Oxygenated Biofuel

Subjects: Energy & Fuels
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The need for lowering the environmental impacts has incentivized the investigation of biomass and biofuels as possible alternative sources for energy supply. Among the others, oxygenated bio-derived molecules such as alcohols, esters, acids, aldehydes, and furans are attractive substances as chemical feedstock and for sustainable energy production. Indeed, the presence of oxygen atoms limits the production of aromatic compounds, improves combustion efficiency (thus heat production) and alleviates the formation of carbon soot. On the other hand, the variability of their composition has represented one of the major challenges for the complete characterization of combustion behaviour. This work gives an overview of the current understanding of the detailed chemical mechanisms, as well as experimental investigations characterizing the combustion process of these species, with an emphasis on the laminar burning velocity and the ignition delay time.

Keywords: oxygenated molecules ; biofuel ; kinetic models ; sustainable energy

1. Introduction

Fossil fuels are still the main feedstock for global energy production [1][2]. However, sustainable sources like biofuels may offer many economic, technological, and environmental advantages due to the significant reduction of particulate matter, soot formation, unburned hydrocarbon, and NO_x emissions [3]. On the contrary, their incomplete combustion produces a small amount of harmful chemical components for the environment and human health (e.g., acetic acid, aldehydes, and ketones) [1][2][4]. Recently, the use of oxygenated bio-derived fuels (oxy-biofuels) such as alcohols, esters, acids, aldehydes, and furans have attracted the attention of researchers worldwide [5][6][7][8][9]. This trend is due to their positive answers to the environmental issues and also complying with the strict emission regulations of transportation sectors [2][4]. Indeed, the existence of oxygenated functional groups in the molecular arrangement changes the electronic structure of the fuel, thus limiting the production of aromatic compounds, carbon soot [3][10][11]. Besides, the presence of oxygen reduces the C–H bond strength being bond dissociation energies 80.6 kcal mol^{-1} and 257.3 kcal mol^{-1} in the absence and presence of oxygen, respectively [12]. In this framework, the design and optimization of any combustion process based on oxy-biofuels need the definition of a detailed chemical kinetic model. However, many experimental studies are hindered by technical difficulties [13][14][15] related to the different functionality of oxygen-rich biomass, intermediates, and products; to the temperature sensitivity of the products [4][16]; to the short lifetime of intermediate products; and the product dependency on the residence time of volatiles.

2. Combustion Chemistry of Oxy-Biofuels

Oxygenated species as a potential replacement to conventional fuels must be strictly reviewed from different practical viewpoints. In addition to the sustainability of the source, the compatibility of the fuel within transportation sectors and combustion machinery need to be analyzed [17]. In advance, it is worth knowing the common pyrolysis products and pathways of biomass degradation in general. Besides, the chemical behaviours of flammable mixtures can be estimated by aggregating the kinetic mechanisms of each component, in agreement with the hierarchical approach adopted for mechanism generations [18]. Biomass can be transformed into biofuel by using different processes, as recently reviewed by Cossu et al. [19]. A schematic representation of alternative routes to produce biofuels is given in Figure 1.

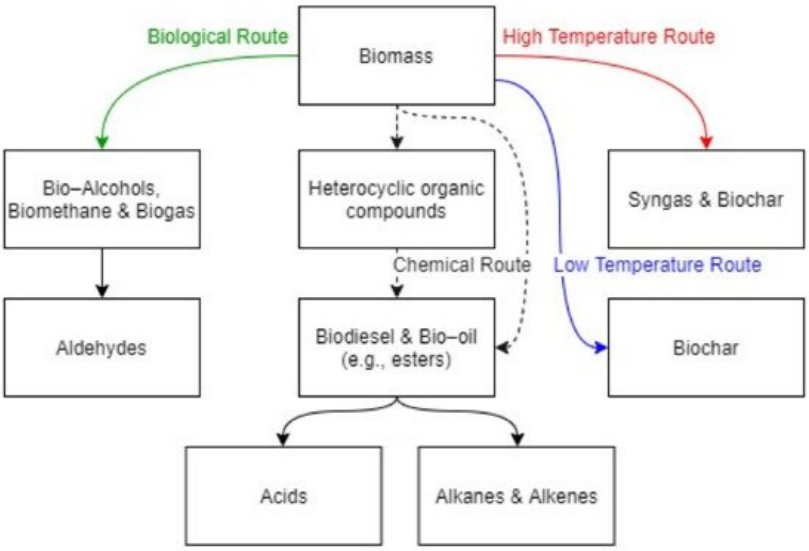

Figure 1. Simplified pathway representative of alternatives for biomass transformation toward biofuels, adapted from Cossu et al. [19].

2.1. Light Alcohols

The energy production via alcohols is primarily satisfied by using them as alternative fuels or additive in blends [7][20]. However, in the kinetic field, alcohols are commonly adopted as per the definition of a surrogate to mimic the combustion behaviour of more complex mixtures characterized by flexible compositions (e.g., biodiesels) [21]. Among them, the primary alcohols (such as methanol, ethanol, and butanol) are ideal for engine combustion [22]. These fuels have no negative temperature coefficient (NTC) behaviours and are all water-soluble [22]. Additionally, their moderate tendency to form soot and elevated octane rating make the light alcohols (i.e., $\leq C_5$) good aspirants for lean to rich stratified combustion [23] and low-temperature combustion [7][24]. Moreover, in homogeneous charge compression ignition, methanol and ethanol have limited sensitivity to the equivalent ratio but high sensitivity to the temperature, while *n*-butanol has similar reactivity to equivalent ratios and temperatures like that of gasoline [25][26]. The average bond dissociation energies of alcohol fuels are around 105 kcal mol^{-1}. Due to the good electron losing the ability of the hydroxyl functional group, the bond dissociation energies of the secondary C−H bond in the α-position largely decreases to ~95 kcal mol^{-1} and that of β-position to ~100 kcal mol^{-1} [7]. In addition, the location of the hydroxyl group (–OH) attached to the carbon atom in alcohol plays a crucial role in the physical-chemical properties. Further, this functional group acts as a radical chain terminating group following H-abstraction, which ends up hindering the cool flame reactivity [27][28]. The presence of the –OH functional group also helps them to suppress the NTC bearing of other fuels [22].

2.2. Carboxylic Acids

Oxygenated fuels with carboxylic acid functionality, especially acetic acid, are the dominant fractions in the tar released from biomass pyrolysis [29][30][31], and an accurate description of biofuel combustion must take into account the formation of these relevant intermediates. Most importantly, on top of their use as fuel surrogate components [30], oxygenated species can be intended as intermediates formed through the decomposition of hydrocarbon. Hence, they are essential in the hierarchical nature of kinetic models [7].

2.2.1. Acetic Acid

The experimental research of acid combustion poses a huge challenge to the combustion community due to issues related to adsorption [32], corrosion [14], and dimerization [33]. Indeed, only a few experimental studies in the literature are available, as reviewed in recent works [14][15]. Many researchers have measured and reported organic acid emissions from spark-ignition engines [34] and rapid compression engines [35]. The studies indicated that, out of the total hydrocarbon emissions from the combustion engines, organic acid emissions measured in spark-ignition engines are 4–27%, with acetic acid being the most important. Numerical and experimental studies of acetic acid combustion in laminar premixed flames were reported by Leplat and Vandooren [36]. Apart from its combustion chemistry, the study also reported ketene as an intermediate product. Mackie and Doolan [37] studied the thermal decomposition kinetics of acetic acid and its products in a single pulse shock tube within the temperature range of 1300–1950 K. As part of this, decomposition kinetics having 21 species and 46 reactions were modelled and simulated using experimental data. From the decomposition kinetics, decarboxylation and dehydration were confirmed to be the two key decomposition reactions producing methane and carbon dioxide, on the one hand, through (Equation (8)) and ketene and water, on the other, through (Equation (9)), respectively. Ketene further decomposed to a methyl radical and CO_2, followed by a further reaction of the methyl radical

with CH to form C_2H_4 and CO. Besides, methyl radicals were revealed to play an important role in determining the main products.

$$CH_3COOH \rightarrow CH_4 + CO_2 \text{ (8)}$$

$$CH_3COOH \rightarrow CH_2CO + H_2O \text{ (9)}$$

Similarly, Gg. Wagner and Zabel [38] studied the further decomposition kinetics of ketene (CH_2CO) behind reflected shocks at low pressure and reported the degradation rate constant-coefficient $K = 3.6 \times 10^{15} \exp(-248 \text{ kJ mol}^{-1} \text{ K}^{-1})$ $\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. In the same way, the gas-phase reactivity analysis of acetic acid, rate constant estimation, and kinetic simulation were studied by Cavallotti et al. [39]. The 1D master equation was also integrated on the potential energy surface (PES) to determine the rate coefficient of acetic acid degradation under a wide range of temperatures (700–2100 K) and pressures (0.1–100 atm). The simulation showed a gradual decrease in the reaction rate at a temperature above 1200 K and a pressure of smaller than 10 atm. Besides, H-abstraction by H, OH, OOH, O_2, and CH_3 was reported to be the responsible radicals in the decomposition of acetic acid [39]. Lately, Zhang et al. [13] studied the laminar flame propagation and kinetic modelling of acetic acid at a low initial temperature and atmospheric pressure. The authors indicated the pathway related to ketene consumption (Equation (10)) as the main in the propagation of acetic acid flames.

$$CH_2CO + H \rightarrow CH_3 + CO \text{ (10)}$$

The laminar burning velocity measured by Christensen and Konnov [14] of acetic acid at different initial temperatures are reported in Figure 2. Based on the reported observations, a simplified reaction pathway representative of the oxidation of acetic acid is produced and reported in Figure 3.

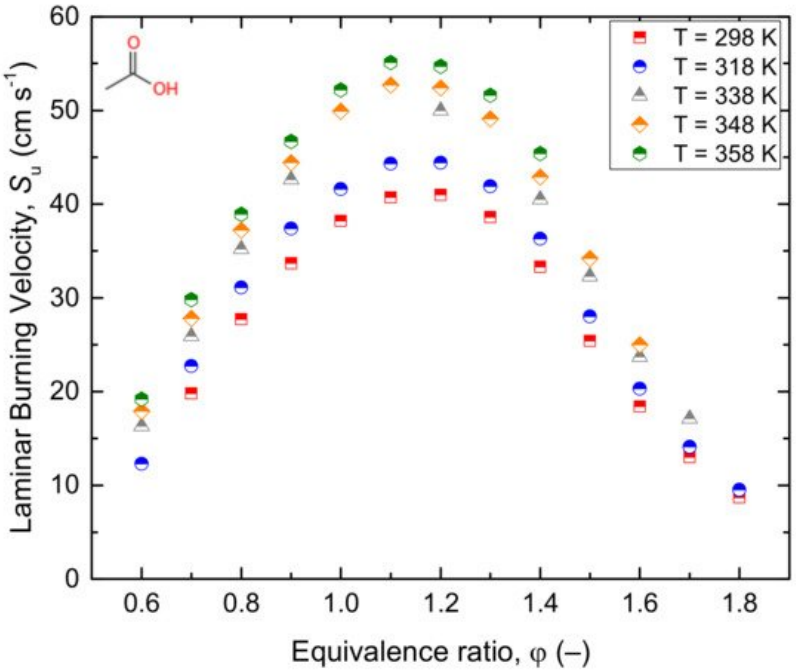

Figure 2. Laminar burning velocity data for the acetic acid/air mixture at atmospheric pressure [14].

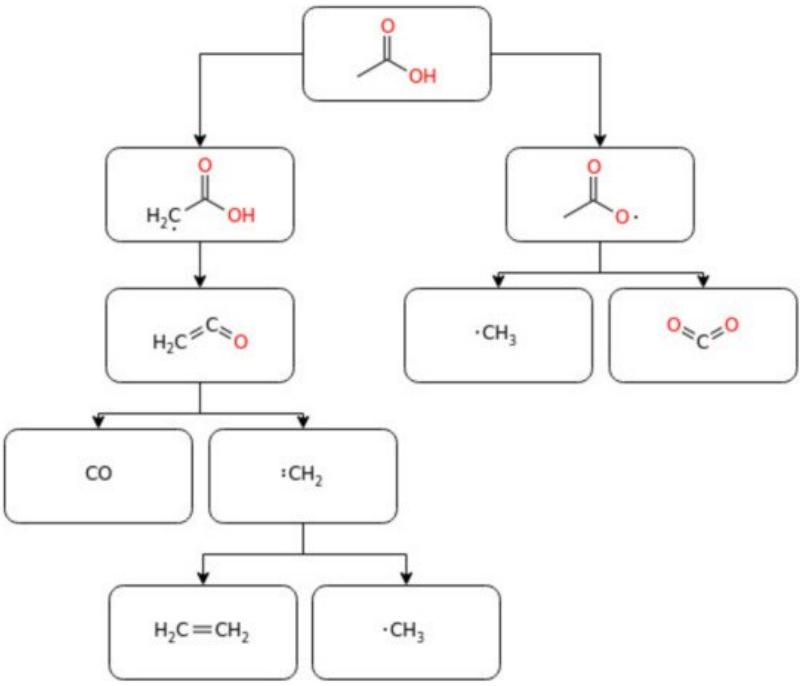

Figure 3. A simplified reaction pathway for acetic acid oxidation.

2.3. Light Aldehydes

Acetaldehyde is a key intermediate in the oxidation of hydrocarbons and alcohols, especially ethanol, which is increasingly being used as a fuel for automobiles. However, it is one of the most abundant toxic oxidative emissions from the combustion of biofuels [40][41], and its atmospheric reaction generates several secondary pollutants [42][43]. Thus, the pyrolysis mechanism study of this intermediate at various reaction conditions can help to understand the overall combustion mechanism of hydrocarbons and alcohol-based fuels [44]. In this regard, several authors reported on the degradation kinetics and combustion chemistry of acetaldehyde. For instance, Sivaramakrishnan et al. [45] conducted a study on the theoretical calculations of acetaldehyde (C_2H_4O) and ethoxide (C_2H_5O) potential energy surfaces (PES) and updated the kinetic model of acetaldehyde pyrolysis. The study revealed C–C bond fission with a minor contribution from the roaming mechanism to form CH_4 and CO as the main decomposition pathway of acetaldehyde during high-temperature processing. The model developed by the author incorporates a master equation for the analysis of H + CH_2CHOH as a primary reaction mechanism for the removal of CH_2CHOH. The governing H-abstraction route at the aldehydic site was found to form a carbonyl radical (R_n–CO), which quickly further decomposes to an alkyl radical (R_n) and CO. Based on that, there is a general implication that the low-temperature oxidation of the generic C_n aldehyde degraded to C_{n-1} alkyl radicals [46].

To better understand the combustion parameters, the ignition delay times of acetaldehyde behind shock tube waves under ranges of reaction conditions were reported by Mével et al. [47]. additionally, a sensitivity analysis, energy release, and rate of production were conducted, indicating four important elementary reactions (Equations (11)–(14)) taking place during acetaldehyde pyrolysis and oxidation:

$$CH_3CHO \rightarrow CH_3 + HCO \quad (11)$$

$$CH_3CHO + CH_3 \rightarrow CH_3CO + CH_4 \quad (12)$$

$$CH_3CHO + H \rightarrow CH_3CO + H_2 \quad (13)$$

$$CH_3CHO + CH_3 \rightarrow CH_2HCO + CH_4 \quad (14)$$

In the end, due to the huge differences observed during the research, the authors recommended the need for new experimental and detailed numerical studies. Tao et al. [48] reported nearly 40 species in laminar and premixed flames of acetaldehyde. Christensen et al. [49] studied the laminar burning velocities at atmospheric pressure and different initial temperatures. Similarly, Christensen and Konnov [50] reported the laminar burning velocity of diacetyl and the updated sub-mechanism model of acetaldehyde and CH_3CO in their model. Halstead et al. [51] studied the kinetic development of acetaldehyde in the perspective of the cool flame feature and suggested models containing 14 steps. From the study, acetyl was found to play a significant role in the chain-branching process through $CH_3CO \rightarrow CH_3CO_3 \rightarrow CH_3CO_3H \rightarrow$

CH_3CO_2 + OH. The theoretical work reported by Felton et al. [52] and the detailed kinetic model developed by Cavanagh et al. [53] supported the result of Halstead et al. [51].

Nevertheless, Gibson et al. [54] came up with another cool flame phenomena of acetaldehyde to be processed by CH_3OOH (CH_3 → CH_3OO → CH_3OOH → CH_3O + OH). On the other hand, the study conducted by Kaiser et al. [55] revealed the radical decomposition reaction (Equation (15)) and O_2 addition to acetyl (Equation (16)) as the main determining step of the chain-branching process.

$$CH_3CO \rightarrow CH_3 + CO \quad (15)$$

$$CH_3CO + O_2 \rightarrow CH_3CO_3 \quad (16)$$

Recently, researchers [56][57] have developed a kinetic model for the low-temperature oxidation of acetaldehyde, as well as C_3 and C_4 aldehydes. Zhang et al. [58] studied the oxidation of acetaldehyde under a wide range of conditions and revealed CH_3OO, CH_3OOH, and HOOCOCHO as the main oxidation products. Besides, H-abstracting agents were found to be processed by H, OH, HO_2, CH_3, O_2, CH_3COOO, CH_3OO, and CH_3O. At the lean condition, OH was found to be the most important H-abstracting agent. It was concluded that CH_3COOOH and CH_3OOH are the main decomposition pathways of acetaldehyde oxidation via the chain-branching reaction, and the reactions related to methyl oxidation were reported to be very sensitive to CH_3OO and CH_3OOH under the studied conditions [58]. Bentz et al. [59] studied the shock tube thermal decomposition of CH_3CHO and CH_3CHO + H at a temperature within 1250–1650 K and a pressure range of 1–5 bar. Combining their results and the low-temperature data from other studies, the authors reported the acetaldehyde rate constant expression as $K = 6.6 \times 10^{-18} \exp(-800\ K/T)\ cm^3\ s^{-1}$ for the temperature range of 300–2000 K. Moreover, Hidaka et al. [60] studied the pyrolysis of acetaldehyde oxidation behind reflected shockwave tubes using single-pulse methods. The study considered different fuel concentrations (2.0% CH_3CHO, 4.0% CH_3CHO, and 5.0% CH_3CHO) diluted with Ar under the temperature range of 1000–1700 K and pressure of 1.2 and 3.0 atm. The (Equations (17)–(19)) reactions were mentioned to be the most important initiation reactions and (Equations (20) and (21)) as the most crucial reactions responsible for acetaldehyde pyrolysis.

$$CH_3CHO \rightarrow CH_3 + CHO \quad (17)$$

$$CH_3CHO \rightarrow CH_4 + CO \quad (18)$$

$$CH_3CHO \rightarrow CH_2CO + H_2 \quad (19)$$

$$CH_3CHO + H \rightarrow CH_2CHO + H_2 \quad (20)$$

$$CH_3CHO + CH_3 \rightarrow CH_2CHO + CH_4 \quad (21)$$

Similarly, Ernst et al. [61] conducted acetaldehyde pyrolysis behind reflected shockwaves under a temperature range of 1350–1650 K. The results revealed the decomposition as a first-order reaction with a rate constant expression of $K = 1.2 \times 10^{16} \exp(-81.74\ kcal/RT)\ s^{-1}$. The experimental ignition delay time and laminar burning velocity data of acetaldehyde oxidation reported in the current literature are shown below in Figure 4. Furthermore, Figure 5 reports a simplified schematization of the oxidation pathway of acetaldehyde.

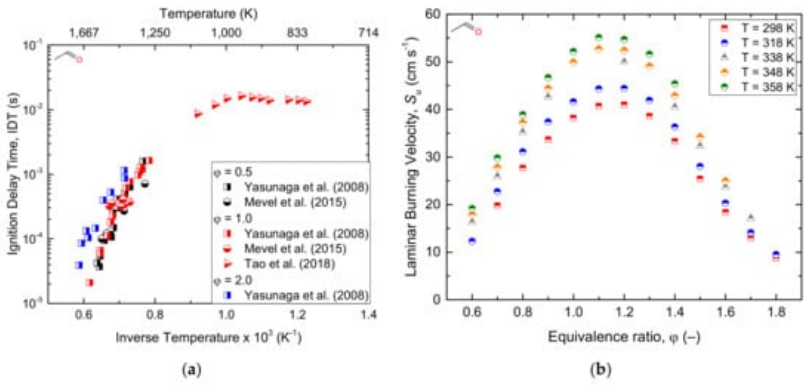

Figure 4. Ignition delay time (**a**) and laminar burning velocity (**b**) of the acetaldehyde/air mixture under different conditions. Note that laminar burning velocity measurements refer to the data reported by Christensen and Konnov [14] exclusively.

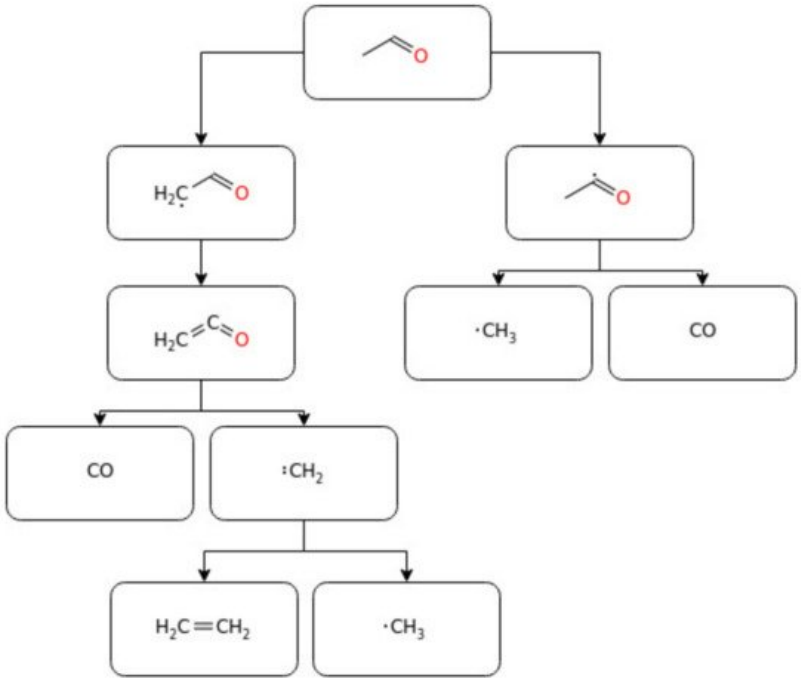

Figure 5. A simplified reaction pathway for acetaldehyde oxidation.

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