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AUTOIGNITION CHARACTERISTICS OF GASEOUS FUELS AT REPRESENTATIVE GAS TURBINE CONDITIONS

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ABSTRACT

The autoignition properties of gas turbine fuels have been studied for many years and by numerous researchers. The advent of ultra low emission industrial gas turbines using lean premixed technologies has given rise to premixer designs with longer residence times. This, in conjunction with the ever-increasing pressure ratios of aeroderivative machines, leads to the potential for autoignition within premix ducts, and has therefore renewed the interest in this field. Although much has been published, data in the region of interest to high pressure ratio gas turbines is extremely sparse. Similarly, modelled autoignition delay times are not very accurate, as most reaction mechanisms were not generated to cover this range of conditions. Hence the uncertainties of autoignition delay times at gas turbine conditions are significant, thereby either imposing over-stringent design limitations or introducing risks of ignition occurrence in the early design process.

A series of experiments have been carried out for methane and simulated natural gas fuels in the region of interest, using shock tubes as the test vehicle. The experimental technique was chosen to isolate only the chemical kinetic component of the autoignition delay time, without any additional delays due to mixing and heating of the test gases. Predictive correlations and a chemical kinetic model (the GRI mechanism) have also been used to predict autoignition delay times at the same conditions. The correlation between experiment and prediction has been shown to be poor at representative temperatures. This paper discusses some of the possible explanations for this poor agreement.

INTRODUCTION

As world-wide emissions legislation is becoming ever more stringent, there is a requirement for combustion engineers to design gas turbine combustors with the capability to produce extremely low levels of NOx and CO in the exhaust. Such low levels of pollutant emissions can only be achieved by extending our understanding of current premixers, to maximise the mixing quality of fuel and air prior to entry into the combustion process. However, with the elevated inlet temperatures and pressures characteristic of high pressure ratio aero-derivative machines, a limit is reached where the time required to fully premix the fuel and air streams becomes comparable with the autoignition delay time for the combustible mixture. A compromise is therefore sought between optimum mixing quality and freedom from autoignition. During the design process, this compromise is currently achieved by experiment. This approach is costly and time-consuming, as it involves the manufacture and testing of many design iterations. If validated predictive chemical kinetic schemes were available, and incorporated into computational fluid dynamics (CFD) codes, then the combustion engineer could have access to a predictive tool, for the optimisation of future designs at minimum cost and in shorter timescales.

There is currently very little autoignition data available in the public domain covering the range of initial temperatures and pressures relevant to high pressure ratio gas turbines. Many researchers (including Spadaccini et al (1999), Burcat et al (1971) and Petersen et al (1999)) have studied the autoignition characteristics of natural gases in shock tubes at high temperatures, typically above 1200 K, which is significantly above the inlet temperature range applicable to aero-derivative

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gas turbines. Much work has also been performed in flowing rigs at representative gas turbine temperatures, but to only moderate pressures (e.g. Cowell and Lefebvre (1986)). A gap exists in our knowledge over the range of temperature from 800 to 1000 K, and pressure from 10 to 40 atm. It is crucial that data is gathered in this region, to enable the validation of chemical kinetic reaction mechanisms for use in combustion design tools.

This paper presents the results of a series of shock tube experiments, aimed at determining the autoignition delay time of methane and natural gas mixtures at representative gas turbine combustor inlet conditions. The main objective is to determine the major factors influencing autoignition delay time in gas turbine combustion systems. Firstly, the autoignition characteristics of methane were determined over a range of temperatures and pressures. Then, to determine the sensitivity of autoignition delay time to variations in natural gas fuel composition, a series of tests were carried out with both ethane and propane added to the methane test gas. The effects on autoignition due to variations in stoichiometry and humidity levels were also investigated. The validity of the current experimental data is discussed, particularly in the lowest temperature range, where the measured autoignition delay times approach the observation time limit of the shock tube.

The resulting experimental data is compared against predictions from the GRI chemical kinetic mechanism of Smith et al (1999) and correlations from Spadaccini et al (1999) and Li and Williams (2000), to assess their suitability in predicting autoignition delay times in the gas turbine combustor. Finally, several suggestions are offered to explain why the agreement is poor at lower temperatures.

NOMENCLATURE

τ	Autoignition delay time, in seconds
T	Temperature, in Kelvin
P	Pressure, in atmospheres
$[O_2]$	Oxygen concentration
$[CH_4]$	Methane concentration
$[HC]$	Non-methane hydrocarbon concentration (all in molecules / cubic centimetre)

MEASUREMENTS OF AUTOIGNITION DELAY TIME

All of the experimental data was generated in a shock tube of length 6.75 m and internal diameter 64 mm, shown schematically in the upper part of Figure 1. The driver and test section lengths were 3 m and 3.75 m respectively, and a double Mylar diaphragm separated the two sections prior to initiation of the test. Helium gas was used in the driver section, to minimise boundary layer effects in the tube.

For the majority of the work presented here, the test gas simulated a methane / air mixture with an equivalence ratio of 0.5. Experiments were also performed on a number of other test

gases, to investigate the effect on autoignition delay time of variable fuel composition, stoichiometry and humidity. Each test gas mixture was produced in a vessel by the method of partial pressures, and allowed to mix thoroughly before its introduction into the shock tube. Before filling, the tube was brushed clean of debris from the previous test, and then evacuated. The length of the shock tube enabled a maximum test observation time in the reflected shock region of approximately 6 milliseconds, as shown schematically by the progression of the shock fronts with time in the lower part of Figure 1. The long observation times required for lower temperature autoignition measurements can cause the experiment to be compromised, due to low shock velocities in a long tube enabling boundary layer build-up and hence bifurcated shocks within the test section. This will be discussed later.
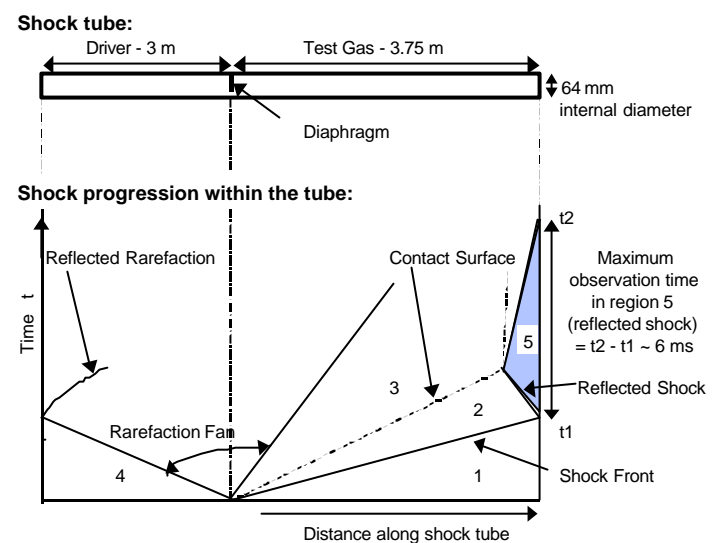

Figure 1: Schematic of shock tube

For all of the experimental work presented here, the onset of pressure rise at the test section end wall was used as the indicator of an autoignition event. This was chosen because an increase in pressure is a definite indicator of exothermic reaction. As the ignition occurs at the end wall of the shock tube, the autoignition delay time is defined as the time interval between the shock front reaching the tube end wall and the pressure rise due to combustion. Light emission was recorded near the end wall of the shock tube at two wavelengths, corresponding to chemiluminescence from OH (308 nm) and CH (431 nm), and this gave good agreement with pressure rise data where all were measured simultaneously. The experimental results cover a range of initial temperatures from 900 to 1700 K, and initial pressures from 5 to 20 atm. The results are described for each test gas composition in turn.

During the course of the current experimental programme, a series of control tests were performed, to determine the characteristics of the shock tube without any fuel in it. The test gas mixture used in this case was bottled dry air. The results in

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Figure 2 show that, over the entire temperature range, light emission was observed at 431 nm in the unfuelled tests at delay times of the same order as the recorded pressure rise during equivalent methane-fuelled tests. At temperatures below 1000 K, the light emission was seen after shorter delay times than were typically expected for the autoignition of methane. This indicates that there may be some other source of ignition within the tube, which may affect the validity of the lower temperature data. However, no corresponding pressure rise was observed during the control tests, indicating that there was no significant exothermic reaction in the tube. As the current fuelled tests used pressure rise as the indicator of autoignition, the presence of light emission in the control tests is not likely to affect the results presented here. This will be discussed later.
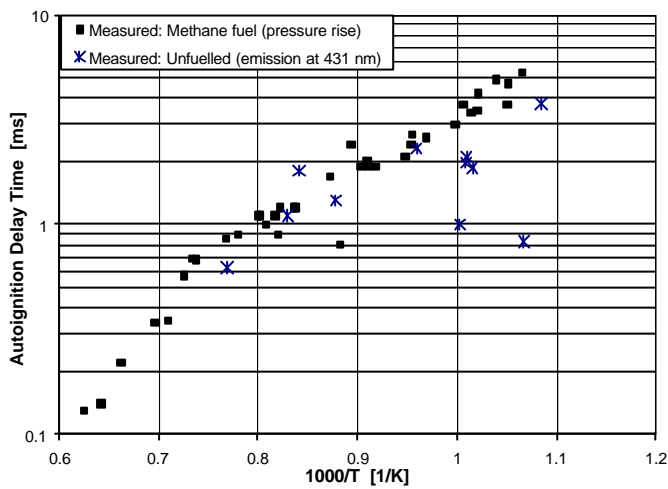

Figure 2: Emission from unfuelled shock tube tests (initial pressure: 10 atm)

The autoignition delay time for methane is presented as a function of temperature and pressure in Figure 3. Predictions made using the GRI mechanism are also plotted; these will be discussed in the next section. The experimental data in Figure 3 shows that the delay time is strongly dependent upon initial temperature, and is affected by pressure to a lesser extent; autoignition delay time reduces when either temperature or pressure is increased. Similar results have been published elsewhere (including Cowell and Lefebvre (1986), Spadaccini et al (1999), Burcat et al (1971) and Petersen et al (1999)), although not under the range of conditions studied here.

At the upper temperature limit of the present data, it is shown to be in good agreement with Burcat et al (1971). No other shock tube data was readily available for comparison with the lower temperature results, but flow rig data from Cowell and Lefebvre (1986), indicated on Figure 3, suggests a marked difference between the two experimental techniques at these conditions. Significantly longer delay times were observed in the flowing tests, possibly due to the influence of fuel / air mixing time on the overall time taken for autoignition. The

current data appears to show a change in the activation energy at an initial temperature of approximately 1100 K at 20 atm. Similarly, the 10 atm data undergoes a change in activation energy around 1300 K.
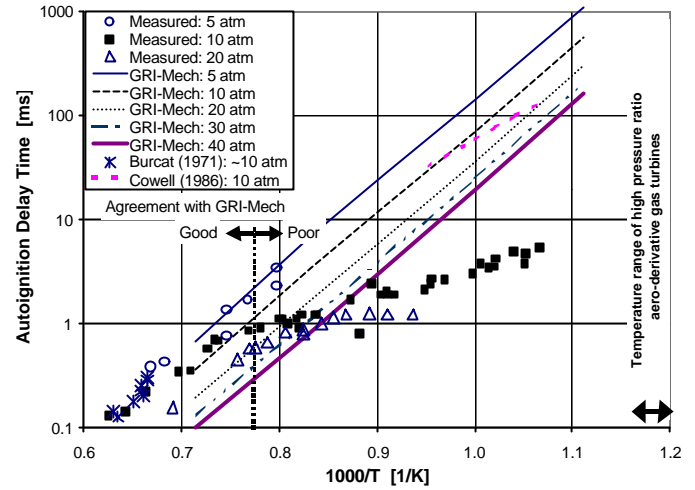

Figure 3: Methane autoignition delay time as a function of temperature and pressure

Having characterised the autoignition behaviour of methane, the effect of adding 15% ethane (by volume) to the test fuel was investigated, to simulate a possible extreme of natural gas composition. The results are shown in Figure 4, where an initial pressure of 10 atm and overall equivalence ratio of 0.5 were maintained for all tests. The data indicate that the autoignition delay time is significantly shortened by the addition of ethane for initial temperatures greater than 1200 K. Below this temperature, the added ethane appears to have no effect on the autoignition characteristics of methane.
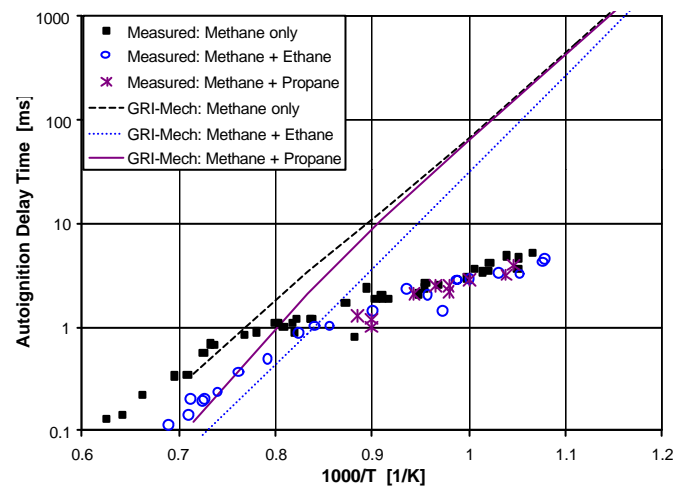

Figure 4: Effect of non-methane natural gas fuel constituents on autoignition delay time

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To further assess the impact of natural gas constituents on autoignition, a similar series of tests was performed with 15% propane added to methane. This data series does not extend to a sufficiently high temperature to fully determine its behaviour relative to ethane. However, for all three test gas mixtures, shown graphically in Figure 4, the delay times begin to tend almost asymptotically towards the observation time limit of the shock tube at temperatures below 1200 K. Under these lower temperature conditions, the results collapse onto one curve, such that the effect of adding this amount of higher hydrocarbons to methane is negligible below 1100 K.

Lean premixed gas turbine combustion systems tend to be optimised to operate at equivalence ratios of around 0.5 at full load conditions, but this may vary widely during engine manoeuvres. It is therefore important to understand the effect of variations in equivalence ratio on autoignition delay time, to prevent ignition events occurring during transient operation. Much of the data in the public domain (e.g. Cowell and Lefebvre (1986)) suggests that the equivalence ratio has only a limited effect on the autoignition delay time. The current data, presented in Figure 5, confirms that varying the stoichiometry between 0.5 and 1 at 10 atm has only a small effect on the measured delay time. At temperatures above 1200 K the effect was negligible, but at lower temperatures the higher equivalence ratio tended to give rise to slightly shorter autoignition delay times.
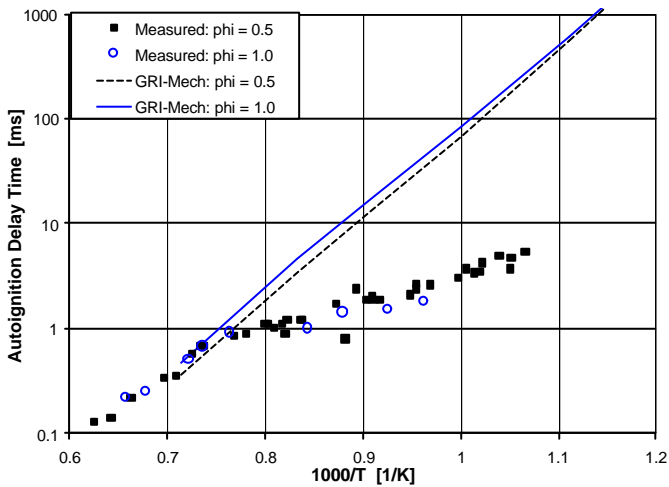

Figure 5: Effect of stoichiometry on the autoignition delay time of methane

In the final series of autoignition tests, varying amounts of water were added to the test gas to simulate the effects of high air humidity on autoignition delay time. A simulated methane / dry air mixture was used as the baseline test gas, with all experiments carried out at an initial pressure of 10 atm.

Although only a limited number of experiments were carried out with added water, the results in Figure 6 indicate that its

effect was to slightly increase the autoignition delay time relative to the baseline test. It is also interesting to note that, for the test series with 8% water added, a sharp cut-off temperature was defined (at approximately 1250 K), below which no autoignition occurred.
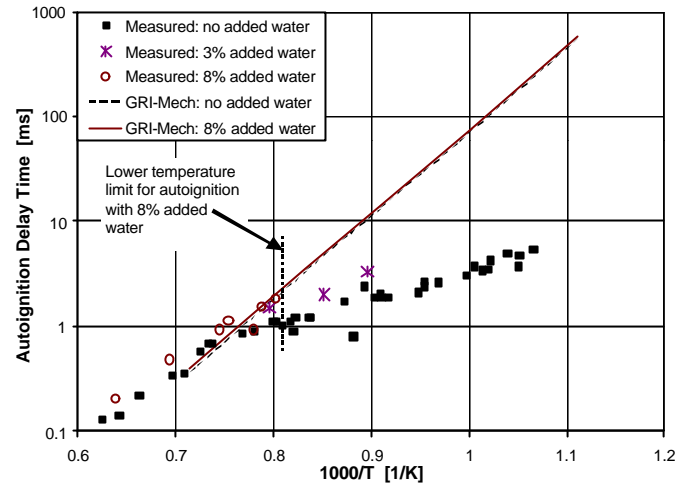

Figure 6: Effect of added water on the autoignition delay time of methane

MODELLING OF AUTOIGNITION DELAY TIME

To complement the experimental work presented here, attempts have been made to predict the autoignition delay time of natural gas mixtures at relevant gas turbine combustor inlet conditions. Comparison is made between the predictions and the experimental data presented in the previous section. The chosen predictive methods are all publicly available: the GRI mechanism (version 3.0) of Smith et al (1999) using the CHEMKIN software package (assuming adiabatic, constant volume conditions), two correlations from Spadaccini et al (1994) and one correlation from Li & Williams (2000). It should be noted that all experimental data used in the validation of these predictions were derived from high temperature tests (> 1200 K), and generally at high pressures (> 50 atm for Li & Williams (2000)). There is currently very little data available in the public domain which relates closely to the combustor inlet conditions of high pressure ratio gas turbines. This is a severe limitation when attempting to make predictions of autoignition delay time in this temperature and pressure range, and so the predictions presented here should be viewed with caution.

GRI Mechanism

Version 3.0 of the GRI kinetic mechanism is validated only for temperatures above 1350 K. Indeed, Figure 3 shows that the agreement with the current experimental data is extremely good for temperatures above 1300 K. But the predicted and measured delay times rapidly diverge at lower temperatures, as the GRI mechanism does not predict the change in activation energy seen experimentally. Where the current test data is available (up

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to 20 atm), the pressure effect on autoignition is predicted well at high temperature. The experimental observation that variations in stoichiometry have little effect on autoignition delay time is shown in Figure 5 to agree fairly well with the prediction. Although the GRI mechanism includes reactions for ethane and propane as minor constituents, the results plotted in Figure 4 suggest that it does not adequately predict the autoignition delay time for mixtures containing as much as 15% ethane. Comparison cannot be made with the prediction for added propane, as the experimental data does not extend to sufficiently high temperatures. The predicted effect of added water is similar to the experimental findings; Figure 6 shows that the GRI mechanism predicts a very small effect.

Empirical Correlations

The correlation for the autoignition delay time of methane generated by Spadaccini et al (1994) covered many published data sources, using both shock tubes and flowing rigs, and over a wide range of initial pressures, but is limited to temperatures of 1300 K and above. In fact, a small quantity of data published by Spadaccini at temperatures around 1000 K gave rise to delay times significantly shorter than the correlation:

Autoignition delay time,
$$t = 2.21x10^{-14} \exp(22659/T)[O_2]^{-1.05}[CH_4]^{0.33}$$

However, its validity is assessed here against the present data. Figure 7 shows that, as with the GRI mechanism, the agreement with the current data is good at high temperature (above 1300 K).
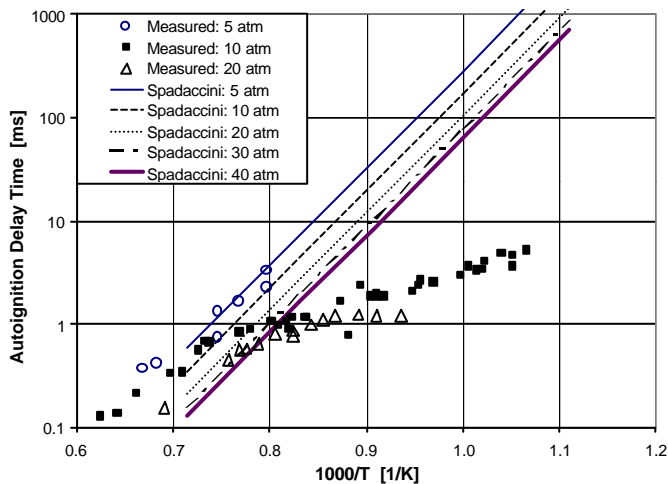

Figure 7: Correlation of Spadaccini et al (1994) for the autoignition delay time of methane

Similarly, the correlation from Spadaccini et al (1994) for methane with added higher hydrocarbons is only validated by high temperature data, above 1200 K:

$$t = 1.77x10^{-14} \exp(18963/T)[O_2]^{-1.05}[CH_4]^{0.66}[HC]^{-0.39}$$

To enable direct comparison with three sets of experimental data of varied fuel compositions and at two pressures, the data in Figure 8 are plotted as a function of autoignition delay time normalised for oxygen, methane and higher hydrocarbon molar concentrations. The agreement between correlation and experiment is again good at high temperature, but does not extend successfully beyond the validated range, as indicated in Figure 8.
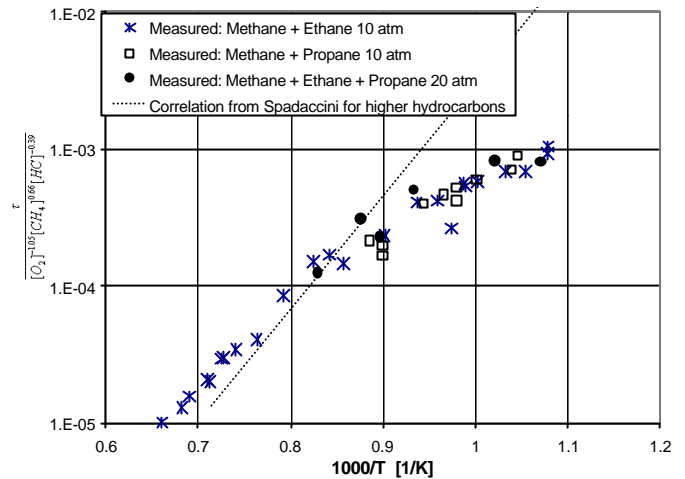

Figure 8: Correlation of Spadaccini et al (1994) for the autoignition delay time of methane with added higher hydrocarbons

The correlations published by Li & Williams (2000) were generated from experimental data published by Petersen et al (1999), and acknowledged a difference in activation energy at "high" and "low" temperature. The effect was similar to that seen in the present data, although the reported change in activation energy occurred at higher temperatures than observed here. The difference in the temperature at which the change occurs could be due to the initial test pressure being much greater in Petersen's work than here.

For Li & Williams' correlations, "low temperature" was defined as less than 1300 K, and as most of the experimental data presented here was below 1300 K, only the low temperature correlation is used:

$$t = \frac{2.6x10^{-15}[O_2]^{-4/3}[CH_4]^{1/3}}{T^{-0.92}\exp(-13180/T)}$$

Figure 9 shows that the slope of the correlation fits the higher temperature experimental data (above 1100 - 1200 K) very well, but there is an offset causing the correlation to consistently over-predict the autoignition delay time, by around 50 to 80%.
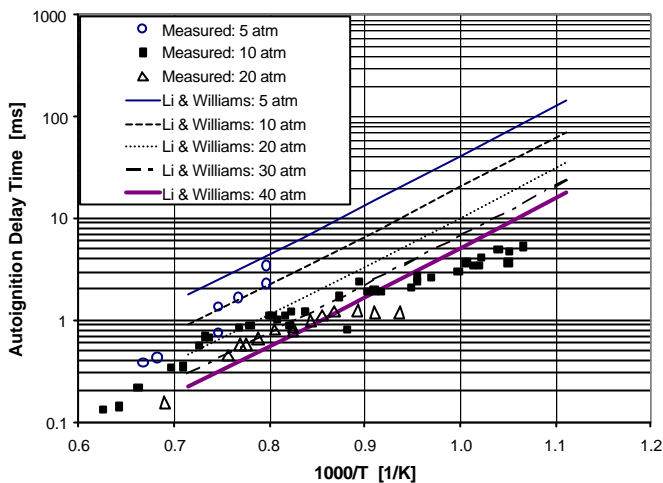
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Figure 9: Low temperature correlation of Li and Williams (2000) for the autoignition delay time of methane

DISCUSSION

Where other published shock tube data is available, the agreement with the current data is good. However, it is acknowledged that there is a shortage of data in the region of interest to gas turbine combustion. The data tend to be at high temperature (greater than 1200 K), and pressures which are either too low (below 10 atm) or too high (over 50 atm).

The experimental data suggest a change in activation energy at low temperature (below ~ 1200 - 1300 K, depending on the initial pressure conditions). This is depicted by a change in the slope of the data series. The change in slope could be due to other factors than a change in activation energy. Several possible explanations are briefly discussed below:

- ♦ **A change in the chemistry important to autoignition** (i.e. change in activation energy). It is possible that the dominant chemistry at lower temperatures differs from that at higher temperatures. This has also been reported by Petersen et al (1999) and Li and Williams (2000). The lower temperature chemistry may be dominated by simpler reactions, such as oxygen abstraction, the result of this being that the effects of temperature, pressure and added higher hydrocarbons become small, as was observed experimentally in Figure 3 to Figure 6;

- ♦ **A physical limitation of the shock tube.** As the delay time approaches the shock tube's observation time limit, the measurements may be affected. Autoignition events may be spuriously recorded after artificially short delay times. The validity of this statement could be determined by the study of similar tests in different lengths of shock tube;

- ♦ **Ignition of the mylar diaphragm initiates reactions in the test gas.** The series of unfuelled shock tube tests revealed light emission from the shocked gases, and a possible source of this emission is combustion of fragments of the mylar diaphragm. At high initial temperatures, where the autoignition delay time of the test gas is shorter than the delay time to emission from the mylar, the data is representative of the test gas mixture. However, at lower temperatures, where the delay time of the test gas becomes longer than that suspected of the mylar, the resulting data may be affected by the diaphragm material. As no pressure rise was observed, it is unlikely that sufficient heat would be generated to accelerate the methane reactions, but it is possible that it could act as a source of ignition. A study of the effect of alternative diaphragm materials would assess this risk;

- ♦ **Initial heating of the test gas by the incident shock.** The current work used the reflected shock technique for the determination of autoignition delay time. As the incident shock passes through the test gas section, it will heat and pressurise the gas, which may cause the initiation of some reactions. This may result in the measurement of artificially low delay times;

- ♦ **Non-ideal conditions in the shock tube.** When studying longer observation times, the likelihood of boundary layers forming in the test section increases. Replacing the Nitrogen in the test gas mixture with a monatomic gas such as Argon will minimise this effect, however preliminary comparison tests at 10 atm showed this to have a negligible effect on the resulting autoignition delay times.

If the integrity of the lower temperature data is shown to be good, there are several significant implications which arise. Firstly, the suggestion that the actual composition of a natural gas fuel has no impact on the autoignition delay time for temperatures below 1100 K would, if confirmed, offer the potential to greatly simplify the predictive schemes. Also, for practical systems, the ability to elevate the minimum autoignition temperature by the addition of water could signify additional benefits for humid air cycles.

Without exception, all of the predictive methods assessed here show good agreement with the high temperature experimental data. The GRI mechanism predicts the measured autoignition delay times almost exactly for methane at temperatures above 1300 K. The activation energies of the various correlations vary slightly, but all demonstrate a fairly close relationship with the current experimental data over a range of temperatures. However, because of the experimentally observed change in activation energy at or around 1200 K, all of the predictions fail to agree with the measured data at lower temperatures. This is because the validation data used for the predictions was in all cases undertaken at temperatures greater than 1200 K, and is therefore no criticism of the predictive

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methods. Of the correlations assessed, the "low temperature" equation of Li and Williams (2000) predicted the temperature dependence most closely below 1200 K, but gave rise to significant over-prediction of autoignition delay time under all conditions. From the data presented here, there is strong evidence to suggest that the dominant chemistry at these lower temperature conditions differs from the reactions incorporated into version 3.0 of the GRI mechanism.

For the test mixtures with other constituents than methane, oxygen and nitrogen, the GRI mechanism demonstrates a degree of success in predicting the autoignition delay time. A very small increase was observed when water vapour was added to the test gas; and the prediction of the effect of added ethane and propane appeared to be qualitatively correct.

The above discussion relates to the measurement and prediction of a pure kinetic time for autoignition of a fuel / air mixture. The shock tube is therefore a particularly good test vehicle, as it measures only this chemical kinetic time. However, in any real premixer geometry (or in a flowing test rig), the true overall autoignition delay time is hard to determine, as it will be defined by some combination of:
- the time taken for fuel and air to mix,
- the time for the fuel temperature to rise to that of the combustion air, and
- the chemical kinetic time for the autoignition reactions to initiate.

Shock tubes cannot therefore be directly compared to flowing rigs; it is quite possible that the results of Cowell and Lefebvre (1986) differ from the current data because of the associated mixing and heating times of the flowing rig. The interaction of the above processes is complex, and requires an integrated solution of chemical kinetics and CFD to enable the accurate prediction of autoignition delay time in a varying time / temperature field.

CONCLUSIONS
There is currently very little experimental data available at conditions relevant to high pressure gas turbine combustion. Consequently, the predictive mechanisms are not validated and the correlations do not extend to sufficiently low temperatures.

The apparent change in activation energy highlighted by the experimental work is particularly important, as it occurs at a temperature slightly lower than the limit of the validated predictions. It is therefore dangerous to extrapolate any of the predictions to lower temperatures, as this poses a risk of significantly over-predicting the autoignition delay time. The implication of this is that if the extrapolated predictions are used to specify design criteria, the resulting designs will have a high likelihood of failure due to unwanted autoignition.

Several uncertainties exist in the current experimental data, which must be addressed before proceeding further. These include the possibility of non-ideal behaviour in the shock tube and possible interference of the results caused by the diaphragm material. Further experimental data covering this range of temperatures and pressures is urgently required to provide validation for lower temperature kinetic schemes. To achieve this objective, the ability to measure autoignition delay times greater than 10 milliseconds is required.

To enable the generation of a useful design tool, a reliable mechanism for prediction of the chemical kinetic autoignition delay time must be combined with a good CFD model to take account of the effects of mixing and heating the fuel and air streams. Only then will a combustion designer be able to optimise the configuration of a premix duct for lowest emissions but with freedom from autoignition.

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