For these additional experiments, the combustion cells were placed in a large airtight PVC box continuously flushed with dry nitrogen and in which desiccant was introduced in order to mitigate the contributions of background oxygen and water vapor.

Identification of the carbonyls formed during the thermal treatment was attempted using UV absorption. An Ocean Optics USB-4000 UV-vis spectrometer was used. It has a resolution of 1 nm and an optical bandwidth from 200 to 900 nm. A 0.1 Hz sampling rate was used. The UV-vis absorption experiments were conducted using an ENERGETIQ EQ-99XFC laser driven light source. It delivers 80 mW of white light over the spectral range 190–2100 nm.

A He-Ne laser emitting at 3.39 μm was employed to monitor the evolution of the fuel concentration in terms of C–H bond equivalent [20]. To avoid saturation of the detector (Thorlabs PDA20H), the incident light beam was mechanically chopped at 100 Hz.

Oxygen was detected near 763.5 nm using scanned wavelength modulation spectroscopy (WMS) with a 1f-normalized 2f detection [21,22]. A saw-tooth signal with frequency of 2 Hz and amplitude of 120 mV was employed to scan across the absorption line while a sine waveform with frequency of 1 kHz and 4 mV amplitude was used for modulation. A dual-pass scheme was employed for this diagnostic. Detection was made with a Thorlabs PDA10A.

Detection of water vapor was also performed using scanned WMS with a 1f-normalized 2f detection. The absorption features near 1392.5 nm were scanned across at a 2 Hz frequency with a saw-tooth signal of 2.5 V of amplitude. The modulation was performed with a sine waveform with amplitude of 22 mV and frequency of 1 kHz. An off-axis multi-pass Herriot scheme was implemented for this diagnostic. A Thorlabs PDA50B detector was employed for monitoring the signal.

For both WMS diagnostics, two SR830 lock-in amplifiers were employed to enable the simultaneous monitoring of both 1f and 2f signals. Acquisition was performed using National Instruments acquisition cards and an in-house Labview program.

All the species profiles were normalized using the maximum value of the raw signal observed during the course of one experiment. It is noted that we did not intend to obtain quantitative information for the species concentrations (except for CO₂ partial pressure) and the value of these data is in the qualitative trends. As a consequence, it is not really meaningful to define uncertainties. For quantifying the CO₂ partial pressure, we have performed a separate calibration with an uncertainty on the order of 5%. For the other absorption diagnostics, quantitative assessment of the species concentrations was complicated by (i) the need for performing calibrations, (ii) the unknown absorption cross-section (mostly for hydroperoxy-ketones), and (iii) the need for using a complex simulation procedure (for WMS [22]) which requires significant development.

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