

## AUTOIGNITION OF GASEOUS FUEL-AIR MIXTURES NEAR A HOT SURFACE

A.Ungut<sup>1</sup> and H. James<sup>2</sup>

<sup>1</sup> Shell Global Solutions, P.O. Box 1, Chester CH1 3SH, UK

<sup>2</sup> Health & Safety Executive, Grove House, Skerton Road, Manchester M16 0RB, UK

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An experimental investigation of the hot surface autoignition temperatures for methane, natural gas, propane, and butane mixtures with air was conducted. A stainless steel cartridge heater was installed, with the exposed surface pointing downwards, within a thermally insulating ceramic plate, and heated up to 1000 °C in an enclosed volume of flammable fuel/air atmosphere. Exposed surface temperatures that caused autoignition in mixtures of varying stoichiometry were determined by slowly heating up the cartridge heater until combustion occurred. The measured hot surface temperatures, representing the most favourable conditions for ignition to occur near an exposed stainless steel surface, were found to be approximately 1.5-1.75 times higher than the reported minimum autoignition temperatures determined by standard test methods. These observations were used to validate a CFD based chemical kinetics modelling method. This validated model could form the basis of a predictive tool for general use.

### INTRODUCTION

In many industrial applications the presence of heated surfaces, and pipework may present an ignition hazard if an accidental leakage of fuel or lubricants comes into contact with the hot surface. This is particularly important in onshore or offshore gas turbine power plants where the engine is sound-insulated in an acoustic-chamber, and the gaseous fuel under usually very high pressure is delivered through a complex network of pipes[1]. In the absence of adequate ventilation an accidental fuel leak may lead to the build-up of a combustible gas cloud near the gas turbine exhaust diffusers which operate at elevated temperatures (450-550 °C). Conditions which lead to spontaneous ignition are controlled by the balance of the heat generated by low temperature combustion reactions, rates of which are determined by the time history of the mixture temperature, and the heat losses from local hot spots to nearby surfaces. The type of the metal surface also affects the ignition phenomenon to a lesser extent. In practice, the buoyancy effects caused by the temperature differential near the hot surface induce a natural convection flow which makes the onset of spontaneous ignition dependent on the geometry. This may be sometimes referred to as the Damköhler number criterion[2], where a critical value of the ratio of a characteristic flow time to a characteristic chemical reaction time affects the onset of ignition. Because of the rather complex nature of this phenomenon risks associated with hot surface autoignition are poorly understood, and measures taken to minimise the risk are usually based on tabulated minimum autoignition temperatures which can be considerably lower than the actual hot surface autoignition values.

Standard test methods for determination of autoignition temperatures of liquid and gaseous fuels involve heating up of a known quantity of fuel in a uniformly heated 500 ml [3], or 200 ml test flasks[4]. These tests provide a quantitative description of the likelihood of autoignition for various fuels but the reported values have a limited range of applicability.

The standard test conditions correspond to near adiabatic conditions where heat losses from the reaction centres, and the effect of the buoyant convective flow are minimised. Thus, they provide a minimum ignition temperature for the fuel in question. It is also reported that the use of larger flasks reduces the autoignition temperature even further by restricting the heat losses [5]. Similar observations are also reported in [6]. A detailed study of the autoignition temperatures of methane, propane and methane/propane mixtures as a function of fuel concentration is also reported in a slightly different test apparatus [7]. We shall refer to the standard test measurement as minimum autoignition temperature (MAT) in this paper.

In realistic hazard scenarios both the buoyant flow, and the presence of hot metal surfaces which serve as a conductive heat sink for the reaction hot spots, reduce the likelihood of autoignition by increasing the minimum wall temperature to much higher values than the MAT. An API publication[8] has concluded that, based on the experimental results, ignition by a hot surface in the open air should not be assumed unless the surface temperature is about 200° C above the MAT. Recently, Smyth & Bryner[9] reported similar results in an experimental apparatus where a jet of fuel/air mixture impinged on a small heated surface.

The surface ignition temperatures of heated rods, pellets, and strips of metal sheets that cause ignition in fuel/ air mixtures have been an area of historical interest [10]. Detailed reviews of the subject are given in references [11], [12], and will not be repeated here. In general, reported hot surface ignition temperatures for methane and natural gas are higher than 1273 K, and the lowest ignition temperatures are observed for leaner mixtures ( equivalence ratio of 0.7). For surfaces with small areas (<400 mm<sup>2</sup> ) the ignition temperature increases with decreasing surface area [13]. Catalytic surfaces such as platinum have been reported to have higher hot surface ignition temperatures than inert surfaces [14], [15] such as nickel and stainless steel. There is also an observed dependence on the orientation of the surface, mixture velocity and surface heating / cooling rates. Hot surface ignition temperatures for propane mixtures vary from 1073 to 1273 K for horizontal hot tubes, and vertical hot plates, respectively in tests reported by Kong et al. [7]. The observed hot surface temperatures that cause ignition increase with increasing equivalence ratio for methane or hydrogen mixtures with air, and reverse is true for higher alkanes [11]. Similar observations were reported in [7] for measurements of MAT for methane and propane mixtures.

The purpose of this paper is to provide hot surface autoignition data for the most commonly used gaseous fuels such as methane, natural gas, propane, and butane in a systematic way covering a wide range of the mixture stoichiometries. The experimental data, representing a 'worst case' scenario of a typical industrial application, is intended to be used for assessing the spontaneous ignition hazards for exposed, clean, non-catalytic metal surfaces, such as stainless steel. The data is also to be used for the validation of a computational fluid dynamics (CFD) based hot surface autoignition model which will be published elsewhere[16]. This model involves the calculation of the buoyant gas flow over the heated plate using a commercial CFD code. The steady state streamlines calculated are used to provide temperature-time histories to a kinetics integration program which also simulates the heat losses to the wall from the reacting gas volume. As the surface temperature increases, the likelihood of autoignition is predicted along the streamlines.

The total exposed area of the heated metal surface should be large enough to provide sufficient residence time for the reactions to occur (Damköhler number criterion), the practical limit to the size of the surface is determined by the maximum surface temperature

that could be attained despite the increasing radiation cooling. The cartridge heater chosen for this study has an exposed stainless steel surface of dimensions 0.025 m x 0.080 m, with a maximum attainable surface temperature of approximately 1300 K. In order to maximise the residence time of the gas pockets near the hot surface the heater is placed pointing downwards in a recess. This arrangement is considered to represent the most likely geometry for the occurrence of the spontaneous ignition ('worst case'). CFD simulation of the buoyant convective air flow near the experimental geometry indicated that the flow residence time is greater than approximately 1.5 s which is much longer than the chemical induction period of the mixtures investigated.

## EXPERIMENT

The experimental apparatus consisted of an open-sided steel compartment of 0.6 m<sup>3</sup> volume (internal dimensions: length 1.0 m; depth 0.6 m; width 1.0 m). A vent was located in the roof of the compartment. Gases entered through a line at the base of the compartment fitted with an air mover to aid mixing. Gas sample points (protected by flame arrestors) were situated at the base of the compartment and within the roof vent. A ceramic board (0.48m x 0.48m) with a centrally located heated surface was suspended from the roof. The base of the compartment was water cooled. Fig. 1 shows the rig in more detail. The board was suspended from the roof by four rods and its height within the compartment could easily be adjusted. Thermocouples monitored the temperature of the heated surface and the gases at the surface of the plate and within the compartment.

The cartridge heater was installed into a recess within the thermally insulating ceramic block with a 0.7 mm diameter type 'K' thermocouple welded at the centre of the unexposed surface. Each leg of the thermocouple was welded separately by a capacitance discharge welder to the back of the heater, approximately 5 mm apart. Thus the stainless steel surface becomes part of the thermocouple junction and the thermocouple accurately and unambiguously measures the steel temperature. The thermocouple cable was extended out of and beyond the auto-ignition chamber into type 'K' connector blocks. These were used to transfer the thermocouple output signals into type 'V' compensating cable and to the data collection point. This thermocouple was linked to a Eurotherm controller which regulated the rate of temperature rise and to the data logger used to measure the temperature at which ignition occurred. Fig. 2 shows the details of the cartridge heater.

As the heater was located in the insulated block there was a temperature differential across the heater between the unexposed face with the thermocouple welded to it and the face exposed to the flammable gas atmosphere because of radiation losses. The validity of the autoignition data depended on knowing with a certain degree of confidence, the temperature of the exposed surface when the gas mixture ignited. Therefore, the exposed surface temperature needed to be calibrated in relation to the unexposed surface. To do this, three extra thermocouples were welded onto the exposed surface of the heater at approximately 25%, 50%, and 75% of the distance along its length. These were all connected into a Netdaq data logger together with the control thermocouple signal. With the data logger running the heater was put under load via the Eurotherm controller to rise at a rate of 33.3 °C. per minute. For mapping purposes, this was continued up to a maximum of 1050 °C. The heater was then set to decrease to room temperature at exactly the same rate. On examining the data, the average value of the temperature of the exposed surface was compared with the

co-incident value on the unexposed surface and a calibration curve-fit expression was derived over the range in excess of 700 °C. Fig. 3 shows the variation of the exposed surface temperature as a function of the back surface temperature. The solid black line shows the centrally located thermocouple, and the dotted lines show the thermocouples positioned at the edges of the heated surface. The variation of the temperature across the length of the cartridge heater introduced an uncertainty in the measurement of the autoignition temperature and this is shown as error bars in the results. Because of the excessive thermal loading it was necessary to replace the cartridge heaters regularly, and repeat the calibration procedure described above. During the tests these extra thermocouples were removed from the exposed surface of the heater and the surface smoothed to eliminate the possibility of any 'hot spots'.

Four extra thermocouples were used to monitor the gas temperature inside the autoignition chamber. These were located inside the recess cavity, on the lower surface of the insulation block, in the volume between the insulation block and the cling-film wall, and inside the cable conduit above the heater. The details of the thermocouples, and the cartridge heater used in these tests are given in the appendix.

A suitable span gas was used to calibrate the analyser before each test. During the experiment, the open sides of the compartment were sealed with cling-film (held in place using magnetic strip) and the volume filled with the fuel/air mixture. The gaseous fuel and air used were supplied in standard gas cylinders. These were stored externally in gas bottle racks and piped directly into the lab. The pressure of the gases was controlled using regulators and the lines downstream were protected by pressure relief and non-return valves. The flow and mixing of the gases were controlled remotely through valves operated from within a control room. With the vent valve at the top of the chamber open, the fuel and the air were introduced in separate bursts into the chamber and mixing was achieved by relying on turbulent mixing within the chamber. The mixture was sampled from both the upper and the lower levels of the chamber to assess the homogeneity of the mixture, and when the desired gas concentration had been reached the gas supply and vent valves were closed.

In the event of the gases failing to ignite upon the hot surface a nitrogen purge was used to remove the flammable gas mixture from the rig and supply lines. As a back up to the nitrogen purge system the gases could also be safely removed from the compartment by a controlled ignition. For this purpose a spark plug, which could be triggered remotely from the control room, was situated in the roof of the compartment. All data produced was collected and digitised using transient recorders and stored on a PC for further analysis.

A TV camera was set up to monitor the conditions inside the chamber close to the surface of the heater. The heater was then powered up. The Eurotherm controller was set to increase the heater temperature by 33.3 °C. per minute. During the heating up period the contents of the chamber were sampled through the gas analyser to ensure the concentration was still within specification. The temperature rise continued until either ignition occurred or the temperature reached approximately 1150 °C at the back surface of the heater which corresponds to an average temperature of approximately 1000 °C at the exposed front surface. If ignition did not occur, the heater was set to cool down and the atmosphere within the chamber was purged with nitrogen.

## RESULTS

Tests for butane, propane, natural gas, and methane mixtures with air were conducted with varying stoichiometries. Table 1 shows the details of the mixture compositions and the average, minimum, and maximum hot surface temperatures that caused the autoignition of the fuel air mixture. An artificial natural gas (NG) mixture similar to the Shell Gannet platform production gas composition (77.7% methane, 10.34% ethane, 6.67% propane, 2.9% butane, 0.74% pentane, 0.09% hexane, balance carbon dioxide) was used in this investigation. The ignition of the mixture was determined from the colour video recordings, and the response of the gas phase thermocouples to the arrival of the flame front. Fig. 4 shows a typical thermocouple measurement during the tests. A sharp spike on the temperature profiles of the gas phase thermocouples is related to the flame front arrival, and the occurrence of ignition is further confirmed by the colour video recording of the test. The temperature of the exposed surface of the cartridge heater was than determined from the calibration data.

Measured hot surface autoignition temperatures are shown in Figs. 5-7 as a plot of the surface temperature against the mixture stoichiometry for mixtures in air of butane, propane, natural gas, and methane respectively. Recent data published by Smyth & Bryner[3] is also shown for butane, propane, and methane mixtures for comparison. Although the method used to measure the hot surface ignition temperatures is very different their results agree well with the data from the current study, with the exception of methane where their measurements are unexplainably low for stoichiometric, and richer methane/air mixtures. In our methane tests, mixtures with stoichiometries greater than 0.8 failed to ignite within the maximum temperature range of the heater. Results agree with published data [7, 11] that the observed hot surface temperatures that cause ignition increase with increasing equivalence ratio for methane or hydrogen mixtures with air, and the reverse is true for higher alkanes.

## DISCUSSION

A small number of repeat experiments for near stoichiometric butane/air mixtures show significant scatter of the hot surface autoignition temperatures (standard deviation of 42 °C). Although not representative of the tests with other mixtures this variation may be considered as typical for the present data. The average values of the hot surface ignition temperatures in Kelvin for a given mixture stoichiometry, normalised with the tabulated minimum autoignition temperatures, are plotted for all of the tests in Fig.8. This ratio varies between 1.5 to 1.75 depending on the mixture composition and stoichiometry which is in good agreement with the API recommendation[8].

Results are used to validate a CFD based model using detailed chemical kinetics calculations [16], details of which will be published elsewhere. The experimental geometry reported is modelled to simulate the convective buoyant flow near a heated surface, and the detailed chemical kinetics model was used to predict the gas phase self ignition. Fig. 9 shows the comparison of the predictions with the experimental results for the butane / air mixture (see Fig. 5). The empty circles show the average hot surface ignition temperature for each mixture stoichiometry investigated. The horizontal lines show the model predictions that failed to ignite, and the plus signs indicate predicted ignitions as a function of surface temperature, and mixture stoichiometry. The agreement between the model predictions and the

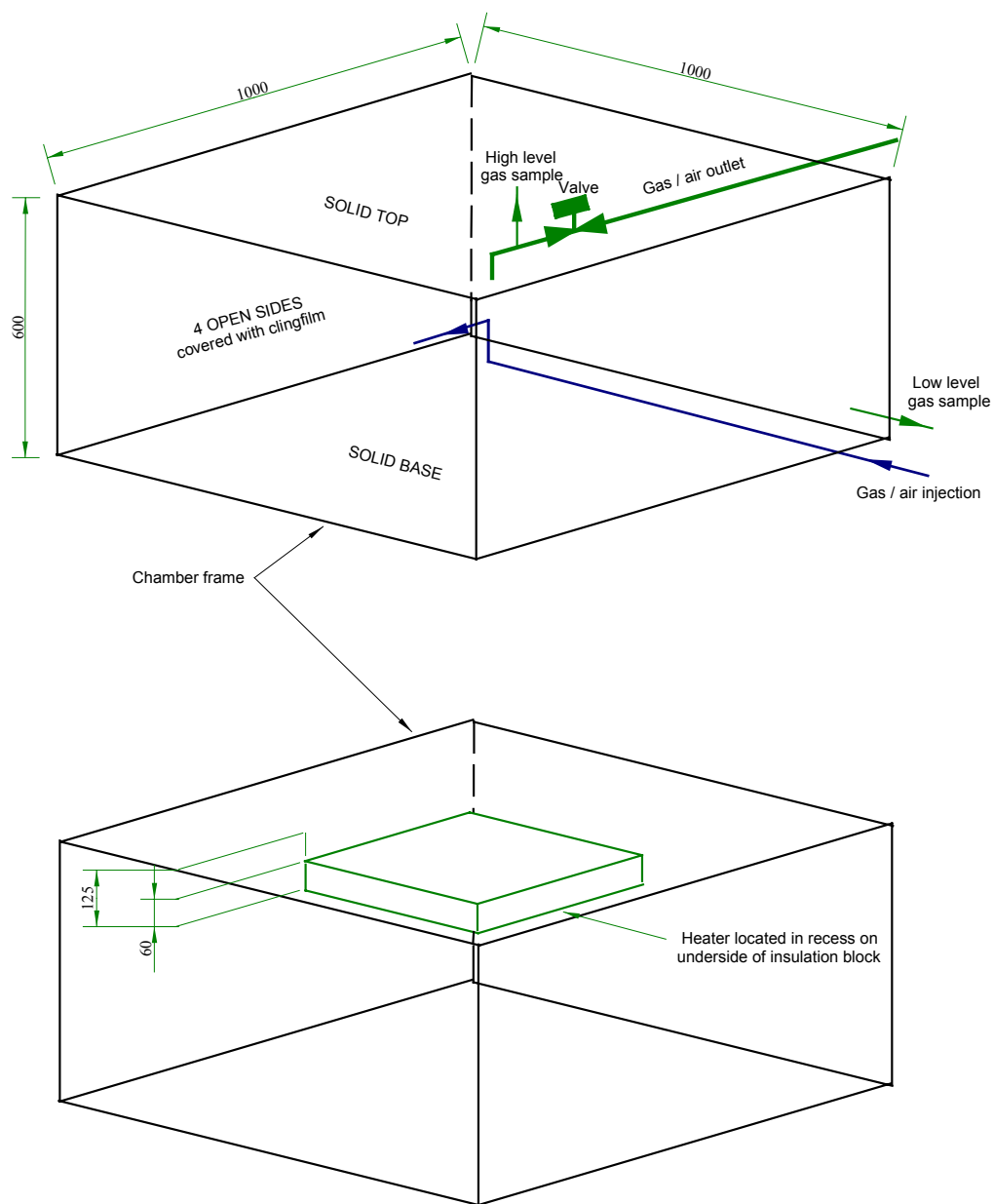
experimental data is excellent [16] and the use of this methodology in accident investigations and hazard assessment will be potentially very valuable.

## CONCLUSIONS

- In this study, autoignition in mixtures in air of methane, natural gas, propane, and butane near a hot stainless steel surface occurred at temperatures (in K) approximately 1.5-1.75 times higher than the minimum autoignition temperatures measured using the standard test method.
- Results are in good agreement with other published data, and represent a realistic accident geometry which can be modelled using the available computational fluid dynamics and chemical kinetics methods. The results also provided much needed validation data for the model.
- The experimental results reported here are specific to the experimental arrangement in this study, and should be used with care, taking into account the possible influence of other variables that could affect autoignition temperature.

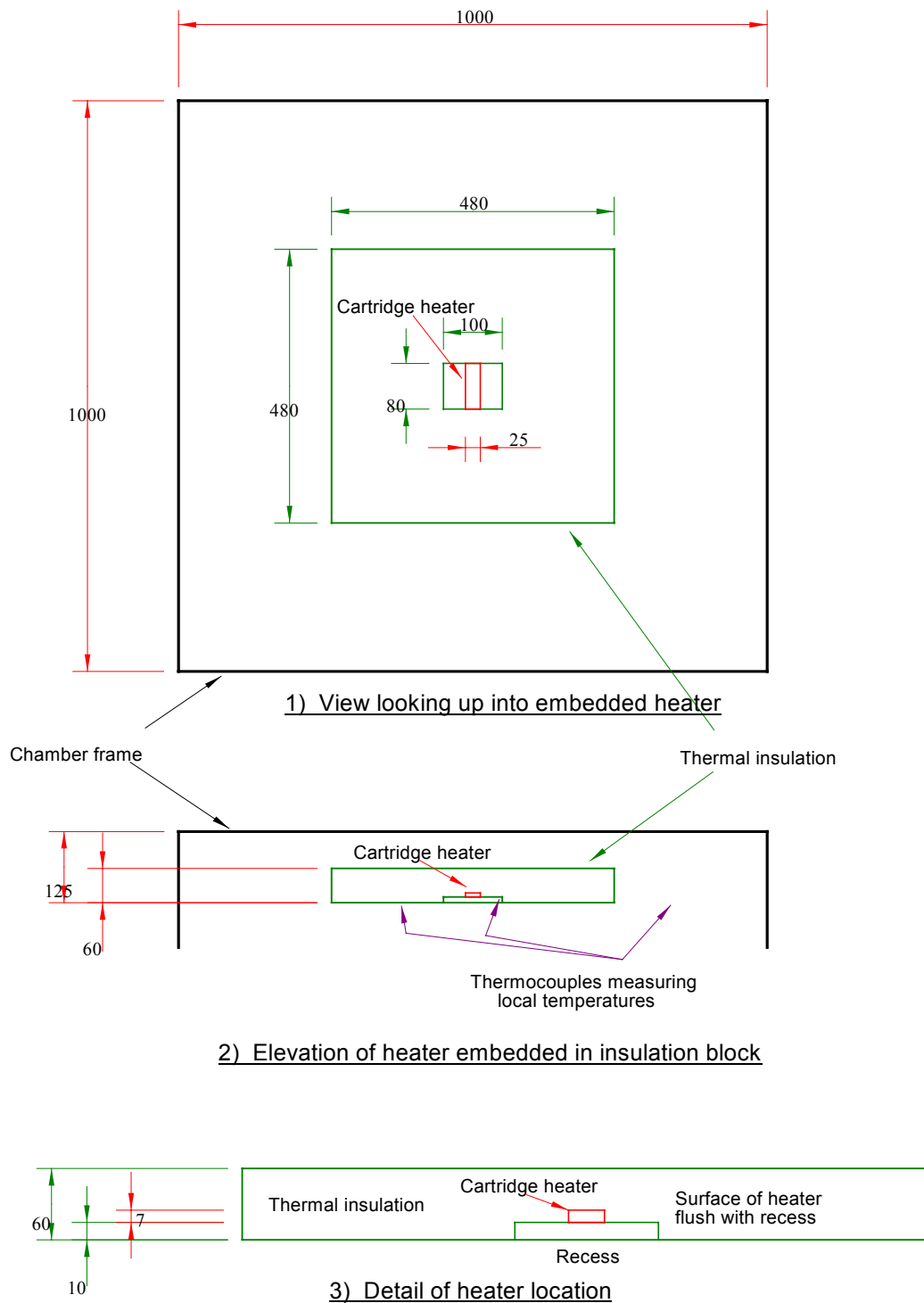
**Table 1 Details of the mixture compositions tested and the average, maximum, and minimum surface temperatures that ignited the fuel air mixture.**

FUEL	STOICHIOMETRY	AVERAGE SURFACE TEMPERATURE (K)	MAXIMUM SURFACE TEMPERATURE (K)	MINIMUM SURFACE TEMPERATURE (K)
Butane	0.46	1264	1291	1249
	0.5	1107	1124	1093
	0.7	1089	1100	1078
	0.8	1099	1115	1085
	0.81	1091	1102	1080
	1.1	1096	1113	1082
	1.07	1013	1023	1003
	1.11	1070	1081	1059
	1.71	1097	1108	1086
Propane	0.71	1110	1123	1101
	1.1	1113	1126	1104
	1.57	1127	1141	1118
NG	0.5	1152	1168	1140
	0.51	1145	1160	1134
	0.6	1159	1175	1147
	0.71	1163	1180	1151
	0.71	1164	1181	1151
	1.1	1197	1217	1181
	1.15	1197	1217	1181
	1.15	1196	1216	1180
	1.3	1227	1250	1207
Methane	0.71	1209	1227	1209
	0.76	1223	1246	1204

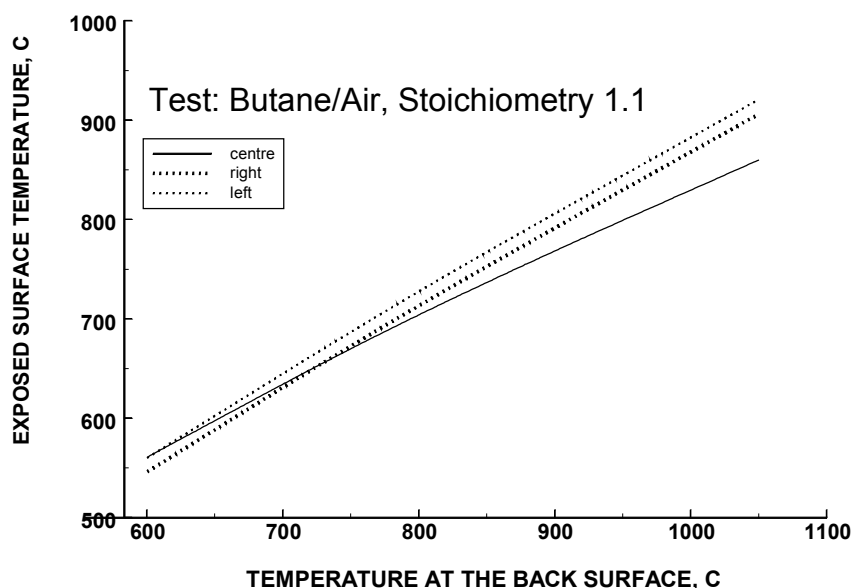


**Figure 1** Details of the autoignition rig showing locations of services and the ceramic heater block. Units are in mm.

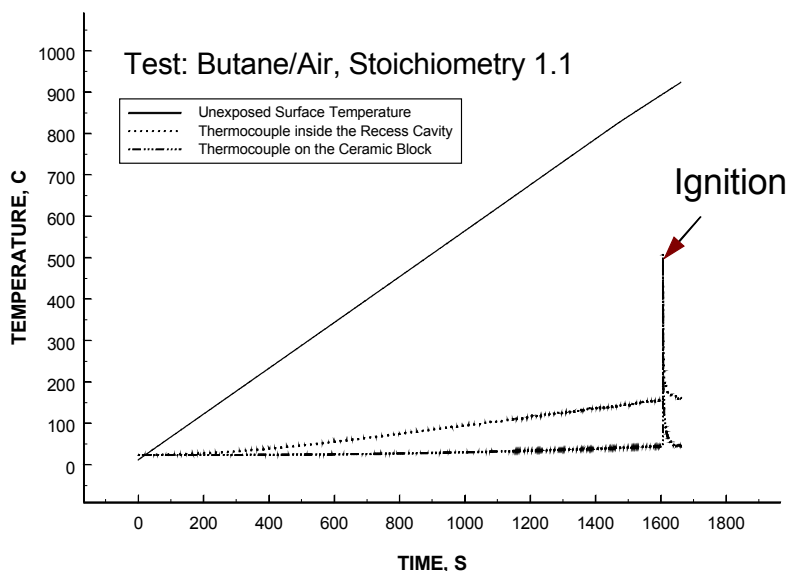




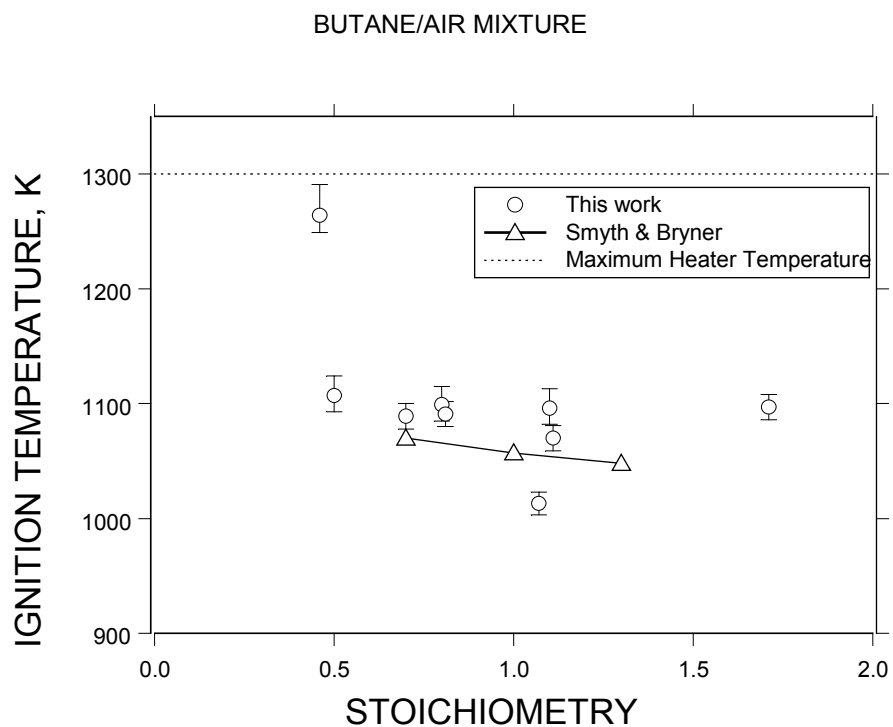
**Figure 2 Details of the cartridge heater, and positioning of thermocouples. Units are in mm.**



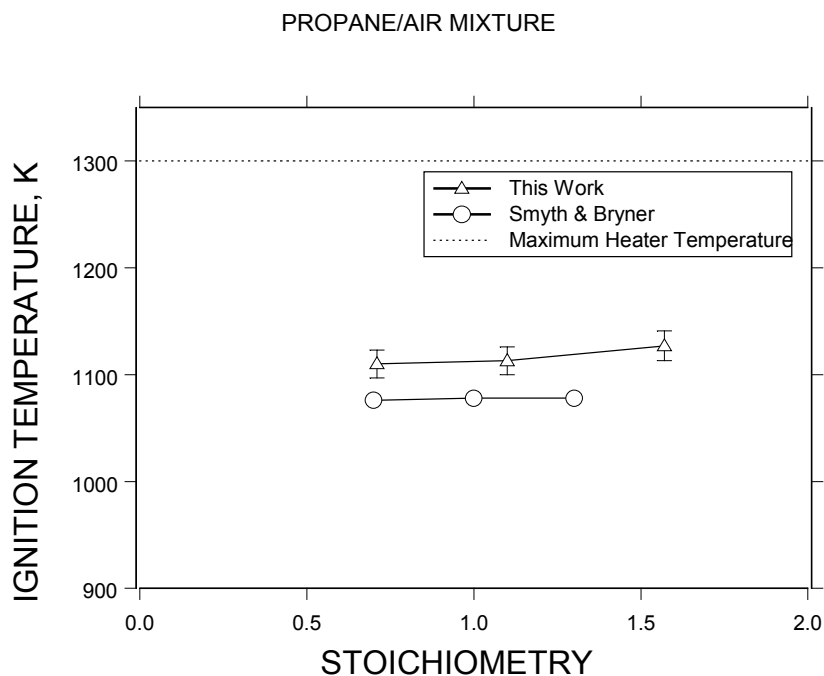
**Figure 3** Calibration of the exposed surface temperature against the temperature measured at the back of the cartridge heater. The solid black line shows the centrally located thermocouple, and the dotted lines show the thermocouples positioned at the edges of the heated surface.



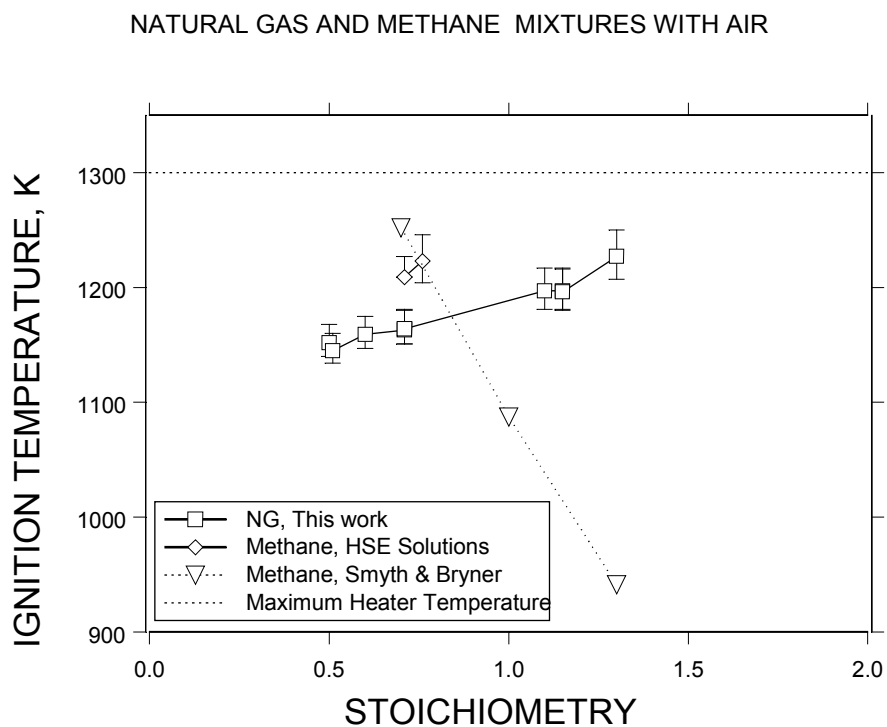
**Figure 4** Thermocouple measurements that show the measured temperature behind the cartridge heater, and the gas phase temperature during a test.



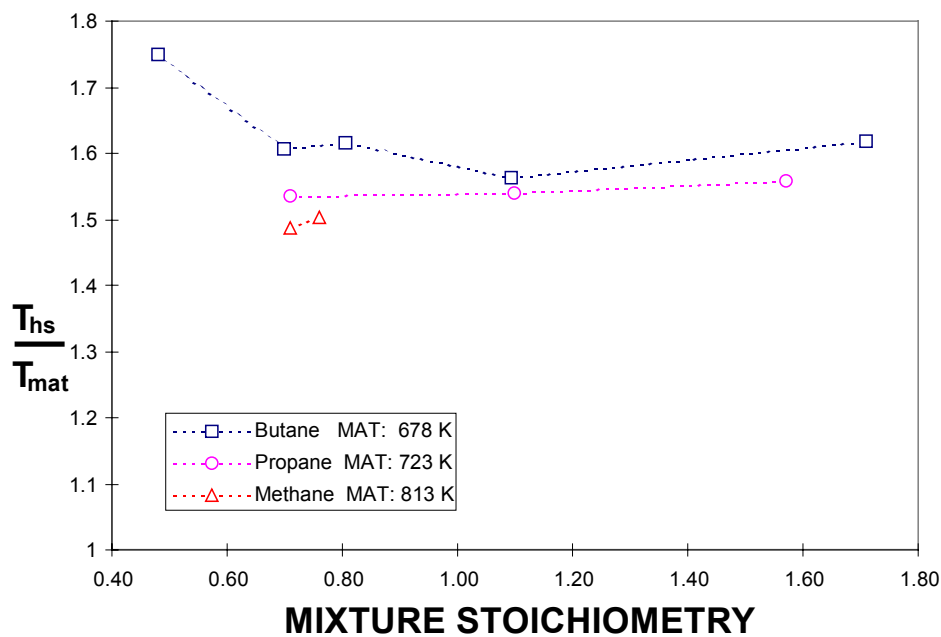
**Figure 3** Hot surface ignition temperatures for butane air mixtures



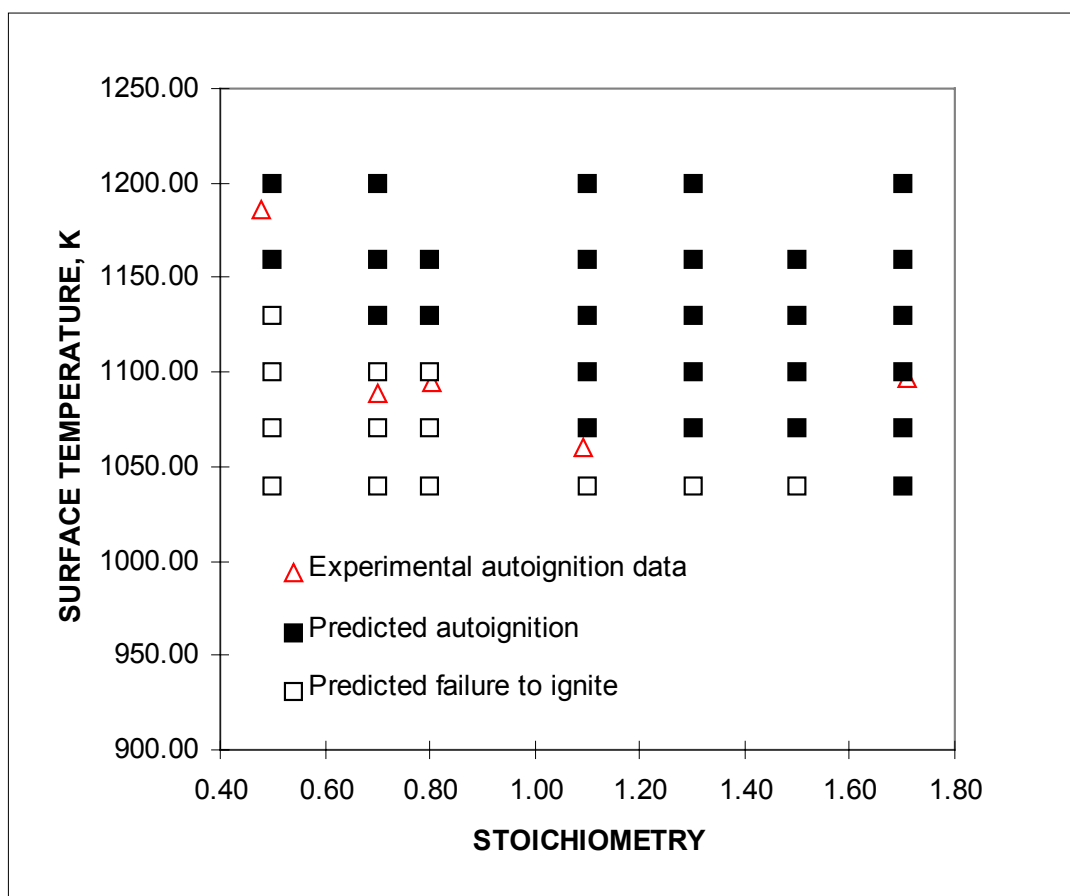
**Figure 4** Hot surface ignition temperatures for propane air mixtures



**Figure 5** Hot surface ignition temperatures for methane and natural gas mixtures with air.



**Figure 6** Ratio of the measured hot surface ignition temperatures ( $T_{hs}$ ) to MAT ( $T_{mat}$ ) measured by the standard method for all of the mixtures investigated.



**Figure 7** Comparison of the model predictions[16] with the experimental data. The experimental data points are the average hot surface autoignition temperatures for a given stoichiometry.

## APPENDIX

### Cartridge heater details

Type:	Hotwatt SR 16-5.
Construction:	Stainless steel sheath with magnesium oxide packing.
Dimensions:	7mm thick by 25mm wide by 127mm long
Power consumption:	Up to 500 Watts
Maximum continuous temperature:	650°C.

Thermocouples welded to the surface of the Cartridge heater

Thermocouple welded to the centre of the unexposed surface

Type:	Solid wire
Construction:	Type 'K' Chromel Alumel

Dimensions: 0.7mm diameter.  
Measuring range: -80 to 1350°C.  
Tolerance: Class 2, +/- 2.5°C to 333°C or 0.0075 x T between 333°C to 1200°C.

Thermocouples used to monitor the gas temperature in the enclosure

Type: Mineral insulated, stainless steel sheath with exposed junction.  
Construction: Type 'K' Chromel Alumel  
Dimensions: 0.5mm diameter sheath.  
Measuring range: -80 to 1350°C.  
Tolerance: Class 2, +/-2.5°C to 333°C or +/-0.0075 x T between 333°C to 1200°C.

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