

THE AUTO-IGNITION TEMPERATURE OF METHANE

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Summary

An improved method for measuring auto-ignition temperatures of gaseous fuels has been developed. Results are reported for methane–air mixtures and compared with previous work. It appears that the normally accepted minimum auto-ignition temperature for methane of 537 (or 540)°C was theoretically rather than experimentally derived. No values with a firm experimental basis lie below 600°C. Our minimum auto-ignition temperature of 600°C is the lowest available. We believe this could be considered as the new standard value.

Introduction

The phenomenon of auto-ignition is important to chemical engineers and others concerned with safe industrial operations, since it is a major source of industrial fires. The minimum temperature at which a fuel will ignite is a useful parameter, as it sets a maximum safe limit for operations involving that fuel. However, it should be borne in mind that the minimum auto-ignition temperature (MAIT) is not a fundamental property of a fuel, since its value depends (to some extent) on the means of measurement.

A variety of methods have been used to measure ignition temperatures, but most adopt the principle of introducing fuel and air into an ignition vessel pre-heated to a selected temperature, and observing whether or not ignition occurs. In subsequent trials, the temperature is raised or lowered until the minimum is located. This forms the basis of the methods approved by the American Society for Testing and Materials (Methods D2155-66 and E659-78 [1, 2]).

Although these standard methods now exist, not all workers have used them. This is certainly true for methane for which many studies have been made. By common convention, the lowest reported value is generally taken as the MAIT of a fuel, irrespective of the method by which it was obtained. For methane, this value is 537°C [3], often quoted as 540°C [4].

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In this paper we report a new study of methane ignition, compare our data with previous measurements, and comment on the normally accepted MAIT.

Experimental

An improved technique has been devised for measuring ignition temperatures of gaseous fuels. A roughly spherical test vessel was used, made of stainless steel and with a volume of 0.8 dm³. Fuel and air were premixed to allow good control of the mixture composition. The vessel was evacuated, heated to the selected temperature (controlled to $\pm 2^\circ\text{C}$) and the mixture admitted. Although the vessel was closed, a relief valve ensured that ignitions were carried out at constant pressure, very close to atmospheric. Ignition was monitored by a thermocouple in the centre of the vessel, and by pressure transducer. Ignition temperatures could be determined with a reproducibility of 5°C or less.

We were concerned that the use of a metal test vessel might lead to higher ignition temperatures than would have been obtained in glass. To examine the possible influence of the nature of the wall on ignition, a series of tests was carried out with the inside of the vessel liberally coated with boric acid. The coating was applied by adding a saturated solution of boric acid in ethanol and evaporating the solvent. Boric acid is converted to the oxide on heating.

Results and discussion

The results for the ignition temperatures of methane as a function of methane concentration are shown in Fig. 1. Several key points emerge from the results:

- Ignition temperatures vary with stoichiometry, reaching a minimum at about 7% fuel. Naylor and Wheeler [5] observed a similar pattern, though their temperatures were higher.
- Ignition delays at the MAITs vary between 17 and 20 seconds, essentially independent of methane content.
- Boric acid coating reduces the ignition temperatures significantly (by $7\text{--}12^\circ\text{C}$). Further coatings produce no further reduction in ignition temperature.
- The MAIT for methane is 601°C occurring at 7% methane and obtained in a boric acid coated vessel.

Before comparing our results with other data, there are two preliminary points to comment on.

a. Validity of present experimental method

The apparatus and procedure adopted in this work do not conform to either of the ASTM standards (D2155 or E659). We were unhappy about

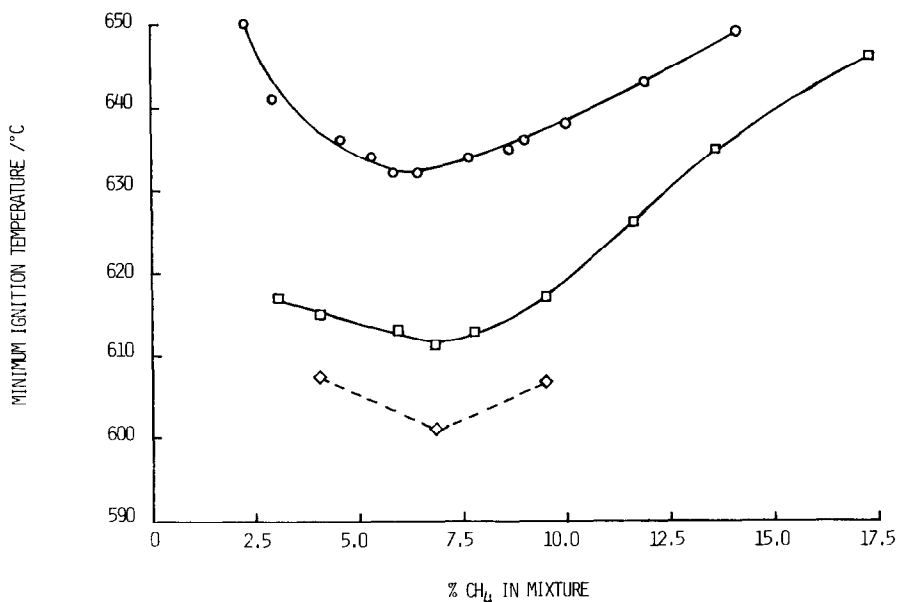


Fig. 1. Auto-ignition temperatures of methane-air mixtures: variation with stoichiometry. □ — this work, untreated vessel; ◇ — this work, boric acid coating; ○ — Naylor and Wheeler [5].

using these for our work for two reasons; first, control over mixing is poor and hence knowledge of fuel-air ratio uncertain, and secondly, they were devised for liquid and solid fuels and are unsuited to gaseous ones. In the early part of our study we attempted to use the D2155 method (with an open-necked 200 ml conical pyrex reaction flask) but injecting methane as a gas. No detectable reaction occurred even at 650°C — the upper limit of our apparatus.

There is a further difference between our procedure and ASTM standards: that is in the volume of test vessel. ASTM standards refer to 200 ml or 500 ml vessels, whereas we used 800 ml. This would tend to make our determinations lower than those based on ASTM methods, because of the well-known reduction of ignition temperature with increase in vessel size.

b. Use of metal ignition vessel

Although the ASTM standard methods prescribe glass reaction vessels, we opted for stainless steel. In our method, the vessel was closed (though vented). So if it had been of glass, it would have been liable to fracture, thus causing inconvenience and possible hazard. There is some evidence [6, 7] that metal surfaces lead to higher ignition temperatures than glass. This is probably due to reactions, occurring on the walls, that destroy reactive species necessary for oxidation to proceed. Such reactions occur more readily on metals than on glass [8].

The present work certainly demonstrates that methane ignition is significantly affected by the nature of the wall. We believe we have overcome the problem of using metal vessels by the use of boric acid coatings. Boric acid was chosen because of its ability in pyrex vessels drastically to reduce the efficiency of wall termination reactions [9]. Although coatings on metal surfaces may not act in precisely the same way, it seems its effect is similar. We think it unlikely that untreated pyrex surfaces (as used in ASTM standards) would have lower wall reaction efficiencies than our coated ones.

Thus we conclude that experiments in a glass vessel would probably not yield ignition temperatures lower than those reported here. As further support for this contention, we note also our ignition temperatures for other hydrocarbons. For propane and butane, our data are consistent with normally accepted values [4], for ethane our value is somewhat lower (490–500°C rather than 515°C [4]).

Comparison with previous data

It was stated earlier that a variety of methods has been used to measure ignition temperatures of methane. None of them follow closely the ASTM standard methods. Indeed most of them predate the establishing of the standards. In Table 1 are presented all reported data we can find on measured ignition temperatures of methane by hot surface.

It will be noticed that the table contains no reference to the commonly accepted value of 537°C. This has been deliberately excluded. The earliest reference we can find for it is from Factory Mutual in 1940 [3]. But despite a thorough literature search, we have been unable to trace details of any experiments performed. We conclude that the value is in all probability not an experimental one, but rather is derived from some theoretical method unknown to us. But because it is the lowest figure available, it has been passed on through successive compilations and has become firmly established as the standard value. There appears to be no rational basis for its continued acceptance.

TABLE 1

Comparison of experimentally determined MAITs of methane in air

| MAIT (°C) | Ignition vessel | Reference and date |
|-----------|---|---------------------------------|
| 606–650 | 0.24 dm ³ glass cylinder | Freyer and Meyer [10], 1893 |
| 675 | 0.275 dm ³ glass cylinder | Taffenel and LeFloch [11], 1913 |
| 632 | 0.44 dm ³ quartz cylinder | Naylor and Wheeler [5], 1931 |
| 656 | Ceramic tubing, volume not known | Dixon [12], 1934 |
| 748 | Steel tubing, diameter about 10 mm, length 165 mm | Bunte and Bloch [13], 1935 |
| 673 | 0.190 dm ³ silica cylinder | Townend and Chamberlain [7] |
| 659 | 0.2 dm ³ stainless steel sphere | Fenstermaker [14], 1982 |
| 601 | 0.8 dm ³ stainless steel sphere, boric acid coated | This work |

Returning to those values which do have a firm basis in experiment, the lowest is the present determination of 601°C. Although our measurement technique does not conform to either ASTM standard method, we have argued above that the data obtained are valid. For convenience, this can be rounded down to 600°C. We believe this figure could be considered as the new standard MAIT of methane.

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References

- 1 American Society for Testing and Materials, Autoignition temperature of liquid petroleum products, D2155 Part 17, 1970, p. 724.
- 2 American Society for Testing and Materials, Autoignition temperature of liquid chemicals, E659 Part 25, 1981, p. 1235.
- 3 The Associated Factory Mutual Fire Insurance Companies, Properties of flammable liquids, gases, and solids, *Ind. Eng. Chem.*, 32 (6) (1940) 880.
- 4 M.G. Zabetakis, Flammability characteristics of combustible gases and vapors, Bureau of Mines Bulletin No. 627, AD 701576, 1965.
- 5 C.A. Naylor and R.V. Wheeler, The ignition of gases. Part VI. Ignition by a heated surface. Mixtures of methane with oxygen and nitrogen, argon or helium, *J. Chem. Soc., II* (1931) 2456.
- 6 N.J. Thompson, Auto-ignition temperatures of flammable liquids, *Ind. Eng. Chem.*, 21 (2) (1929) 134.
- 7 D.T.A. Townend and E.A.C. Chamberlain, The influence of pressure on the spontaneous ignition of inflammable gas-air mixtures. IV. Methane, ethane, and propane-air mixtures, *Proc. Roy. Soc.*, A154 (1936) 95.
- 8 D.E. Hoare, G.B. Peacock and G.R.D. Ruxton, Efficiency of surfaces in destroying hydrogen peroxide and hydroperoxyl radicals, *Trans. Faraday Soc.*, 63 (1967) 2498.
- 9 C.H. Bamford and C.F.H. Tipper, *Comprehensive Chemical Kinetics*, Vol. 17, Gas-Phase Combustion, Elsevier Scientific Publishing Co., Amsterdam, 1977.
- 10 F. Freyer and V. Meyer, On the ignition temperatures of explosive gas mixtures, *Z. Phys. Chem.*, 11 (1893) 28.
- 11 J. Taffenel and LeFloch, Combustion of gaseous mixtures, and kindling temperatures, *Comptes Rendus*, 157 (1913) 469.
- 12 H.F. Coward, Ignition temperatures of gases. "Concentric tube" experiments of the late Harold Bailey Dixon, *J. Chem. Soc., II* (1934) 1382.
- 13 K. Bunte and A. Bloch, Ignition temperatures of gases, *Gas- Wasserfach*, 20 (1935) 349.
- 14 R.W. Fenstermaker, Study of autoignition for low pressure fuel-gas blends helps promote safety, *Oil and Gas Journal*, (15 Feb.) (1982) 126.