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Global sensitivity analysis of n-butanol reaction kinetics using rate rules

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ABSTRACT

We investigate the sensitivity of the ignition delay time, τ_{ign}, of n-butanol to uncertainties in the rate-rule kinetic rate parameters, at various initial temperatures (600–1000 K), pressures (10–80 bar) and equivalence ratios (0.5–2.0). We start by considering a 30-dimensional stochastic germ in which each random variable is associated with one reaction class, and build a surrogate model for the ignition delay time using polynomial chaos expansions. The adaptive pseudo-spectral projection technique is used for this purpose. The surrogate model is used to estimate first-order and total-order sensitivity indices characterizing the dependence of the ignition delay time on the uncertain inputs. Results indicate that τ_{ign} is mostly sensitive to variations in four dominant reaction classes, namely, H–atom abstraction from the fuel (reaction class 2), addition of O_2 to the fuel radicals (reaction class 11), fuel radical isomerization including Waddington type reactions (reaction class 15), and concerted elimination reactions (reaction class 16). We consequently focus our attention on these four reaction classes, and consider variations within corresponding subrules. We explore two approaches to define the subrules of reaction class 2, one based on the radical abstracting from the fuel resulting in eleven subrules and another based on the abstraction site resulting in five subrules. Hence, we investigate the sensitivity of τ_{ign} due to variability in the rate parameters of 26 and 20 subrules of the resulting models. In particular, the simulations indicate that in reaction class 2 H–atom abstraction by HO_2 dominates the variability in τ_{ign} at all initial conditions considered. Analysis of this finding reveals that correlations inherent in the rate rule construction plays an important role in the resulting sensitivity predictions, and suggests a hierarchical approach to the calibration of elementary reaction rates.

1. Introduction

Interest in renewable and sustainable biofuels for the transportation sector is driven by the need to reduce greenhouse gas emissions and pollutants [1]. One of the prevailing next-generation biofuels is n-butanol [2]. Interest in n-butanol arises due to its varied advantages over other biofuels, such as ethanol, including its higher energy density and better fuel economy [3], lower corrosion and volatility, and higher calorific values [4]. Thus, n-butanol has been used as a fuel and as a blending agent with gasoline or diesel in several engine studies [5–11]. In order to characterize the combustion characteristics of n-butanol, different experiments have been conducted, including shock tube [12,13], rapid compression machine [14,15], jet stirred reactor [3,16], premixed laminar flame and opposed-flow diffusion flame experiments [3]. Hence, several elaborate chemical kinetic models were developed and validated against these different experimental setups [2].

Compiling comprehensive chemical kinetic models is of great importance to ensure an extensive description of the combustion process. Detailed chemical kinetic models are also a critical component for simulation tools in combustion. For these reasons, various methods have been proposed to aid in assembling and calibrating these representative models. For instance, the hierarchical approach [17] aims at mimicking the combustion process, which sequentially breaks down the fuel molecules into smaller intermediate species and ultimately products. Thus, the chemical kinetic model describing the overall complex combustion process is built by accumulating sequences of elementary reactions into a single mechanism. A fundamental difficulty in this approach concerns the scarcity in experimental data, which impedes the process of

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Table 1
Rate rules and their corresponding uncertainty factors (UF) for n-butanol mechanism.

30 reaction classes in n-butanol mechanism	UF
1. Unimolecular fuel decomposition	2
2. H-atom abstraction from the fuel	see Table 2
3. Fuel radical decomposition	2
4. Fuel radical isomerization	3.5
5. H-atom abstraction reactions from enols (i.e. unsaturated alcohols)	3
6. Enol - Keto tautomerizations and isomerizations catalyzed by H, HO_2 and formic acid	3
7. Addition of H radicals to enols	4
8. Enol radical decomposition	2
9. Unimolecular decomposition of enols	2
10. Reaction of O_2 to 1-hydroxybutyl radicals to directly form an aldehyde/ketone + HO_2	3
11. Addition of O_2 to fuel radicals ($R + O_2 = ROO$)	2
12. $R + ROO = RO + RO$	2
13. $R + HO_2 = RO + OH$	3
14. $R + CH_3O_2 = RO + CH_3O$	3
15. ROO radical isomerization (ROO = QOOH) including Waddington type reaction mechanism	4
16. Concerted eliminations (ROO = enol + HO_2)	4
17. $ROO + HO_2 = ROOH + OH$	3
18. $ROO + H_2O_2 = ROOH + HO_2$	3
19. $ROO + CH_3O_2 = RO + CH_3O + O_2$	3
20. $ROO + ROO = RO + RO + O_2$	3
21. $ROOH = RO + OH$	3
22. RO decomposition	3
23. Formation of epoxy alcohols via cyclization	4
24. QOOH = enol + HO_2 (radical site beta to OOH group)	3
25. QOOH = alkene/enol + carbonyl + OH (radical site gamma to OOH group)	3
26. Addition of O_2 to QOOH ($QOOH + O_2 = OOQOOH$)	2
27. Reaction of O_2 with 1-hydroxybutylhydroperoxide radicals	3
28. Isomerization of OOQOOH and formation of carbonyl alkylhydroxy hydroperoxides and OH including Waddington type reactions mechanism	4
29. Decomposition of carbonyl alkylhydroxy hydroperoxides to form oxygenated radical species and OH	3
30. Epoxy alcohol reactions with OH and HO_2	3

assigning rate coefficients to all reactions in the model. Consequently, it is necessary to obtain a set of rate coefficient estimations for appreciably similar reactions. This was well established by the concept of reaction classes and rate rules [17], in which one estimates the rate parameters of substantially similar reactions to be the same. A systematic approach was thus deployed to assemble kinetic mechanisms for fuel surrogates and large hydrocarbons [18–22]. This approach however, propagates uncertainty in the rate parameters in a two-fold fashion: uncertainty in the reference rate constants and uncertainty in the rate rule itself. Consequently, in order to build a reliable model, uncertainty in individual reaction rate coefficients and rate rules must be examined.

The usefulness of any chemical kinetic model is directly correlated with its accuracy and reliability in predicting measured quantities of interest (QoIs) [23,24]. Because uncertainties in the input parameters of a kinetic model propagate to uncertainties in the model outputs, a key step to any calibration effort concerns the quantification of uncertainties in the predictions. Traditionally, uncertainty quantification (UQ) in chemical systems is based on either a local sensitivity analysis or random sampling methods. In general terms, local sensitivity analysis considers the impact of individual perturbations in the model parameters without accounting for mixed interactions. On the other hand, random sampling techniques, which are typically employed to propagate parametric uncertainties, do not efficiently provide information about the sensitivity of QoIs to individual parameters or to collections on uncertain inputs. UQ based on spectral representation of uncertain quantities using polynomial chaos (PC) expansions was proposed to overcome these hurdles. PC [25–27] provides an explicit functional dependence of QoIs in terms of uncertain inputs. This can be readily and efficiently exploited to estimate variance based global sensitivity indices [28]. PC methods have been extensively used in various applications [29–31], and in particular for combustion and reacting flow [32–34].

In this work, we aim at quantifying the variability of the ignition delay time of n-butanol combustion in air, at various initial conditions of temperature, pressure and equivalence ratio, and characterizing the dependence of this variability on uncertainty in rate rules. The detailed chemical kinetic model from [2] is adapted for this purpose. We first consider a 30-dimensional stochastic space for the 30 rate rules underlying the kinetic model. We apply the adaptive pseudo-spectral projection technique [35] to build PC surrogates and consequently perform global sensitivity analysis (GSA). The GSA is initially used to identify the rate rules whose uncertainties dominate the variability of the ignition delay time. Once these dominant parameters are identified, the GSA is exploited to propose and test a reduction in the dimensionality of the germ. An additional layer of detail is then introduced, namely by considering the impact of individual subrules belonging to the dominant rules. This enables us to explore in a cost-effective fashion the variability sources at different levels of detail.

This paper is organized as follows. In Section 2 we introduce the rate rules and reaction classes, specify the corresponding uncertainty factors, outline the adaptive pseudo-spectral projection technique used to build the PC surrogates, and highlight their use for GSA. The computational study of the sensitivity of the ignition delay time to uncertainty in rate rule parameters is presented in Section 3. The analysis is further refined in Section 4 by analyzing variability in the sub-rules of the dominant reaction classes. Major conclusions are summarized in Section 5.

2. Methodology

2.1. Reaction classes and rate rules

In the rate-rule approach, rate parameters are assigned to reactions that have not been studied or measured, using rate parameters of reactions that are deemed to be sufficiently similar. In this study we investigate the combustion of n-butanol and rely on the