

Laminar Burning Velocity Measurements in DIPK-An Advanced Biofuel

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ABSTRACT

The biofuel and engine co-development framework was initiated at Sandia National Labs. Here, the synthetic biologists develop and engineer a new platform for drop-in fuel production from lignocellulosic biomass, using several endophytic fungi. Hence this process has the potential advantage that expensive pretreatment and fuel refining stages can be optimized thereby allowing scalability and cost reduction; two major considerations for widespread biofuel utilization. Large concentrations of ketones along with other volatile organic compounds were produced by fungi grown over switchgrass media. The combustion and emission properties of these new large ketones are poorly known. Therefore, fundamental measurements of representative molecules are needed to provide feedback on their desirability in advanced combustion engines (e.g., HCCI: homogeneous charge compression ignition engines) and their impact on emissions, as well as other combustion devices such as micro-combustors. 2,4-Dimethyl-3-pentanone, also known as diisopropyl ketone (DIPK), is a promising candidate biofuel for automotive applications produced by the fungal conversion process. Laminar burning velocity (LBV) is an important fundamental property of a fuel/air mixture and it depends on the composition, temperature, and pressure. Therefore, the knowledge of the dependence of the laminar burning velocity on above mentioned parameters can be used to design advanced engines as it can affect efficiency and heat release rates. We provide LBV measurements for DIPK, using the University of Central Florida (UCF) spherical flame chamber connected to a modified spark plug. Both pressure and direct flame visualization (shadowgraph) were utilized to ensure that the flame is spherical and stable (no cellular structure was observed within the flame) in order to provide reliable results with the constant volume approach. LBV measurements were also performed in iso-octane (C_8H_{18}), a relatively well characterized fuel, in order to validate our facility and measurement technique. The LBV results of C_8H_{18} /air and DIPK/air mixtures are compared with several oxygenated fuels in the literature and numerical values predicted by two chemical kinetic mechanisms.

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INTRODUCTION

Consumption of crude oil derived hydrocarbons is growing due to an increase in the general standard of living of the global population. Power generation and transportation sectors are the primary two sources of fuel consumption, which have raised the demand for crude oil and led to serious environmental problems [1, 2]. These reasons, along with new government legislation increasing regulations on exhaust emissions are the driving forces for researchers to find new fuel alternatives (e.g. biofuels) [3]. Due to the fact that internal combustion engines will still dominate the market for the immediate future [1], biofuels [4, 5] and advanced combustion strategies (e.g., lean combustion, HCCI [6, 7], and dual fuel engines) are important. Research in these areas must run simultaneously to meet more stringent exhaust emissions regulations, without compromising engine efficiency.

One of the most promising platforms for cellulosic biofuel generation is to harness the metabolic processes of endophytic fungi that directly convert the lignocellulosic material into a variety of volatile organic compounds. Recently, many classes of endophytic fungi have been used to convert

cellulosic biomass to a range of ketones and other oxygenated molecules [8]. There is a vast potential for these new biofuels (ketones) in automotive applications due to their advantages in mitigating greenhouse gases, improve air quality and reduce the dependence on foreign oil [9]; however, their oxidation chemistry is not well understood. 2,4-Dimethyl-3-pentanone, also known as diisopropyl ketone (DIPK), is a promising biofuel for high-load HCCI engines [9]. Long-chain ketones such as DIPK, show an unusually low-temperature heat release for intake pressure above 1.78 atm [10]. The auto-ignition enhancement at increasing boost pressures and DIPK's higher temperature and pressure sensitivities provide significant advantages over gasoline [9, 10]. The high pressure-sensitivity reduces the required inlet temperature for DIPK as the inlet pressure increases in HCCI engines; which allows for more advanced combustion timing. As a result, DIPK provides a higher thermal efficiency compared to gasoline at high-load boosted conditions $P_{in} \geq 2.36$ atm [9].

The laminar burning velocity (LBV) is defined as the velocity at which unburned gases moves through the combustion wave in the direction normal to the wave surface [11]. The LBV is not only important in understanding several aspects of combustion in spark

ignition engines, and fuel comparisons; it is commonly used to validate the chemical kinetic schemes [11, 12]. Also, oxygenated fuels like methanol and ethanol are used as an octane booster or to reduce emissions; in the United States and part of Europe ethanol is blended with gasoline at 10% by volume [13]. The effect of equivalence ratio (Φ) on LBV, and the Φ value for maximum LBV have been shown by many authors to vary significantly depending on the type of biofuel fuel used [14]. Beeckmann et al. investigated LBV experimentally and numerical for many oxygenated fuels [15]. Specifically, methanol, ethanol, n-propanol, and n-butanol were tested at 373K and 10 atm in a spherical combustion chamber. Flame fronts tracked by a schlieren cinematography system and a nonlinear extrapolation model was used. Beeckman et al. found that the maximum methanol burning velocity occurs at an equivalence ratio of 1.1-1.2 experimentally and 1.15-1.2 numerically. Among the oxygenated fuels, methanol has the lowest burning velocity while ethanol has the highest value [15]. Burluka et al. [16] obtained the LBV of three C_3H_6O isomers, propylene oxide (cyclic ether), acetone (ketone), and propionaldehyde (aldehyde) at room temperature and atmospheric pressure. Both constant pressure and constant volume methods are used in the analysis of LBV. The maximum burning velocity occurs at Φ slightly lower than 1.2 for propylene oxide, while the highest acetone LBV happens at $\Phi > 1.2$. Furthermore, the propionaldehyde has almost constant LBV values in the range of $\Phi = 1.1$ -1.4. Studies were conducted by Daly et al. [17] and Huang et al. [18] for obtaining the LBV and Markstein number of dimethyl ether (DME) by tracking the flame at room temperature and several initial pressures. A positive Markstein number was found, and the maximum LBV value was observed at $\Phi = 1.13$ and 1.1 in [17] and [18], respectively. It is apparent from the previous studies of oxygenated fuels that the maximum burning velocity tends toward a richer mixture compared with a non-oxygenated fuel. This behavior is believed to be due to the change in the Lewis number and differential diffusion (the oxygenated fuel diffuses at a slower rate compared to the oxygen which results in a leaner mixture within the reaction layer). The deviation of the Lewis number (from unity) and differential diffusion effects on the burning velocities are discussed in references [19] and [20], respectively.

Recently, Yang and Dec investigated the auto-ignition characteristics of DIPK in both HCCI and spark ignition engines [9]. Experiments were conducted over a wide range of operating conditions to characterize the fuel reactivity for auto-ignition and its sensitivity to the variations of temperature and pressure. Allen et al. carried out an experimental and modeling study on DIPK combustion chemistry [8]. Ignition delay time, pyrolysis, and oxidation measurements were conducted under a wide range of operating conditions, but LBV measurements were not made. They found that the DIPK ignition delay time is substantially shorter than that of structurally similar hydrocarbons, and their experiments showed a region of negative temperature coefficient behavior in the range of 650 to 750 K [8]. Barari et al. [21] ran a numerical simulation of HCCI engines by using single and multi-zone models. Their single zone model provided reasonable agreement during the compression stage until the onset of ignition, however, it over-predicted the peak pressure after the ignition process. The kinetics mechanisms used by Allen et al. [8] and Barari et al. [21] were generated by utilizing the Reaction Mechanism Generator [22] and are not compatible for simulating

laminar burning velocity under automotive combustion conditions. Typically, combustion bombs, flow reactors, rapid compression machines, and shock tube experiments are utilized to obtain fundamental combustion data which are utilized to develop and validate chemical kinetic mechanisms [23, 24, 25, 26, 27].

In this paper, the LBV of DIPK/air is measured using a recently constructed spherical chamber set up utilizing spark ignition and dynamic pressure traces. Also, flame propagation by shadowgraph imaging is used to ensure a stable flame. LBV is obtained for various equivalence ratios at an initial temperature of 393 K and initial pressures of 1 and 5 atm. Also, LBV's are determined in iso-octane/air mixtures (since iso-octane is a widely studied and well-characterized reference fuel [28, 29]) as a validation of our new set up and liquid fuel experimental strategy. Comparisons with numerical predictions and literature data are presented to assess the behavior of DIPK. This study is conducted to provide fundamental combustion data needed for developing kinetics mechanisms for DIPK and enable engine designers to assess the suitability of DIPK as a fuel.

EXPERIMENTAL SETUP

The experimental setup in this study is similar to the one used by Farrell and co-workers [30, 31] and consists of the spherical combustion chamber, mixing tank, optical system, ignition systems, high-speed camera, and data acquisition system. A brief description of the experimental setup is presented below; more details can be found in our recent laser ignition work [32]. The combustion chamber is made of 316 stainless steel with an internal diameter of 165 mm and 10 mm shell thickness. The shell is designed to withstand a maximum pressure of 140 atm. The spherical chamber has four optical access points with different sizes that can be used for schlieren, shadowgraph imaging, laser ignition, mounting a pressure transducer, and spectroscopic diagnostic techniques. The spherical combustion chamber is placed in an oven to raise the combustion chamber temperature uniformly to the desired value (393 K in the present experiments) before undertaking experiments to ensure that liquid fuel is in vapor form. The oven is designed for a maximum temperature of 1375 K, optical access added on each side to provide a path for schlieren and shadowgraph imaging. The schematic representation of the experimental setup is shown in [figure 1](#).

The optical system was constructed to visualize the ignition, flame kernel development, and flame propagation by a shadowgraph imaging. It consists of a continuous wave He-Ne laser (633 nm) that was expanded and collimated to a 2" diameter before passing it perpendicular to the ignition system electrodes. The Lucas ignition circuit was assembled and controlled by a LabVIEW program (though a transistor connected to the ignition circuit relay) to provide spark ignition mechanism. Also, a spark plug (NGK BR4HS) was modified by welding two tungsten electrodes (1 mm) in order to produce a spark at the center of the combustion chamber. In our design both electrodes were introduced from the same side as opposed to diametrically opposite configuration found in many spherical chamber configurations [33]. Because there are no electrodes in one hemisphere, this configuration would avoid thermal conduction losses and thereby producing a theoretically undisturbed

flame in that section (opposite to electrodes). A Phantom v12.1 high-speed camera (capable of 1million fps) was used to capture frames with a resolution of 512×512 pixels at a rate of 20,000 fps.

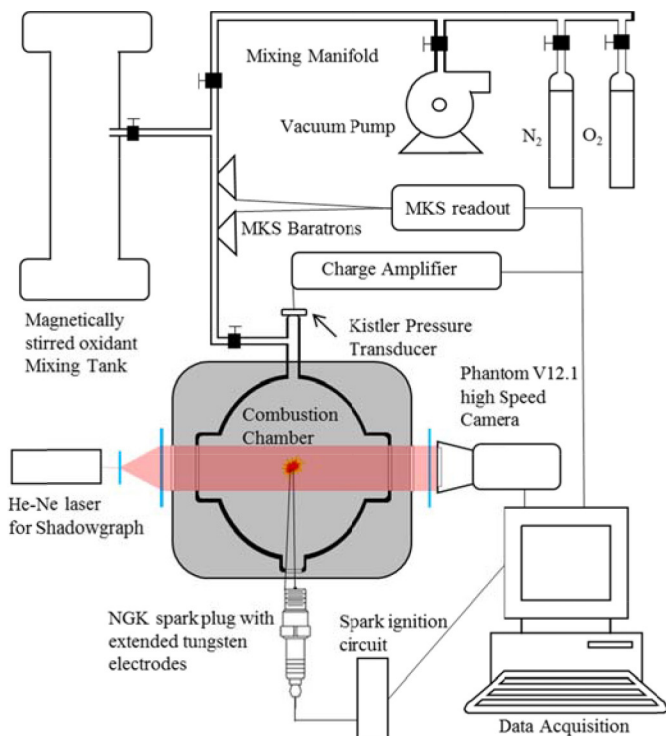


Figure 1. Schematic representation of the spherical experimental setup inside an oven designed for up to 1375K (Note: image not to scale).

Fuels

Iso-octane and DIPK were supplied by Fisher Scientific; Table 1 presents their properties and purities. Research grade (purity 99.999%) oxygen (Praxair) and nitrogen (Air Liquide) were utilized to create synthetic air (1 O₂: 3.76 N₂).

Table 1. Physical and chemical properties for C₈H₁₈ and DIPK fuels.

	Isooctane	DIPK
Molecular Formula	C ₈ H ₁₈	C ₇ H ₁₄ O
Density, [g/mL]	0.692	0.8
Molecular Weight, [g/mol]	114.23	114.19
Boiling Point, [°C]	98-99	124-125
Vapor Pressure, [mbar @ 20°C]	51	5
Flash Point, [°C]	-12	15
Assay (Purity), [%]	≥99	≥98

Experimental Procedure

The following procedure was developed to ensure that each mixture is homogeneous and uncertainties in composition is minimized. The heated (using heating jackets to 393K) synthetic air (1 O₂: 3.76 N₂) was created inside a mixing tank (using partial pressure) after evacuating for several hours. A capacitance manometer (MKS Baratron 628, 0-26 atm) connected to the mixing manifold section was used to monitor the pressure. First, oxygen and then nitrogen were filled after determining the required partial pressure based on a

desired final value (10-20 atm). The oven was used to raise the temperature of the evacuated combustion chamber to 393 K. Mixtures of fuel and air were prepared by using the partial pressure method after first injecting a specified volume of fuel (Luer lock and syringe connection). Since the combustion chamber is maintained at high temperature, injected fuel evaporates completely because the partial pressure of the fuel was much below its vapor pressure. The combustion chamber temperature was monitored by using three thermocouples attached to different locations on the outside surface of the combustion chamber. The differences between the three thermocouple readings were less than 0.1°C. A second temperature controlled MKS E27 Baratron with a pressure range of 0-0.13 atm was employed to increase the accuracy of determining the partial pressure of the injected fuel. Preheated air at 393 K was filled to achieve the target equivalence ratio and fuel/air mixtures were allowed to mix for roughly 15 minutes to ensure homogeneity.

The Kistler 603B1 dynamic pressure transducer and 5010B1 charge amplifier were used to record the combustion pressure at 100 kHz. The pressure before the ignition event was referenced to the value obtained by the MKS Baratron 628 which was attached to the manifold to be utilized for both the mixing tank and the spherical chamber. The data were recorded using National Instruments DAQ system NI 6259 capable of recording up to 1.25 Ms/s (Mega samples per second) on a single channel. The ignition circuit and the high-speed camera were triggered by using a LabVIEW program to synchronize the pressure signal with the captured image. Half a second of pressure signal was recorded before employing a 1-D Matlab smoothing function [34] to minimize the pressure fluctuation at the beginning of the combustion process. The smoothed trace was compared to the original signal at each experiment to ensure that the mean value of the pressure fluctuations were captured.

COMBUSTION MODEL

There are many methods used for determining the LBV in the literature; each method has its difficulties and limitation as described by Egolopoulos et al. [33]. The outwardly propagating spherical flame is the most favorable method for obtaining laminar burning velocity at relevant engine condition (high pressure and temperature) according to Metghalchi [35]. In this study, LBV is calculated by using the constant volume approach which requires evident pressure change (obtained from the Kistler pressure transducer) during the analysis. By definition, the laminar burning velocity is proportional to the instantaneous mass of burned gases (m_b) passing through the area of the flame (A_f) [35], shown in equation 1. O'Donovan and Rallis [36], and Bradley and Mitcheson [37] among others derived expressions for the flame radius by dividing the control volume into burned and unburned gases assuming the isentropic compression, spherical flame, and spatially uniform pressure. The derivation of the flame radius (R_f) and its inclusion in the definition of LBV (equations 2 and 3) are described in the literature [38, 39] (also developed in Appendix A).

$$\rho_u S_u = \frac{1}{A_f} \frac{dm_b}{dt}$$

