

Kinetic modelling of Biofuels: Pyrolysis and Auto-Ignition of Aldehydes

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Aldehydes are involved in practically all the oxidation processes of solid and liquid fuels, and they are of concern as pollutants from different combustion systems such as conventional spark-ignition gasoline engines and compression-ignition diesel engines. In the case of biofuel combustion, aldehydes are not only pollutants whose emissions have to be controlled, but also, they are primary products of bio-oil, influencing the combustion properties. A similar statement can be applied to biomass combustion and/or gasification processes, where aldehydes (also including aromatic aldehydes) have been highlighted as products of biomass and coal gasification. With the rising interest in biofuels and biomasses for energy applications, there is a need to assess the combustion of aldehydes, in order to better understand the influence of the carbonyl group on the combustion properties of these species.

While formaldehyde and acetaldehyde have been studied in detail in the recent and past literature, just a few works have focused on long chain aldehydes. A few recent combustion studies on C₃-C₅ aldehydes provide new fundamental data for a better understanding of their pyrolysis and combustion behaviour which in turn form the basis for a more reliable extension of the kinetic knowledge towards oxygenated biofuels.

A detailed mechanism has been developed at the Combustion Chemistry Centre (NUI Galway, Ireland) and a lumped one developed within the research activity of the CRECK Modeling group (Politecnico di Milano, Italy). Both the models, validated over a wide range of new and previously published data (flame speeds, ignition delay time, pyrolysis speciations), showed good capability to reproduce the main experimental observations and the kinetic analysis highlighted key consumption channels, mainly related to the carbonyl moiety of the molecule.

Only the results for the lumped mechanism referring to the auto-ignition behaviour of aldehydes are discussed in this paper. This work constitute a first step towards a better knowledge of the combustion behavior of oxygenated bio-oil and biofuels.

1. Introduction

The depletion of fossil fuel reserves and the stringent goals on air pollution reduction has led to a focus on gaseous, liquid and solid biofuels as a sustainable source of energy for transport, domestic and industrial applications. Within this scenario small and large molecular weight aldehydes play a key role, being products of partial or incomplete oxidation of conventional hydrocarbon fuels and primary decomposition products derived from biofuel (liquid and solid) oxidation and pyrolysis in mobile or industrial combustion systems. Furthermore they are known as being toxic, some of them carcinogens and precursors of free radicals leading to the formation of ozone and urban smog, they belong to the class of non-regulated pollutants and they are classified as mobile sources air toxic (MSAT) compounds. Different studies focused on the experimental detection of aldehydes emissions from conventional diesel and gasoline engines, both using hydrocarbon fuels, biofuels or both in blending, and from biomasses treatments.

From a pure chemical kinetics point of view, aldehydes are primary stable intermediate products of biofuels oxidation and pyrolysis, influencing reaction pathways and important combustion properties, and

they are not negligible in order to design more efficient and environmental friendly combustion systems. For these reasons, the understanding of combustion kinetics of aldehydes and furthermore, a deeper understanding of the reactivity of the carbonyl side of the molecule ($R-CH=O$), play a vital role in the capability of kinetic mechanisms to better predict pollutants release from both conventional and renewable liquid or solid fuels.

While oxidation of formaldehyde and acetaldehyde has been studied in details over a wide range of conditions in recent and past years just a few works focused on long chain aldehydes. Propanal was studied in flames by Kasper et al. (2009), flame speeds and speciation profiles in jet stirred reactor were measured by Veloo et al. (2013a), a pyrolysis study in shock tube was carried out by Lifshitz et al. (1990) and ignition delay times were measured by Akih-Kumgeh and Bergthorson (2011). Butanal oxidation was studied in flames and jet stirred reactor by Veloo et al. (2013b), the auto-ignition behaviour has been investigated at pressure close to atmospheric by Davidson et al. (2010) and up to 10 atmospheres pressure by Zhang et al. (2013). da Silva and Bozzelli (2006) calculated the enthalpies of formation of C_2 to C_7 n -aldehydes through ab initio calculations and determined bond dissociation energies (BDE) for all C–C and C–H bonds in the molecules.

Further experimental data for the auto-ignition in shock tube have been collected by Pelucchi et al. (2013) at the National University of Ireland, Galway (NUIG) and are part of an ongoing comprehensive study on C_3 – C_5 aldehydes high temperature oxidation and pyrolysis. A comparative study of the auto-ignition behaviour of propanal, n -butanal and n -pentanal is presented in this work. A description of the approach used to develop a consistent lumped kinetic scheme to describe C_3 – C_5 aldehydes oxidation will be given and mechanism performances will be discussed.

2. Kinetic mechanism development

The thermodynamic data for propanal, n -butanal and n -pentanal (Figure 1) and related radical species were calculated using the THERM program by Ritter and Bozzelli (1991), based on group additivity methods developed by Benson and further optimized by Burke (2013). The computed enthalpies of formation were found to be in very good agreement with those suggested by da Silva and Bozzelli (2006).

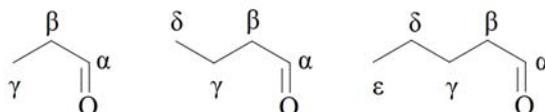


Figure 1: propanal, n -butanal and n -pentanal chemical structure and named carbon sites

A three-frequency version of QRRK (Quantum-Rice-Ramsperger-Kassel) theory (Dean, 1985, Chang et al., 2000) was used to calculate the temperature and pressure dependency of the unimolecular decomposition reactions for the three aldehydes. Collisional stabilization was calculated using a modified strong collision approximation. The high-pressure limit rate constants were calculated from microscopic reversibility using estimates for radical-radical recombination reactions. Table 1 shows results from our calculations compared to those by da Silva and Bozzelli (2006). The weakest C–C bond is the C_{β} – C_{γ} bond, as would be expected from the proximity to the electron withdrawing carbonyl group, followed by C_{α} – C_{β} . The weakest C–H bond is the C_{α} –H, followed by C_{β} –H. From a branching ratio analysis, the reactions involving a C–H bond breaking were found to contribute less than 1% to the fuel decomposition in the temperature range 1,000–2,000 K. Nevertheless they have been included in the mechanism due to possible effect on the laminar flame speed evaluation.

H-atom abstractions are treated according to the systematic approach described by Ranzi et al. (1993). With reference to the primary H-atom from a methyl group, rate constant parameters for the abstraction of the H-atom sited in α , are obtained by correcting the activation energy by $-4,500 \text{ cal mol}^{-1}$. With regards to the abstraction from the β -site, leading to resonantly stabilized radicals, a correction factor of 2 has been applied to the frequency factor of the secondary H-atom abstraction. Reactivity of primary, as well as the remaining secondary H-atoms, are considered as being the same as those for alkanes.

Rate constants for the β -scission reactions were based on analogy with alkanes and alcohols or taken from literature. The α -radical derived from the C_n aldehyde can decompose via β -scission forming either ketene and a C_{n-2} alkyl radical or CO and a C_{n-1} alkyl radical. Isomerization reactions tend to give the thermodynamically favoured α -radical. Rate constants for the internal H-transfer were explained on the basis of 6-, 5- or 4- membered ring intermediates (Dente et al., 2007), accounting for the ring strain and internal rotations.

Table 1: Calculated Bond Dissociation Energies [kcal mol^{-1}] of C–C and C–H bonds and comparison to *ab initio* computed values by da Silva and Bozzelli (2006)

	propanal		<i>n</i> -butanal		<i>n</i> -pentanal	
	This work	da Silva	This work	da Silva	This work	da Silva
C _α –C _β	84.4	83.8	84.6	84.1	84.5	83.4
C _β –C _γ	83.5	83.7	82.3	82.5	82.5	82.3
C _γ –C _δ			89.1	90.1	87.9	88.5
C _δ –C _ε					89.1	89.4
C _α –H	89.0	89.3	89.0	89.1	89.0	88.8
C _β –H	91.9	90.2	91.9	90.6	91.9	89.5

When competitive reaction paths are well defined and not strongly dependent on the temperature, larger radicals can be conveniently and directly substituted by their reaction products. This is the advantage of a lumped approach. On a theoretical basis this is supported by the fact that, for radical species higher than C₄, it is possible to assume them as directly decomposed, without further interaction with the reacting mixture (i.e. their lifetimes are short).

This sub-mechanism of aldehydes has been coupled with the complete PoliMI kinetic mechanism of pyrolysis and oxidation of hydrocarbon fuels (Ranzi et al., 2012), available on the CRECK modelling group website.

3. Results and discussion

The OpenSMOKE code by Cuoci et al. (2011) was used to simulate the shock tube reactor, considered as a batch constant volume reactor.

3.1 Propanal

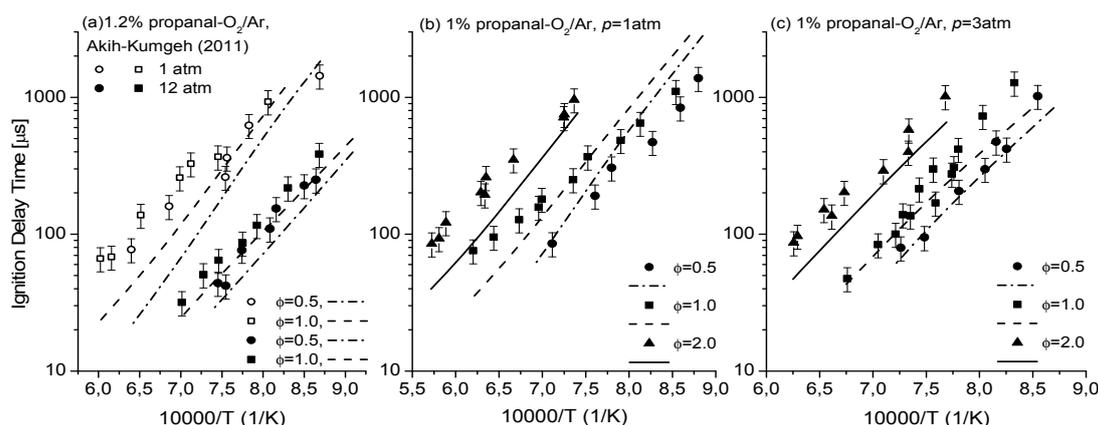


Figure 2: (a) Data by Akih-Kumgeh and Bergthorson (2011), (b) and (c) data by Pelucchi et al. (2013). Predicted (lines) and experimental (symbols) IDT

Akih-Kumgeh and Bergthorson (2011) measured ignition delay times (IDT) for three different mixtures of propanal–O₂/Ar, corresponding to equivalence ratios (Φ) of 0.5, 1.0 and 2.0 at reflected pressures of 1 and 12 atm. The experimental and computed results are shown in Figure 2a. Figure 2b and 2c show further ignition delay time measurements, carried out by Pelucchi et al. (2013), for mixture of 1 % propanal–O₂/Ar at $\Phi=0.5$, 1.0 and 2.0, at reflected pressures of 1 and 3 atm. While the predicted apparent activation energy tends to be higher than the one experimentally observed for the 1 atm experiments, the kinetic model reasonably reproduces the measured ignition delay times for both the high pressure data (12 atm) in Figure 2a and the 3 atm experiments in Figure 2c. Both the negative dependency on temperature and oxygen concentration are well captured by the mechanism. For similar lean conditions ($\Phi=0.5$), it is relevant to observe that different apparent activation energies (E_{a^*}) are deduced from the experiments performed by Akih-Kumgeh ($25.5 \text{ kcal mol}^{-1}$) and by Pelucchi ($31.2 \text{ kcal mol}^{-1}$). Furthermore, the model shows a clear decrease in the apparent activation energy, when pressure increases. This behaviour is not experimentally verified in the case of aldehydes, while it was observed for large methyl esters by Campbell et al. (2013).

3.2 Butanal

Butanal ignition delay time measurements were carried out by Zhang et al. (2013) at 1.3, 5 and 10 atm. Two different fuel concentrations (1.2 % and 0.6 %) and three different equivalence ratios (0.5, 1.0 and 2.0) were tested. Comparison between calculations and experimental data are shown in Figure 3a-3c. The model agreement improves as the pressure increases, and moving from lean to fuel rich conditions. Further ignition delay times were measured by Davidson et al. (2010) for mixtures of 1% *n*-butanal–O₂/Ar, at equivalence ratios of 1.0 and 2.0 and reflected pressures of 1.7 atm. These data are compared with model predictions in Figure 4a. Similarly, Figure 4b and 4c show comparisons with Pelucchi et al. (2013) experimental data, obtained at the same pressure and equivalence ratios as described for propanal. These data are very well reproduced by the model under all conditions tested. Focusing on fuel rich conditions at very similar pressures (1, 1.3 and 1.7 atm), the mechanism is able to reproduce very well the Davidson data, on the contrary, IDT are overestimated at lower temperatures for Zhang data and underestimated in respect of the high temperature data of Pelucchi. Again, a slightly higher activation energy is predicted.

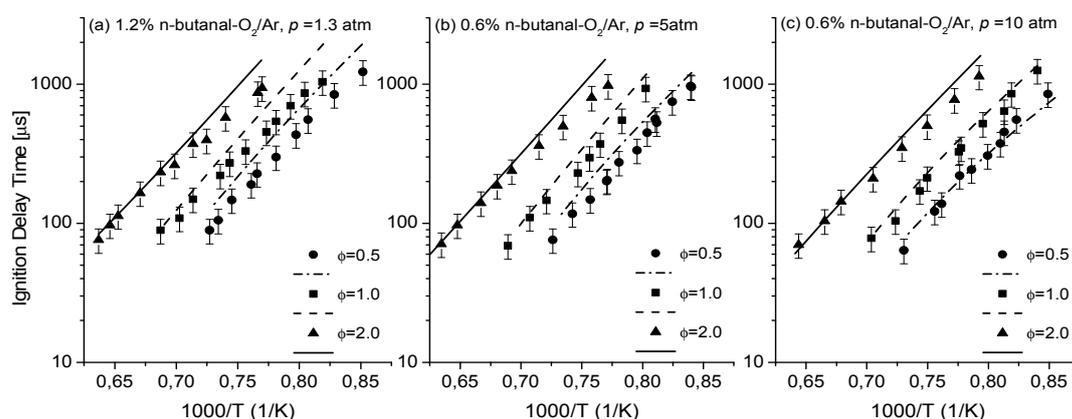


Figure 3: *n*-butanal–O₂/Ar mixtures, data by Zhang et al. (2013). Predicted (lines) and experimental (symbols) IDT

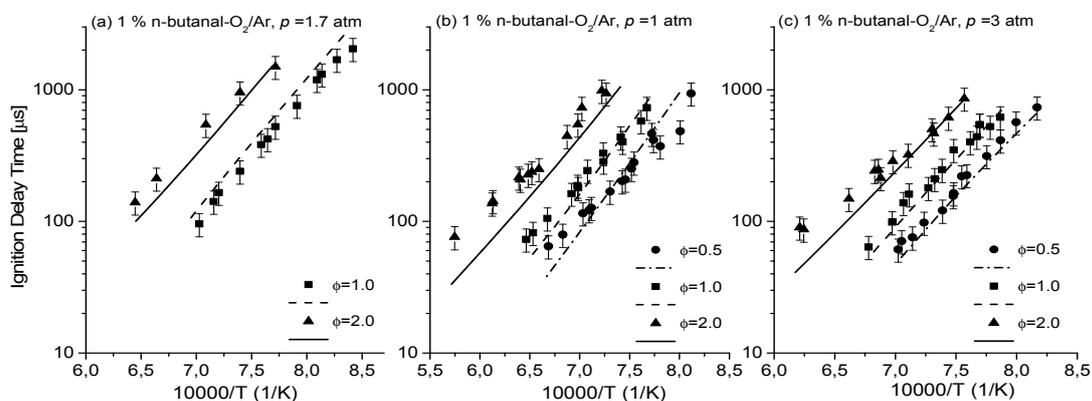


Figure 4: *n*-butanal–O₂/Ar mixtures, (a) data by Davidson et al. (2010), (b) and (c) data by Pelucchi et al. (2013). Predicted (lines) and experimental (symbols) IDT

3.3 Pentanal

Ignition delay times for mixture of 1 % *n*-pentanal–O₂/Ar were obtained by Pelucchi et al. (2013) at the same equivalence ratios and reflected shock pressure conditions described above for propanal and *n*-butanal. Figure 5a and 5b present comparisons between experiments and calculated ignition delay times. While the model predictions agree satisfactorily with the experimental measurements at both pressures for fuel lean and stoichiometric conditions, the maximum deviations are obtained for fuel rich conditions.

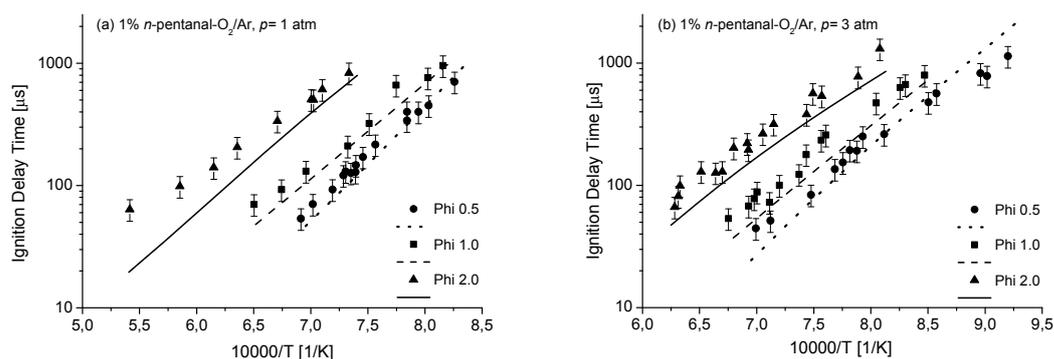


Figure 5: *n*-pentanal–O₂/Ar mixtures, data by Pelucchi et al. (2013). Predicted (lines) and experimental (symbols) IDT

4. Conclusions

Comparing the auto-ignition behaviour of aldehydes at 1 % fuel concentration, *n*-pentanal is the most reactive. This is justified by both the higher oxygen concentration in the mixture and by the longer carbon chain. While one would expect *n*-pentanal to be followed by *n*-butanal in this hierarchy, propanal reactivity is comparable or even higher than that of *n*-pentanal, with *n*-butanal being the slowest to ignite. Results of this comparison are shown in Figure 6, for lean mixtures ($\Phi=0.5$) at 1 % fuel concentration and 1 atm pressure. At fuel rich conditions, where the oxygen concentration in the mixtures becomes closer for the three aldehydes (2.00 %, 2.75 % and 3.50 % respectively), the ignition characteristics become similar. This experimental behaviour is well reproduced by the kinetic model. This is justified by the fact that the primary propagation reactions of propanal involve the production of a larger amount of H radical, promoting the reactivity of the system. In fact, while the decomposition of β -radical leads to the formation of methyl radical for butanal and ethyl radical for pentanal, it directly leads to the production of H radical and acrolein (or methyl ketene) when the propanal is considered.

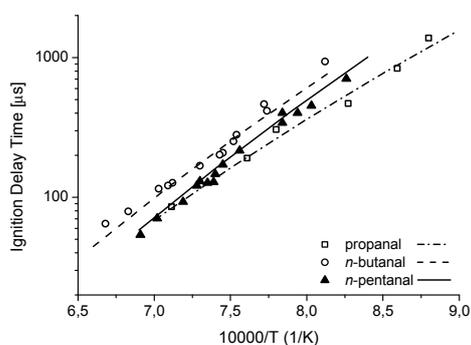


Figure 6: 1% fuel–O₂/Ar mixtures; $\Phi=0.5$, $p=1$ atm, experimental data and linear fit

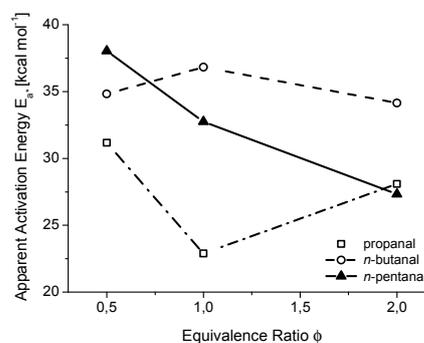


Figure 7: 1% fuel–O₂/Ar mixtures, $p=1$ atm; experimental activation energies [kcal mol⁻¹]

As already observed, the kinetic mechanism tends to systematically over predict the activation energy by about 4 kcal mol⁻¹ with respect to the experimental one. This over prediction has also been observed previously for alcohols and methyl esters, underlining that improvements are possibly needed in the C₀–C₃ portion of the overall mechanism.

It is relevant to observe that some inconsistencies within the apparent activation energies (E_{a^*}) have been highlighted also in respect of different experimental data. Thus, data sets from different authors at similar operating conditions gives dispersed values of E_{a^*} . Also, the expected decrease of E_{a^*} with increasing equivalence ratios is not unequivocally observed in the experiments. Figure 7 presents comparison of apparent activation energies for 1 % fuel–O₂/Ar mixture at 1 and 3 atm reflected pressures obtained for the three fuels by Pelucchi et al. (2013).

Concluding, the overall performance of the model is satisfactory, also considering that the validation has been carried out on a wider set of experimental data, including laminar flame speed, jet stirred and shock tube reactors in pyrolysis environment.

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