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Combustion and pyrolysis of *iso*-butanol: Experimental and chemical kinetic modeling study

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ABSTRACT

The first reaction mechanism for *iso*-butanol (372 species and 8723 reversible elementary reactions) pyrolysis and combustion that includes pressure dependent kinetics and proposes reaction pathways to soot precursors has been automatically generated using the open-source software package RMG. High-pressure reaction rate coefficients for important hydrogen abstraction reactions from *iso*-butanol by hydrogen, methyl and HO_2 were calculated using quantum chemistry at the CBS-QB3 level. The mechanism was validated with recently published *iso*-butanol combustion experiments as well as new pyrolysis speciation data under diluted and undiluted conditions from 900 to 1100 K at 1.72 atm representative of fuel rich combustion conditions. Sensitivity and rate of production analysis revealed that the overall good agreement for the pyrolysis species, and in particular for the soot precursors like benzene, toluene and 1,3-cyclopentadiene, depends strongly on pressure dependent reactions involving the resonantly stabilized *iso*-butenyl radical. Laminar flame speed, opposed flow diffusion flame speciation profiles, and autoignition are also well-captured by the model. The agreement with speciation profiles for the jet-stirred reactor could be improved, in particular for temperatures lower than 850 K. Flux and sensitivity analysis for *iso*-butanol consumption revealed that this is primarily caused by uncertainty in *iso*-butanol + OH, *iso*-butanol + HO_2 and the low temperature peroxy chemistry rates. Further theoretical and quantum chemical studies are needed in understanding these rates to completely predict the combustion behavior of *iso*-butanol using detailed chemistry.

1. Introduction

The demand for a clean, renewable biofuel increases as new benchmarks are legislated amid increased pressure to reduce the world's dependence on fossil fuels for energy and chemicals. Biobutanol is in pole position to become a major game changer in the 21st century [1]. It is considered an advanced biofuel – superior to ethanol in almost every way – and convertible to jet fuel and biogasoline [2]. Not only are the fuel properties of butanol better than ethanol, butanol is also considered a 'greener' fuel than ethanol [3]. One of the remaining unanswered questions is which of the four butanol isomers (*n*-butanol, sec-butanol, *iso*-butanol, and tert-butanol) should be favored in the coming decades.

Although today the butanol isomers are largely produced from petrochemicals, all isomers, apart from tertiary butanol, can be developed independently in renewable forms [4] to be marketed as biobutanol at competitive prices to oil based fuels. *n*-Butanol was initially considered to be the logical favorite to replace ethanol because of its mature production technology via the well-known acetone–butanol–ethanol process by anaerobic fermentation of sugar substrates using solventogenic clostridia [5]. However, this technology is handicapped in competitiveness by high energy cost due to low concentrations of butanol produced and significant volumes of water processed, even with new clostridia strains [2]. That is why in recent years *iso*-butanol has gradually become favored by industry. One of the main advantages of the *iso*-butanol technology is that it can be produced at adapted ethanol plants from corn and other grains or sugarcane and even from cellulose, as demonstrated by among others Gevo Inc. [6,7]. With diminishing subsidies on conventional fermentation ethanol, producers looking for higher margin derivatives are potential candidates for switching to *iso*-butanol. Looking at the fuel properties of both isomers the differences are relatively small with the exception of *iso*-butanol having a higher octane rating (motor octane number of 89)

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compared to *n*-butanol (motor octane number of 78), this gives it a slightly higher value as gasoline blend stock.

The strong interest from industry in butanol as a potential replacement for ethanol in combustion engines has resulted in many recent combustion studies of the different butanol isomers. Only a brief summary, focusing on *iso*-butanol, is presented in this work. *iso*-Butanol has received considerable attention from the engine community with studies performed in spark-ignition engines [8,9] and in compression–ignition engines [10,11]. These studies are essential for assessing the feasibility and performance of *iso*-butanol in practical systems and are complementary with more fundamental combustion science research. The latter include experimental studies on premixed laminar flame propagation [12,13], premixed laminar flame structure [14], non-premixed laminar diffusion flame structure [13,15,16], shock tube and rapid compression machine ignition delay [17–19], and jet-stirred reactor oxidation chemistry [20].

All this recent experimental work has certainly helped the development and validation of detailed chemical kinetic models for *iso*-butanol, such as those presented by [13,16,21–23]. These fundamental kinetic models have the ambition to be predictive in nature with the ultimate goal of advancing design and optimization of practical engine systems through coupling with computational fluid dynamic (CFD) models. However, despite the recent leaps in butanol kinetic modeling, a comprehensive model for *iso*-butanol pyrolysis and combustion – valid at the temperature and pressure ranges found in practical engines – is still lacking. Moreover the experimental dataset for *iso*-butanol is far from complete. For example, although pyrolysis reactions are an essential part of any combustion mechanism [24], prior to this work accurate pyrolysis data for *iso*-butanol have not been available. These pyrolysis reactions play an important role in areas of fuel rich conditions in internal combustion engines, e.g. in case of incomplete mixing.

The goal of the present study is to develop a detailed kinetic mechanism for *iso*-butanol pyrolysis and combustion building on the mechanisms developed for other isomers in earlier work [32,54]. This study differentiates itself from other *iso*-butanol chemical kinetic model studies by consistently including pressure dependent kinetics, with most rate coefficients from high-pressure limit rate rules built into the open source mechanism generator RMG [25]. Most rate rules originate from literature but for the most important reactions in our system new rate rules have been determined from quantum calculations. The mechanism is tested against a large number of new and recently published data including – pyrolysis product profiles in plug flow reactor, jet-stirred reactor mole fraction profiles, opposed flow diffusion flame mole fraction profiles, laminar flame speeds at different pressures and autoignition delays in rapid-compression machine and high-pressure shock tube experiments. Furthermore, this study attempts to guide future *iso*-butanol pyrolysis and combustion chemistry research by elucidating those reactions that are the most significant and uncertain for the experimental conditions that have been studied.

2. Experiment and computational procedures

2.1. Pyrolysis experiments

The experimental set-up has been described in detail elsewhere [26–28] and therefore only a brief description based on Djokic et al. [28] and Pyl et al. [27] will be given here. A schematic overview of the experimental set-up as well as a more extensive description are given in the Supplementary information section. It consists of three parts: the feed section, the furnace/reactor section and the analysis section. *iso*-Butanol (Acros Organics, Belgium, purity 99.5%+, used as obtained) is pumped towards an evaporator kept at 523 K using a peristaltic pump (Heidolph, Germany). The mass flow rate of the feed is calibrated using an electronic balance. The diluent, N_2 (Air Liquide, Belgium, purity 99.999%), is heated separately to the same temperature. Both the evaporators/heaters and the subsequent mixer are electrically heated and filled with quartz beads, enabling a smooth evaporation of the feed and uniform mixing of the feed and diluent. The flow rate of the latter is controlled by a coriolis mass flow controller (Bronkhorst, The Netherlands). Typical experimental conditions for diluted and undiluted *iso*-butanol are provided in Table 1. The overall residence time varies between 1.1 s and 0.57 s. Working with fixed mass flow rates for diluted and undiluted conditions respectively results in a difference in residence time at higher temperatures of 0.18 s because of a difference in molar flow rate due to the decomposition of *iso*-butanol into predominantly species with lower molecular weight. Due to this increase in residence time, the conversion for the diluted experiments is higher for an identical temperature profile in the plug flow reactor.

The reactor is a 1.475 m long, 6 mm internal diameter tube, made of Incoloy 800HT (Ni, 30–35; Cr, 19–23; and Fe, >39.5 wt%). Prior to its use in these experiments, the reactor tube was passivated to suppress potential catalytic activity of the wall. Control experiments with a second reactor having a two times larger surface to volume ratio showed that the influence of the wall on conversion and product selectivities was negligible. The reactor is placed vertically in an electrically heated rectangular furnace. In all experiments discussed in this work, the reactor is operated nearly isothermally, i.e. with a steep temperature increase at the inlet and a steep temperature drop at the reactor outlet. Eight thermocouples along the reactor monitor the process gas temperature at different positions. The temperature profiles of experiments are provided in Supplementary information. The pressure in the reactor is controlled by a downstream back pressure regulator. Two manometers, positioned at the inlet and outlet of the reactor, record the coil inlet pressure (CIP) and the coil outlet pressure (COP), respectively. The pressure drop over the reactor was found to be negligible. During a typical 6-h operation the pressure drop did not increase noticeably since the amount of coke deposited on the reactor inner wall was found to be marginal. Even under the most severe conditions ($T > 1073$ K) no significant pressure drop was observed, with the pressure remaining constant in the coil at 1.7 bar. No entrained coke particles were collected.

The analysis section of the pyrolysis set-up is similar to the one discussed previously [29,30]. A detailed description of the columns used and analysis procedure can be found in the Supporting information. More than 100 different components are observed and identified using the on-line comprehensive 2D gas chromatograph (GC × GC) equipped with a flame ionization detector (FID) and a Time-of-Flight Mass Spectrometer (TOF-MS). Figure 1 shows part of the GC × GC chromatogram during one of the *iso*-butanol experiments. The settings and the characteristics of the GC × GC can be found elsewhere [27]. The increased separation power of GC × GC makes it very suitable for analyzing complex effluents containing

Table 1
Overview of experimental conditions for the pyrolysis of *iso*-butanol in the bench scale set-up.

	Diluted	Undiluted
T_{inl} (K)	550–660	550–660
T_{avg} (K)	913–1093	913–1093
Outlet pressure (10^5 Pa)	1.72	1.72
Hydrocarbon flow rate ($g\ s^{-1}$)	1.666×10^{-2}	6.666×10^{-2}
Nitrogen flow rate ($g\ s^{-1}$)	1.889×10^{-2}	0
Conversion (%)	15–98	15–94

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