Effect of hydrogen addition on the counterflow ignition of *n*-butanol at atmospheric and elevated pressures

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Abstract

The present experimental and computational study describes the non-premixed counterflow ignition of nitrogen-diluted pre-vaporized *n*-butanol/hydrogen mixtures impinging on a heated air stream for pressures of 1–4 atm and hydrogen molar percentages in the binary fuel blends ranging from $\xi_H=0\%$ (pure *n*-butanol) to $\xi_H=100\%$ (pure hydrogen). The experimental data show that hydrogen addition results in a non-linear decrease in ignition temperatures that can be broken into two regimes; a hydrogen-enhanced regime of $\xi_H=0\text{--}40\%$, where the addition of more hydrogen significantly decreases ignition temperature, and a hydrogen-dominated regime in the range of $\xi_H=40\text{--}100\%$, where ignition temperatures exhibit minimal sensitivity to further hydrogen addition. The experimental results are then simulated using *n*-butanol-specific skeletal mechanisms developed from two comprehensive butanol models available in the literature. The ability of these mechanisms to predict the variation of ignition temperatures associated with hydrogen addition to the *n*-butanol “base” fuel is assessed. Comparison between the experimental and computational results reveals that both chemical kinetic models capture the two-regime behavior associated with hydrogen addition observed in the present experiments, though both models over-predict experimental ignition temperatures. Further chemical kinetic analysis of the mechanisms reveals that the two-regime behavior is controlled by the production of hydroperoxyl radicals, with production via the reaction of formyl radicals and oxygen molecules dominating at low hydrogen addition levels, and production via the three-body $\text{H}+\text{O}_2+\text{M}=\text{HO}_2+\text{M}$ reaction dominating at high hydrogen addition levels.

Keywords: Ignition, Non-premixed, Butanol, Hydrogen, Binary fuel blends, Hydrogen addition

1. Introduction

For transportation energy purposes, the internal combustion engine will likely remain the dominant energy conversion device for the foreseeable future. As recently observed by Chu and Majumdar [1], while vehicle electrification via battery or fuel-cell technology holds promise, significant practical and technical challenges preventing their widespread adoption remain, including energy system weight, range, and the development of new fuel supply infrastructure. As a result, combustion-based transportation energy solutions that both improve efficiency and lower emissions are critically needed.

As a method for improving a wide range of combustion properties including efficiency and emissions characteristics, hydrogen addition to a base hydrocarbon fuel presents a variety of interesting opportunities. As early as the 1980s, Milton and Keck [2] and Yu *et al.* [3] recognized that laminar flame speed data for hydrocarbons with hydrogen addition were of both fundamental and practical interest. More recently, as a result of a significant push towards fuel-efficient, ultra-low emissions engines, numerous studies have investigated hydrogen addition for practical engines fueled by hydrocarbons. In spark-ignited engines, several studies have noted performance improvements, including extended lean operation limits, improved thermal efficiency, and reduced cycle-to-cycle pressure variations at lean operating conditions (e.g. [4–7]). Similar studies in diesel engines have noted improvements in NO_x emissions and thermal efficiency (e.g. [8,9]). In addition, benefits have been observed for aviation turbine engines (e.g. [10–13]), with hydrogen addition improving flame stability and blowout under lean conditions, leading to potentially lower NO_x emissions as a result of stable, fuel lean combustion.

In recent years, alternative fuels have also emerged as a leading prospect for efficiency and emissions improvements, both as blends or neat fuels in existing engine technologies, and as

stand-alone fuels for novel engine concepts. With respect to internal combustion engines, butanol has shown significant promise. As a fuel blend with gasoline, its higher energy density allows butanol to be mixed at a higher ratio – compared to ethanol – before engine modifications are required, facilitating phase-in to existing fuel infrastructure. In addition, whereas ethanol is fully miscible with water, both *n*- and *iso*-butanol isomers exhibit limited water solubility and are less corrosive, making efficient distribution via pipelines feasible. As a result, numerous fundamental studies have been conducted with an aim to develop robust chemical kinetic models for butanol isomers. Though not a comprehensive review, such studies have investigated laminar flame speeds [14–17], flame extinction [18–20], pyrolysis [21], flame structure [16,22–25], species and temperature measurements in a flow reactor [22] and jet-stirred reactors (JSRs) [16,26], and ignition delays in rapid compression machines (RCMs) [27–29] and shock tubes [30,31]. Recent efforts by the authors have also explored the ignition temperatures of the butanol isomers under the convective-diffusive conditions of the non-premixed counterflow configuration [32,33].

In addition to extensive investigations using butanol as a pure fuel, several fundamental efforts have explored blending butanol with other transportation-relevant fuels, focusing largely on mixtures relevant to butanol/gasoline blends. Dagaut and Togbé investigated species concentration profiles emanating from a JSR using butanol-gasoline surrogate mixtures [34] and butanol/*n*-heptane mixtures [35] at 10 atm and a range of lean and rich equivalence ratios. Saisirirat *et al.* [36] conducted further experiments on 1:1 mixtures of ethanol and *n*-butanol with *n*-heptane in a JSR for lean conditions. Broustail *et al.* [37] investigated laminar flame speeds of ethanol and butanol mixtures with *iso*-octane in a spherically-expanding flame configuration, observing that the addition of alcohols linearly increased the propagation velocity relative to *iso*-octane at atmospheric conditions as blending ratios of ethanol and butanol increased, with similar

but more muted effects at elevated pressures. Similar experiments at atmospheric pressure were conducted by Zhang *et al.* [38], coming to similar conclusions. Using a rapid compression facility, Karwat *et al.* [39] explored the effects of blending *n*-heptane/*n*-butanol on ignition delays, finding that butanol slowed ignition relative to pure *n*-heptane. In addition, Karwat *et al.* [39] found that the presence of *n*-heptane caused *n*-butanol to react at temperatures it would otherwise be non-reactive. Similar behavior for *n*-heptane/*n*-butanol mixtures was observed by Zhang *et al.* [40] in a shock tube for pressures of 2 and 10 atm and equivalence ratios of 0.5 and 1.0. In a recent RCM study, Kumar *et al.* [41] studied the effect of blending *n*-butanol on the ignition delay times of *n*-heptane and *iso*-octane for a pressure of 20 bar and equivalence ratios of 0.4 and 1.0. For blends with *n*-heptane, Kumar *et al.* [41] showed that both first-stage and total ignition delay increased with the addition of *n*-butanol. However, for *iso*-octane/*n*-butanol blends, the addition of *n*-butanol to *iso*-octane was found to lead to shorter total ignition delays under fuel lean conditions [41].

The present study develops novel counterflow forced ignition data for *n*-butanol with varying levels of hydrogen addition, and for varied ambient pressures. This effort is motivated by advanced engine concepts such as low temperature combustion (LTC), which have been proposed for the purpose of reducing emissions while simultaneously maintaining or improving performance. For example, the homogeneous charge compression ignition (HCCI) concept has been discussed extensively as a potential way to reduce emissions and increase fuel economy by combining a high compression ratio with a nearly homogenous fuel-air charge. However, despite a long track record of related research, this effort has not resulted in a commercially-viable engine due to a wide variety of technical hurdles including difficulties in ignition timing, low-load efficiency, a limited operability range, and high heat release rate at high-load conditions (*cf.*

[42–44]). Reactivity controlled compression ignition (RCCI) – an offshoot of the HCCI concept – attempts to resolve these issues via the staggered injection of two or more fuels of differing reactivity to control the timing and magnitude of the combustion event. In general, a low-reactivity fuel is injected into the cylinder prior to compression to create a well-mixed charge of fuel and air. Just prior to ignition, a high-reactivity fuel is injected directly into the cylinder to promote and control the ignition event. As recently reviewed by Reitz and Duraisamy [45], the RCCI concept has shown significant promise in terms of **greater** efficiency, significantly improved emissions characteristics, and controllable ignition timing with a variety of fuel configurations including gasoline/diesel, natural gas/diesel, methanol/diesel, and gasoline/gasoline+additive. **As its octane rating is similar to that of gasoline**, butanol may have promise as the low reactivity fuel in an RCCI-type engine. **Moreover, the inclusion of an in-situ fuel reformation system to reform on-board butanol fuel to hydrogen offers the potential to provide the necessary high reactivity fuel without the necessity of dual-fuel on-board storage. The complications associated with hydrogen distribution and dual-fuel distribution and on-board storage may thus be circumvented, while still providing the operability benefits**, improved efficiency, and reduced emissions of the RCCI concept. Such reforming has been demonstrated extensively for ethanol [46], while butanol reforming has also been investigated by several studies [47–49].

Recognizing that developing the above advanced engine concepts into practical devices will **require** high-fidelity combustion models able to capture the chemical kinetic effects of fuel blending, the present study aims to progress two objectives. First, novel non-premixed counterflow ignition data exploring the effect of hydrogen addition to *n*-butanol for mixing ratios, defined as the mole percentage of hydrogen in the hydrogen/*n*-butanol blends, of 0–100% and

pressures of 1–4 atm are obtained. As has been described in detail in previous studies by the authors [32,33], the non-premixed counterflow ignition configuration provides a unique opportunity to explore a diverse set of chemical kinetics under convective/diffusive conditions due to its high degree of sensitivity to both chemical kinetic and transport effects. Such data are relevant to the development of robust, predictive combustion models suitable for engine development and design. This dataset is furthermore simulated using *n*-butanol skeletal mechanisms developed previously by the authors [32] from two comprehensive butanol mechanisms available in the literature. The experimental and simulated results are compared to assess the performance of the two literature butanol models for predicting ignition temperatures of *n*-butanol/hydrogen mixtures. Second, chemical kinetic analysis of the simulated results is performed to understand the controlling chemistry causing changes in fuel blend reactivity due to hydrogen addition. This understanding suggests the possibility of generalized rules for estimating the effect of hydrogen addition on forced ignition temperatures for a given “base” fuel, and highlights an area for future investigation.

2. Experimental and computational descriptions

2.1 Experimental apparatus

The details of the non-premixed counterflow ignition apparatus, including a comprehensive experimental characterization, have been previously described by the authors [32]. A schematic is provided in Fig. 1. In brief, the counterflow burner consists of a quartz straight-tube upper section directing heated air downward against a nitrogen-diluted fuel stream emanating from a stainless steel lower section. The air and fuel streams are surrounded by concentric nitrogen co-flow to isolate the test section from the ambient atmosphere and maintain the quality of the resulting flow field. The air and fuel tubes have inner diameters of $D=19$ mm and the co-flow

tubes have 28 mm inner diameters. The air and fuel streams are separated by $L=20$ mm, resulting in an L/D ratio for all experimental conditions of 1.05.

Figure 1: Diagram of the flow control, heating, and measurement systems for the present counterflow ignition apparatus.

The air boundary is heated to 1250–1300 K using an internal helical SiC heater, supplemented by an external heater used to reduce heat loss along the air tube's length. The ignition temperature, measured as the air-side centerline temperature at the tube exit using a K-type bare wire thermocouple, is determined by processing the thermocouple reading with a radiation correction. The fuel boundary is monitored using a bare wire K-type thermocouple, and the temperature is controlled by electric heating on the exterior of the fuel duct. Throughout this study the fuel boundary temperature is set to a nominal value of 380 K. The details of the air-

boundary thermocouple design and radiation correction methodology can be found in the supplementary material of Ref. [32].

As discussed in previous work by the authors [32], knowledge of the ignition location is critical to ensure that the ignition event itself occurs in a quasi-one-dimensional manner, consistent with the quasi-one-dimensional modeling assumptions **implicit in the counterflow configuration**. The location of the ignition event is monitored in the present study using a Photron SA5 high-speed camera acquiring visible-light images at frame rates ranging from 60 to 3000 Hz. While high speed images are desirable to precisely locate the ignition event, for high hydrogen content cases the extremely low luminosity associated with the ignition event prevents high frame-rate imaging. These frame rates are nonetheless adequate to ensure consistency amongst experimental data sets. For all the experimental data reported herein, the onset of ignition is observed to take place near the middle of the test section and then propagate radially **outwards**. A detailed discussion of the importance of monitoring ignition location has been described previously [32].

Flow control is accomplished through the use of sonic nozzles for all gases. The air stream is synthesized by a 21%/79% O₂/N₂ mixture by mole, while the nitrogen-diluted fuel stream can be set at a particular fuel mole fraction of interest. **For the present study, the total fuel loading (mole fraction of hydrogen and *n*-butanol combined) is held constant at $X_f = 0.15$.** When investigating the ignition of various hydrogen/*n*-butanol blends, hydrogen is introduced into the fuel stream after the liquid *n*-butanol has been vaporized, and is mixed in a glass-bead-filled mixing chamber before proceeding to the fuel duct. The flow rate of liquid *n*-butanol is controlled using a precision Teledyne Isco 1000D high-pressure syringe pump, with fuel vaporization accomplished through a heated spray system. The liquid fuel vaporization system

and the subsequent fuel lines are heated to a surface temperature just above the boiling point of *n*-butanol. To ensure proper vaporization, the partial pressure of *n*-butanol in the fuel stream is maintained well below its saturation vapor pressure, calculated using the correlation from Yaw's Chemical Handbook [50] at the temperature/pressure conditions within the fuel line. Validation of the fuel stream concentration has been conducted previously [32].

2.2 Experimental procedure

In the present experiments, the oxidizer boundary temperature at the onset of ignition is denoted as the ignition temperature (T_{ig}). The procedure for acquiring this temperature is as follows: 1) The internal, external, and flow system heaters are brought up to a steady-state temperature close to the ignition state, the desired gaseous mass flow rates (excepting any fuel) for a given strain rate condition are set on the flow system, and the chamber is pressurized to the desired set point. 2) The fuel mixture is introduced through the flow system and allowed to come to steady state. 3) The high-speed camera begins acquiring data, and the air temperature is gradually raised by increasing power to the internal heater until a flame ignites. 4) The fuel supply is shut off to extinguish the flame. 5) The thermocouple solenoid is activated, rotating the thermocouple bead to the center of the air duct and the air temperature is recorded. The fuel-side gas temperature is also recorded. 6) The images acquired from the high-speed camera are checked to verify that ignition occurs at or near the longitudinal axis, and that it occurs near the middle of the test section, ± 2 mm. If ignition occurs too far towards the fuel or oxidizer exits, the flow rates are adjusted to move the stagnation plane in the appropriate direction while maintaining a constant global strain rate, as defined in the following paragraph. In addition, if ignition occurs at a temperature more than 10 K away from the estimated temperature used to compute flow rates for a given global strain rate, the flow rates are updated and steps 2–6 are repeated. Moreover, steps

2–6 are repeated a minimum of three times once the proper flow settings are achieved to ensure a consistent value for T_{ig} .

Here, the global strain rate (k) is defined based on the relation of Seshadri and Williams [51]: $k = \frac{2V_O}{L} \left(1 + \frac{V_F \sqrt{\rho_F}}{V_O \sqrt{\rho_O}} \right)$, where V is the bulk velocity at the boundary, L is the separation distance, ρ is the density, and the subscripts F and O represent the fuel and air boundaries, respectively. The adequacy of this global strain rate definition for accounting for the effects of varying density due to the temperature gradients inherent to counterflow ignition has been demonstrated in [32]. Following the work of Fotache *et al.* [52], the pressure-weighted strain rate (k'), defined as $k' = \frac{P_C}{P_{ref}} k$, is used to isolate the chemical kinetic effect of pressure variations by keeping the thickness of the spatial scalar structure (temperature and concentration profiles) approximately constant. In the definition of k' , P_C is the chamber pressure and P_{ref} is a reference pressure, taken throughout this work as 1 atm.

The fuel loading, X_f , is defined as the molar fraction of fuel (neat component or blend) in the fuel stream, with nitrogen accounting for the remainder of the fuel stream. In the present study, the total fuel loading (including both *n*-butanol and hydrogen) is held constant at $X_f = 0.15$, while the percentage of hydrogen within the fuel portion of the fuel stream is varied. The blending ratio of hydrogen is characterized by ξ_H , defined as the mole percentage of hydrogen in a hydrogen/*n*-butanol blend. Thus, the fuel loading of hydrogen in the fuel blend ranges from $\xi_H = 0\%$ (pure *n*-butanol) to $\xi_H = 100\%$ (pure hydrogen).

As has been described in previous work [32], both systematic and random uncertainties are relevant to the analysis of the present experimental results. Systematic uncertainty stems from defects in a parameter model (e.g., Nusselt number for thermocouple radiation correction) or

measuring equipment (e.g., pressure gauges) which cause system-wide deviations from true behavior. Such uncertainties result in reproducible inaccuracies that tend to impact the entire dataset in an equivalent manner. Random error, on the other hand, represents statistical fluctuations in measured data based upon the precision of the measurement device. Such errors are typically minimized through the averaging of multiple observations. These definitions are crucial to interpreting the results of the present study. While the total uncertainty (including both systematic and random errors) is relevant for the comparison of experimental and numerical ignition temperatures, only the random error is applicable when comparing amongst the experimental results, since all data should be equally affected by systematic errors. As a result, comparisons amongst the experimental data sets should be compared using the random error (± 5 K), while comparisons between experimental and numerical data are best compared using the total estimated uncertainty (systematic plus random), which ranges from 12 K for the lowest ignition temperature to 25 K for the highest one in the present study. The maximum uncertainty in molar percentage of hydrogen is estimated as $\pm 1\%$. Representative total uncertainties in experimental ignition temperatures are shown in the following figures to facilitate comparison with the simulated results. The interested reader is referred to the supplementary material included with [32] for a detailed discussion of the sources of uncertainty and the uncertainty estimation methodology.

2.3 Computational specifications

The ignition state is modeled using an in-house counterflow non-premixed ignition code based on the **potential-flow** formulation of Smooke *et al.* [53] and identical to that used previously [32,33]. While experimentally the flow field more closely follows the behavior of a plug-type flow [32], as demonstrated by Sung *et al.* [54], the scalar structures of different flow descriptions

– potential, plug, or an intermediate flow – collapse onto each other within the thermal mixing zone for properly matched boundary velocities. Fotache *et al.* [55] further indicated the insensitivity of the ignition process to the flow description used. As a result, the choice of potential-flow model should have a minimal effect on the ignition temperatures computed.

As in the work of Kreutz *et al.* [56], the ignition temperature corresponds to the turning point of the lower-branch ignition response curve (“S-curve”) with respect to air boundary temperature, while navigation of the ignition turning point is achieved through the two-point flame-controlling continuation method developed by Nishioka *et al.* [57], using the H-radical as the controlled species. For more details on the nature and computation of the system response curve, the interested reader is referred to the works of Kreutz *et al.* [56] and Nishioka *et al.* [57]. In this study, the H radical is chosen as the controlled species due to its crucial role in governing ignition, although other key radicals are equally applicable [57]. For a given strain rate, the use of the two-point H-controlling continuation requires boundary conditions of the mixture compositions at both fuel and oxidizer boundaries, the fuel boundary temperature (380 K in the current work), and the H concentration values at two different locations as internal boundary conditions [57]. As such, the mass fluxes at the fuel and oxidizer boundaries are solved as edge values, while the air boundary temperature becomes the system response [57]. By varying the H concentration values at the two selected locations, continuous mapping of the ignition response curve is then obtained.

The current code utilizes the CHEMKIN chemical kinetics and transport properties libraries [58,59]. Typically, absolute and relative tolerances are set as 10^{-9} and 10^{-6} , respectively; variation of these values has no impact on the computed ignition temperature. The solution is computed on a non-uniform grid consisting of 227 points that have been adaptively placed to

achieve a dense grid within the thermal mixing zone/ignition kernel. The gradient and curvature parameters of the resulting solution typically have values of 0.05 or less.

The skeletal mechanisms used in the present work are those developed previously [32] for *n*-butanol based upon the comprehensive butanol mechanisms of Sarathy *et al.* [60] and Merchant *et al.* [61], and will be referred to throughout the remainder of the text as the SN and MN mechanisms, respectively. These skeletal mechanisms are generated by eliminating unimportant species and reactions for the conditions of interest and are used in place of the detailed mechanisms since, despite being of modest size compared to many reaction mechanisms of large hydrocarbons, the Sarathy *et al.* [60] and Merchant *et al.* [61] mechanisms are nonetheless too large to allow efficient computing of ignition turning points. While the authors are aware of the additional comprehensive butanol mechanism of Frassoldati *et al.* [62], as mentioned in previous works [32,33] the inclusion of non-integer stoichiometric coefficients in this mechanism makes it incompatible with the current CHEMKIN-based ignition code, as well as running exceedingly slowly in batch reactor simulations in CHEMKIN-PRO [63]. Hence, only the mechanisms of Sarathy *et al.* [60] and Merchant *et al.* [61] are included and compared in the present study.

The detailed mechanisms of Sarathy *et al.* [60] and Merchant *et al.* [61] are reduced using the Directed Relation Graph with Error Propagation (DRGEP) implementation of the Mechanism Automatic Reduction Software (MARS) package of Niemeyer and co-authors [64–67]. The skeletal reduction utilizes constant-volume ignition delays for equivalence ratios of 0.5–2, pressures of 1–40 atm, and temperatures of 1000–1800 K, using *n*-butanol, N₂, and O₂ as target species. In addition, the reduction procedure utilizes perfectly stirred reactor (PSR) extinction profiles for inlet temperatures of 400 and 500 K, covering the same range of pressure and

equivalence ratio as the autoignition results. For both ignition delay and PSR targets, the maximum error tolerance during the reduction process is set at 10%. Further validation data for the skeletal mechanisms can be found in previous work by the authors [32].

3. Ignition results and discussion

3.1 Effects of hydrogen addition

Figure 2 demonstrates the effect of hydrogen addition to *n*-butanol, with accompanying simulated results using the SN and MN mechanisms. For atmospheric pressure conditions, fuel loading $X_f = 0.15$, a pressure-weighted strain rate of $k' = 350 \text{ s}^{-1}$, and a fuel boundary temperature of 380 K, ignition temperature decreases by $\sim 250 \text{ K}$ as the hydrogen content in the fuel stream increases from $\xi_H = 0\%$ to $\xi_H = 40\%$. However, as the hydrogen content increases further beyond 40% the effect of further hydrogen addition is significantly more muted, with ignition temperature decreasing by less than 40 K between $\xi_H = 40\%$ and $\xi_H = 100\%$. Similar, but less dramatic effects are observed when pressure is increased to 3 atm, where ignition temperature decreases by $\sim 100 \text{ K}$ from $\xi_H = 0\%$ to $\xi_H = 40\%$, and $\sim 25 \text{ K}$ from $\xi_H = 40\%$ to $\xi_H = 100\%$.

The reduced ignition temperature sensitivity to hydrogen addition at elevated pressure can be readily explained by considering the disparate behavior of the pure component fuels. Unlike hydrocarbon fuels, which exhibit a monotonic decrease in ignition temperature as pressure rises (e.g., previous butanol results [32,33]), hydrogen exhibits a unique three-limit behavior wherein ignition temperature falls with rising pressure below $\sim 0.2 \text{ atm}$, increases between 0.2 and 3–4 atm, then decreases again as pressure rises further beyond 4 atm [52]. As the pressure range of 1–4 atm in the present study generally falls within the “second limit” regime for hydrogen ignition [52], hydrogen and *n*-butanol exhibit qualitatively opposite ignition temperature trends,

with the ignition temperature of *n*-butanol falling with increasing pressure while the ignition temperature of hydrogen rises. This behavior results in a crossover point between the fuel blend ignition results at 1 and 3 atm, which is observed to occur between $\xi_H = 20\%$ and $\xi_H = 30\%$ for the present conditions.

Figure 2: Counterflow ignition temperatures as a function of molar percentage of hydrogen in the fuel blend. Total fuel loading $X_f = 0.15$, $k' = 350 \text{ s}^{-1}$, and fuel boundary temperature of 380 K. Solid lines represent results from the SN mechanism, while dashed lines indicate results from the MN mechanism.

The simulated results from both the SN and MN mechanisms are also included in Fig. 2 and generally capture the above trends, including the transition in behavior at $\sim 40\%$ hydrogen addition for a given pressure and the crossover point between the 1 and 3 atm results, suggesting that both mechanisms capture the controlling chemistry and that further analysis of the mechanisms can yield meaningful explanations of the observed trends. Several other interesting features are also worth mentioning. As was observed by the authors in previous study [32], the MN mechanism predicts ignition temperatures 50–60 K higher than those predicted by the SN

mechanism for pure *n*-butanol ignition. However, both mechanisms converge to appreciably similar results for pure hydrogen ignition, with predictions from each mechanism at both 1 and 3 atm falling within 10 K of each other. In addition, Fig. 2 demonstrates that the simulated results for pure hydrogen lie substantially closer to the experimental results than the simulated results for pure *n*-butanol, with the simulations exceeding the experiments by just 25–35 K – nearly within the bounds of total estimated uncertainty – at 1 atm, and 50–60 K at 3 atm. In comparison, for the same operating conditions the SN and MN mechanisms predict *n*-butanol ignition temperatures 90–100 K higher and 140–160 K higher, respectively, than experimental values across the pressure range.

Figure 3 provides additional detail on the effect of pressure for selected percentages of hydrogen addition for both experimental and simulated results. The conditions of Fig. 3 are a total fuel loading $X_f = 0.15$, a pressure-weighted strain rate of $k' = 350 \text{ s}^{-1}$, and a fuel boundary temperature of 380 K. Focusing on the experimental results, at $\xi_H = 0\%$ and 10%, increasing pressure results in a monotonic decrease in ignition temperature. The 10% hydrogen addition level decreases the overall ignition temperatures relative to the pure *n*-butanol case, and reduces the slope of the ignition temperature change with respect to pressure. Furthermore, as suggested by the crossover point observed in Fig. 2, when the hydrogen content reaches 25% the ignition temperature is nearly invariant with pressure, with ignition temperature increasing only slightly between 1 and 2.5 atm prior to a small decrease above 3 atm. Hydrogen addition at 25% therefore delineates a transitional point between butanol-dominated behavior and hydrogen-dominated behavior. As more hydrogen is added to the fuel blend, ignition temperature behavior as a function of pressure becomes progressively more similar to that of pure hydrogen, with the 50% hydrogen addition results showing a great degree of similarity to the pure hydrogen (100%)

results both in trend and in absolute ignition temperatures. The effect of the aforementioned trends is a convergence in ignition temperature amongst the various mixtures as pressure increases, indicating more clearly the pressure effects observed in Fig. 2. Both the SN mechanism (Fig. 3(a)) and the MN mechanism (Fig. 3(b)) capture the above trends quite well, including the transitional behavior at 25% hydrogen, although both mechanisms predict ignition temperatures exceeding those observed experimentally.

Figure 3: Counterflow ignition temperatures as a function of pressure for varying hydrogen addition percentages in the fuel blend. Total fuel loading $X_f = 0.15$, $k' = 350 \text{ s}^{-1}$, and fuel boundary temperature of 380 K. (a) Comparison of experimental data to simulated data from the SN mechanism. (b) Comparison of experimental data to simulated data from the MN mechanism. (c) Comparison of 100% hydrogen experimental data to simulated results using the SN and MN skeletal mechanisms, as well as the H₂/O₂ model of Burke *et al.* [68].

In addition to the broad trends observed in Fig. 3, several more subtle features are also worthy of mention. First, comparing the experimental results for $\xi_H = 25\%$, 50% , and 100% , a non-monotonic response with pressure variation is exhibited for each case; ignition temperature first reaches a maximum as pressure increases, then begins to decrease as pressure increases further. The locations of the maxima also appear to change as ξ_H varies. At $\xi_H = 25\%$, the maximum ignition temperature is reached at 2.5 atm, while for $\xi_H = 50\%$ and 100% the maximum ignition temperature occurs between 3 and 3.5 atm. This shift is interesting in that it suggests the presence of *n*-butanol may impact the critical pressure of the typical second-to-third limit transition. Such behavior is not observed in the simulated results using either the SN or MN mechanism within the simulated pressure range, suggesting that this phenomenon may warrant further study.

Second, observing Fig. 3(c) – which shows the experimental and simulated results for 100% hydrogen in detail – it is apparent that the simulated results from the SN and MN mechanisms fall within 10 K of each other throughout the pressure range tested and additionally show good agreement with corresponding results using the recent detailed hydrogen-oxygen model proposed by Burke *et al.* [68]. This suggests that despite not being specifically reduced for prediction of hydrogen ignition, the SN and MN mechanisms nonetheless capture the hydrogen ignition behavior predicted by the Burke *et al.* [68] mechanism quite well.

Third, it is seen from Fig. 3(c) that whereas the experimental hydrogen results appear to transition from the second to third limit at ~ 3.5 atm (indicated by a slight decrease in ignition temperature at 4 atm relative to 3.5 atm), none of the mechanisms predict a transition below 4 atm. Taken in conjunction with the increasing level of disagreement between the experimental and simulated results as pressure increases, the conclusion reached by Burke *et al.* [68] – namely

that uncertainties in the model parameters for the formation and consumption of hydroperoxyl significantly impact the model’s predictive capabilities, particularly at elevated pressures and lower temperatures – would appear to be supported by the present dataset.

3.2 Controlling ignition chemistry

The results of Figs. 2 and 3 can best be understood as a transition between the thermokinetically-controlled behavior of butanol and the kinetically-controlled behavior of hydrogen. As has been described previously by Kreutz *et al.* [56] and Fotache *et al.* [55], while thermal feedback plays an insignificant role in most situations for hydrogen ignition, for hydrocarbons it is indispensable for the prediction of ignition turning point behavior. To begin to understand what is responsible for the enhancement of *n*-butanol ignition with hydrogen addition, this transition is demonstrated in Fig. 4, which shows the ignition turning point as well as the lower branch of the characteristic “S-curve” using the MN mechanism. Since similar results are obtained using the SN mechanism, only the results from the MN mechanism are presented in this section for the sake of clarity.

Figure 4: Comparison of the ignition turning points and lower-branch “S-curve” behaviors for varying levels of hydrogen addition at 1 atm, $X_f = 0.15$, $k' = 350 \text{ s}^{-1}$, and fuel boundary temperature of 380 K. Simulated results are derived from the MN mechanism.

As shown in Fig. 4, the pure butanol case (0% hydrogen) exhibits a consistent increase in **air boundary** temperature as the peak H-radical mole fraction **rises towards the** ignition turning point. However, **when** hydrogen is introduced the lower branch exhibits a region of strong temperature sensitivity, what Fotache *et al.* [69] in their methane-hydrogen ignition study termed a “hydrogen chemistry kinetic growth” or HKG zone. At low hydrogen addition percentages (e.g., $\xi_H = 10\%$) this zone terminates ahead of the ignition turning point and returns to a lower temperature sensitivity more commensurate with the pure butanol case. As hydrogen addition level increases beyond 10%, the ignition turning point begins to merge with the HKG zone. This merging coincides with the end of the $\xi_H = 0\text{--}40\%$ hydrogen addition region, after which the ignition temperature is insensitive to further hydrogen addition (*cf.* Fig. 2). As a result, the two ignition regimes observed in the previous section may be roughly described as hydrogen-enhanced ($\xi_H = 0\text{--}40\%$) or hydrogen-dominated ($\xi_H = 40\text{--}100\%$).

In order to identify the underlying cause of the ignition enhancement due to hydrogen addition, it is first useful to identify the chemistry underlying the HKG zone. Recognizing that this enhancement must be related to hydrogen consumption, a path flux analysis utilizing the MN mechanism reveals that the following four reactions account for the majority of H_2 and H radical consumption.

Reactions R1 and R2 are the primary consumption reactions for the H radical, while R3 and R4 represent the major consumption reactions for H_2 . To identify the controlling reactions of the

HKG zone, each of the four reactions is artificially removed from the MN mechanism to create individual “test” mechanisms. The resulting solutions on the lower branch and in the region of the turning point for conditions of 10% hydrogen addition, $X_f = 0.15$, $k' = 350 \text{ s}^{-1}$, and a fuel boundary temperature of 380 K are shown in Fig. 5, with the ignition response curve for the pure *n*-butanol (0% H_2) and unmodified $\xi_H = 10\%$ cases shown for comparison.

Figure 5: Comparison of the effect on the lower branch and ignition turning point of removing several key hydrogen-related reactions from the MN mechanism. Solid lines represent the unmodified MN mechanism solutions for 0% and 10% hydrogen addition. Symbols represent solutions for 10% hydrogen addition with selected reactions artificially removed from the MN mechanism. Solutions are for atmospheric conditions, $X_f = 0.15$, $k' = 350 \text{ s}^{-1}$, and fuel boundary temperature of 380 K.

Figure 5 shows that the removal of **R1** results in identical solutions to the unmodified 10% case **leading** up to the HKG zone, but significantly departs from **the unmodified solutions** thereafter, displaying no HKG zone or ignition turning point within the range of air boundary temperatures calculated. Since R1 represents a basic chain branching reaction, this result is not surprising. Removing R2, which competes for reactants with R1, reduces the ignition temperature while significantly enlarging the HKG zone and translating it to ~800 K, 200 K

lower than the baseline unmodified 10% hydrogen case. Removal of R3 results in lower- and middle-branch solutions closely related to those seen in the pure *n*-butanol (0% H₂) case, with significant deviations occurring only near the ignition turning point. No HKG zone is observed when removing R3. Finally, R4 has a less dramatic effect, slightly reducing the size and translating the HKG zone to a higher air boundary temperature, while exerting minimal influence on the ignition turning point. Although all four reactions impact the HKG zone to a greater or lesser extent, Fig. 5 clearly demonstrates that R3 serves as a gateway reaction for the enhancement associated hydrogen addition, as it effectively isolates the effect of hydrogen addition and reverts to the pure *n*-butanol results in the lower and middle branches.

Further flux analysis considering the production and consumption of the H radical reveals that R3 represents the primary reaction both in consuming H₂ and producing H for all conditions involving hydrogen addition. The H radicals produced via R3 are then primarily consumed via R1 and R2, with R1 dominating consumption in the hydrogen-enhanced regime and R2 taking over as hydrogen addition levels move into the hydrogen-dominated regime. It is noted that the net effect of hydrogen addition is a significant enhancement in terms of the size of the radical pool available in the hydrogen-enhanced regime, as demonstrated in Fig. 6 through a spatially-resolved profile comparison between O, OH, and H radicals with 0% and 10% hydrogen addition at their respective ignition turning points. Per Fig. 2, the computed ignition temperatures using the MN mechanism for the 0% and 10% hydrogen addition cases are 1371.4 K and 1255.5 K, respectively. Figure 6 shows that the mole fractions of key radicals increase by more than two orders of magnitude as a result of hydrogen addition, providing a significantly larger radical pool from which *n*-butanol breakdown reactions can draw. The larger radical pool size leads to a dramatic reduction in ignition temperature, as observed in the hydrogen-enhanced regime in Fig. 2. In light of the observed effects on the radical pool, it is also interesting to note the greater

sensitivity to hydrogen addition displayed by the MN mechanism relative to the SN mechanism in Fig. 2. As discussed in previous study by the authors [32], the MN mechanism predicts that *n*-butanol consumption proceeds in large part through enol and butyraldehyde pathways via a series of H-abstraction reactions, which require significant input from the radical pool. In contrast, the SN mechanism predicts relatively rapid breakdown via unimolecular decomposition reactions. The present results thus demonstrate the greater sensitivity of the MN mechanism to radical pool growth, and additionally explain the differing sensitivities of ignition temperature to ξ_H between the SN and MN mechanisms in the hydrogen-enhanced regime.

Figure 6: Comparison of the H, O, and OH radical profiles for 0% and 10% hydrogen addition at the corresponding ignition turning point. Results computed for atmospheric pressure, $X_f = 0.15$, $k' = 350 \text{ s}^{-1}$, and fuel boundary temperature of 380 K using the MN mechanism. Axial position is relative to the fuel stream boundary.

In addition to the root cause of the ignition enhancement via hydrogen, Fig. 2 also begs the question of what causes the ignition enhancement effect to be confined to low levels of hydrogen addition (i.e. below $\sim 40\%$ addition). This question is particularly interesting in light of previous work by Fotache *et al.* [69] on hydrogen-enriched methane mixtures, which showed the hydrogen-enhanced regime confined to a significantly smaller hydrogen addition range of approximately 0–10% at atmospheric pressure and similar total fuel loading conditions. This

disparate behavior suggests that the nature of hydrogen enhancement has some dependence on **fuel** molecule size, which could be a critical consideration for the application of hydrogen addition in practical engines. A useful starting point for investigating this behavior is the observation that, somewhat counterintuitively, spatially-integrated H_2 consumption exhibits significant non-monotonicity as hydrogen addition increases, as shown in Fig. 7. As the mole percentage of hydrogen in the fuel blend increases from $\xi_H = 0\%$ to $\xi_H = 40\%$, H_2 consumption increases by an order of magnitude, reaching peak consumption at $\xi_H \sim 40\%$ before decreasing as hydrogen content increases further. This is in contrast to the behavior of *n*-butanol, for which consumption remains nearly constant up to 20–30% hydrogen addition before dropping off as the total fraction of *n*-butanol in the fuel blend reduces further. That the observed peak consumption coincides with the end of the hydrogen-enhanced regime suggests that increased hydrogen consumption supports and promotes radical production, which in turn leads to reduced ignition temperatures.

Figure 7: Spatially-integrated *n*-butanol and hydrogen **production** rates as a function of hydrogen addition at atmospheric pressure, total fuel loading $X_f = 0.15$, $k' = 350 \text{ s}^{-1}$, and fuel boundary temperature of 380 K.

Figure 8 shows the spatially-resolved profiles of H, O, OH, and HO₂ radical species at the ignition turning point as a function of hydrogen addition for atmospheric pressure. It is clear from the profiles of H, O, and OH that low levels of hydrogen addition result in a significantly larger ignition kernel, with 10% addition raising the peak mole fraction of each radical by several orders of magnitude. However as hydrogen content is further increased, the size of the kernel does not change significantly, with peak mole fractions of O and OH remaining essentially constant, and the H radical increasing only slightly between 10% and 40% hydrogen addition. After $\xi_H = 40\%$, the ignition kernel size progressively decreases as hydrogen percentage increases, with the kernel for pure hydrogen stabilizing at peak mole fractions two to three orders of magnitude greater than those observed in the pure *n*-butanol ignition kernel. The spatial profiles of HO₂ exhibit similar trends in terms of magnitude. However, the shape of the HO₂ profile changes dramatically between 50% and 80% hydrogen content. At low hydrogen addition levels, a significant drop in HO₂ mole fraction is apparent at ~ 1.2 cm (measured from the fuel stream boundary), with the magnitude of this drop progressively decreasing from $\xi_H = 10\%$ to $\xi_H = 50\%$, and disappearing entirely by $\xi_H = 80\%$. This significant change in the shape of the HO₂ profile suggests appreciable changes in the production/consumption routes of HO₂ as ξ_H increases.

It is further seen from Fig. 8 that by keeping k' constant, the overall width of the ignition kernel, characterized by the full-width-at-half-maximum (FWHM) of the spatially-resolved profiles of key radicals, remains similar at varying ξ_H . The thermal diffusivity values of the fuel stream differ by approximately a factor of two between $\xi_H = 0\%$ (pure *n*-butanol) and $\xi_H = 100\%$ (pure hydrogen) cases, representing a maximum deviation at different hydrogen addition levels. However, within the thermal mixing zone, as well as the ignition kernel, the difference between

these two extreme cases is reduced due to diffusive intermixing with the high-temperature air stream. As a result, neither the thermal structure nor the ignition kernel width substantially vary as a result of hydrogen addition, which is confirmed computationally.

Figure 8: Spatially-resolved profiles of (a) H, (b) O, (c) OH, and (d) HO₂ radicals as a function of hydrogen content of the fuel blend. Results computed using the MN mechanism for atmospheric pressure, total fuel loading $X_f = 0.15$, $k' = 350 \text{ s}^{-1}$, and fuel boundary temperature of 380 K.

To investigate the cause of **the changing behavior for the HO₂ profiles**, Fig. 9 compares the spatially-resolved molar production rates of some important HO₂-related reactions – identified via path flux analysis – accounting for the greatest proportion of HO₂ production and consumption. For atmospheric conditions, $X_f = 0.15$, $k' = 350 \text{ s}^{-1}$, and hydrogen addition levels

of 10%, 40%, and 80%, it is apparent that the primary production and consumption reactions change significantly as hydrogen addition increases. At 10% hydrogen addition, the majority of HO_2 is produced via reaction R5, with reaction R2 playing a significantly smaller role.

As hydrogen addition increases to 40%, R2 becomes significantly more prominent, and overtakes R5 in terms of total HO_2 production rate. By 80% addition, R5 accounts for a minimal proportion of overall HO_2 production, while R2 is responsible for ~90% of its production. The major consumption reactions also change as a function hydrogen addition, with the chain branching reaction R6 and the chain propagating reaction R7 becoming relatively more important than the terminating reaction R8 and the H_2O_2 -formation reaction R9 as hydrogen addition increases.

The drop in HO_2 mole fraction near 1.2 cm – and its decreasing magnitude with increasing hydrogen addition – can be explained by the spatial distribution of the production and consumption reactions shown in Fig. 9. At 10% hydrogen addition, the peak consumption rates of the two major consumption reactions R7 and R8 occur just after the peak production rate via R5, resulting in a steep drop near 1.2 cm. As hydrogen addition increases, the magnitude of this drop diminishes as reaction R2 becomes more prominent, due to R2's peak production rates occurring farther towards the oxidizer side. Ultimately the drop disappears entirely by $\xi_H = 80\%$ due to the relatively broadly-distributed R2 becoming the primary HO_2 production reaction.

Figure 9 Spatially-resolved molar production rates of the hydroperoxyl radical related reactions; (a) 10%, (b) 40%, and (c) 80% hydrogen addition. Results computed using the MN mechanism for atmospheric pressure, total fuel loading $X_f = 0.15$, $k' = 350 \text{ s}^{-1}$, and fuel boundary temperature of 380 K.

The transition between R5 and R2 as a function of hydrogen addition is summarized in Fig. 10 by comparing the spatially-integrated molar production rates **for total HO₂ (i.e. via all related reactions)**, R2, and R5. A clear crossover point between molar production rates of R2 and R5

occurs at 30% hydrogen addition, while overall HO_2 production rate peaks at 40%. This crossover is important, as when R2 takes over from R5 as the primary pathway leading to HO_2 , production of HO_2 begins to compete with the critical chain branching reaction R1, and the reaction pathways begin to strongly resemble the competition between R1 and R2 that typifies the second limit in the hydrogen-oxygen system. Thus, the relative importance of reactions R5 and R2 determine the transition point between hydrogen-enhanced and hydrogen-dominated behaviors.

Figure 10: Spatially-integrated molar production rates of total HO_2 , R2 ($\text{H} + \text{O}_2(+\text{M}) \leftrightarrow \text{HO}_2(+\text{M})$), and R5 ($\text{HCO} + \text{O}_2 \leftrightarrow \text{HO}_2 + \text{CO}$) as a function of hydrogen addition. Results computed using the MN mechanism for atmospheric pressure, total fuel loading $X_f = 0.15$, $k' = 350 \text{ s}^{-1}$, and fuel boundary temperature of 380 K.

The above-mentioned phenomena can also aid in understanding the cause behind the observed pressure-insensitivity of the 25% hydrogen fuel mixture in the 1–4 atm pressure range shown in Fig. 3. As the gap between the R5 and R2 production rates closes between 20–30% hydrogen content, HO_2 production is approximately evenly split between the pressure-insensitive reaction R5 and the pressure-sensitive reaction R2. After $\xi_{\text{H}} = 30\%$, R2 dominates HO_2

production and the mixture begins to take on pressure behaviors similar to those of hydrogen, as demonstrated in Fig. 3. This counteracts the typical pressure dependency of hydrocarbon ignition – namely an increase in reaction rate with increasing pressure – and results in the largely constant ignition temperatures for 25% hydrogen addition. Finally, this competition helps to explain the differing transition behavior observed between the methane/hydrogen results of Fotache *et al.* [69] and the present *n*-butanol/hydrogen results. As mentioned earlier, for hydrogen addition to methane, Fotache *et al.* [69] observed a transition to the hydrogen-dominated regime at hydrogen addition percentages near 10%, whereas the present study observes transition at much higher hydrogen addition percentages near 40%. As described above, the transition between these regimes is mediated by the competition between R2 and R5, with R5 relying on the availability of HCO to proceed. As methane contains only a single carbon atom, appreciably less HCO will be available with methane as compared to *n*-butanol for similar total fuel loading and hydrogen addition conditions. As a result, R2 will overtake R5 more quickly for the methane/hydrogen blends, resulting in earlier transition between regimes. This conclusion is further supported by the dataset of Fotache *et al.* [69], which examined the effect of increasing total fuel loading on methane-hydrogen blends. Fotache *et al.* [69] found that as total fuel loading is increased, the transition between hydrogen-enhanced and hydrogen-dominated regimes is delayed to higher hydrogen addition percentages. By adding more hydrocarbon fuel, the availability of carbon in the system will increase, thus leading to a delayed transition point. This observation further suggests that as the carbon chain length of the “base” fuel increases – with a commensurate increase in total carbon atoms – greater hydrogen addition is required to reach the hydrogen-dominated regime, and thus the effect of hydrogen in the hydrogen-enhanced regime should be more muted for longer chain hydrocarbons as compared to smaller

hydrocarbons. As this suggests potentially more limited effects for longer carbon chain molecules of practical interest for transportation purposes (e.g., diesel, gasoline, kerosene), the effect of carbon chain length on the transition point should be examined in more detail in future study.

3.3 Effect of pressure variation on controlling chemistry

The preceding discussion of the controlling chemistry has focused largely on atmospheric conditions, based on the great degree of similarity between trends observed in the 1 and 3 atm ignition temperature results in Fig. 2, and the greater magnitude of hydrogen addition effects for atmospheric conditions. Despite the significantly more muted effect of hydrogen addition at elevated pressures, the controlling reactions under these conditions deserve attention. Figure 11 replicates the analysis found in Fig. 4 for 3 atm pressure conditions. As is particularly evident for the $\xi_H = 10\%$ result, the HKG zone at this elevated pressure is less dramatic, lacking the near-vertical region observed in Fig. 4 for the same ξ_H . However, the overall effect of hydrogen addition appears quite similar, with the ignition point merging into the HKG zone as ξ_H increases.

Replicating the analysis of Fig. 8, Fig. 12 also reveals significant similarity in the effects of hydrogen addition on the ignition kernel, with all cases involving hydrogen addition replicating the trends discussed previously for atmospheric conditions. Moreover, as in Fig. 8, Fig. 12 demonstrates that the FWHM of the spatially-resolved profile of each key radical - and hence the ignition kernel width - is minimally affected by the effect of differing thermal diffusivity of the fuel stream with hydrogen addition, when k' is kept constant.

Figure 11: Comparison of the ignition turning points and lower-branch “S-curve” behaviors for varying levels of hydrogen addition at 3 atm, $X_f = 0.15$, $k' = 350 \text{ s}^{-1}$, and fuel boundary temperature of 380 K. Simulated results are derived from the MN mechanism.

However, the $\xi_H = 0\%$ case exhibits significantly higher peak mole fractions for key radical species than are observed under atmospheric conditions. In fact, the $\xi_H = 0\%$ kernel is comparable to those predicted for the $\xi_H = 100\%$ case **at 3 atm**, in contrast to the atmospheric results where peak mole fractions of key radical species differ by as much as three orders of magnitude. Flux analysis further reveals that such an increase is supported at least in part through the increased production of OH from H_2O_2 via reaction R10.

At atmospheric conditions, R10 is responsible for 24% of OH production, while R1 produces 29% and the remainder is produced via several reactions involving HO_2 . However at 3 atm conditions, the production rate of OH via R10 more than doubles, accounting for nearly half (48%) of OH production. Nonetheless, aside from the increase in the importance of R10 the

controlling chemistry at 3 atm conditions are identical to those observed at atmospheric conditions, resulting in the similar – but **more** muted – trends observed in Fig. 2.

Figure 12: Spatially-resolved profiles of (a) H, (b) O, (c) OH, and (d) HO_2 radicals as a function of hydrogen content of the fuel blend. Results computed using the MN mechanism for 3 atm, total fuel loading $X_f = 0.15$, $k' = 350 \text{ s}^{-1}$, and fuel boundary temperature of 380 K.

In closing this section, it is worth noting that the SN and MN mechanisms predict different trends with respect to the effect of pressure on the ignition kernel. While the MN mechanism predicts increases in all major radical species as a function of pressure within the present range of interest, the SN mechanism – as has been shown previously [32] – predicts that the peak mole fractions of H, O, and OH fall with increasing pressure, while HO_2 remains approximately

constant and H_2O_2 increases slightly. The differing behavior between the two mechanisms is attributed to the MN mechanism's increased reliance on H, O, and OH for *n*-butanol breakdown, as described in Section 3.2 and in our previous study [32].

4. Conclusions

The present study explores the impact of hydrogen addition on the counterflow ignition temperature of *n*-butanol in a non-premixed counterflow configuration for total fuel loading $X_f = 0.15$, a fuel stream boundary temperature of 380 K, pressure-weighted strain rate of $k' = 350 \text{ s}^{-1}$, pressures varying between 1 and 4 atm, and hydrogen addition ranging from $\xi_H = 0\%$ (pure *n*-butanol) to $\xi_H = 100\%$ (pure hydrogen). Two ignition temperature regimes are observed and are termed the hydrogen-enhanced regime and hydrogen-dominated regime. Within the hydrogen-enhanced regime (0–40% hydrogen addition), ignition temperature is appreciably more sensitive to hydrogen addition at atmospheric pressure than at elevated pressure within the current pressure range due to a convergence in ignition temperatures of the two pure component fuels as pressure increases. Within the hydrogen-dominated regime (40–100% hydrogen), ignition temperature is largely insensitive to further hydrogen addition. Comparison to numerical results simulated using two previously-developed skeletal *n*-butanol mechanisms of [32] reveals that both mechanisms capture this two-regime behavior at both atmospheric and elevated pressures. Additionally, the location of the transition between the two regimes is predicted well. Further analysis reveals that the controlling mechanism behind the reduction in ignition temperatures in the hydrogen-enhanced regime is a significant increase in the size of the available radical pool, which promotes ignition. This increase in radical pool size is primarily mediated by the reaction $\text{H}_2 + \text{OH} \leftrightarrow \text{H}_2\text{O} + \text{H}$ (R3), which serves as a gateway reaction to further chain branching reactions. Furthermore, flux analysis reveals that the reactions $\text{HCO} + \text{O}_2 \leftrightarrow \text{HO}_2 + \text{CO}$ (R5) and

$H + O_2(+M) \leftrightarrow HO_2(+M)$ (R2) are the primary reactions producing hydroperoxyl, which in turn provides 30–50% of the hydroxyl radicals needed by reaction R3. In the hydrogen-enhanced regime, R5 is primarily responsible for hydroperoxyl production, however as hydrogen addition levels increase, R2 becomes more prominent, eventually overtaking R5 as the mixture transitions to the hydrogen-dominated regime. While this effect is most prominent at atmospheric pressures, a more muted effect is observed at elevated pressures, and is mediated by identical chemistry. The competition between these reactions also suggests that the extent of the hydrogen-enhanced regime and the impact of hydrogen addition within that regime may be impacted by “base” fuel molecule size, as an increase in the number of carbon atoms available will enhance R5 and delay the transition point between R2 and R5 to higher hydrogen addition levels. Based on the fact that many practical transportation fuels involve relatively long-chain hydrocarbons, this subject merits further investigation.

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