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Low Temperature Ignition Properties of *n*-Butanol: Key Uncertainties and Constraints

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Abstract

A recent kinetic mechanism (Sarathy et al., 2012) describing the low temperature oxidation of *n*-butanol was investigated using both local and global sensitivity/uncertainty analysis methods with ignition delays as predictive targets over temperature ranges of 678-898 K and equivalence ratios ranging from 0.5-2.0 at 15 bar. The study incorporates the effects of uncertainties in forward rate constants on the predicted outputs, providing information on the robustness of the mechanism over a range of operating conditions. A global sampling technique was employed for the determination of predictive error bars, and a high dimensional model representation (HDMR) method was further utilised for the calculation of global sensitivity indices following the application of a linear screening method. Predicted ignition delay distributions spanning up to an order of magnitude indicate the need for better quantification of the most dominant reaction rate parameters. The calculated first-order sensitivities from the HDMR study show the main fuel hydrogen abstraction pathways via OH as the major contributors to the predicted uncertainties. Sensitivities indicate that no individual rate constant dominates uncertainties under any of the conditions studied, but that strong constraints on the branching ratio for H abstraction by OH at the and sites are provided by the measurements.

Introduction

Due to the need to address the issue of climate change, there is interest in seeking fuels which may be generated from renewable sources including from biomass [1]. Alcohols such as methanol, ethanol and butanol are being projected as satisfactory fuels that could be produced from renewable sources, and used successfully within internal combustion engines. Alcohols, along with other oxygenated fuels, have been shown to have the potential to improve engine performance and emissions because of some of their unique physical and chemical properties [2-6].

There is presently some support for bio-butanol as a potential replacement for ethanol in spark ignition (SI) and compression ignition (CI) engines due to several advantages. Its higher heating value combined with higher stoichiometric air-fuel ratio, allow higher blending levels of butanol in gasoline than can be achieved for ethanol without changing regulations, engine control systems, and distribution networks. Moreover, butanol has a lower latent heat of vaporization than ethanol reducing issues with fuel atomization and combustion during cold start [7]. It is less corrosive and less prone to water absorption than ethanol, allowing it to be transported using existing fuel pipelines. It also has a higher cetane number than ethanol, lower vapour pressure, similar viscosity to diesel and improved miscibility in diesel [8].

Experimental testing of bio-butanol in SI and CI engines has shown promise. However, a detailed investigation and understanding of the behaviour of this new fuel in real engines can be greatly assisted through modelling, particularly to improve our understanding of the key kinetic processes that drive combustion over a range of temperatures and pressures. In order to accurately reproduce the combustion and emission characteristics of the target fuel during the simulation of SI and CI engines, accurate and reliable detailed chemical kinetic models of fuel oxidation are needed. While the combustion chemistry of common hydrocarbon fuels such as ethanol and dimethyl ether are qualitatively relatively well understood, much work is still needed to clearly identify the most important reaction steps that determine the key predictive targets within combustion devices fuelled by larger alcohols, such as butanol [9].

A number of recent studies addressing the chemical kinetic modelling of bio-butanol combustion have been performed [10-16]. Most of the mechanisms developed to date focus on high temperature reaction classes and have not been specifically designed for application to the prediction of ignition behaviour at lower temperatures. However, very recently, Sarathy et al. [17] proposed a detailed reaction mechanism that includes both low and high temperature reaction pathways for the four isomers of butanol, with reaction rate parameters determined from experimental data, *ab initio* studies and estimations based on bond dissociation energies. For certain key reactions, modifications to rate constants were made (within parameter uncertainties) as part of the validation study of [17], in order to improve agreement with experimental data.

The current work is fundamentally driven by the search for suitable scheme of *n*-butanol oxidation for subsequent simulations of *n*-butanol combustion in CI and SI engines. The detailed chemical kinetic scheme of *n*-butanol proposed by Sarathy et al. [17] is investigated in a rapid compression machine (RCM) with ignition delays forming the set of predictive targets. The predictive capability of the Sarathy mechanism, in terms of its ability to accurately reproduce the low temperature chemistry

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*Corresponding author: A.S.Tomlin@leeds.ac.uk (auto-ignition regime) of *n*-butanol is investigated by comparing predicted data from simulations with measured experimental data over temperature ranges of 678-898 K, = 0.5-2.0, at 15 and 30 bar.

Kinetic models of complicated fuels are usually made up of a large set of elementary reactions which are quantitatively described by rate parameters and thermodynamic and transport data for the species. A large number of the rate parameters are, by necessity, determined using semi-empirical estimation approaches (e.g. group additivity methods) because of the difficulties associated with the experimental measurement of such large numbers of rate parameters. This however has the disadvantage of potentially introducing large uncertainties in the determined parameter values and therefore the model as a whole [18]. As a result, even if validated against a range of target experimental data sets using more fundamental combustion apparatuses (such as RCMs, jet stirred reactors, premixed and diffusion flames etc.), a model could quite easily fail when utilised under practical engine conditions that are outside the range in which it is validated or constrained.

Although local sensitivity methods have been applied to the butanol scheme in previous modelling work [17,19] for importance ranking of key reactions that influence the predicted target quantities, it does not however account for the impact of the inherent uncertainties in the input rate parameters on the predictive uncertainties. On the other hand, global uncertainty and sensitivity methods provide an understanding of the predictive output uncertainties as well as details on their main contributing parameters, even where the relationship between the input parameters and predicted target output are highly nonlinear [18]. Therefore, the sensitivity of predicted ignition delays to possible uncertainties within the input data of the kinetic scheme (in this case, rate parameters) is investigated here via global uncertainty and sensitivity analyses.

Methodology

The Cantera software libraries (version 2.1.1) [21] were used within the Python environment to numerically model the *n*-butanol fuelled RCM in line with the experimental conditions and data given by Weber et al. [20] and recent data obtained from the RCM in Leeds. The RCM used by Weber et al. has been described in detail in [22]. In the experimental setup [20], *n*-butanol/O_2/N_2 mixtures were investigated over a compressed temperature range of 679-925 K, compressed pressures of 15 and 30 bar, at equivalence ratios of 0.5, 1.0 and 2.0. The modelling approach adopted here is in line with that of Weber et al. [20], in which both compression and post compression events are accounted for. Volume traces which inherently account for the heat losses during both compression and post compression effects were used as input into the auto-ignition simulations of this study. According to [20], the volume traces for the full event were determined from the measured pressure trace of the non-reactive experiment using the isentropic core relations and temperature-dependent mixture specific heat ratios. The volume profiles were implemented in our Cantera calculations during each time step in which the state of the RCM reactor is advanced. A python-based subroutine obtained from the GitHub account of Weber [23] was used alongside an in-house Cantera RCM code for this purpose. The volume traces used in this study are available from [24]. The Leeds RCM, on the other hand, was modelled as a constant volume adiabatic reactor based on provided experimental data, with heat loss effects of the reactants to chamber walls taken as negligible. *n*-butanol mixtures of different diluents ratio were modelled for compressed temperature ranges of 670K – 865K and compressed pressures of 20 bar under stoichiometric conditions.

Definition of ignition delays

The computed ignition delay time is defined as the time from the end of compression (at TDC) to the point of maximum rate of pressure rise $\left(max\, {}^{dP}/_{dt}\right)$. Appropriate tolerance criteria were chosen to ensure sufficiently stable and well converged solutions for the chosen kinetic scheme.

Chemical kinetic model

The mechanism adopted is the recent and previously validated butanol mechanism, proposed by [17]. The kinetic model was constructed based on the 1-butanol kinetic scheme of [13] by upgrading the mechanism with the primary reactions of tert-butanol, 2-butanol, and iso-butanol and related radical reactions. The mechanism, containing 426 species and 2335 mainly reversible reactions, was validated with reasonable agreement against a wide range of experimental data which includes: speciation data obtained in low pressure laminar premixed flames, premixed laminar flame velocities under atmospheric pressures, species data from a high pressure jet-stirred reactor (JSR), ignition delay times from a high pressure RCM and ignition delay times from atmospheric and high pressure shock tubes (ST). The scheme is available from the Lawrence Livermore website and described in [17].

Calculations of rate coefficients for pressure dependent reactions were achieved within Cantera using both the Troe formulation [21] and interpolation based on the PLOG approach depending on the requirements of the scheme. Using the PLOG approach, Arrhenius expressions are given at particular pressures and logarithmic interpolation is used for pressures in between [21]. The Sarathy et al. kinetic scheme, originally in Chemkin format, was converted to Cantera input format (.cti file including the thermodynamic data) using the Cantera 2.1.1 ck2ti.py subroutine.

Sensitivity screening approach

Since only a few key reactions are likely to greatly influence the accuracy of the predicted targets, computational time can be saved if these reactions are identified for inclusion in global sensitivity analysis, whilst parameters of low sensitivity are retained at their nominal values. This allows for smaller sample sizes to be used without compromising the sparsity of the input space. A screening approach based on the brute force local sensitivity method was therefore performed for a range of conditions in [20] to identify the key reactions that influence the ignition delay at compressed (TDC) conditions of 15 bar, temperatures of 678-898 K and = 0.5-2.0. The local sensitivity setup is a Python based code originally developed in [25] and adapted for implementation within the current bio-butanol RCM model. The ignition delay sensitivity to each reaction in the kinetic model is calculated after multiplying each pre-exponential factor (A-factor) for the reaction rate by a factor of 1.3 (30% increase) and then computing the corresponding ignition delay τ_{after}. The ignition delay computed without perturbation is represented by τ_{before}. The sensitivity coefficient for reaction *i* is given by $S_i = \frac{\partial \tau}{\partial k}$ or in this case:

$$S_i = \frac{\tau_{before} - \tau_{after}}{\tau_{before}}$$

For each condition, reactions to be included in the subsequent global uncertainty and sensitivity analysis were screened based on a threshold of $S_i > 2$ % leading to a total of 40 reactions.

Global uncertainty and sensitivity analysis

In the global approach employed in the study, the uncertainty in the selected input parameters is propagated though the model in order to provide error bars on the predicted ignition delay distribution. Global sensitivity analysis is then performed in order to determine and rank the contribution of each parameter uncertainty to the overall output uncertainty, represented by the output sample variance. The global sensitivity method allows one to be able to investigate the impact of model input parameters (e.g. reaction rates) across their entire uncertainty range and also to account for the effect of parameter interactions.

Prior to performing global uncertainty and sensitivity analysis, uncertainty factors (G_i) were assigned to each of the screened reactions based on values evaluated in the reviews of Baulch [26] where available. For reactions without evaluated uncertainties, data available on National Institute of Standard and Technology (NIST) website representing several studies was employed to estimate the uncertainty of the input parameter. In situations where there was no evaluation and insufficient studies within NIST (experimental or theoretical) to determine uncertainty from spread of data, an uncertainty value of 2 was chosen for the sensitivity calculations in the present study. This is perhaps an optimistic factor for reactions with rates determined by theory, group additivity or estimation, but the results will show that it already leads to quite large uncertainties within the predictive targets.

The global technique employed here is built around a sampling approach in which many simulations are carried out with samples covering the entire domain of the defined input space. A low discrepancy sampling sequence such as Sobol's quasi-random sequence is employed because of its ability to converge faster (in terms of output mean and variance) compared to standard Monte Carlo random sampling. The Sobol' sequence represents a set of quasi-random numbers between 0 and 1 generated for each of the selected input parameters across the chosen sample size *N*. This sequence is then used to create a sample of rate parameters within the uncertainty range (k_i/G_i, $G_i \times k_i$) which is uniform in the space of log(k_i), where k_i is the original rate parameter in the scheme, k_i/G_i is the lower limit and $G_i \times k_i$ is the upper limit. The log rate constants within the chosen uncertainty range are uniformly distributed, as they have been assumed to have equal probability of being the actual rate parameter value. This approach is fairly typical for schemes with estimated parameters since insufficient information is available to take a probabilistic approach.

Following the sampling and performance of model runs, there is a need to estimate the global sensitivity index - a factor that gives an indication of the importance ranking of input parameters that contribute most to the variance in the predicted output. Monte Carlo (MC) simulations and response surface methods (RSMs), are commonly employed to investigate the relationship between the input and output distributions [27-28]. In the RSM method based on high dimensional model representations (HDMR) employed in the study, the sensitivity indices are calculated using a functional meta-model fitted to sample input-output distributions that is based on the quasi-random sample (QRS) of full model runs. The accuracy of the calculated sensitivities is dependent on the accuracy of the constructed meta-model which in turn is a function of the sample size, the fitting approach used in constructing the meta-model and the complexity of the surface response [27]. A total sample size of *N* = 256 was used for the uncertainty study (i.e. in order to estimate error bars on the predicted targets) while a sample size *N* ranging from 2048-4096 was used for the QRS-HDMR study in order to obtain accurate HDMR meta-model fits based on up to 10th order orthonormal polynomials and a coefficient of determination $R^2>90\%$ for ignition delay predictions. A full description of the QRS-HDMR method can be found in [29].

Results and discussion

Comparison with experimental data.

Weber Data

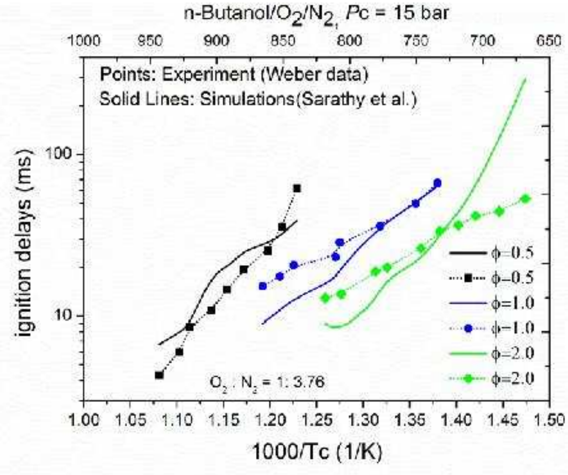

Fig 1 Comparison of predicted ignition delays with experimental data from Weber et al. for conditions of 15 bar and = 0.5-2.0

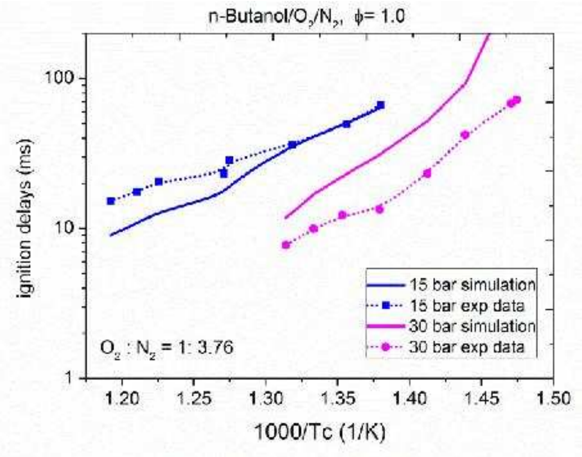

Fig. 2 Comparison of predicted ignition delays with experimental data for = 1at 15 bar and 30 bar

Figure 1 shows a comparison of predicted ignition delays with the data from Weber et al. for a compressed pressure of 15 bar, temperatures ranging from 678K- 925K and = 0.5 -2.0. In common with Sarathy et al. and Weber et al. [17,19], we find (Fig. 1) that under these conditions, the RCM data is predicted to a reasonable level of accuracy across the entire equivalence ratio range. However, under rich conditions, the model's over-prediction of the ignition delay data could be over a factor of 5 for the low temperature region (i.e. T < 700K). Under stoichiometric conditions, at a higher pressure of 30 bar (Fig. 2), which is above the pressure range at which the model was constrained by ignition delays, the model over-predicts the Weber data by a factor of about 2 across a major part of the temperature range. In addition, the decrease in ignition delays when pressure is increased from 15 to 30 bar is under-represented by the model. It is also apparent from Figs. 1 and 2 that *n*-butanol does not exhibit the well-known two-stage, negative temperature coefficient (NTC) behaviour commonly seen for linear alkanes and shown for DME ignition delays in our previous work [29].

Leeds Data

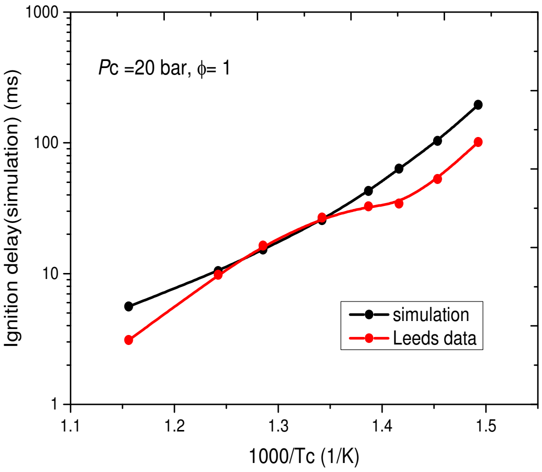

Fig. 3 Comparison of predicted ignition delays with Leeds data for conditions of 20 bar under stoichiometric conditions of ϕ = 1

Figure 3 shows that under constant volume stoichiometric simulation conditions of 20 bar, the kinetic model predicts the Leeds data quite well at high temperatures but over predicts the experimental data by about a factor of 2 at lower temperatures below 700K. The discrepancy is smaller than that shown at 30 bar in Fig. 2 but still significant.

Uncertainty study

Figure 4 shows that for the case of ϕ=1, at 15 bar, and *T* = 725K-839K, uncertainties in the predicted ignition delays are quite large; up to at least plus or minus one order of magnitude. Although the original model appears to predict the ignition delay data at lower temperatures quite well, the experimental values fall only within the 25th percentile of the predicted outputs and are not close to the median of the distributions. This results from the fact that the predicted distributions are skewed with respect to the mean values. At higher temperatures, the agreement at nominal parameter values, is less good, although the experimental values do lie close to the median predictions. Overall, within the suggested uncertainties for the model, there is agreement with the experiments across the temperature range. The large uncertainties in predicted delays do however, indicate the need for a more accurate knowledge of the dominant rate parameters in the scheme if the scheme were to be reliably utilised for auto-ignition predictions under real engine conditions. Particular focus should be paid to temperature dependencies of the rate parameters. Via a global sensitivity study we can determine first of all, which parameters contribute most to these predictive uncertainties.

Secondly we can determine how the experimental measurements constrain these parameters under the different conditions studied.

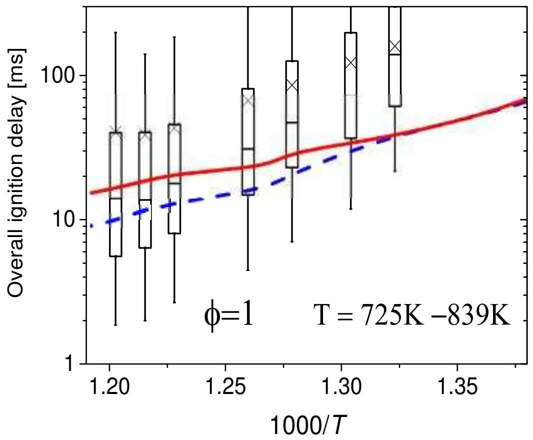

Fig. 4 Comparison of predicted ignition delays (blue) with Weber data (red). Boxes - 25th and 75th percentiles; whiskers - 5th and 95th percentiles

Global sensitivity study

Figure 5 shows the main first-order sensitivity coefficients determined by the HDMR study for selected conditions at 15 bar. The selected reactions are the seven most dominant reactions for predicted *n*-butanol ignition delay predictions and account for over 85 % of the predictive uncertainties, highlighting that the uncertainties are dominated by the first-order effects of just a few reactions.

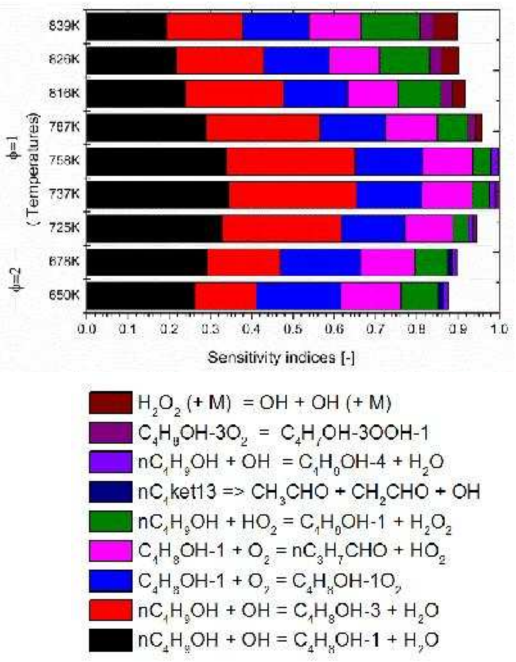

Fig. 5 Main first-order sensitivity indices for simulated ignition delays with respect to reaction rates at selected temperatures and 15 bar

The branching fractions of fuel + OH hydrogen abstraction reactions dominate the predicted uncertainties across the entire temperature range (i.e. low-intermediate temperatures) for stoichiometric conditions. The hydroxybutyl radicals produced as a result of the main fuel oxidation reactions are consumed via two different types of reaction pathways: one is the oxygen addition reaction (alpha-hydroxybutyl+O_2) leading to the formation of the peroxy radical (RO_2) that drives auto-ignition, and the other is termination that inhibits autoignition due to the formation of HO_2. Although it is well known [29] that isomerisation reactions of the peroxy radical (RO_2) dominate auto-ignition chemistry in general low-temperature mechanisms, the dominance of the main fuel hydrogen abstraction reactions in the butanol scheme may be due to its key role in determining the amount of fuel that goes to termination steps compared with how much is available for chain branching and propagation steps. The contribution from the hydrogen abstraction reactions diminishes with increasing in temperature while a contribution from HO_2 chemistry and formation routes for H_2O_2 become more significant.

The sensitivities highlight that constraints in the reaction rate coefficients for the H abstraction reactions by OH are better provided by ignition delays at stoichiometric lower temperature conditions since their uncertainties contribute to a larger percentage of the predictive variance. However, no single rate constant dominates, with the two main H abstractions from the and sites showing first-order sensitivities of 0.32 and 0.29 respectively. This means that a wide range of chosen rate constants for these reactions could reproduce the experimental ignition delays with reasonable accuracy. Sarathy et al. report [17] discrepancies between the *ab initio* studies for abstraction from the site between the studies of Zhou et al. [30] and Zádor et al. [31] and have adopted the temperature dependence of Zádor et al. to give better agreement with experimental data. H abstraction from the site is critical to correctly determining the amount of chain branching which drives low-temperature autoignition. The rate constant for this reaction was however, subject to large discrepancies between [30] and [31] and hence corrections were made in [17]. The low temperature ignition delays at =1 provide some constraints on this reaction channel (S_i=0.29) but there is still a large influence of uncertainties in other key rates.

However, if we plot predicted log ignition delay against a scaled ratio of the log reaction rates for these main abstractions reactions from the and sites, leading to C_4H_8OH-1 + H_2O and C_4H_8OH-3 + H_2O respectively, we see an almost linear relationship (Fig. 6), with the scatter resulting from uncertainties in the other main reactions listed in Fig. 5. The sensitivity index for this branching ratio is 0.7 i.e. twice that for the individual rates. On the contrary the sensitivity index for the sum of reaction rates for H abstraction by OH is <0.1. The analysis therefore demonstrates that ignition delay measurements provide much stronger constraints on the branching ratio than on the overall rate constant for this reaction class. There is still scatter in Fig. 6 however, due to the influence of uncertainties in other channels such as $R+O_2$.

At lower temperatures and richer conditions (=2), where discrepancies between model and experiment were seen in Fig. 1, $R+O_2$ reactions are equally as important as H abstraction (Fig. 5). The reaction to form butanal+HO_2 is included as a high temperature pathway in [17] but actually shows a higher sensitivity at low temperature rich conditions.

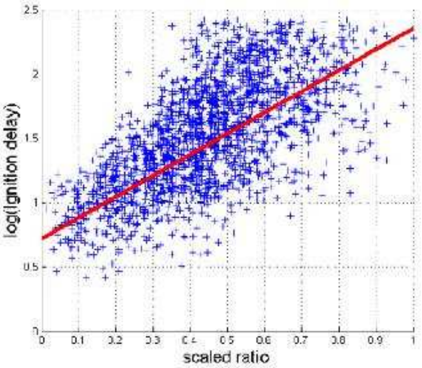

Fig. 6 Scatter plot and HDMR component function for predicted log(ignition delay) against the scaled branching ratio for the two main H abstraction reactions by OH, taking into account uncertainties in the 40 main reactions, T=725 K,   =1, 15 bar.

Conclusions

A global uncertainty and sensitivity study of the low-intermediate temperature of n-butanol combustion has been conducted with ignition delays as predictive targets. The key reactions that dominate the predicted uncertainties were identified through global sampling-based HDMR analysis. Calculated sensitivity indices show that the dominant reaction pathways are H abstraction via OH. The study indicates that low temperature ignition delay measurements provide a high level of constraint on the branching ratio for abstraction from the   and   sites but not on the total rate constant. For rich conditions R + O_2 pathways are equally as important as H abstraction.

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