An Experimental and Kinetic Modeling Approach to a Martian Fuel Combustion

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1 Introduction

2,3-butanediol ($C_4H_{10}O_2$) has recently emerged as a potential rocket propellant. Based on the atmospheric and gravitational differences between Earth and Mars, Kruyer et al. has proposed a potential biotechnological production of 2,3-butanediol on Mars from the Martian sources, such as carbon dioxide, water and sunlight using a biotechnology-enabled in situ resource utilization strategy [1]. The Martian CO_2 is converted by a photosynthetic cyanobacteria into glucose, which is further upgraded to 2,3-butanediol by *Escherichia coli*. They theoretically studied some short-chain diols, among which 2,3-butanediol was found to be the most biotechnologically suitable candidate due to its high titer, yield and productivity.

Despite the fact that this biotechnological route seems feasible on Mars, the combustion mechanism of 2,3-butanediol still remains unexplored, to the best of our knowledge. In this regard, the fundamental combustion characteristics of this fuel, such as flame speeds and ignition delay times need to be studied over a wide range of conditions to understand its combustion mechanism. 2-butanol oxidation kinetics would be a suitable starting point for the kinetic modeling of 2,3-butanediol oxidation due to the absence of studies on its oxidation kinetics. The kinetic mechanisms in literature developed for 2-butanol oxidation have been reported to predict well its fundamental combustion properties such as ignition delay times, flame speeds, species profiles obtained during oxidation [2-6].

Moss et al. developed the first 2-butanol oxidation kinetic mechanism and tested well against ignition delay times data obtained in a shock tube at high temperatures [2]. The consumption of 2-butanol was found to take place mainly by dehydration leading to the formation of alkenes, and ultimately to resonance stabilized radicals with low reactivity. Van Geem et al. [3] proposed a mechanism that successfully predicted different data sets, including ignition delay times and flame speeds. The kinetic mechanism developed for butanol isomers using a hierarchical method by Grana et al. [4] was further improved by Frassoldati et al. [5], who found acetone to be the main product of 2-butanol decomposition. Sarathy et al. [6] developed a detailed kinetic mechanism including the low- and high-temperature reactions of all butanol isomers. The mechanism was well validated against the atmospheric pressure premixed laminar flame velocity data of 2-butanol [7], while it slightly underpredicted 2-butanol ignition delay times reported by Weber et al. [8].

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This study presents the first ever measured 2,3-butanediol flame speeds and ignition delay times. The flame speed measurements were carried out for mixtures with equivalence ratios between 0.8–1.2 at initial pressures of 1 and 2 bar and at an unburned gas temperature of 403 K using the constant volume spherical expanding flame methodology. The flame speeds were obtained as a function of both pressure and temperature which both rise as the flame propagation takes place in the chamber. The ignition delay times were measured in a rapid compression machine at compressed gas pressures of 10, 15 and 20 bars and at compressed gas temperatures ranging from 800 to 1000 K. Furthermore, a detailed 2,3-butanediol kinetic submechanism was developed and tested against the present data.

2 Experimental

Laminar Flame Speeds

A perfectly spherical constant volume vessel was used to carry out the laminar flame speed measurements. It has a 360° fused silica ring that facilitates the full visualization of the flame front propagation from the center of ignition to the walls. Two pressure sensors (AVL GU21D) with a high sensitivity of 35 pc/bar and a high frequency of 85 kHz are placed at the opposite sides of the chamber along its diameter to track the pressure in the combustion chamber. The initial unburned gas temperature is monitored by a K-type thermocouple. The combustion chamber is placed inside a furnace of 32 L volume to achieve a homogeneous heating. The furnace can operate from room temperature to 573 K. This experimental set-up, named OPTIPRIME (Fig. 1.) and located at ICARE-CNRS, Orleans, France, has been previously described in detail by Halter et al. [9].

The flame speeds were determined by applying the spherically propagating flame methodology. During the flame propagation, the centrifugal consumption of fresh gases by the flame front leads to a rise in pressure and the isentropic compression results in an increase in the fresh gases temperature. Thus, the laminar flame speed can be evaluated for a range of pressures and temperatures, as shown in Table 1. The experimental uncertainty for OPTIPRIME has been previously reported [9] to be less than 5%.

Table 1: The experimental conditions for the flame speed measurements.

Oxidizer	φ (-)	p_0 (bar)	T_0 (K)	p (bar)	T (K)
Air (21% O_2/79% N_2)	0.8	1	403	2.23–4.33	491–575
	0.8	2	403	4.10–7.90	481–563
	0.9	1	403	2.26–4.56	491–579
	0.9	2	403	4.05–8.35	478–567
	1.0	1	403	2.26–4.56	489–575
	1.0	2	403	4.49–8.39	489–565
	1.1	1	403	2.28–4.78	489–579
	1.1	2	403	4.06–7.96	476–555
	1.2	1	403	2.31–4.31	489–563

Ignition Delay Times

The ignition delay time measurements were carried out in a rapid compression machine located at PRISME laboratory [10]. The RCM is equipped with a single piston that is pneumatically driven and hydraulically controlled. The piston has a crevice head to prevent vortex roll-up formation and ensure the homogeneity of the core gas [11]. Therefore, the adiabatic core hypothesis can be applied to determine the temperature at the top dead center. The initial temperature is controlled by external wall heating and it is determined based on a 0D thermal law as a function of external temperature [12]. The external intake temperature is measured using a K-type thermocouple having an uncertainty of ±1 K. The A 6054BRU59-3-1 Kistler pressure sensor with a range of 0–300 bars is used to measure the intake pressure (p_0) and the compression pressure (p). The dead volume was adjusted using two shims with the thicknesses of 12.7 and 5 mm, resulting in a volumetric compression ratio of around 10.

The mixtures were prepared prior to the measurements in a separate tank of 4.18 L volume. The liquid fuel was injected into the tank by a syringe and its partial pressure was tracked to ensure the full vaporization to achieve the intended equivalence ratio. The fuel used has > 97.0% purity and a boiling point of 455 K. The temperature in the tank was set to its maximum of 453 K to avoid condensation of the fuel in the tank. Then, the gases are introduced in a specific order to make the full mixture. Having the mixture ready, it is directed into the combustion chamber using pneumatic heated valves to obtain the required initial pressure. When the valves are closed, the piston in its initial position starts to compress the mixture until the top dead center. A Labview software is used to obtain the pressure time profile, which is used to determine the ignition delay time as the time taken from the end of compression until the pressure gradient reaches its maximum. The experiments at the same conditions were further conducted with non-reactive mixtures by replacing oxygen with nitrogen to obtain volume-time profiles to be used in the simulations in order to consider the experimental heat losses during the compression stage. At least three tests were conducted for both reactive and non-reactive mixtures for each condition to ensure the repeatability. The experimental conditions are provided in Table 2.

Table 2: The experimental conditions for the ignition delay time measurements.

Dilution Ratio	φ (-)	p_0 (bar)	T_0 (K)	p_c (bar)	T_c (K)
O_2 / Inert = 1 / 8.00	0.5	0.694–1.052	413–436	15, 20	830–1000
O_2 / Inert = 1 / 8.00	1.0	0.472–1.047	426–434	10, 15, 20	830–930
O_2 / Inert = 1 / 10.0	1.5	0.997–1.019	397–448	20	800–880

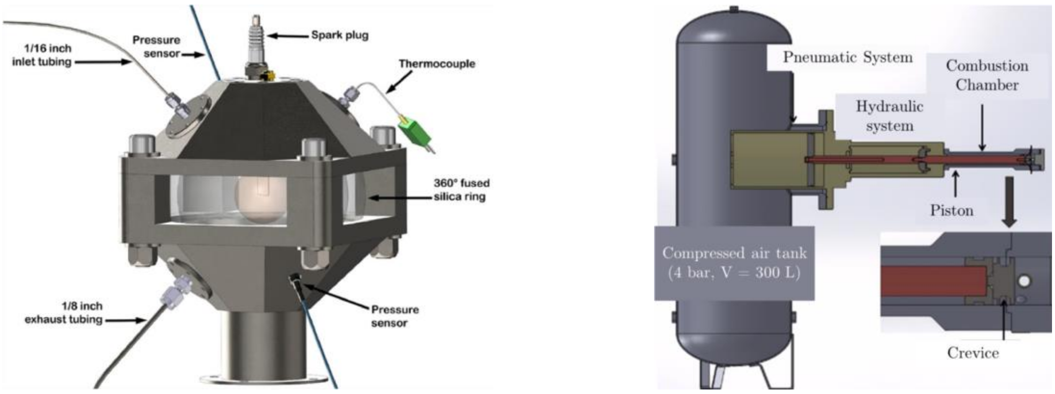

Figure 1: The experimental apparatus. Left: Spherical isochoric combustion chamber [9]. Right: Rapid compression machine [13].

3 Kinetic Modeling

A detailed kinetic mechanism for 2,3-butanediol oxidation, including low- and high-temperature reactions, was developed for the first time in this study. This mechanism consists of the reactions of 2,3-butanediol, 3-hydroxybutan-2-one, 2,3-butanedione, 1-hydroxypropan-2-one, 2-hydroxypropanal, 2-oxopropanal and oxaldehyde. The comprehensive butanol kinetic mechanism developed by Sarathy et al. [6] was used in the present study. Due to the absence of the experimental or theoretical rate parameters for 2,3-butanediol reactions, the reaction rate constants were determined based on analogies to 2-butanol reactions since the α- and β-carbon atoms in a 2,3-butanediol molecule can be considered analogous to those in 2-butanol, as a first approximation. Thus, the rate parameters of the reactions around these C–atoms of 2-butanol can be used to approximate the rate parameters for the corresponding 2,3-butanediol reactions. Unlike 2-butanol, 2,3-butanediol has a symmetric structure. Therefore, the rate constants of 2-butanol unimolecular decomposition and H-abstraction reactions are multiplied by a factor of 2 to account for the equivalent H atoms, except for the C-C bond scission reaction forming two α-hydroxyethyl radicals. This reaction is assumed to proceed at the same rate as the corresponding reaction of 2-butanol resulting in ethyl and α-hydroxyethyl radicals. The rate constants for β-scission reactions of the α and β radicals of 2,3-butanediol were considered to be the same as reported for 2-butanol radicals. The rate constants of 2-butanol reactions were adopted from Sarathy et al. [6]. Following the same methodology, the reactions of 2,3-butanedione were modeled based on analogies to 2-butanone. However, for 3-hydroxybutan-2-one, a non-symmetric molecule, two different set of analogies were used. While its α- and β-C atoms are analogous to those of 2-butanone, the β' and γ C-atoms are analogous to the α- and β-C atoms of 2-butanol. Similarly, for 1-hydroxypropan-2-one and 2-hydroxypropanal analogies were done to acetone-propanol and isopropanol-propanal, respectively. With regards to the 2-oxopropanal and oxaldehyde, the sub-mechanisms reported previously by our team [14] have been used in the present work.

ANSYS CHEMKIN-PRO 2023 R2 [15] was used to perform all flame speed and ignition delay time simulations. The flame speed calculations were carried out using the premixed laminar flame-speed calculation module, while the ignition delay time simulations were performed with the homogeneous reactor model using the volume-time profiles obtained in the non-reactive mixture experiments.

4 Results

Laminar Flame Speeds

The laminar flame speed measurements for lean, stoichiometric and rich 2,3-butanediol/air mixtures were carried out at the initial unburned gas temperature of 403 K and the initial pressures of 1 and 2 bar. The results of the experimental measurements at 1 and 2 bar are plotted in Fig. 2. left and right, respectively. From the data at the initial pressure of 1 bar, it can be seen that the flame speed increases with the equivalence ratio until φ = 1.1, where its maximum is observed at each recorded pressure and temperature during propagation. It follows a decreasing trend from φ = 1.2 onward. The flame speeds at the initial pressure of 2 bar could not be measured for φ = 1.2 due to experimental constraints, as condensation issues of 2,3-butanediol are faced for this rich mixture.

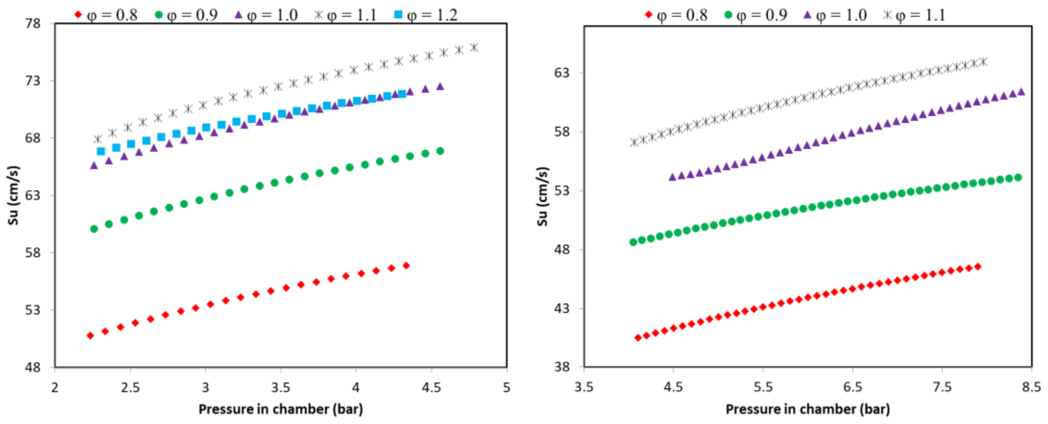

Figure 2: The experimental 2,3-butanediol flame speeds for φ = 0.8–1.2 at an unburned gas temperature of 403 K. Left: p_0 = 1 bar (T ≈ 489-579 K). Right: p_0 = 2 bar (T ≈ 476-567 K).

Ignition Delay Times

The results of the ignition delay time measurements in a rapid compression machine at different compressed gas pressures and temperatures for three different equivalence ratios are presented in Fig. 3. Additionally, pressure profiles at 880 K for three different compressed gas pressures at φ = 1.0 is provided. The inert composition was adjusted to keep the temperature inside the chamber as high as possible to avoid condensation.

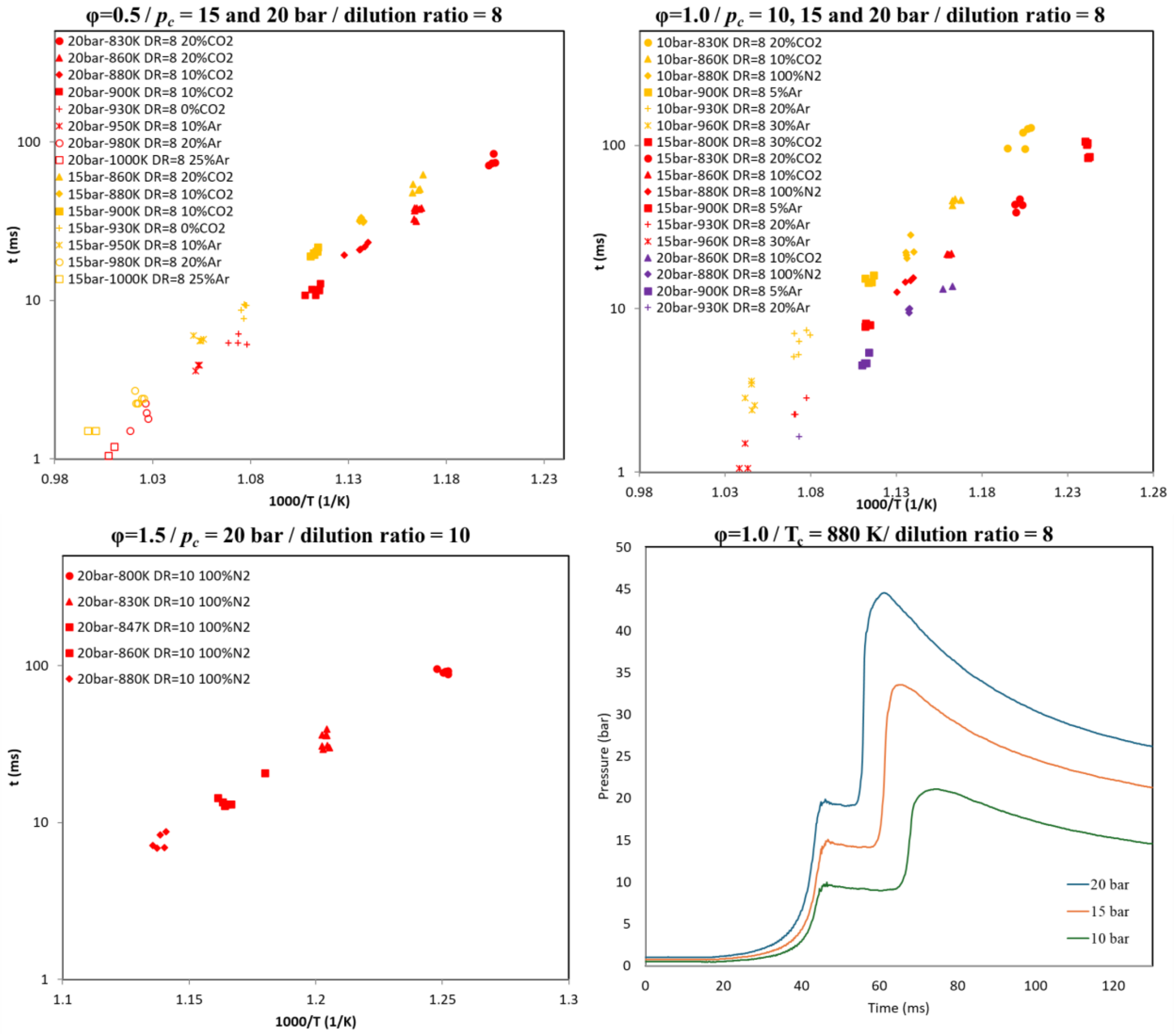

Figure 3: The experimental ignition delay times for φ = 0.5–1.5. Top Left: φ = 0.5, p_c = 15 and 20 bar, and T_c = 830–1000 K (O_2 / Inert = 1 / 8;). Top Right: φ = 1.0, p_c = 10, 15 and 20 bar, and T_c = 830–930 K (O_2 / Inert = 1 / 8;). Bottom Left: φ = 1.5, p_c = 20 bar, and T_c = 800–880 K (O_2 / Inert = 1 / 10;). Bottom Right: Pressure profiles at φ = 1.0, p_c = 10, 15 and 20 bar, and T_c = 880 K (O_2 / Inert = 1 / 8;).

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