



# Construction of a skeletal mechanism for butanol isomers based on the decoupling methodology



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## ABSTRACT

Butanol has been recommended as an alternative for fossil fuels in the transport sector due to its potential for reducing pollutant emissions. Butanol has four isomers, i.e., *n*-butanol, *s*-butanol, *i*-butanol, and *t*-butanol. For the purpose of investigating the effect of molecular structure on the fuel kinetics of butanol, a skeletal mechanism containing 66 species and 196 reactions was constructed for the four butanol isomers using a decoupling methodology. The mechanism was validated against the measurements in various fundamental reactors and a homogeneous charge compression ignition (HCCI) engine. The predictions agree with the measurements reasonably well for all the four butanol isomers covering wide operating conditions. The results indicate that, for the four butanol isomers, the ignition delay time is significantly affected by the fuel-related reactions, whereas the laminar flame speed is dominated by the small species kinetics. The overall reactivity of butanol isomers decreases with the increased number of fuel molecular branch due to the fact that the fuel molecule with branched structure produces more stable branched intermediate species, reducing the reactivity of fuel.

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## 1. Introduction

Biofuels have attracted more and more attentions over the past decades due to its potential of reducing the emissions of greenhouse gas and the dependence on fossil fuel. As an alternative or an additive to gasoline and diesel, butanol is better than ethanol in the aspects of higher hydrophobicity and energy content, lower volatility, and less corrosion [1–4]. Furthermore, butanol is capable of being blended with gasoline and diesel in the present engines with higher concentration than ethanol [5,6]. In order to deeply understand the influence of butanol on engine performance and emissions, understanding its ignition and oxidation behaviors in fundamental reactors is crucial.

Butanol includes four isomers, i.e., normal butanol (*n*-butanol), secondary butanol (*s*-butanol), *iso*-butanol (*i*-butanol), and tertiary butanol (*t*-butanol). The different chemical structure of butanol isomers affects the intermediate species pool, which subsequently influences the ignition and oxidation characteristics [7]. Plenty of experiments has been conducted on the oxidation of butanol isomers in shock tubes [8,9], rapid compression machines [10], jet-stirred reactors (JSR) [11,12], and premixed laminar and

counterflow flames [13–18]. Based on experimental and theoretical analysis, Wu and Law [14] found that the reactivity of butanol isomers was dominated by chemical kinetics in expanding spherical flames. Recently, Liu et al. [17] measured the burning behavior of a single droplet of butanol isomers at atmosphere conditions. The experimental data were simulated by two detailed mechanism [19,20], and the results indicated that the transport data of isomer specific species significantly affected the predicted results. Thus, a reliable chemical mechanism is required to deeply understand the oxidation characteristics of butanol.

Grana et al. [21] employed the hierarchical approach to construct a high-temperature mechanism for the four butanol isomers. The mechanism includes above 300 species and 7000 reactions and is capable of satisfactorily reproducing the pyrolysis and oxidation of different butanol isomers in various reactors. Frassoldati et al. [22] further modified the Grana et al. mechanism [21] in order to improve the predictions on the pyrolysis of *n*-butanol and acetone-butanol-ethanol mixture. By adding the related reactions of *s*-, *i*-, and *t*-butanol into the *n*-butanol mechanism constructed by Black et al. [23], Yasunaga et al. [24] built a detailed mechanism for different butanol isomers based on the measurements in shock tubes at high temperatures.

Recently, Cai et al. [25–27] proposed a set of detailed mechanisms to simulate the combustion of *n*-butanol, *s*-butanol, and *i*-butanol based on the USC Mech II model [28] and three butene

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isomers model [29]. The rate constants of the reactions in the butanol sub-mechanisms were estimated using a series of computational methods. The final mechanism can well reproduce the measurements in shock tubes, JSRs, flow reactors, and premixed laminar flames for butanol isomers.

It is worth noting that the aforementioned butanol mechanisms merely include the high-temperature regime. Because the low-temperature chemistry is extremely important for the engines with advanced compression ignition modes [30–32], it is necessary to consider the kinetics for the construction of the butanol mechanism from low to high temperatures. By dividing the elementary reactions into 30 classes, Sarathy et al. [19] constructed a comprehensive oxidation mechanism composed of both the low- and high-temperature reactions for the four butanol isomers. The mechanism contains 426 species and 2335 reactions, and was extensively validated covering a wide temperatures range. With the open-source software package, Reaction Mechanism Generator (RMG), the detailed mechanisms of the four butanol isomers were constructed by Green et al. [20,33,34]. The comparison between the measured and predicted results indicated that the mechanism can well reproduce the pyrolysis and oxidation behaviors of the butanol isomers in shock tubes, jet-stirred reactors, premixed and diffusion flames at high temperatures.

Most of the present mechanisms for butanol isomers are detailed mechanisms, including more than 300 species and thousands of reactions. Integrating the detailed mechanism for engine computational fluid dynamics (CFD) simulations is still a challenge for the present computer due to the expensive computation cost, thus the skeletal or reduced mechanisms are urgently needed. With the Directed Relation Graph with Error Propagation (DRGEP) method, Brady et al. [35,36] reduced the detailed mechanisms of Merchant et al. [20] and Sarathy et al. [19] to predict the counter-flow ignition of the butanol isomers. The final reduced mechanism includes more than 100 species and 800 reactions for each butanol isomer, which is still relatively large for multi-dimensional CFD simulations. As far as we know, only one skeletal mechanism with compact size including low-to-high temperature chemistry for the four butanol isomers is available [37]. In this study, a new skeletal oxidation mechanism was developed for the four butanol isomers using a decoupling methodology. The structure of the paper is as follows. First, the methodology for the mechanism development is introduced. Then, the mechanism is validated against the experimental data over wide operating conditions in various reactors, and the oxidation behaviors of butanol isomers are analyzed. Finally, major conclusions are summarized based on the computational results.

## 2. Model development

By analyzing the laminar flame speed of different butanol isomers, Wu and Law [14] revealed that the kinetics of butanol isomers were same as that of heavy hydrocarbons. Consistently, Sarathy et al. [19] indicated that the low-temperature chemistry of butanol isomers was similar to that of heavy hydrocarbons. Thus, the available butanol mechanisms were mostly developed on the basis of the previous work for large hydrocarbons. Because the decoupling methodology is effective for the construction of the oxidation mechanisms of heavy hydrocarbons [38], it is employed in the present study to build the skeletal mechanism of the four butanol isomers. Due to space limitations, only a brief introduction of the decoupling methodology is presented below with special emphasis on butanol isomers, and the detailed description can be found in Ref. [39].

In the decoupling methodology for the construction of the mechanism of butanol isomers, a detailed  $H_2/CO/C_1$  sub-

mechanism is employed to predict the laminar flame speed and heat release rate of butanol, and the species concentration evolutions of small species. On the contrary, an extremely simplified fuel-related sub-mechanism is introduced to reproduce the ignition behavior and the consumption of the four butanol isomers. As a transition between the  $H_2/CO/C_1$  sub-mechanism and the fuel-related sub-mechanism, a reduced  $C_2$ – $C_3$  mechanism is used.

Fig. 1 shows the major reaction pathways for butanol isomers over the low-to-high temperature regime. Previous studies [14,19,25] indicate that the primary depletion of the butanol molecule is through the H-atom abstraction reactions (Reaction 1–Reaction 4) from low to high temperatures, while the unimolecular fuel decomposition is only important at high temperatures (Reaction 5). Due to the difference in the fuel molecular structure, different fuel radicals (R) are formed for the four butanol isomers. To reduce the size of the present mechanism, only one representative fuel radical is retained for each butanol isomer.



where X represents H, OH,  $HO_2$ , and  $O_2$ , corresponding to Reaction 1–Reaction 4, respectively.



Consistent with the low-temperature butanol kinetics of Sarathy et al. [19], the fuel radicals of the four butanol isomers first react with oxygen to form hydroxyalkyl peroxy ( $RO_2$ ) radicals (Reaction 6), which subsequently form hydroxyalkyl hydroperoxide (QOOH) radicals via isomerization (Reaction 7) at low temperatures in the present mechanism. Then a second oxygen addition to QOOH forms  $O_2QOOH$  (Reaction 8), and  $O_2QOOH$  releases an OH to form carbonyl alkylhydroxy hydroperoxides ( $C_4ket$ ) (Reaction 9). Finally, the  $C_4ket$  radicals are decomposed into small  $C_0$ – $C_2$  species (Reaction 10).

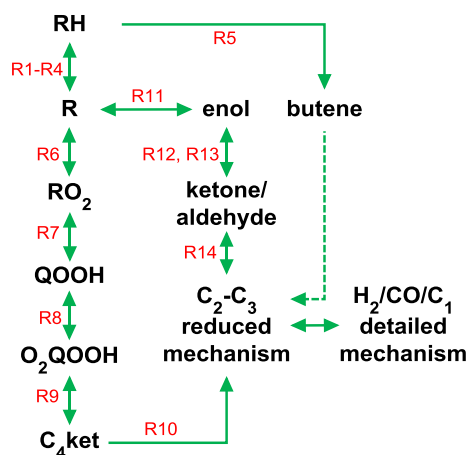


Fig. 1. Diagram of the major reaction paths for butanol isomers (R1–R4 are the initial reactions, R6–R10 are the low-temperature reactions, R5 and R11–R14 are the high-temperature reactions).

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