A comprehensive experimental and detailed chemical kinetic modelling study of 2,5-dimethylfuran pyrolysis and oxidation

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ABSTRACT

The pyrolytic and oxidative behaviour of the biofuel 2,5-dimethylfuran (25DMF) has been studied in a range of experimental facilities in order to investigate the relatively unexplored combustion chemistry of the title species and to provide combustor relevant experimental data. The pyrolysis of 25DMF has been re-investigated in a shock tube using the single-pulse method for mixtures of 3% 25DMF in argon, at temperatures from 1200 to 1350 K, pressures from 2 to 2.5 atm and residence times of approximately 2 ms.

Ignition delay times for mixtures of 0.75% 25DMF in argon have been measured at atmospheric pressure, temperatures of 1350–1800 K at equivalence ratios (ϕ) of 0.5, 1.0 and 2.0 along with auto-ignition measurements for stoichiometric fuel in air mixtures of 25DMF at 20 and 80 bar, from 820 to 1210 K.

This is supplemented with an oxidative speciation study of 25DMF in a jet-stirred reactor (JSR) from 770 to 1220 K, at 10.0 atm, residence times of 0.7 s and at ϕ = 0.5, 1.0 and 2.0.

Laminar burning velocities for 25DMF-air mixtures have been measured using the heat-flux method at unburnt gas temperatures of 298 and 358 K, at atmospheric pressure from ϕ = 0.6–1.6. These laminar burning velocity measurements highlight inconsistencies in the current literature data and provide a validation target for kinetic mechanisms.

A detailed chemical kinetic mechanism containing 2768 reactions and 545 species has been simultaneously developed to describe the combustion of 25DMF under the experimental conditions described above. Numerical modelling results based on the mechanism can accurately reproduce the majority of the experimental data. At high temperatures, a hydrogen atom transfer reaction is found to be the dominant unimolecular decomposition pathway of 25DMF. The reactions of hydrogen atom with the fuel are also found to be important in predicting pyrolysis and ignition delay time experiments.

Numerous proposals are made on the mechanism and kinetics of the previously unexplored intermediate temperature combustion pathways of 25DMF. Hydroxyl radical addition to the furan ring is highlighted as an important fuel consuming reaction, leading to the formation of methyl vinyl ketone and acetyl radical. The chemically activated recombination of $H\dot{O}_2$ or $CH_3\dot{O}_2$ with the 5-methyl-2-furanylmethyl radical, forming a 5-methyl-2-furylmethanoxy radical and $\dot{O}H$ or $CH_3\dot{O}$ radical is also found to exhibit significant control over ignition delay times, as well as being important reactions in the prediction of species profiles in a JSR. Kinetics for the abstraction of a hydrogen atom from the alkyl side-chain of the fuel by molecular oxygen and $H\dot{O}_2$ radical are found to be sensitive in the estimation of ignition delay times for fuel–air mixtures from temperatures of 820 to 1200 K.

At intermediate temperatures, the resonantly stabilised 5-methyl-2-furanylmethyl radical is found to predominantly undergo bimolecular reactions, and as a result sub-mechanisms for 5-methyl-2-formylfuran and 5-methyl-2-ethylfuran, and their derivatives, have also been developed with consumption path-

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ways proposed. *This study* is the first to attempt to simulate the combustion of these species in any detail, although future refinements are likely necessary.

The current study illustrates both quantitatively and qualitatively the complex chemical behaviour of what is a high potential biofuel. Whilst the current work is the most comprehensive study on the oxidation of 25DMF in the literature to date, the mechanism cannot accurately reproduce laminar burning velocity measurements over a suitable range of unburnt gas temperatures, pressures and equivalence ratios, although discrepancies in the experimental literature data are highlighted. Resolving this issue should remain a focus of future work.

1. Introduction

Depletion of fossil energy reserves and increasing concerns over climate change are key incentives for the development of energy technologies which are sustainable from social, economical and environmental perspectives. Biofuels, liquid or gaseous fuels derived from biological sources, are considered as a natural successor to the petroleum derived products which are the dominant energy carriers for the transportation sector.

Ethanol is presently the most abundantly produced biofuel globally, with 86.1 billion litres manufactured in 2011 derived largely *via* fermentation of sugar cane and corn [1]. Yet despite its status as the leading renewable energy source in the transportation sector, problems with its use are now well founded in the literature.

Production feedstocks are in direct competition with food crops and agricultural land [2,3], combustion in unmodified direct-injection spark-ignition engines is only possible when blended with fossil fuels, its energy density is much lower than that of gasoline and its volatility and complete miscibility with water make it difficult to transport and store. Nevertheless, its ability to reduce emissions, CO, CO_2, NO_x and unburnt hydrocarbon (HC), when blended with gasoline and diesel illustrate the environmental benefits which the use of oxygenated biofuels can achieve.

Next-generation production methods have recently been developed [4–10] capable of converting inedible waste biomass, into the platform chemical 5-hydroxymethyl-2-furaldehyde, with subsequent conversion into the novel biofuel, 2,5-dimethylfuran (25DMF). The literature highlights the energy density of 25DMF (30 MJ L^{-1}) as a notable improvement over that of ethanol (21.3 MJ L^{-1}) with its higher boiling point (366 K) and lower aqueous solubility also making it preferable to the alcohol in terms of transportation and storage [7]. Other considerations such as atmospheric lifetimes and ecological and toxicological aspects are covered in a recent review by Simmie and Würmel [11].

Since the development of these production methods, combustion studies have ensued. 25DMF performed wholly similar to commercial gasoline in research engine tests [12,13], the authors concluding that no major modifications to engine design would be necessary to achieve equivalent emissions and performance levels to gasoline. Daniel et al. [14] recently found that total carbonyl emissions from a direct-injection spark-ignition engine fuelled with 25DMF were lower than those of methanol, ethanol, *n*-butanol and gasoline, in particular formaldehyde emissions, which may bear on its suitability as a biofuel. 1,3-cyclopentadiene, methyl vinyl ketone and 2-methylfuran (2MF) were also found in the exhaust gas, with unburnt fuel dominating the characterised emissions.

Wu et al. [15] determined laminar burning velocities of 25DMF–O_2–N_2/CO_2 mixtures as a function of equivalence ratio (ϕ) and dilution ratio at unburnt gas temperatures (T_i) of 393 K and atmospheric pressure. Laminar burning velocity was found to decrease linearly as a function of increased N_2/CO_2 concentrations, with peak burning velocities occurring for ϕ = 1.1–1.2. They com-

plemented this work with studies on the laminar burning velocities of atmospheric pressure 25DMF-air mixtures over a range of equivalence ratios as a function of T_i (393–473 K) [16] and as a function of pressure (0.1–0.75 MPa) [17] for T_i = 393 K.

Tian et al. [18] determined laminar burning velocities of 25DMF, ethanol and gasoline as a function of ϕ and T_i (323–373 K) under atmospheric pressure in a combustion bomb. The laminar burning velocities of 25DMF were found to be the slowest of all three fuels studied, but were within 10% of gasoline between equivalence ratios of 0.9–1.1. Unfortunately, no measurements were made under directly comparable conditions to those of Wu and co-workers [15–17]. These laminar premixed flame burning velocity measurements will form a portion of the kinetic mechanism validation described in *this work*, along with experimental laminar burning velocities measured as part of *this work* using the heat-flux method.

Experimental work to isolate the chemical pathways of 25DMF combustion have also ensued of late, but other than early works by Grela et al. [20] in 1985 and Lifshitz et al. [21] in 1998 the literature remained sparse until very recently. Grela et al. [20] pyrolysed 25DMF in a heated tubular reactor at very low pressures (1 mTorr) from 1050 to 1270 K, analysing the product mixtures *via* on-line mass spectrometry. They detected water, CO, C_5H_6 and C_6H_6 in their effluent stream and hypothesised their formation from 25DMF by isomerisation to 2,4-dimethylfuran through a cyclopropenylcarbonyl intermediate – 25DMF or 2,4-dimethylfuran could then decompose *via* biradical intermediates through simple C-O bond fission. Lifshitz et al. [21] studied the thermal decomposition of 25DMF behind reflected shock waves in the temperature range 1070–1370 K, at pressures of 2–3 atm. They analysed the post-shock mixtures *via* gas chromatography, quantifying the concentrations of 19 intermediate species and reporting a rate constant (pseudo-first order) for the decomposition of 25DMF of $10^{15.81}\exp(-75.1 \times 10^3/RT)$ where R is in units of cal K^{-1} mol^{-1}. A chemical kinetic mechanism consisting of 50 species and 180 elementary reactions was developed to account for the product distributions.

However, it would appear that the mechanistic proposals of Grela et al. [20] and Lifshitz et al. [21] are erroneous, in light of recent theoretical work on the furans, and in particular the quantum chemical calculations by Liu et al. [22,23] and Sendt et al. [24], which went some way to disproving the long held belief that furan decomposition was routed through biradical intermediates [25–27]. The authors showed that the unimolecular decomposition of furan was initiated through singlet carbene intermediates formed from hydrogen atom transfer reactions, with Sendt et al. [24] constructing a kinetic scheme capable of reproducing laboratory pyrolysis experiments, thus validating their kinetic and mechanistic proposals.

More recently, Simmie and Curran [28] applied quantum chemical methods (CBS-QB3, CBS-APNO and G3) and developed isodesmic working reactions to calculate enthalpies of formation for a range of substituted furans and their corresponding furfuryl radicals, thus determining bond dissociation energies. They noted that