1. Introduction

The manufacturing sector relies on combustion systems such as gas turbines, boilers, combined heat and power (CHP) technologies, and internal combustion engines for heat and steam generation. Major end-users include energy-intensive industrial sectors, such as petroleum, metals, and forest products.

To produce more energy efficient combustion systems for both transport and energy production we need to study the fundamental chemistry involved so that this knowledge can be applied to achieve optimal efficiency with minimal emissions. The coupling of experimental chemical studies which measure important fuel combustion characteristics such as ignition delay times, intermediate species concentrations, and laminar flame speeds with detailed chemical kinetic models is now the internationally recognized way to produce validated chemical kinetic mechanisms. These detailed mechanisms can be reduced, while still retaining the accuracy of prediction of the appropriate target, and combined with Computational Fluid Dynamics (CFD) codes to carry out realistic and accurate overall simulations of both the physical and chemical processes associated with engines and gas turbines for example. In addition, detailed mechanisms can be used in expensive Direct Numerical Simulations (DNS) to understand some specific processes in rapid compression machines, shock tubes, flow reactors, etc.

Looking to the future, the composition of fuels is likely to be different compared to those used today, particularly with the expected increase in the use of biofuels for transport. Biofuels typically contain an oxygenated functional group, such as methyl or ethyl esters, but may contain other functionalities such as alcohols, ethers, aldehydes and ketones. Understanding the combustion chemistry of these species will be critical to the generation of future fuels with minimal emission, health, and climate change effects.

Detailed chemical kinetic mechanisms are typically generated based on the hierarchical nature of hydrocarbon mechanisms as described by Westbrook and Dryer [1], Fig. 1, starting with a H2/O2 sub-mechanism, and subsequently adding a CO/CO2 subset, followed by C1-Cn hydrocarbon and oxygenated hydrocarbon species.
In this paper, the important reactions controlling fuel oxidation for several different standard experiments commonly used to validate detailed kinetic mechanisms will be highlighted. Because of recent work on propane, iso-octane, and methyl butanoate, these fuels will be used as illustrative cases studies for this paper.

2. Types of reactor

2.1. Ignition delay times

Ignition delay timing is an important indicator of a fuel's reactivity and is usually measured as a function of temperature, pressure, fuel/air ratio and dilution; in a rapid compression machine (RCM) the accessible temperature range is approximately 600–1100 K, while in a shock tube it is typically in the range 1000–2000 K.

It has been noted in the literature [2, 3] that some experimental studies on hydrogen/syngas [4] and propane [5] mixture oxidation have shown that, at high pressures (≥ 10 atm), and at intermediate temperature (≤ 1100 K), a pre-ignition pressure rise sometimes occurs, the origin of which is still not well understood, which leads to ignition delay time measurements that are typically shorter (sometimes by orders of magnitude) compared to model predictions. Petersen has shown that, an otherwise validated mechanism, can be used to accurately simulate these mixtures if the pre-ignition pressure rise with the corresponding rise in temperature is accounted for. Petersen et al. [2, 4] and Dryer and Chaos [3] have proposed several theories including transport effects, wall and catalytic effects, and inhomogeneous conditions in the test volume. More recently, Pang et al. [6] reported a series of ignition delay time measurements for hydrogen/oxygen mixtures and observed a 2% per ms pressure rise in the absence of reaction prior to ignition. Their data was successfully simulated using validated kinetic models by accounting for this phenomenon.

In a recent study of propane oxidation in a rapid compression machine, Gallagher et al. [5] have shown that ignition times for lean propane mixtures at 30 atm pressure were recorded to be up to two orders of magnitude slower than those measured in a shock tube over the temperature range 800–1050 K, Fig. 2. It was again suggested that a pre-ignition pressure rise in the shock tube experiments may have been responsible for this disparity. Thus, it is recommended RCM experiments be used to study ignition time up to 1100 K and shock tubes be then used to extend the range of study from 1100 to 2000 K.

In simulating these shock tube and RCM data it is important to know which reactions influence and control ignition timing. It has been shown by Curran et al. [7, 8] and others that, in the temperature range 600–1000 K, reactions associated with low and intermediate temperature kinetics have a major influence on delay times. The underlying chemistry was first proposed by Knox [9] and Fish [10], with further understanding and improvements made by Pollard [11], Cox and Cole [12], and Walker and Morley [13], and Griffiths and Mohamed [14]. An example of a sensitivity analysis to ignition times in a RCM is given in Fig. 3.

It is clear that the primary reactions controlling ignition times at lower temperatures (725 and 825 K) are those associated with the classic low-temperature mechanism, in which the fuel alkyl radicals add to molecular oxidation, undergo one or more internal H-atom rearrangements, and proceed to chain branching or propagation processes. However, at 1000 K (and higher) reactions pertaining to low-temperature mechanism are largely unimportant, while those associated with HO₂ and CH₃O₂ radicals, generated in the intermediate temperature regime, become predominant as indicated by the large sensitivity coefficients associated with their reactions with the fuel.

Finally, Fig. 4 shows sensitivity to ignition times for methyl butanoate ignition in a shock tube at 1 atm pressure and at typical high temperature conditions. Similar sensitivity coefficients
would be observed for almost any hydrocarbon or oxygenated hydrocarbon fuel under these conditions. The reaction with the largest overall sensitivity is \( H + O_2 = O + OH \), which, depending on the pressure of the system, is the most important chain-branching reaction in combustion at temperatures above approximately 1000 K.

The next most important reaction type promoting oxidation is unimolecular fuel decomposition. This behaviour is again characteristic of hydrocarbon oxidation under these conditions. The reaction which most inhibits reactivity is hydrogen abstraction from the fuel by hydrogen atom to produce an alkyl radical and molecular hydrogen. Again, this inhibiting effect is common to almost all fuels under these conditions, because the fuel competes with molecular oxygen for hydrogen atoms, which is the main chain-branching process, thus decreasing the system’s overall reactivity.

In this system we also see the importance of methyl and vinyl radical chemistry; methyl-methyl radical recombination inhibits reactivity as ethane is generated. This reaction competes with other reactions of methyl radicals such as: \( CH_3 + HO_2 = CH_3O + OH \).

2.2. Flow and jet-stirred reactor studies

Speciation data versus time and/or temperature taken in flow- and/or jet-stirred reactors are also important in the validation of detailed chemical kinetic mechanisms. Ignition delay time is a global phenomenon but generally tests only that a model predicts the correct overall rate of fuel reaction but does not adequately test the relative rates of decomposition. For example, for methyl butanoate there are five significant unimolecular decomposition reactions that should be considered (typically C–H bond cleavage does not compete with C–C or C–O cleavage), Fig. 5.

These reactions can lead to different sets of products; for example if decomposition occurs predominantly via channels 1, 3 or 5 relatively large concentrations of CO2, ethylene and methyl radicals will be produced. However, channels 2 and 4 will produce formaldehyde, ketene, ethylene and hydrogen atoms. Thus, speciation measurements in flow- and jet-stirred reactors are important in accurately predicting species profiles as they evolve as a function of temperature and/or time.

It is important to note that when one compares the sensitivity coefficients of methyl butanoate oxidation in a JSR, Fig. 6, with those in a shock tube, Fig. 4, it is clear that most of the sensitive reactions are common to both experiments.

This may be contrasted with Fig. 7 which depicts the sensitivity coefficients of important reactions for methyl butanoate oxidation in a flow reactor at a lower temperature of 820 K and at a pressure of 12.5 atm. Under these conditions of temperature and pressure the important reactions are those associated with hydroperoxyl radical chemistry, which as we discussed earlier, are also important at these intermediate temperatures.

We see significant sensitivity to hydrogen atom abstraction.
reactions from the fuel but not to unimolecular fuel decomposition because the temperature is too low for C–C or C–O bond cleavage. Moreover, reactions associated with methyl radical chemistry show significant sensitivity and have predominant importance under these conditions. This illustrates the importance of the use of hierarchically structured mechanisms with detailed modelling of many different systems which incorporate wide ranges of temperature, pressure and mixture composition.

2.3. Opposed flow diffusion flames

Diffusion flame experiments are also used to validate detailed chemical kinetic mechanisms. In this case, species and energy transport modify the environment in which chemistry occurs. Here, sensitivity to methyl butanoate experiments published by Gail et al. [17] will be discussed. A stream of 4.7% MB diluted in N₂ was sent through the bottom burner port, while the oxidizer stream, containing 42% O₂, also diluted in N₂, was sent through the top burner port. At high temperature (1470 K), 93% of MB is consumed by hydrogen abstraction, with H atoms (81%) and OH radicals (9%) the main contributors, and under this condition fuel alkyl radicals are consumed by β-scission. Due to the significant role of H-atoms in fuel consumption, reactions involving this moiety show large sensitivity coefficients, Fig. 8.

Hydrogen abstraction from MB by H atoms is the most sensitive reaction at 1470 K; this is so because this process results in the formation of a fuel alkyl radical and H₂ (i.e., propagation) and is in competition for H atoms with the chain termination reaction of CH₃ + H = CH₄, which shows a large positive sensitivity, slowing the overall rate of reaction. As this reaction is coupled to the dominant methane consumption reaction, CH₄ + H = CH₃ + H₂, this reaction pathway leads to the consumption of two reactive H atoms, and the extent to which it competes for H atoms with hydrogen abstraction from MB is responsible for the overall reactivity of the system at high temperatures.

In this experiment it is very common to see large sensitivity to hydrogen atom chemistry due to its mobility to travel across the flame front, thus controlling the kinetics of the reaction. For accurate prediction of flame speed too we also see large sensitivity coefficients to hydrogen atom reactions.

2.4. Flame speed experiments

The laminar flame speed (also called the burning velocity or flame velocity) can be defined as “The velocity at which the unburned gases move through the combustion wave in a direction normal to the wave surface” [18], and thus can be alternatively defined as the speed at which an unburned gas flow must be injected into a burner for a flame to be stable and fixed (with respect to the burner). Thus, the accurate measurement and prediction of this parameter is crucial for stable operation of a combustor such as a gas turbine.

Many flame speed measurements have been made for methane and some for DME but not many have been performed for large hydrocarbons. Zhao et al. [19] reported on burning velocities of n-decane and used a high-temperature skeletal kinetic model to simulate the experimental data. Fig. 9 shows the most sensitive
3. Problems encountered in using detailed kinetic mechanisms

Thus far, the important reactions at various conditions of temperature, pressure and equivalence ratio have been illustrated. However, one problem that often exists is that a mechanism may be employed over a temperature and/or pressure regime for which it has not actually been validated, or employed to simulate species for which it has not originally been designed.

For instance, GRI-Mech 3.0 [21] was developed and has been widely used to simulate natural gas combustion, including NO formation and re-burn chemistry. There are many things to commend this mechanism. A extensive range of targets were chosen including (i) shock tube ignition delay times for pure methane and ethane fuels in addition to methane/ethane and methane/propane mixtures, (ii) methane and ethane shock tube species profiles, (iii) H₂/CO, methane and ethane flame speed measurements. Moreover, some acetaldehyde and vinyl chemistry are included to better describe ethylene oxidation, and because natural gas contains propane, a minimal set of propane kinetics is included to model this (and other larger) species. GRI-Mech 3.0 also includes as targets shock tube observations sensitive to the oxidation of the formaldehyde intermediate; a set of shock tube, low pressure flame, and flow reactor experiments concerning prompt NO formation and reburn; and a few targets concerning the shortening of methane shock tube ignition delays by small amounts of propane or ethane.

One drawback is that GRI-Mech 3.0 does not include methyl peroxy chemistry and thus cannot be employed to simulate natural gas combustion at the intermediate temperatures (800–1000 K) and high pressures (≥ 10 atm) which are pertinent to gas turbine operation. Petersen et al. [22] published RAMEC which added a methyl-peroxy sub-mechanism to GRI-Mech 1.2 in order to accurately simulate low-temperature, high-pressure (≈ 260 atm) shock tube ignition delay data for methane oxidation. Unfortunately, the timing was such that the new methyl-proxy chemistry was not combined with GRI-Mech 3.0 in order to incorporate the best of both of these studies and an important opportunity was missed for the combustion community.

Another drawback associated with GRI-Mech 3.0 is that propane fuel was included as a minor constituent only, and thus cannot be relied on to accurately simulate propane (or larger hydrocarbon) kinetics.

In the past too, detailed chemical kinetic mechanisms published for the primary reference fuels n-heptane [7] published in 1998 and iso-octane [8] published in 2002 were generated using similar but not identical sub-mechanisms, making it difficult if not impossible to combine these two, into one consistent primary reference fuel mechanism. Moreover, because of the hierarchical nature of kinetic mechanisms the n-heptane mechanism published in 1998 contains detailed chemistry for the hydrogen/oxygen system, in addition to C₁-C₆ chemistry including low-temperature chemistry. However, targets such as methane, ethane and propane were not tested using this mechanism and so no claims as to its reliability in simulating any fuel other than n-heptane could or can be made. In addition, it would probably be a mistake to use this mechanism to make reliable predictions for the oxidation of any sub-species contained within the sub-mechanism. This is a problem with many if not all detailed chemical kinetic mechanisms that currently exist in the literature.

Combining two mechanisms can also have associated problems. For instance, in order to perform fuel flexibility studies for mixtures of n-heptane and/or iso-octane blended with ethanol these mechanisms need to be combined. Marinov published a mechanism for ethanol [23] and so if one was to combine the primary mechanism of Marinov with either of the Livermore primary reference fuel mechanisms it is highly likely that it would not reproduce the ethanol targets used by Marinov in his...
validation, due to the different sub-mechanisms used. Generating mechanisms in this way is then by its very nature very time consuming.

Frequently too a new experimental study is performed and is simulated using an already validated detailed kinetic mechanism. More often than not the mechanism does not accurately represent this new data and so some modifications are made to sensitive rate constants. However, most of the time the modified mechanism is not used to re-simulate the targets for which it was first validated and so one cannot be certain whether or not the new study really is an advance on previous work. Therefore, it is important that when new experimental data are published and simulated, the mechanism used, if modified, should be shown to reproduce at least a representative array of the original targets for which it was validated and should be provided as supplemental material.

4. Application to gas turbine combustion

Finally, we consider a possible kinetic problem relevant to gas turbines. By using humidified air in gas turbines, the efficiency and output power can be augmented [24]. The other important effect is possibly decreasing pollutant emissions, especially NOx [25]. To explore the kinetic effect of water on ignition timing, we simulated a natural gas mixture with and without water, Fig. 10.

We see that replacing 25% by mass of the air stream with nitrogen reduces the reactivity of the fuel at all temperatures. In this example the fuel concentration decreases from 6.59% to 5.78% of the total mixture composition, which corresponds to just over a 12% reduction in fuel concentration. At low temperatures (600–1000 K) and at 40 atm, it is the fuel concentration that determines the reactivity of the mixture, the higher the fuel concentration the faster is the mixture to ignite.

Comparing the results of replacement by nitrogen and water we see that water is not as inhibiting as nitrogen, certainly in the temperature range 800–1000 K. At 900 K, the more important reaction accelerating ignition times under these conditions is the decomposition of hydrogen peroxide: \( \text{H}_2\text{O}_2 (+M) = \text{OH} + \text{OH} (+M) \), a reaction in which water acts as an important third body, with a very high efficiency of 12 compared to most other species. At high temperature (~ 1500 K) water loses its accelerating effect on ignition times (not depicted here). In fact, the greatest chain branching reaction for ignition delay at 1500 K is: \( \text{H} + \text{O}_2 = \text{O} + \text{OH} \) and not \( \text{H}_2\text{O}_2 (+M) = \text{OH} + \text{OH} (+M) \) as was the case at 900 K, thus the water efficiency coefficient doesn't play the same role at high temperature.

Thus, water has an accelerating effect on ignition delay times, at intermediate temperatures, by acting as a third body with a very high efficiency coefficient, and primarily not by self-decomposition generating radicals.

References

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