

Exploring the reactivity of C₄–C₆ linear alcohols: from jet stirred reactor and rapid compression machine experiments to operating regimes in a HCCI engine.

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Introduction

Starting from bioethanol which is blended with gasoline in fractions of up to 85% (E85 gasoline) and used in fuel flexible vehicles, there is currently an increasing interest in higher alcohols, with four or more carbon atoms because of their favorable physical and thermodynamic properties. In the US, the Octamix waiver [1] already allows up to 16% butanol blends with gasoline as an equivalent to E10 gasoline. Many studies investigated the performances of bio-butanol and bio-pentanol as fuels or fuel additives, generally noticing improved emission quality, and promising overall performances when blended with diesel fuels [2, 3]. 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. [4] and Kalghatgi [5].

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

Extensive experimental investigations endorsed *n*-butanol as a promising fuel to be used in HCCI engines [6]. 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. [7, 8] validated a multi-zone model to study the impact of different fuels and engine configurations (speed and boost) on the operability maps.

A systematic investigation of linear C₄–C₆ alcohols was carried out recently in the atmospheric pressure jet stirred reactors at CNRS in Nancy, over the temperature range 500–1100 K. The rapid compression machine based at NUI Galway was used to measure ignition delay times of stoichiometric *n*-C₂–C₅ alcohols/air mixtures at $p = 10$ –30 bar in the temperature range $T = 700$ –925 K. The new validation targets reduced the scarcity of fundamental data on alcohols oxidation, and allowed for a systematic revision of the rate rules to describe alcohols oxidation in the kinetic model developed at Politecnico di Milano (POLIMI) [9-12]. The model of Bissoli et al. [7, 8] was used to investigate the chemical kinetics underlying the operability maps and efficiency of HCCI engines fueled with *n*-butanol, *n*-pentanol and a TRF/butanol gasoline surrogate [12].

Kinetic Model

Figure 1 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 **Errore. L'origine riferimento non è stata trovata.** such effect vanishes after the β -positions.

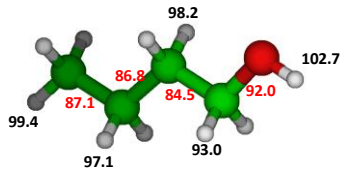


Figure 1: C–H (black) and C–C (red) bond dissociation energies (kcal mol^{-1}). Adapted from [9].

Fuel consumption mostly occurs through H-atom abstraction to form fuel radicals. $\dot{\text{O}}\text{H}$ and $\text{H}\dot{\text{O}}_2$ are the dominant abstracting radicals over the whole temperature range of interest for HCCI combustion. The observed bond strength hierarchy directly impacts the relative selectivity of the different H-atom abstraction sites, as indicated in Figure 2.

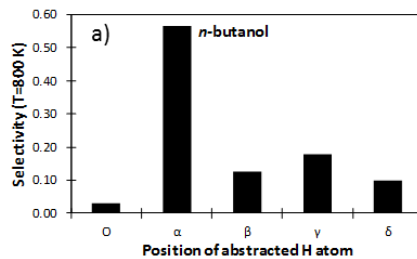


Figure 2: Selectivity of H-abstraction reactions as a function of temperature from Rate of Production Analysis at $T=800\text{ K}$ and $p=30\text{ bar}$.

Similar to alkanes, the fuel radical can isomerize or decompose via β -scission reactions. At lower temperatures, alkyl radicals interact with oxygen forming peroxy radicals, activating the typical low temperature reaction pathways. A schematic representation of the low temperature oxidation mechanism of alcohols is given in Figure 3, highlighting pathways that are particularly relevant or new pathways with respect to alkanes (thicker arrows).

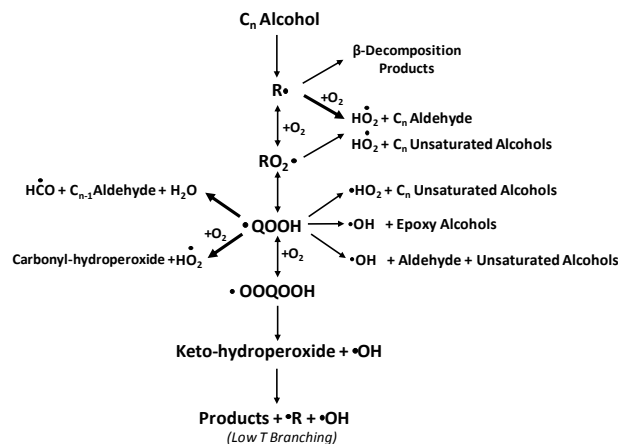


Figure 3: Schematic representation of alcohols low temperature oxidation mechanism. Thicker arrows represent new or particularly relevant pathways in alcohols oxidation with respect to alkanes.

The peculiarity of alcohols oxidation at low temperatures is that the dominant α -hydroxyl-alkyl radical ($\text{R}-\dot{\text{C}}\text{H}-\text{OH}$) reacts with O_2 to rapidly form $\text{H}\dot{\text{O}}_2$ radicals and the parent aldehyde or ketone without forming stable peroxy radicals which usually enhance the low temperature branching pathways. The activation of this reaction pathway is the major motivation for the relatively high RON and MON indices of alcohol fuels (ethanol, propanol and butanol isomers). Clearly, the importance of the α -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. The specific low temperature interactions of ethanol α -hydroxyl-alkyl radical with O_2 have been theoretically investigated in the literature

clearly highlighting low-lying pathway leading to the formation of HO₂ radicals and acetaldehyde. A detailed kinetic analysis of the different pathways and their impact at engine relevant conditions has been presented by Pelucchi et al. [12].

Kinetic Model Validation

Figure 4 compares experimental ignition delay times of *n*-butanol (left panel) and *n*-pentanol (right panel)/O₂/Ar and in air mixtures. A comparison of *n*-butanol and *n*-pentanol reactivity in an atmospheric pressure jet stirred reactor is presented in Figure 5, confirming the reliability of the kinetic mechanism.

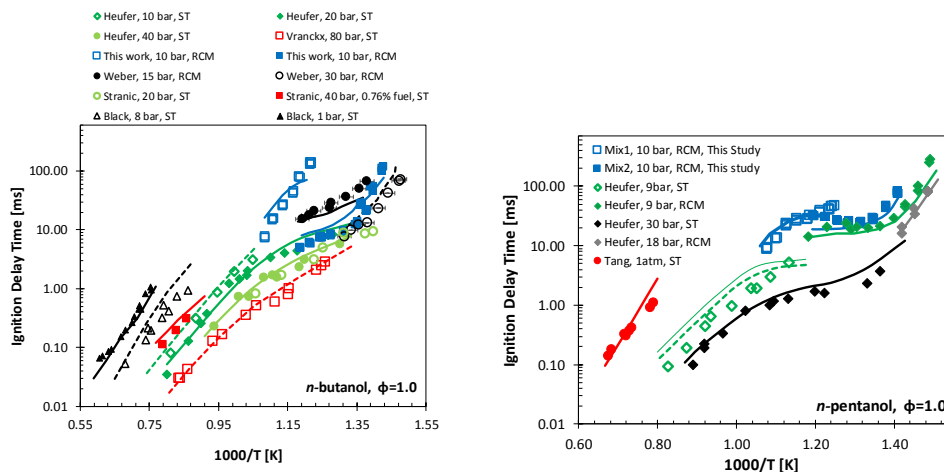


Figure 4: Measured (symbols) and calculated (lines) ignition delay times of stoichiometric mixtures of *n*-butanol (left) and *n*-pentanol (right).

Figure 5 shows some discrepancies between experimental measurements and model predictions. In fact, a slight low temperature reactivity followed by an NTC behavior is predicted by the model in the case of *n*-pentanol, while no such trends are observed experimentally. Deviations at low temperatures for acetaldehyde, *n*-butanol and *n*-pentanol profiles have to be referred to this slight over-prediction of fuel conversion.

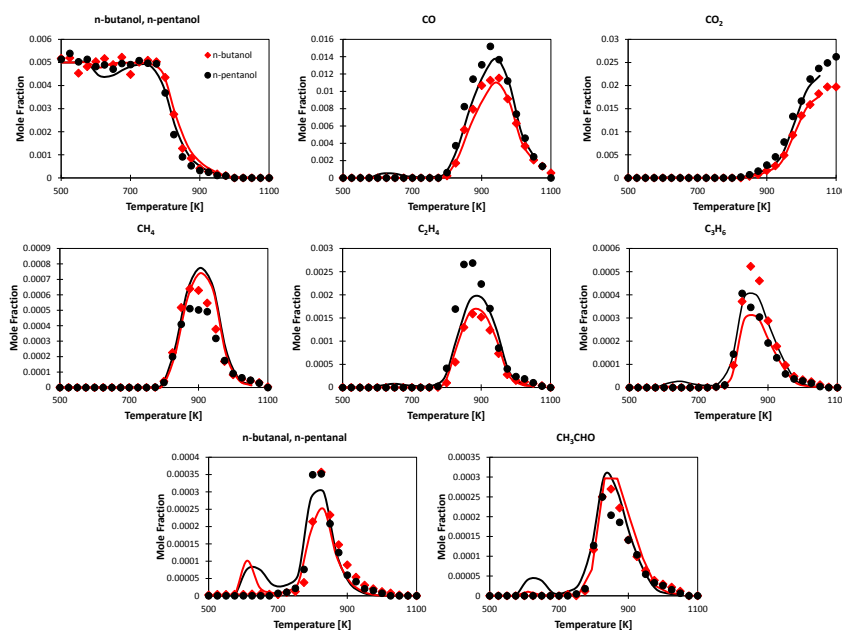


Figure 5: Experimental (symbols) and calculated (lines) mole fraction profiles in the oxidation of *n*-butanol and *n*-pentanol (0.5%)/O₂/He mixtures at $\phi=0.5$, $p=1.05$ atm and $\tau=2$ s.

HCCI Operability Maps

Figure 6 shows typical stability maps of HCCI engines as a function of engine load ($\lambda = 1$ stoichiometric fuel/air conditions, $\lambda > 1$ air excess) and amount of exhaust gas recirculation (mass %) obtained with the kinetic model discussed above from HCCI engines simulations [7, 8]. The areas within the lines represent the conditions at which the fuel guarantees a stable HCCI regime. Pure alcohols and butanol/gasoline blends (TRF/butanol, RON = 95) largely extend the stability region of gasoline reference mixtures (PRF100, RON = 100, PRF80, RON = 80). These observations further confirm the suitability of alcohols for HCCI technology.

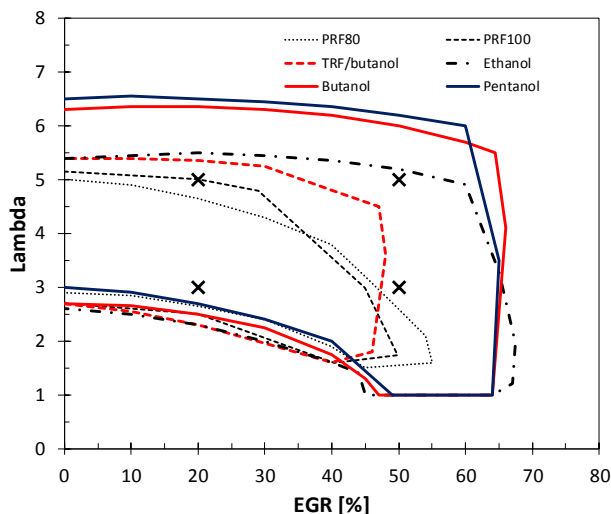


Figure 6: Comparison of predicted HCCI operating limits for different fuels [12].

Acknowledgements

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