Experimental and numerical investigations on the laminar burning velocity of n-butanol+air mixtures at elevated temperatures

Amit Katoch\textsuperscript{1,2*}, Adamu Alfazazi\textsuperscript{2,3}, S. Mani Sarathy\textsuperscript{2}, Sudarshan Kumar\textsuperscript{1}

\textsuperscript{1} Department of Aerospace Engineering, Indian Institute of Technology Bombay, Powai, Mumbai 400 076, India

\textsuperscript{2} King Abdullah University of Science and Technology (KAUST), Clean Combustion Research Center (CCRC), Thuwal 23955-6900, Saudi Arabia

\textsuperscript{3} Department of Chemical Engineering, University of Jeddah, Jeddah 21589, Saudi Arabia

Corresponding author *: amitkatoch15@gmail.com
Abstract

Laminar burning velocities of n-butanol+air mixtures were measured experimentally at elevated mixture temperatures using an externally heated meso-scale channel configuration. The measurements were carried out at atmospheric pressure for an equivalence ratio range 0.7-1.3 and unburnt mixture temperature range of 350 - 600 K. Planar, stretch free and nearly adiabatic flames were stabilized in the diverging channel and used to extract the laminar burning velocity data based on mass conservation between the channel inlet and flame stabilization point. A skeletal kinetic-mechanism (124 species and 943 reactions) based on a previous model of Sarathy (2014) was developed to compare the present experimental results with mechanism predictions. Besides the skeletal model predictions, n-butanol experimental results were also compared with other recent kinetic models reported in literature. The effect of unburnt mixture temperature on burning velocity of n-butanol+air mixtures was evaluated using the power-law correlation: $S_u = S_{u,0} \left(\frac{T_u}{T_{u,0}}\right)^\alpha$. The variation of temperature exponent ($\alpha$) with equivalence ratio ($\Phi$) was reported also for the first time. The values exhibit a non-linear inverted parabolic profile with a minimum value occurring for slightly rich mixtures at $\Phi = 1.1$.

Keywords: Laminar burning velocity, n-butanol, Kinetic mechanism reduction, Planar flames, Meso-scale diverging channel, Temperature dependence

Nomenclature:

- **LHV** - Lower Heating Value
- **RON** - Research Octane Number
- **MON** - Motor Octane Number
- **EGR** - Exhaust Gas Recirculation
GDI- Gasoline Direct Injection

BTE- Brake Thermal Efficiency

PID- Proportional Integral Derivative
1. Introduction

Increasing fossil fuel demand has motivated both developed and developing nations to venture into biofuels research to address the ever-growing needs of combustion-based transport and energy generation systems. The production methods for biofuels vary from plant based (edible and non-edible) production units to micro-algae to gasification of biomass to produce syngas [1]. The C\textsubscript{1}-C\textsubscript{4} normal alcohols i.e. methanol, ethanol, propanol and butanol are promising and reliable fuels in the global biofuel market. Numerous studies have been reported in literature to evaluate the performance characteristics and feasibility of using blends of various biofuels such as butanol, biodiesel [2] and also blending biofuels with conventional fuels such as gasoline and diesel in automotive spark-ignition and compression-ignition engines [3-6] besides gas turbine engines [7, 8]. Table 1 summarizes the important physical properties of the n-butanol fuel and its comparison with ethanol, gasoline and diesel.

**Table 1.** Summary of physical properties of n-butanol and comparison with ethanol, gasoline and diesel fuels [7, 9, 10].

<table>
<thead>
<tr>
<th></th>
<th>Ethanol</th>
<th>n-Butanol</th>
<th>Gasoline</th>
<th>Diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>C\textsubscript{2}H\textsubscript{5}OH</td>
<td>C\textsubscript{4}H\textsubscript{9}OH</td>
<td>C\textsubscript{8}H\textsubscript{15}</td>
<td>C\textsubscript{14}H\textsubscript{30}</td>
</tr>
<tr>
<td>Molar weight (g.mol\textsuperscript{-1})</td>
<td>46.06</td>
<td>74.11</td>
<td>111.19</td>
<td>198.4</td>
</tr>
<tr>
<td>(A/F) (\phi=1)</td>
<td>8.98</td>
<td>11.17</td>
<td>14.58</td>
<td>14.95</td>
</tr>
<tr>
<td>Density at 20°C (kg/m\textsuperscript{3})</td>
<td>789</td>
<td>810</td>
<td>718-780</td>
<td>810-890</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>78.37</td>
<td>117.7</td>
<td>27-225</td>
<td>125-400</td>
</tr>
<tr>
<td>%\textsubscript{O\textsubscript{2}} (wt.)</td>
<td>0.35</td>
<td>0.22</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>LHV (MJ/kg)</td>
<td><strong>26.9</strong></td>
<td><strong>33.1</strong></td>
<td><strong>43.5</strong></td>
<td><strong>41.7</strong></td>
</tr>
<tr>
<td>RON</td>
<td>109</td>
<td>98</td>
<td>88-98</td>
<td>&lt; 0</td>
</tr>
<tr>
<td>MON</td>
<td>90</td>
<td>85</td>
<td>80-88</td>
<td>&lt; 0</td>
</tr>
</tbody>
</table>

Although ethanol is currently the preferred choice for blending with gasoline due to the ease in its bulk production as compared to butanol, however, recent advances in biotechnology have shown promising results to engineer bacteria for higher production rates.
of butanol through various biological pathways[11-13]. In comparison to ethanol, n-butanol has higher energy density, higher cetane number, lower vapor pressure, lesser hygroscopic, lower corrosion tendency and better blending potential. In direct injection based diesel engines, n-butanol blending has been reported to produce lower NO\textsubscript{x} emissions due to high heat of vaporization, which in turn leads to lower combustion temperatures[4].

Elfasakhany[14] used a single cylinder SI engine to compare the emissions and engine performance of neat gasoline and gasoline with n-butanol blends (up to 10 \% by vol.), which can be used without engine modifications. The author reported that for the aforementioned blending ratio, n-butanol addition produces a leaning effect primarily due to the extra oxygen content, which leads to lower CO, CO\textsubscript{2} and UHC emissions. This is accompanied by a small reduction in engine performance due to its high latent heat and lower calorific value compared to gasoline. Major petroleum companies like DuPont, BP and Gevo are involved in the production of bio-butanol for blending with gasoline. Rakopoulos et al. [15] have recently developed a robust two-zone model to investigate the effects of EGR rate and temperature on the combustion performance and emissions in direct injection diesel engines at various injection timings and loading conditions. A recent study has shown that except for low load conditions, EGR with butanol blended gasoline as fuel in GDI engines could help reduce emissions while maintaining BTE, when compared to engines operating only on gasoline[16]. Saini et al. [17] have been able to produce butanol by tweaking the metabolic pathways of E.Coli bacteria with a conversion yield of 87 \% of the theoretical yield. Sooting tendencies of n-butanol and gasoline blends are reported to be similar to ethanol-gasoline blends [18].

Laminar burning velocity is an important parameter used for characterizing the reactivity, thermo-diffusivity and heat release behavior of a fuel. It is also used in the estimation of turbulent burning velocity and at sufficiently small length scales, some turbulent combustion
regimes can be modeled as laminar flamelets [19]. With the advancements in the integration of fuel-chemistry to flow physics in chemically-reacting flows, it is imperative to accurately model the reaction-rates for the elementary reactions, thus improving the overall prediction capability of detailed kinetic models [20]. Laminar burning velocity is used in the validation of such chemical kinetic mechanisms. A robust and well-established model is able to reproduce the parameters such as laminar burning velocity, ignition delay timings, flame structure accurately. It is also measured as one of the explosion characteristics of various fuels [21-23] for the design of explosion suppression devices. Laminar burning velocity of a fuel-oxidizer mixture depends on the initial pressure, mixture temperature and mixture equivalence ratio. The dependence of burning velocity on mixture temperature can be described using following power-law correlation[24]:

\[ S_u = S_{u,0} \left( \frac{T_u}{T_{u,0}} \right)^{\alpha} \]

Where, \( S_{u,0} \) = laminar burning velocity at reference temperature \( T_{u,0} \) and \( \alpha \) is the temperature exponent. Only a few experimental studies reporting the measurement of laminar burning velocity of n-butanol+air mixtures are reported in the literature. The available experimental data at 1 atm for n-butanol+air mixtures is summarized in Table 2. It is clear from the table, that for n-butanol+air mixtures at atmospheric pressure, the highest unburnt mixture temperature reported in literature is 473 K [25]. To date, there are no experimental studies to assess the effects of increasing mixture temperature (in terms of temperature exponent \( \alpha \)) on the variation of laminar burning velocity for this fuel at various mixture equivalence ratios.

Majority of the work on development of n-butanol mechanisms has been reported during the past one decade [26-33] and very little experimental data is available for validation of these mechanisms at higher mixture temperatures. This necessitates the measurement of
laminar burning velocities at high mixture temperatures to further help in the validation of the developed mechanisms at these conditions.

Table 2: Summary of experimental data for burning velocities of n-butanol+air mixtures at 1 atm. CV - Constant volume, HF - Heat flux burner and CF - Counter flow burner method

<table>
<thead>
<tr>
<th>Reference</th>
<th>Method</th>
<th>φ_range</th>
<th>T_range(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[25]</td>
<td>CV</td>
<td>0.7-1.5</td>
<td>413,443,473</td>
</tr>
<tr>
<td>[34]</td>
<td>CV</td>
<td>0.8-1.7</td>
<td>428</td>
</tr>
<tr>
<td>[35]</td>
<td>CF</td>
<td>0.7-1.5</td>
<td>343</td>
</tr>
<tr>
<td>[36]</td>
<td>CV</td>
<td>0.6-1.6</td>
<td>353</td>
</tr>
<tr>
<td>[37]</td>
<td>CV</td>
<td>0.7-1.4</td>
<td>428</td>
</tr>
<tr>
<td>[38]</td>
<td>CV</td>
<td>0.8-1.4</td>
<td>393</td>
</tr>
<tr>
<td>[39]</td>
<td>CV</td>
<td>0.6-1.8</td>
<td>393,433,473</td>
</tr>
<tr>
<td>[40]</td>
<td>HF</td>
<td>0.7-1.5</td>
<td>373,423</td>
</tr>
</tbody>
</table>

Therefore, the objective of the present work is to measure the laminar burning velocity for n-butanol+air mixtures at atmospheric pressure, up to an unburnt mixture temperature of 600 K, with Φ = 0.7 - 1.3, and to assess the dependency of laminar burning velocity on mixture temperature through temperature exponent. Externally heated meso-scale diverging channel method has been used in this work [41-43]. This technique has been used to measure the laminar burning velocities of various gaseous fuels [44-47] and liquid fuels [48-51] at high temperatures using planar stretch-free flames.

2. Experimental method

In the present study, externally heated meso-scale diverging channel method [41, 46, 48, 52] was employed to measure the laminar burning velocity. A schematic diagram of the experimental setup is shown in Fig. 1. Quartz channels with divergence angles 10° and 15°
with a high aspect ratio (> 12) were used for the measurements. The depth of the channels was varied between 1.5 mm – 2.0 mm. The starting of the diverging portion is referred to as the inlet with a fixed width of 25 mm. An external infrared heater was employed to establish a positive temperature gradient along the direction of the fluid flow [41, 46]. Quartz material is transparent, with high heat capacity, low thermal conductivity and low thermal expansion. Therefore, it facilitates the creation of a linear temperature gradient besides helping in flame visualization and avoiding radical quenching at the walls [53]. The temperature gradients can be altered by varying the input power to the heater through a PID (proportional-integral-derivative) driven digital voltage controller and by changing the horizontal and the vertical clearance between the channel and the heater.

Figure 1. Schematic of the experimental setup

The mixture flow rates in such small domains are very small and thus the corresponding Peclet number (Pe) has a low value [54]. Therefore, the unburnt mixture temperature is assumed to be equal to the wall temperature at the flame stabilization location [55]. The fuels
used in the present study were in liquid state at ambient conditions. Therefore, they need to be pre-vaporized and mixed with oxidizer before being fed to the channels for combustion. The incoming air is preheated using a heating unit comprising of two plate type heaters of 1.5 kW each and the temperature control is achieved using a PID temperature controller driven unit. The air is preheated to a temperature close to the boiling point of the fuel, such that the required mixture can be formed based on saturation vapor pressure at that temperature. It is to be noted that no pyrolysis occurs in the present setup where the maximum unburnt mixture temperature is below 600 K. This is substantiated by the findings reported by Harper et al. [29]. The authors stated that, in their pyrolysis experiments, no pyrolysis or deposition of coke was observed for temperatures below 550˚C or 823 K. The air flow rate is controlled using thermal mass flow controllers from AALBORG with an accuracy of ± 1.5 % and flow velocity ranging from 20 – 80 % of full scale flow. Since the fuel flow rates were of the order of a few mlph (milliliters per hour), the fuel was dispensed using an infusion pump. The preheated air is directed into a copper tube of 2 mm inner diameter where the fuel is also injected using a micro-syringe. This leads to instant vaporization and mixing of the fuel due to its impingement into a high velocity hot air jet. To avoid vapor mixture condensation all fluid flow lines are insulated and maintained at high temperatures using tape heaters. The mixture is subsequently fed to the channel and ignited at the open end using a nichrome ignitor. The temperature profile in the channel is measured using a 0.25 mm K-type thermocouple (accuracy ± 5 K). The laminar burning velocity is calculated using mass conservation equation between the channel inlet and flame stabilization point as:

\[ S_u = U_{inlet} \left( \frac{A_{inlet}}{A_f} \right) \left( \frac{T_f}{T_{inlet}} \right) \]

Where \( T_{inlet} \) is the mixture temperature at the channel inlet (with area, \( A_{inlet} \)) and \( T_f \) is the mixture temperature at the flame stabilization location (with area \( A_{flame} \)). Both these
temperatures are known from temperature profiles. Since the mass flow rates of fuel and air are controlled externally, $U_{inlet}$ can be easily computed using inlet mixture temperature, $T_{inlet}$. Flame stabilization location is measured using image processing of the flame photographs with an accuracy of $\pm 0.25$ mm. A variety of flame dynamics are observed upon varying the inlet velocity and temperature gradient across the channel [41]. Only planar flames (as shown in Figure 2) are used for extracting the mixture burning velocity. An uncertainty of $\pm 5\%$ is associated with the experimental measurements and same has been indicated through uncertainty bars in the results. The various factors contributing to the uncertainty in the measurements have been discussed in previous works [44, 48, 56].

![Figure 2](image.png)

Figure 2. Planar stabilized flame for $U_{inlet} = 0.75$ m/s at $\Phi = 0.8$

3. Chemical kinetic Mechanisms and Numerical predictions

3.1 Model Reduction and simulation procedure

The high temperature alcohol mechanism developed by Sarathy et al. [9] was used for these simulations. The detailed high temperature model has 354 species and 2462 reactions. In order to minimize computational time, this model was reduced using the method of direct relation graph with expert knowledge (DRG-X) [57]. As reported in previous studies, this method is based on the assumption that during combustion reactions, some species are weakly connected to others and barely contribute to the combustion process [57, 58]. Such loosely coupled species can be removed from the mechanism and still retain the chemical
fidelity of the detailed kinetic model. Furthermore, the DRG-X method is not restricted by an overall error tolerance, as it allows a specific controlled reduction error for heat release and other species of interest. In the present work, the detailed model was reduced for high temperatures with an error tolerance for heat release set at 0.01. The error tolerance for species relevant to high temperature heat release; H and OH radicals is 0.3 and 0.1 respectively, while the default error tolerance for other species is 0.4. A resulting skeletal mechanism with 124 species and 943 reactions was generated. The model is provided in the supplementary material as well as a species dictionary for those species mentioned in this text. The term “skeletal” is used here to denote a mechanism wherein only species and reactions were eliminated, as opposed to “reduced,” wherein isomer species and reactions are lumped together. The resulting model is referred to as “skeletal” in all further figures and related discussions in this paper.

Figure 3: Comparison of mechanism performance in terms of a) Laminar burning velocity predictions b) Temperature exponent

The skeletal model was used to simulate the present experimental data. Simulations were performed with CHEMKIN-PRO, using the PREMIX solver[59], with thermal diffusion and mixture-averaged transport accounted for at different conditions. A large number of grid
points were used (~ 1500), employing convergence parameters of GRAD = 0.01 and CURV = 0.03. GRAD and CURV are adaptive grid control parameters that control the extent to which the solution gradient and curvature is resolved. The other mechanisms used for comparison with experimental results are listed in Table 3.

**Table 3**: Summary of chemical kinetic mechanisms used in the present work

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Mechanism</th>
<th>Species</th>
<th>Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-C₄H₉OH</td>
<td>Feng et al. [60]</td>
<td>75</td>
<td>285</td>
</tr>
<tr>
<td></td>
<td>Liu et al. [61]</td>
<td>161</td>
<td>622</td>
</tr>
<tr>
<td></td>
<td>Skeletal (present)</td>
<td>124</td>
<td>943</td>
</tr>
</tbody>
</table>

The performance of the skeletal model was assessed in terms of the laminar burning velocity and the associated temperature exponents as shown in Fig. 3. The skeletal mechanism accurately reproduces the important trends related to these two important parameters, for instance, the peaking of the burning velocity at $\Phi = 1.1$ and existence of the minimum value of the temperature exponent at $\Phi = 1.1$. In terms of the magnitude of laminar burning velocity, the skeletal model predictions match really well even at elevated mixture temperature with a slight over-prediction in the leaner regime.

4. Results and Discussion

4.1 Influence of Initial temperature on laminar burning velocity
Figure 4. Variation of laminar burning velocity of stoichiometric n-butanol+air mixtures with temperature ratio and its comparison with predictions of various kinetic models.

Figure 4 shows the variation of laminar burning velocity for a stoichiometric n-butanol+air mixture with temperature ratio. A reference temperature of 300 K is used for normalization of the unburnt mixture temperature in Fig. 4. The present experimental measurements are shown with open circles with an uncertainty band of ± 5 %. Power-law correlations are used to fit the present data for extracting the temperature exponent values. The data indicates that the burning velocity increases with an increase in unburnt mixture temperature with $\alpha = 1.6771$.

The results are compared with numerical predictions using the skeletal model, Feng et al. model [60] and Liu et al. model [61]. The experimental results are compared only with the numerical predictions as there are no other experimental data available across this temperature range.

Amongst all the three mechanisms, Liu et al. mechanism [61] predicts the lowest values. The skeletal mechanism shows a good agreement across the entire range of mixture temperatures. The predictions of Feng et al. mechanism [60] are slightly lower than experimental measurements till a temperature ratio of ~1.55. Above this value, the predictions are in reasonably good agreement with experiments.
Figure 5. Comparison of the measured laminar burning velocity for lean (Φ = 0.8) and rich (Φ = 1.2) n-butanol+air mixtures at elevated temperatures with the skeletal mechanism and other kinetic models.

Figure 5 shows the variation of laminar burning velocity for lean (Φ = 0.8) and rich (Φ = 1.2) n-butanol+air mixtures with temperature ratio for unburnt mixture temperatures up to 600 K. For Φ = 0.8, the predictions of Liu et al. [61] mechanism show noticeable underprediction when compared with the measured values. Numerical predictions of Feng et al. [60] mechanism and the skeletal model show excellent agreement with the experimental data. For Φ = 1.2, the predictions from Feng et al. [60] are slightly lower than measured values, whereas the Skeletal mechanism gives slightly higher values across the measured temperature ratios albeit within the uncertainty range.

4.2 Influence of mixture equivalence ratio on temperature exponent

The influence of unburnt temperature on laminar burning velocity for different equivalence ratios was assessed through the variation of temperature exponent, α, with mixture equivalence ratio. The burning velocity data was fitted using power-law correlations to obtain the temperature exponent values. Figure 6 shows the variation of temperature...
exponent with equivalence ratio. Since there is no other experimental data available for comparison, a comparison with the numerical predictions of different kinetic models is presented here. The temperature exponent shows an inverted parabolic variation, qualitatively similar to other alcohols with the existence of a minimum value for slightly rich mixtures ($\Phi = 1.1$). Such variations have also been reported by Konnov et al. [62] and Katoch et al. [48] for other alcohol-based fuels. The mechanisms used for comparison also show a similar trend. The variation of temperature exponent $\alpha$ with equivalence ratio, $\Phi$ can be correlated using a fourth order polynomial as:

$$
\alpha = 14.28\Phi^4 - 60.927\Phi^3 + 99.549\Phi^2 - 73.717\Phi + 22.497
$$

The uncertainty in temperature exponent, $\alpha$ was evaluated using the least-square method proposed by Sileghem et al. [63], Vancoillie et al. [64] and Alekseev et al. [65]. In a quantitative sense, the skeletal model shows a closer match with experimental results except at $\Phi = 0.7$ (under prediction) which could be ascribed to the lack of high temperature data in literature, further leading to less accurate rate constants. The predictions from the Liu et al. [61] kinetic model show an excellent agreement with present experimental results except at $\Phi = 0.7$ (under prediction).
Figure 6. Variation of temperature exponent, $\alpha$ with equivalence ratio for n-butanol+air mixtures

4.3 Comparison of laminar burning velocity at low and elevated temperatures:

As stated earlier, the highest unburnt mixture temperature for which measurements are reported in literature is 473 K by Gu et al. [25]. They used the spherical bomb method, where the burning velocity was obtained through linear extrapolation of stretched flame speed to zero stretch rates during the early stages of flame propagation. Most of the experimental data available in literature are reported at temperatures less than 430 K. Therefore, two mixture temperatures of 343 K and 423 K were chosen for detailed comparison of present results as shown in Figs. 7 and 8. The data points used in the figures were extracted from the power-law correlations for the respective equivalence ratios. As could be seen in Fig. 7, the maximum deviation between various predictions and experimental values at 343 K is $\approx 5$ cm/s. At 343 K, the present values are in excellent agreement with the skeletal model, with a maximum deviation of $\approx 3$ cm/s (on the lower side) at $\Phi = 1.2$ and 1.3. Veloo et al. [35] used the counterflow burner configuration with a non-linear stretch extrapolation (based on the direct numerical simulation of experiments [66, 67]) for measurements at 343 K. Liu et al. [36] used a dual-chamber, constant-pressure apparatus to record spherical flame propagation and a non-linear regression technique [68] for extracting the un-stretched burning velocity at 353 K mixture temperature with an uncertainty of $\pm 2$ cm/s. The present data shows a good match with 343 K predictions of the present skeletal mechanism as well as with the measured data of Veloo et al. [35]. The measurements of Sarathy et al. [27] at $P_u = 0.89$ and $T_u = 350$ K do not agree with the rest of the data perhaps due to much lower pressure of 0.89 atm. The predictions from Feng et al. [60] kinetic model are slightly lower than the predictions from the skeletal model and other experimental results for lean mixture ratios of 0.9. At $\Phi = 1$ and 1.1, the models under predict the experimental results. At $\Phi = 1$ and 1.1 the models of Feng
et al. [60] and Liu et al. [61] predict lower values than the experimental measurement (lower by $\approx 5$ cm/s). At $\Phi = 1.2$ and 1.3 the experimental measurements agree well with the predictions of the kinetic models of Feng et al. [60] and Liu et al. [61]. The predictions of the model of Liu et al. [61] are in good agreement with the predictions of the skeletal model as well as experimental data from Veloo et al. [35] and the present study.

Knorsch et al. [40] used a modified heat-flux method called ‘HeatFluxER’ to measure the burning velocity of n-butanol+air mixtures at 423 K. The present experimental data is in close agreement with predictions from Feng et al. [60] model in the leaner regime and for $\Phi = 1.2$ and 1.3. Predictions from the Liu et al. [61] model match well with the present experiment only at $\Phi = 1.3$. The predictions from the skeletal show a closer agreement with present results except at $\Phi = 1.3$ where the measured value is lower by $\approx 6$ cm/s.

Figure 7. Comparison of present measured laminar burning velocity of n-butanol+air mixture at ambient pressure and 343 and 423 K with numerical predictions. Open symbols represent experimental measurements and lines are numerical predictions.
Figure 8. Comparison of present measured laminar burning velocity of n-butanol+air mixture at 343 K and 423 K mixture temperature with experimental data from literature. Open symbols represent experimental measurements.

Figure 9 shows a comparison between the present experimental values and numerical predictions from the three models at 400 – 600 K mixture temperatures. For 400 K mixture temperature, all three models show good agreement with the measured values. At 500 K and 600 K, slightly rich mixtures show the existence of maximum burning velocity for slightly rich mixtures at $\Phi = 1.1$. The agreement between the skeletal model and the experiment measurements is reasonably good till $\Phi = 1.2$. Feng et al. model [60] shows a good agreement for all equivalence ratios at 500 K and 600 K mixture temperatures. The predictions of Liu et al. model [61] are slightly lower than the experimental measurements at elevated temperatures.
Figure 9. Comparison of measured laminar burning velocity with the numerical predictions at higher mixture temperatures (n-butanol+air mixtures). Open symbols represent experimental measurements and lines are numerical predictions.

4.4 Sensitivity and Path Flux Analysis

Sensitivity analysis was carried out with the skeletal model to understand the role of kinetics in the changes in the laminar burning velocity with increasing mixture temperature across equivalence ratios. To understand the role of important reactions in the mechanism, analysis was carried out at 335 K and 600 K mixture temperatures as shown in Fig. 10. Overall, the
Figure 10. Normalized sensitivity coefficients for laminar burning velocity of n-butanol + air mixtures a) 335 K b) 600 K

Sensitive reactions are similar at both 335 K and 600 K mixture temperatures, except for few cases. For example, at 335 K and Φ = 1.3, the reaction C2H3 + O2 ⇋ CH2CHO + O is sensitive, while it is not at 600 K. Also, in some instances, the magnitude of the sensitivities is slightly different. The main radicals, which enhance the burning velocity are H and OH, whereas radicals like C2H3 act as sink for such radicals and hence decelerate the rate of flame propagation.

In addition to this, a reaction path flux analysis was carried out at 335 K and 600 K to compare how the fuel is consumed at these conditions. The result is shown in Fig. 11. The analyses showed that the fuel decomposes almost in a similar manner at both the mixture temperatures. The magnitude of initial fuel abstraction is very close, although, notable differences occur in the percentage flux of some certain pathways leading to the formation of more active radicals at 600 K and less active radicals at 335 K. For example, 63% of C4H8OH-2 reacts to produce a butene (C4H8-1) radicals at 600 K, while around 70% of
C4H8OH-2 produces it at 335 K. Also, more of ethylene (C2H4) is converted to vinyl (C2H3) radicals at 335 K than at 600 K. Butene and vinyl radicals are resonantly stable species and they act as radical sinks.

5. Conclusions:
Meso-scale diverging channel method was employed to measure the burning velocity variation with equivalence ratio and its temperature dependence for n-butanol + air mixtures.
Measurements were carried out at temperature ranges much higher (upto 600 K at 1 atm) than those reported previously in the literature (473 K). Laminar burning velocities were found to increase with an increase in unburnt mixture temperature. The maximum burning velocity occurs at slightly rich equivalence ratios even at elevated temperatures. The temperature exponent variation with mixture equivalence ratio exhibits an inverted parabolic profile with a minimum value at $\Phi = 1.1$. For the purpose of validation and analysis, a skeletal kinetic model was developed based on a detailed model of Sarathy et al. [9]. The detailed model was reduced to develop a skeletal model with less number of species and reactions. The skeletal model shows a good match with experiments even at high temperatures with the only exception of noticeable overprediction for richest case of $\Phi = 1.3$. The higher burning velocity predictions at richer equivalence ratios call for further investigations into the chemistry development in these regimes.

**Acknowledgments**

The first author would like to acknowledge the financial support for this work from Department of Science and Technology, Govt. of India wide grant no. SB/S3/COMB-001/(2014). Research conducted by AF and SMS of Clean Combustion Research Center was supported by competitive research funding from King Abdullah University of Science and Technology (KAUST).

**Supplementary material:**

The present work includes the following supplementary mechanism: The skeletal kinetic model along with the associated thermochemistry, and transport data. A species dictionary for those species discussed in the paper.
References:


Rakopoulos CD, Rakopoulos DC, Mavropoulos GC, Kosmadakis GMJE. Investigating the EGR rate and temperature impact on diesel engine combustion and emissions under various injection timings and loads by comprehensive two-zone modeling. 2018;157:990-1014.


