Combustion characteristics of butanol isomers in multiphase droplet configurations

Yu Cheng Liu [a],[*],[1], Fahd E. Alam [b],[1], Yuhao Xu [c], Frederick L. Dryer [d], C. Thomas Avedisian [c], Tanvir I. Farouk [b],[*]

[a] Department of Computer Science, Engineering and Physics, University of Michigan – Flint, Flint, MI 48502, USA
[b] Department of Mechanical Engineering, University of South Carolina, Columbia, SC 29208, USA
[c] Sibley School of Mechanical and Aerospace Engineering, Cornell University, Ithaca, NY 14853, USA
[d] Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08544, USA

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ABSTRACT

This study reports results of experiments on the isolated droplet burning characteristics of butanol isomers (n-, iso-, sec-, and tert-) under standard atmosphere conditions in an environment that promotes spherical combustion. The data are compared with predictions from a detailed numerical model (DNM) that incorporates complex combustion chemistry, radiative heat transfer, temperature dependent variable fluid properties, and unsteady gas and liquid transport. Computational predictions are generated using the high temperature kinetic models of Sarathy et al. (2012) and Merchant et al. (2013).

The experiments were performed in a free-fall facility to reduce the effects of buoyancy and produce spherical droplet flames. Motion of single droplets with diameters ranged from 0.52 mm to 0.56 mm was eliminated by tethering them to two small-diameter SiC filaments ($\sim$14 μm diameter). In all the experiments, minimal sooting was observed, offering the opportunity for direct comparison of the experimental measurements with DNM predictions that neglect soot kinetics.

The experimental data showed that the burning rates of iso- and sec-butanol are very close to that of n-butanol, differing only in flame structure. The flame stand-off ratios (FSR) for n-butanol flames are smaller than those for the isomers, while tert-butanol flames exhibited the largest FSR. DNM predictions based upon the kinetic model of Sarathy et al. over-predict the droplet burning rates and FSRs of all the isomers except n-butanol. Predictions using a kinetic model based upon the work of Merchant et al. agree much better with the experimental data, though relatively higher discrepancies are evident for tert-butanol simulation results. Further analyses of the predictions using the two kinetic models and their differences are discussed. It is found that the disparity in transport coefficients for isomer specific species for Sarathy et al. model fosters deviation in computational predictions against these newly acquired droplet combustion data presented in this study.

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1. Introduction

Liquid fuels have been widely used to power aerospace and ground transportation vehicles. Despite projected decreases in petroleum resources in the future, forecasts suggest that demand for liquid transportation fuel will continue to grow. Liquid fuels are preferred over other forms due to their high energy content, matured engine technologies that utilize them, and fuel manufacturing/distribution infrastructure [1]. In particular, sustainable liquid fuels derived from biomass (biofuels) have demonstrated potential to be used to augment petroleum derived resources through blending. Creating a self-sustaining, profitable biofuels industry that does not compete with agricultural food supply is a challenge recognized by government mandates in the U.S. and European Union [2,3].
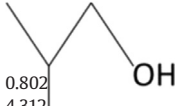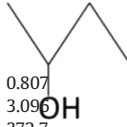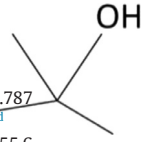
Butanol (C_4H_9OH), as an emerging biofuel, has been identified because of the readiness and continuous development of conversion processes for biomass feedstocks [4]. Selected properties of butanol isomers are shown in Table 1 [5–7]. Butanol isomers have comparatively superior fuel properties, e.g. higher energy density, lower vapor pressure, less corrosive compared to ethanol [6] and also have been considered for use in commercial compression ignition (CI) engines due to their relatively high cetane number [8,9].

Table 1
Selected fuel properties of butanol isomers (C$_4$H$_9$OH, M.W. = 78.123 g/mol [9]).

	n-Butanol	*iso*-Butanol	*sec*-Butanol	*tert*-Butanol
Molecular structure				
Liquid density, ρ (kg/m^3) at 298 K[a]	0.81	0.802	0.807	0.787
Liquid viscosity μ (mPa s) at 298 K[b]	2.544	4.312	3.096	_[d]
Boiling point, T_b (K) [a]	390.9	381	372.7	355.6
Freezing point T_{fr} (K) [a]	183.9	165.2	158.5	298.8
Critical pressure, P_c (atm)[a]	43.6	42.4	41.4	39.2
Research octane number[b]	96	113	101	105
Motor octane number[b]	78	94	32	89
Enthalpy of vaporization, ΔH_f (kJ/kg) at T_b[b]	582	566	551	527
Heat of combustion, $\Delta H_{c,liq}$ (kJ/kg)[c]	−36,087	−36,001	−35,895	−35,669

[a] [5].
[b] [6].
[c] Values converted from [7].
[d] *tert*-Butanol is solid at 298 K.

The interests in butanol have attracted much effort towards engine studies. The performance and emission behaviors of both spark ignition (SI) and CI engines fueled by blends of petroleum fuels and *n*-butanol have been extensively reported [10–19]. The addition of *n*-butanol was found to increase the brake specific fuel consumption (bsfc) and brake thermal efficiency [13] and slightly reduce CO and NO$_x$ emissions [10] of diesel engines except for turbo-charged operations [14,15]. In direct injection SI engines, *n*-butanol/gasoline blends promote better anti-knock behaviors and reduction of CO, NO$_x$ and unburned hydrocarbons (UHC) [11]. Pure *n*-butanol combustion has been reported in some homogeneous charged CI (HCCI) engine studies [16,17] and it could increase CO and UHC emissions compared to gasoline in SI engine operations [12]. Regalbuto et al. [18] reported that among butanol isomers, *n*-butanol exhibits the highest NO$_x$, *iso*-butanol the highest CO, and *sec*-butanol the highest UHC in SI engine experiments. However, Fushimi et al. [19] claimed few isomer effects on NO$_x$ and smoke emission are found in butanol/diesel blend operations.

Oxidation kinetics of butanol isomers have received attention since about a decade ago [20,21]. Development of combustion chemistry of butanol isomers includes a direct comparison with combustion properties measured in configurations that are amenable to detailed numerical modeling (DNM). Currently, such modeling has been widely performed for configurations in which the fuel is pre-vaporized (e.g., jet-stirred reactor (JSR) [22–25], shock tubes [26–29], rapid compression machines/facility (RCM/RCF) [30,31], opposed diffusion flame [32–34] burners, flow reactors [34,35] and pyrolysis reactor and premixed flame probed by a molecular beam mass spectroscopy (MBMS) [21,35–39]). Recently, Sarathy et al. [40] utilized experimental results from MBMS, shock tube, RCM, and JSR configurations to validate a comprehensive oxidation kinetics model for butanol isomers that cover high and low temperature ranges. Van Geem and coworkers [41], Harper et al. [42] and Merchant et al. [43] validated the mechanisms for *n*-, *sec*-, *iso*- and *tert*-butanol pyrolysis and/or oxidation with combustion properties from JSR, opposed flame, laminar flame velocity, and shock tube configurations. This kinetic model has been used in simulating the combustion in more practical systems like a homogeneous charge compression ignition (HCCI) engine [44].

Non-premixed liquid pool ignition experiments [45] of *n*-butanol and *iso*-butanol have been modeled using a reduced version [46] of *n*-butanol oxidation scheme by Sarathy et al. [23] coupled with phase equilibrium parameters. Soot prediction from *n*-heptane/*n*-butanol/PAH mechanisms has also been pursued [47]. However, the performance of the kinetic models developed has not yet been assessed in detailed numerical models of multi-phase

combustion configurations that, at the least, may be considered to provide a bridge to spray combustion.

An important attribute of combustion properties obtained from the experimental configurations mentioned above for validating detailed kinetic mechanisms is that those configurations promote a zero or one-dimensional transport process, because doing so significantly reduces computational overhead for modeling while incorporating detail chemistry. However, none of them includes some of the unique multiphase features found in a spray, including fuel vaporization, coupled liquid and vapor transport, moving boundary effects, or the sub-grid spray configuration of droplets. Currently the only combustion configuration that is amenable to detailed numerical modeling which does incorporate such elements is a single isolate droplet burning with spherical symmetry [48–54] such that the droplet and flame are concentric and gas transport is radially symmetric. This paper applies this modeling capability to combustion of butanol isomer droplets under conditions that promote such spherical symmetry.

Experimental studies are noted on butanol isomer droplets at standard [52] and elevated pressures [54–56] as well as under various ambient temperatures [57]. Pure evaporation of *n*-butanol droplets has also been studied [58]. The present study is motivated by the dearth of data for butanol isomers droplet combustion specifically under conditions that promote spherical droplet flames to simplify the transport processes involved as well as representing a multi-phase combustion system. The predicted combustion properties using DNM as described in [50,51] are compared with measurements. Building upon the prior work on *n*-butanol [52], the present study shows both experimental and numerical comparison of droplet burning of all four butanol isomers.

2. Experimental methods

To promote spherically symmetric droplet burning, a combination of low gravity (to minimize buoyancy effects), physically restricting motion of the droplet by tethering it to support structures (to eliminate forced convection) and employing small droplets were used. A gravity level of 10^{-4} g/g$_0$ was achieved by carrying out the experiments in a laboratory configuration that was in free-fall over a distance sufficient to observe the complete droplet burning history (free-fall over 7.6 m to provide 1.2 s experimental time). The details of the experimental setup and procedures can be found elsewhere [59,60] and a brief summary is provided below.

Figure 1 outlines the procedure for the experiment. Test droplets were deployed onto an X-shape configuration of two 14 μm SiC fiber filaments intersecting at 60° (cf. Fig. 1a). Previ-