

A Kinetic Modelling Study of Alcohols Operating Regimes in a HCCI Engine

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ABSTRACT

Pursuing a sustainable energy scenario for transportation requires the blending of renewable oxygenated fuels such as alcohols into commercial hydrocarbon fuels. From a chemical kinetic perspective, this requires the accurate description of both hydrocarbon reference fuels (*n*-heptane, *iso*-octane, toluene, etc.) and oxygenated fuels chemistry. A recent systematic investigation of linear C₂-C₅ alcohols ignition in a rapid compression machine at $p = 10\text{--}30$ bar and $T = 650\text{--}900$ K has extended the scarcity of fundamental data at such conditions, allowing for a revision of the low temperature chemistry for alcohol fuels in the POLIMI mechanism. Heavier alcohols such as *n*-butanol and *n*-pentanol present ignition characteristic of interest for application in HCCI engines, due to the presence of the hydroxyl moiety reducing their low temperature reactivity compared to the parent linear alkanes (i.e. higher octane number). The promising performances of ethanol in a HCCI engine have been recently discussed by Bissoli et al. (*Energy & Fuels*, 2017, Submitted), observing wider stable operability conditions in terms of fuel/air load (λ) and exhaust gas recirculation (EGR) extent compared to PRF80 and PRF100. The aim of this study is to present briefly the reliability of the updated POLIMI mechanism for heavier alcohols and to investigate the fundamental role of chemical kinetics on the performance maps of HCCI engines fueled with *n*-butanol and *n*-pentanol, in terms of operability limits and engine efficiency.

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1. INTRODUCTION

Modern society is facing multifaceted and complex energy-related challenges. Projection for the next 20-30 years foresee the combustion of fossil fuels to keep driving energy production, mostly due to higher energy demands for road, air and sea transport [1]. While suitable alternatives to combustion exist for power generation, transportation requires high energy density sources, i.e. petroleum-derived liquid fuels (gasoline, diesel, kerosene, naphta). Moreover, environmental issues associated to combustion, pollution reduction targets [2] and other political and economic strategies endorse the use of biofuels (neat or in blends with commercial fuels) as the most promising near term alternative to fossil fuels for internal combustion engines.

First-generation fatty acid methyl-esters [3, 4] together with second-generation biofuels such as alcohols [5] and furans [6] have been one of the main topic of combustion chemistry research in the last decade. Particularly, large interest has been devoted to alcohols, due to the viable production pathways from biological matter [7, 8].

Starting from bioethanol, nowadays blended with gasoline up to 85% (E85 gasoline) and used in fuel flexible vehicles, an increasing interest in higher alcohols, with four or more carbon atoms has emerged because of favorable physical and thermodynamic properties [5]. Energy density, heating value, viscosity, hygroscopicity and volatility of higher alcohols are in fact compatible with the requirements of

existing distribution infrastructure (pipe lines, tanks etc.) and most importantly with modern engines. Therefore, the interest in C_4 - C_6 alcohols as fuel additives or as replacements for fossil fuels.

In the United States, the Octamix waiver [9] already allowed up to 16% butanol blends with gasoline as an equivalent to E10 gasoline. Many studies investigated the performances of biobutanol as a fuel or fuel additive. Rakopoulos et al. [10] as well as Siwale et al. [11] investigated blends of up to 24% v/v butanol in diesel, observing generally improved exhaust emission quality. Also a decrease in soot emissions was highlighted by Valentino et al. [12], due to the lower ignitability of butanol/diesel blends.

Pentanol is also an attractive second-generation bio-fuels and can be produced from renewable feedstock. Its higher energy density, higher heating value, higher viscosity, lower hygroscopicity and lower volatility [5] motivated the interest in pentanol isomers. Campos-Fernandez et al. [13] investigated power and fuel economy performance of diesel/pentanol blends (10-25% v/v of pentanol) in a direct injection compression ignition engine. Wei et al. [14] tested blends with up to 30% pentanol by volume. Li et al. experimentally investigated the emission performance, fuel economy and combustion characteristic of neat pentanol in a diesel engine [15]. Overall these studies highlighted the potentials of the use of n-pentanol in diesel engines. Table 1 shows some important properties of several alcohols, gasoline and diesel fuels such as the lower heating value (LHV), research octane number (RON), motor octane number (MON) and cetane number (CN).

Table 1. Properties of alcohols, gasolines and diesel fuels. Adapted from Sarathy et al. [5] and Kalghatgi [16].

Fuel	LHV (MJ/L)	RON	MON	CN
Gasoline	~30-33	88-98	80-88	n.d.
Diesel	~35	n.d.	n.d.	40-55
n-butanol	26.9	98	85	12
n-pentanol	28.5	80	74	20
n-hexanol	29.3	56	46	24

Correctly assessing the reactivity of a new fuel or a new gasoline or diesel formulation is largely a chemical kinetics problem. A better understanding of a specific chemical compound's effects on combustion performances (flame speed, auto-ignition etc.) and emission allow the design of a fuel or fuel blend for an existing technology, the tuning of an engine for an assigned fuel or the concerted development of fuels and engines [17]. Typical surrogate mixtures such as primary reference fuels (PRFs) and toluene reference fuels (TRFs) have started to include different alcohols to investigate their possible impact on commercial fuels [18]. From a chemical kinetic perspective, an accurate description of the combustion chemistry of every surrogate component (n-heptane,

iso-octane, toluene, ethanol, butanol etc.) is imperative. The recent review of Sarathy et al. [5] discussed the state of the art understanding of alcohols combustion chemistry, synoptically pointing out many improvement margins and open questions. Following the inputs of Sarathy et al. [5], a joint research effort between the CRECK group at Politecnico di Milano (POLIMI) and the C3 group at National University of Ireland, Galway (NUIG) investigated the auto-ignition propensity of n - C_2 - C_5 alcohols in a twin-piston Rapid Compression Machine (RCM), with the aim of systematically revising alcohols low temperature chemistry.

Along with new fuel formulations to be used in conventional spark ignition (SI) and compression ignition (CI) engines, new engine technologies are also being investigated [16]. Homogeneous Charge Compression Ignition (HCCI) engines have received great attention in the last few decades because of the possibility to obtain high power output with a cleaner combustion [19]. In HCCI engines, fuel and air are fully premixed, as in conventional SI engines, and the charge is ignited through compression, relying on its auto-ignition characteristics, like in CI engines. Although the use of a premixed air-fuel charge ensures reduced NO_x and soot emissions, it also causes High Heat Release (HRR) and Pressure Rise Rates (PRR) leading to ringing events [20], strongly limiting the power output. Charge dilution by means of lean equivalence ratio and Exhaust Gas Recirculation (EGR) allow preventing these phenomena, but excessive charge dilution leads to very low power output and unburned hydrocarbon emissions. Typical undesired phenomena such as knock, already limiting the efficiency of SI engine, are also an issue in HCCI engines, with the additional criticism derived from the lack of cycle control measures such as spark timing (SI engine) or fuel injection timing (CI engine).

Beside extensive experimental investigations of HCCI operating ranges, also including neat n -butanol or blends in the most recent literature [21, 22, 23, 24, 25], some computational model providing a time- and cost-effective solution to analyze and optimize the engines, have been reported in the literature [26, 27, 28, 29, 30, 31, 32]. In particular, stemming from the well-recognized fundamental role of chemical kinetics in HCCI combustion, and from the general lack of knowledge about the chemical phenomena ruling HCCI operability maps, Bissoli et al. (*Energy & Fuels*, 2017, Submitted) validated a multi-zone model to study the impact of different fuels and engine configurations (speed and boost) on the operability maps, from a chemical point of view, by means of advanced tools like Sensitivity Analysis and Rate of Production Analysis [32].

Starting from the description and validation of the updated POLIMI alcohols mechanism, this study investigates the chemical kinetics underlying the operability maps and efficiency of HCCI engines fueled with n -butanol, n -pentanol and a TRF/butanol gasoline surrogate [33].

The manuscript is organized as follows. Section 2 briefly discusses the experimental approach at NUIG also comparing alcohols ignition-delay time measurements with previous measurements from the literature. The kinetic mechanism of n -butanol and n -pentanol is

then discussed, mostly focusing on the low temperature oxidation pathways. Comparison of experimental data with POLIMI model predictions for *n*-butanol, *n*-pentanol and PRF-TRFs/butanol mixtures is presented to prove reliability of the chemistry. Section 3 describes the main features of the multi-zone HCCI model and its validation method. Section 4 discusses operability and performance maps of HCCI engines charged with the same fuels for which ignition propensity is discussed in Section 2.

2. KINETIC MODEL OF N-BUTANOL AND N-PENTANOL LOW TEMPERATURE COMBUSTION

Modelling the autoignition in HCCI engines requires an accurate description of low and high temperature combustion kinetics of alcohols. Moving from the studies on propanol isomers by Frassoldati et al. [34] and of butanol isomers by Grana et al. [35], the high temperature kinetic mechanism has been recently revised and extended to pentanol isomers (*n*- and *iso*-pentanol) [36]. A lumped low temperature mechanism to describe *n*-butanol oxidation was proposed by Pelucchi et al. [37]. Starting from a systematic evaluation of the influence of different oxygenated functional groups on C-C and C-H bonds strength, a description of the main features and reaction pathways characterizing the reactivity of different oxygenated fuels (alcohols, aldehydes, ketones, methyl esters) was provided, with particular focus on intermediate and low temperature regimes [37]. The same rules applied to *n*-butanol, were then extended to describe *n*-pentanol oxidation at low temperatures, according to the assumption that the effect of the functional group vanishes after the β position [37, 38, 39], as schematically represented in Figure 1.

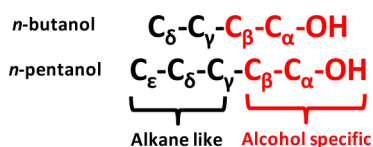


Figure 1. treatment of different carbon positions in *n*-butanol and *n*-pentanol.

Stemming from the lack of a systematic investigation of alcohols auto-ignition chemistry under engine relevant conditions and from the scarcity of measurements at low temperatures and high pressures [5], ignition delay times were measured in the twin-piston rapid compression machine (RCM) at NUIG for *n*-butanol and *n*-pentanol/“air” stoichiometric mixtures at $p=10$ -30 bar and $T=700$ -925 K. The extended experimental targets for model validation guided a revision of the lumped low temperature mechanism, as discussed in Section 2.2.

New fuel formulations require the coupling of alcohols chemistry with standard PRFs and TRFs surrogates, representative of commercial fuels [33, 40]. The global POLIMI mechanism has been thoroughly validated for pure component such as *n*-heptane, *iso*-octane and toluene and their mixtures [41, 42, 43]. The

mechanism uses a lumped description of the primary propagation reactions of larger species and primary intermediates [44, 45]. This approach, together with an extensive use of structural analogies and similarities within the different reaction classes, easily allows extension of the scheme to new species (e.g. *n*-hexanol), still maintaining a relatively low number of species (298 species, 11095 reactions). The kinetic mechanism, together with thermodynamic properties is provided in the Supporting Information.

2.1. Experimental Methodology

Ignition delay time measurements were carried out in the rapid compression machine described by Darcy et al. [46] at NUIG. *n*-butanol ($\geq 99\%$) and *n*-pentanol ($\geq 99\%$) were obtained from Sigma- Aldrich, while helium (99.9%), oxygen (99.5%), argon (99.9995%), nitrogen (99.95%), and carbon dioxide (99.5%) were supplied by BOC Ireland. Auto-ignition measurements for *n*-butanol and *n*-pentanol/“air” stoichiometric mixtures were conducted at temperatures of ~ 700 -925 K, and pressures of 10-30 bar. Mixture compositions are reported in Table 2.

Table 2. $\Phi=1.0$ alcohols / “air” mixture compositions (% mole fraction) tested in this study.

n-butanol					
Mixture	Fuel	O2	N2	Ar	CO2
Mix1-C4, p=30 bar	3.38	20.29	68.70	7.63	0.00
Mix2-C4, p=10 bar	3.38	20.28	15.26	61.09	0.00
Mix3-C4, p=30 bar	3.39	20.36	53.61	0.00	22.63
n-pentanol					
Mixture	Fuel	O2	N2	Ar	CO2
Mix1-C5, p=10 bar	2.72	20.43	76.85	0.00	0.00
Mix2-C5, p=10 bar	2.72	20.43	38.42	38.42	0.00

The experimental data thus obtained agree well with previous literature measurements in RCM and Shock Tubes (ST). Deviations between measurements at similar conditions have to be attributed to differences in the facility design and in diluent compositions ($N_2/Ar/CO_2$) in data from different authors. Deviations from ideal behavior caused by heat loss and complex fluid dynamics were taken into account for RCM simulations. Volume histories necessary for the correct simulation of the new data presented in this study are reported in the Supporting Information.

Figure 2a shows simulated pressure profiles for *n*-butanol and *n*-pentanol at $T_c=830$ K and 838 K, respectively. Experimental ignition delay times of the two alcohols at $p=10$ bar are compared in Figure 2b, highlighting the higher low temperature reactivity of *n*-pentanol, and a converging ignition propensity for $T > \sim 950$ K.

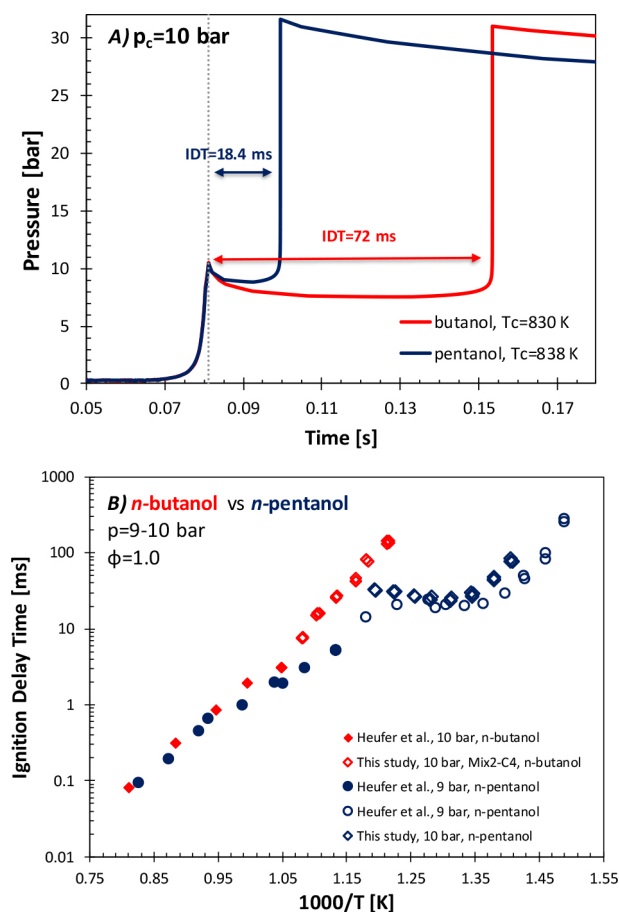


Figure 2. A) Calculated pressure history for n -butanol and n -pentanol stoichiometric mixtures at $T_c \sim 830$ – 840 K and $p_c \sim 10$ bar. B) Comparison between n -butanol and n -pentanol ignition delay measurements at $p_c \sim 10$ bar. Open symbols: RCM experiments (this study $\square$ and Heufer et al. $\diamond$ [38]), full symbols: shock tube experiments [38].

2.2. Kinetic Mechanism

Prior to the systematic revision of n -butanol and n -pentanol kinetics, the thermodynamic properties of the fuels, fuel radicals (alkyl, peroxy, hydroperoxy alkyl etc.) and stable species (enols, ketohydroperoxides etc.) have been obtained based on the revised group contributions by Burke et al. [47]. Properties of the lumped low temperature species have been obtained as a selectivity based average of the different possible isomers. It has to be noted that, according to the lumping procedure proposed by Ranzi et al. [44, 45] both the forward and the reverse rate constant in the low temperature pathways are explicitly assigned, nullifying the effect of updated thermochemistry of typical low temperature species. Figure 3 shows bond dissociation energies (BDE) for n -butanol C-H and C-C bonds, highlighting the weakening effect of the hydroxyl functional group on vicinal bonds. As summarized in Figure 1 such effect vanishes after the β -positions.

Fuel consumption mostly occurs through H-abstraction to form fuel radicals. OH and HO_2 are the dominant abstracting radical over the whole temperature range of interest for HCCI combustion. The

observed bond strength hierarchy directly impacts relative selectivity to the different H-abstraction channels. Rate constants for H-abstraction by OH, HO_2 and CH_3 on alcohols-specific positions have been adopted from Zhou et al. [48, 49, 50]. Alkane-like positions are treated according to the systematic approach of Ranzi et al. [51], as already reported in previous studies [34, 35, 36].

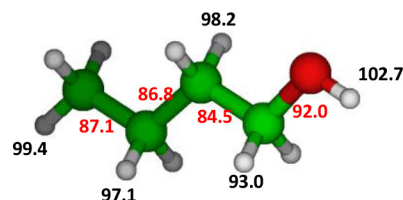


Figure 3. C-H (black) and C-C (red) bond dissociation energies (kcal mol⁻¹). Adapted from [37].

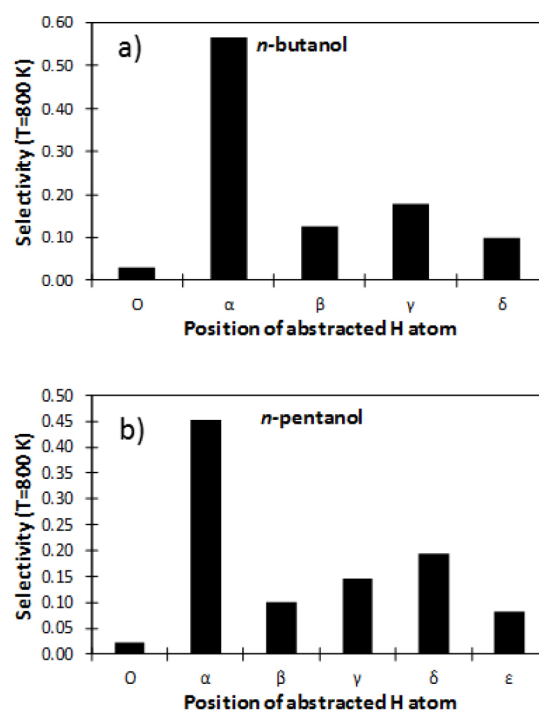


Figure 4. H-abstraction selectivity as a function of temperature from Rate of Production Analysis at $T=800$ K and $p=30$ bar. Panel a) n -butanol, panel b) n -pentanol.

Figure 4 shows selectivity of H-abstractions by OH for both n -butanol and n -pentanol. As expected from the BDEs, the formation of α radical largely dominates, followed by the secondary alkane-like positions (γ in n -butanol or γ and δ in n -pentanol), and by the secondary β position, whose C-H bond is ~ 1 kcal mol⁻¹ stronger than the alkane-like secondary positions. H-abstraction from the hydroxyl group only accounts for $\sim 5\%$ of the overall selectivity.

Similarly to alkanes, the fuel radical can isomerize or decompose via β -scission reactions [52]. At lower temperatures alkyl radicals interact with oxygen forming peroxy radicals, activating the typical low temperature reaction pathways [5, 44, 53]. A schematic representation

of the low temperature oxidation mechanism of alcohols is given in Figure 5, highlighting pathways that are particularly relevant or new pathways with respect to alkanes (thicker arrows).

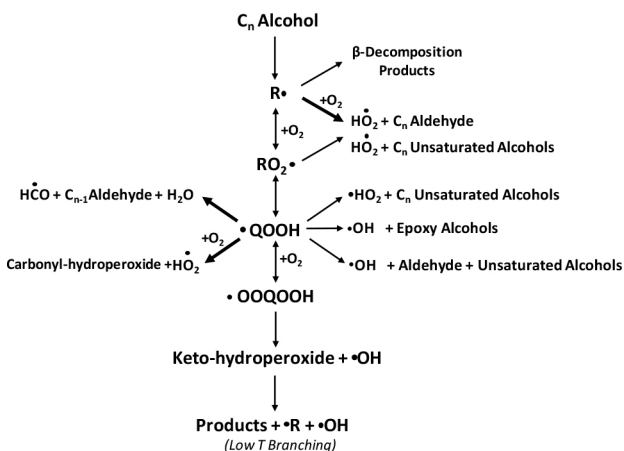


Figure 5. Schematic representation of alcohols low temperature oxidation mechanism. Thicker arrows represent new or particularly relevant pathways in alcohols oxidation with respect to alkanes.

The peculiarity of alcohols oxidation at low temperatures is that the α -hydroxyalkyl radical ($R\cdot\text{-CH-OH}$) reacts with O_2 to rapidly form HO_2 and the parent aldehyde or ketone. This alcohol-specific propagation pathway strongly competes with the conventional alkane-like low temperature branching channel, largely justifying the relatively high RON and MON indices of alcohol fuels (ethanol, propanol and butanol isomers). As clear from the comparison between panel A and B of Figure 4, the importance of this reaction channel decreases with increasing chain length, making longer alcohols (pentanol, hexanol, etc.) gradually more similar to linear alkanes and therefore more suitable for diesel engines or new combustion technologies such as gasoline compression ignition (GCI) engines. As summarized by Kalghatgi [16], GCI engines could efficiently reduce NO_x and soot by running CI engines using low octane gasoline (RON~70-85), spanning gasoline and diesel volatility ranges. n-pentanol and n-hexanol fall within such specifications both in terms of boiling temperatures (138 and 157 °C respectively) and ignition propensity.

The specific low temperature interactions of ethanol α -hydroxyalkyl radical with O_2 have been theoretically investigated by Zádor et al. [54] and by da Silva et al. [55], clearly highlighting in the potential energy surface analysis the low lying pathway leading to the formation of HO_2 and acetaldehyde. Despite a more systematic theoretical evaluation of $R\cdot\text{-CH-OH} + \text{O}_2$ for a series of alcohols would be necessary in order to extrapolate meaningful rate rules, the high pressure limit rate constant of da Silva et al. [55], already adopted by Sarathy et al. [5] and Heufer et al. [38], has been corrected accounting for the extra ~4 kcal/mol reported by Zádor [54] and co-workers at a higher level of theory. Figure 6 compares such rate constants.

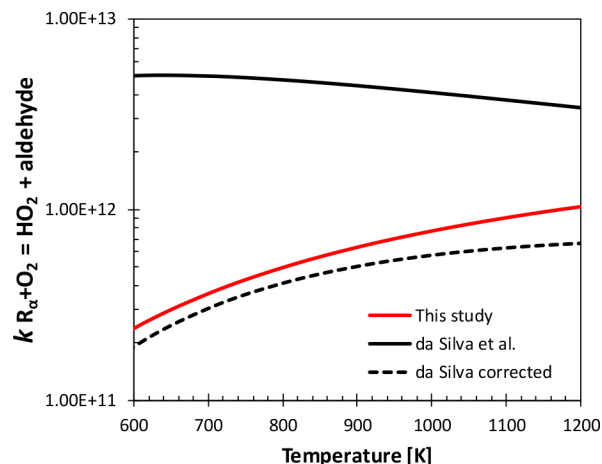


Figure 6. $R\cdot\text{-CH-OH} + \text{O}_2 \leftrightarrow R\text{-(C=O)-H} + \text{HO}_2$ high pressure limit rate constant, $k = 4.5 \cdot 10^{12} \exp(-3500/RT)$. Units are $\text{cm}^3, \text{mol}, \text{s}, \text{cal}$.

The formation of a carbonyl compound and HO_2 is also considered in successive steps when internal isomerization reactions ($\text{RO}_2 \leftrightarrow \text{QOOH}$) lead to the formation of a α -hydroxy-hydroperoxyalkyl radical, and its successive interactions with O_2 undergo similar pathways, as summarized in Figure 7.

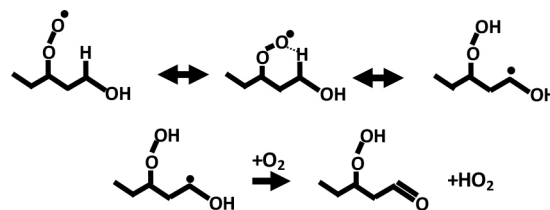


Figure 7. formation of α -hydroxy-hydroperoxyalkyl radical and its interactions with O_2 to form a carbonyl-hydroperoxide (e.g. hydroperoxy pentanal) and HO_2 .

The remaining fuel radicals produced by H-abstraction reactions follow the conventional low temperature pathways, whose rate constant are obtained from established alkanes rate rules [44] accounting for the different bond dissociation energies (i.e. C-H in α and β) in isomerization and decomposition steps or from the mechanism of Sarathy [5] (e.g. tautomerization reactions, Waddington reactions etc.). The unconventional dehydration pathway of hydroperoxyalkyl (QOOH) radicals proposed by Welz et al. [56] is also included, and the rate constant is estimated taking into account the formation of a cyclic transition state and the calculated energy barrier (~13 kcal/mol). Further activity should be devoted to obtain a more accurate kinetic rate constant for this channel, whose steps are reported in Figure 8.

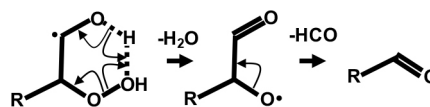


Figure 8. Dehydration channel of QOOH radicals [56] and successive decomposition.

As clearly highlighted in the above discussion and schematically summarized in Figure 5, a large amount of aldehydes is produced in alcohols oxidation. In particular, the $R\cdot\text{CH-OH}+\text{O}_2$ pathways directly produce the parent aldehydes $R\text{-(C=O)-H}$, whose high and low temperature oxidation have been included according to the work of Pelucchi et al. [57, 58].

The primary reaction in the lumped kinetic mechanism to describe the oxidation of *n*-butanol and *n*-pentanol is reported in Table 3.

Table 3. Kinetic parameters of the lumped oxidation reactions of *n*-butanol and *n*-pentanol (units are mol, cm, s, cal).

Lumped reactions	n-butanol			n-pentanol		
	<i>A</i>	<i>n</i>	<i>E_a</i>	<i>A</i>	<i>n</i>	<i>E_a</i>
$R + \text{O}_2 \rightarrow \text{O}_2$	7.50E+12	0.0	0	1.00E+13	0.0	0
$\text{RO}_2 \rightarrow R + \text{O}_2$	3.00E+13	0.0	30000	4.00E+13	0.0	30000
$\text{RO}_2 \rightarrow \text{Unsat Alcohols} + \text{HO}_2$	0.80E+37	-7.5	39500	1.20E+37	-7.5	39500
$\text{RO}_2 \rightarrow \text{OH} + \text{CH}_2\text{O} + \text{C}_{n-1}\text{aldehyde}$ (Waddington)	1.00E+10	0.0	22000	1.00E+10	0.0	22000
$\text{RO}_2 \rightarrow \text{QOOH}$	8.36E+9	0.39	19621.3	2.16E+03	2.463	17204.05
$\text{QOOH} \rightarrow \text{RO}_2$	3.55E+05	1.596	11124.06	5.97E+03	2.186	10839.18
$\beta\text{-QOOH} \rightarrow \text{HO}_2 + \text{Unsat Alcohols}$	4.04E+07	1.823	23182.1	4.79E+12	0.48	27344.5
$\gamma/\delta\text{-QOOH} \rightarrow \text{OH} + \text{Olefins}$	8.19E+15	1.013	23327.45	1.07E+17	1.335	23538.5
$\text{QOOH} \rightarrow \text{Cyclic Ether} + \text{OH}$	2.78E+10	0.371	17120.7	2.78E+10	0.371	17120.7
$\text{QOOH} \rightarrow \text{H}_2\text{O} + \text{C}_{n-1}\text{Aldehyde} + \text{HCO}$	3.00E+10	0	13000	3.00E+10	0	13000
$\text{QOOH} + \text{O}_2 \rightarrow \text{OOQOOH}$	7.50E+12	0.0	0	1.00E+13	0.0	0
$\text{OOQOOH} \rightarrow \text{QOOH} + \text{O}_2$	3.00E+13	0.0	30000	4.00E+13	0.0	30000
$\alpha\text{QOOH} + \text{O}_2 \rightarrow \text{HO}_2 + \text{Aldehyde}$	3.00E+12	0.0	35000	3.00E+12	0.0	35000
$\text{OOQOOH} \rightarrow \text{OQOOH} + \text{OH}$	8.36E+9	0.39	19621.3	2.16E+03	2.463	17204.05
$\text{OQOOH} \rightarrow \text{OH} + \text{Products}$	9.00E+15	0.0	41500	9.00E+15	0.0	41500

Beyond the kinetic details of Table 3 it is possible to explain the higher reactivity of *n*-pentanol (Figure 2) through some rather simple observations. Beside the higher rate of consumption due to H-abstraction reactions by OH, the longer alkane-like carbon chain allows for enhanced isomerization steps in the low temperature branching pathways, as reported in Figure 9. In particular, Figure 9a shows forward (solid lines) and backward (dashed lines) $\text{RO}_2 \leftrightarrow \text{QOOH}$ isomerization lumped rate constants, whose ratio results in a ~20% higher equilibrium rate constant (Figure 9b) in *n*-pentanol oxidation compared to *n*-butanol.

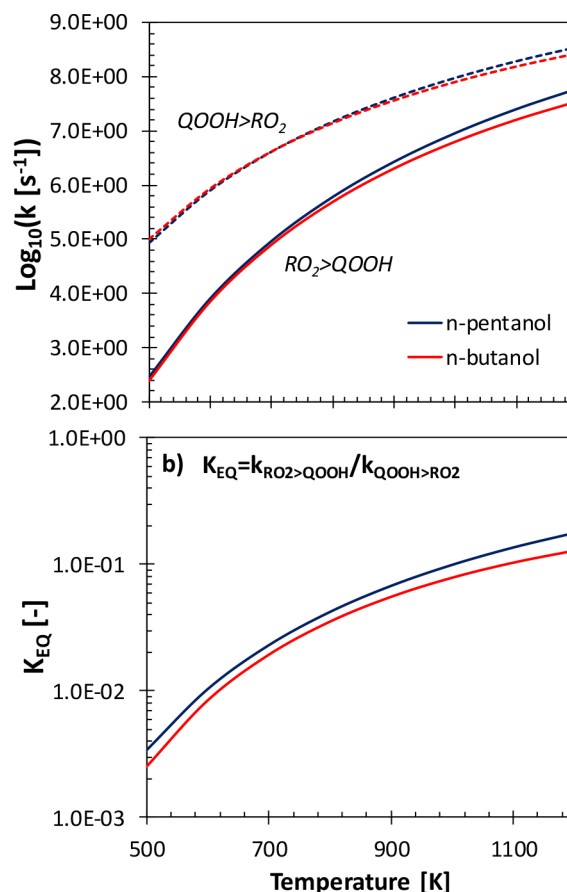


Figure 9. A) $\text{RO}_2 \rightarrow \text{QOOH}$ (solid lines), $\text{QOOH} \rightarrow \text{RO}_2$ (dashed lines) isomerization rate constants of *n*-butanol (red) and *n*-pentanol (blue). B) equilibrium rate constant defined as $k_{\text{RO}_2 \rightarrow \text{QOOH}}/k_{\text{QOOH} \rightarrow \text{RO}_2}$.

This enhanced isomerization step translates into a more effective low temperature branching for *n*-pentanol, highlighted in terms of normalized ketohydroperoxides mole fraction in Figure 10. The ignition delay time also corresponds to the time at which complete consumption of ketohydroperoxides occurs.

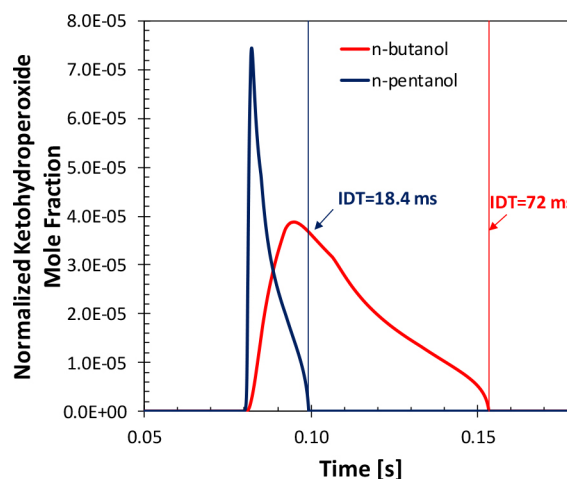


Figure 10. Normalized ketohydroperoxide mole fraction ($x/x_{0,\text{fuel}}$) for *n*-butanol and *n*-pentanol stoichiometric mixtures at $T_c \sim 830\text{--}840\text{ K}$ and $P_c \sim 10\text{ bar}$.