Comparative study of the counterflow forced ignition of the butanol isomers at atmospheric and elevated pressures

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ABSTRACT

In support of the development of robust combustion models, the present study describes experimental and computational results on the non-premixed counterflow ignition of all four butanol isomers against heated air for pressures of 1–4 atm, pressure-weighted strain rates of 200–400 s^{-1}, and fuel molar fractions in nitrogen-diluted mixtures of 0.05–0.25. Comparison of the parametric effects of varied pressure, strain rate, and fuel loading among the isomers facilitates a comprehensive evaluation of the effect of varied structural isomerism on transport-affected ignition. The experimental results are simulated using isomer-specific skeletal mechanisms developed from two comprehensive butanol models available in the literature, and are used to validate and assess the performance of these models. Comparison of the experimental and computational results reveal that while both models largely capture the trends in ignition temperature as functions of pressure-weighted strain rate, fuel loading, and pressure, for all isomers both models over-predict the experimental data to an appreciable extent. In addition, neither model captures the experimentally-observed ignition temperature rankings, with both models predicting a large spread among n-/iso-/sec-butanol which does not appear in the experimental results. Sensitivity and path analyses reveal that the butene isomers play a significant role in determining the ignition temperatures of the butanol isomers in both models, with the relative branching ratios likely accounting for the ignition temperature rankings observed using each model. It is observed that the reactivity of the butene isomers varies appreciably between the two butanol models, which may account for some of the variability in predictions between the two models. Furthermore, effects of transport properties and their uncertainties on ignition temperature predictions are discussed.

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1. Introduction

Despite recent advances in electric vehicle technologies, their limited range, long recharge cycles, and limited at-large charging options have constrained their consumer appeal [1]. Moreover, while significant advances in terms of energy density over current lithium battery technology are conceivable, attaining such performance will require major technological breakthroughs in terms of electrode/electrolyte materials and chemistry [2]. Alternative technologies such as fuel cell vehicles can potentially address both range and recharge/refuel time issues; however such vehicles have largely been based upon hydrogen fuel cells, which would require an entirely new, world-wide fuel distribution infrastructure to be developed. As a result, there is a clear need for combustion-based near- and intermediate-term alternative transportation energy solutions that address the pressing issues of improved efficiency, reduced emissions, and lowered lifecycle carbon footprint. While both novel engine designs and alternative fuels promise to provide efficiency gains and emissions improvements, their success is predicated upon a robust understanding of the coupled effects of chemical kinetics and convective-diffusive transport, and their accurate representation in predictive reactive-flow models under engine relevant conditions.

As part of a push towards renewable fuels and reduced emissions, alcohols have emerged as a leading prospect both for near-term performance and sustainability improvements, as well as for the long-term replacement of fossil fuels in novel engine concepts. Ethanol, the most successful of these to date, currently comprises up to 10% of all gasoline purchased in the United States and has facilitated the elimination or phase-out of both tetra-ethyl lead (TEL) and methyl tert-butyl ether (MTBE) as anti-knock additives. Through its long history, ethanol has received significant research attention and has been investigated in shock tube, flame, and reactor experiments (cf. [3]). However, the fermentation process by which the majority of ethanol is produced has been criticized for both its use of food-grade

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feedstocks as well as its low conversion efficiency, and second generation production from cellulosic plant waste has yet to be proven commercially viable. Partly as a result, so-called "second generation" alcohol-based alternative fuels such as butanol have recently received significant research attention. As a stand-alone alternative transportation fuel or as a fuel blend with gasoline, butanol offers several advantages over ethanol. Whereas ethanol is fully miscible with water, both *n*- and *iso*-butanol isomers exhibit limited solubility with water and are less corrosive, opening up the possibility of more efficient distribution methods though pipelines. In addition, its higher energy density allows higher blending ratios with gasoline without engine modifications, and its lower vapor pressure would greatly reduce evaporative emissions. Aside from its potential impact as a transportation fuel, chemical kinetics of butanol is scientifically interesting as it represents the smallest alcohol exhibiting all forms of structural isomerism. As a result, by comparing the behavior of the butanol isomers in well-defined combustion configurations, the impacts of molecular structural variations on combustion chemistry can be better understood and broadly applied to the modeling of alcohol-based transportation fuels.

Due to the interest from both practical and scientific points of view, an appreciable body of fundamental research has been developed for butanol isomers in recent years. Though by no means a comprehensive review, numerous fundamental studies have been conducted using a variety of experimental systems including laminar flame speeds [4–7], flame extinction [8–10], pyrolysis [11], flame structure [6,12–15], species and temperature measurements in a flow reactor [12], jet-stirred reactors (JSR) [6,16], and ignition delays in rapid compression machines (RCM) [17–19] and shock tubes [20,21]. Several of these studies have investigated the impact of isomeric variations on global combustion properties. Veloo and Egolfopoulos [7] determined atmospheric pressure laminar flame speeds of the butanol isomers in the equivalence ratio range of $0.7-1.5$, finding highly similar flame propagation rates for *n*-/*iso*-/*sec*-butanol but significantly lower flame speeds for *tert*-butanol. Gu et al. [4] observed laminar flame speed differences between the various isomers, finding that the isomers followed a ranking of *n*-butanol > *iso*-butanol ≈ *sec*-butanol > *tert*-butanol for atmospheric pressure. Stranic et al. [20] investigated ignition delay times of the butanol isomers in a shock tube at $1050-1600$ K, $1.5-43$ atm, and equivalence ratios of 0.5 and 1.0, finding that the butanol isomers exhibited noticeably different ignition delay times, with the relative rankings changing as a function of pressure. At 1.5 atm, *n*-butanol exhibited the shortest ignition delay times, followed by *iso*- and *sec*-butanol, with *tert*-butanol exhibiting considerably longer ignition delays, whereas at 43 atm the rankings followed *n*-butanol ≈ *iso*-butanol < *sec*-butanol < *tert*-butanol. In an RCM configuration Weber and Sung [17] found quite different ignition delay trends for stoichiometric mixtures at $715-910$ K and 15 and 30 bar pressures. At both pressure conditions *n*-butanol exhibited significantly faster ignition delay times than other isomers, additionally finding that the ignition delay ranking followed *n*-butanol < *iso*-butanol ≈ *sec*-butanol < *tert*-butanol at 15 bar, but *n*-butanol < *tert*-butanol < *sec*-butanol < *iso*-butanol at 30 bar. In addition to global combustion properties, the effect of structural isomerism on intermediate species production has been explored by several studies. McEnally et al. [15] conducted speciation studies on the butanol isomers in a doped methane co-flow flame at atmospheric pressure, and concluded that the dominant decomposition process was unimolecular decomposition rather than H-abstraction. Oßwald et al. [14] conducted a molecular beam mass spectrometry (MBMS) study of the butanol isomers in a fuel-rich low-pressure laminar premixed flame, noting significant differences among the butanol isomers in terms of the intermediate species pool. In particular, large disparities were observed for butene, enol, and aldehyde species in [14].

From these and similar works, several detailed combustion models have recently been compiled and developed that comprehensively describe the chemical kinetics of butanol isomers. The model of Frassoldati et al. [22] – an update of the mechanism of Grana et al. [13] – includes all four isomers and has been validated against pyrolysis, shock tube ignition delay time, and premixed and non-premixed flame structure data. The model of Merchant et al. [23] – including all four isomers, and based upon the comprehensive model of Van Geem et al. [24] – has been validated against pyrolysis, laminar flame speed, low-pressure premixed flame structure, and shock tube ignition delay data. Additionally, the comprehensive model of Sarathy et al. [25] has been validated against laminar flame speeds, low-pressure premixed flame structures, RCM and shock tube ignition delays, and JSR species profiles.

Despite the research attention that butanol isomers have garnered, there is relatively little data exploring limit phenomena in convective/diffusive environments for these fuels. In fact, to the authors' knowledge, the only available forced ignition data comes from the stagnation-pool study of Liu et al. [26] for *n*- and *iso*-butanol, while flame extinction data are limited to the *n*-butanol studies of Veloo et al. [10] and Hashimoto et al. [9], and the *n*-, *iso*-, and *sec*-butanol study of Mitsingas and Kyritsis [8]. Ignition and extinction data in convective/diffusive systems are relevant to the operation of practical combustion devices, and can also offer a highly-sensitive experimental platform for the validation of both chemical kinetic and transport models. As such, the present work compares the impact of ambient pressure, strain rate, and fuel loading on the counterflow ignition temperatures of all four butanol isomers in order to understand the effects of isomeric structure variations on diffusive ignition. The experimental results are further simulated using isomer-specific skeletal mechanisms derived from comprehensive butanol models available in the literature. A comparison of experimental and simulated results is then used to validate and assess the performance of these literature butanol models.

2. Experimental and computational descriptions

2.1. Experimental apparatus

The details of the non-premixed counterflow ignition apparatus, including a detailed experimental characterization, have been previously described by the authors [27]. Briefly, 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 improve the quality of the resulting stagnation-point 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. Heating on the air side is accomplished using an internal helical SiC heater, capable of heating the airflow to 1250–1300 K at the tube exit depending on operating conditions, and an external heater that is used to reduce heat loss. The ignition temperature, measured as the air-side centerline boundary temperature, is determined from a K-type bare wire thermocouple with proper radiation correction. The location of the ignition event is monitored using a Vision Research Phantom v710 high-speed camera acquiring visible-light images at a frame rate of 3000 Hz. This frame rate is sufficient to capture the onset of ignition and facilitates determining its precise location within the test section to ensure consistency among data sets as well as ensure quasi-one-dimensional ignition behavior. For all the experimental data reported herein, the onset of ignition was observed to take place near the middle of the test section and then propagate radially in a fairly one-dimensional manner. The thermocouple design, details of the radiation correction, and discussion of the importance of monitoring ignition location have been described previously [27].