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XIV. THE CAUSE OF THE EFFECT OF HYDROGEN SULPHIDE TO REDUCE
THE COMPRESSION RATIOS AT WHICH FUEL GASES CAN BE USED
IN SPARK IGNITION ENGINES

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✓ By R. O. KING,² E. J. DURAND,³ BERNARD D. WOOD,⁴ AND A. B. ALLAN⁵

Abstract

Experimental results are given for trials of the C.F.R. engine at 900 r.p.m. and 12 : 1 C.R. on Toronto town gas alone and with an addition of hydrogen sulphide. The sulphide led to such severe preignition that measurements of power were impossible except for very weak or very rich mixtures. The former included the 50% weak mixture for which thermal efficiency is a maximum. The sulphide was then of beneficial effect, a maximum value of 44% for indicated thermal efficiency being obtained as compared to a maximum of 42.5% without it. The experimental results are interpreted in the light of combustion tube experiments showing that hydrogen in mixtures with air is not ignited by red hot surfaces on which it is oxidized with sufficient rapidity to steam, but that ignition occurs at relatively low temperatures if the surface reaction is inhibited by hydrogen sulphide. The conclusion is that fuel gases containing hydrogen in large proportion can be used for full power engine operation at compression ratios even higher than 12 : 1 if the oxidation of the hydrogen in part to steam, on the hot surfaces in the combustion chamber, is not inhibited by the poisoning effect of the hydrogen sulphide commonly present in the gases.

Introduction

The compression ratio of 12 : 1 at which Toronto town gas was used for the engine trials described in Part XIII (7) is impossibly high according to accepted standards. Ricardo, for example, states (15, p. 32) that the usable compression ratio for town gas is 5 to 6 : 1, for producer gas 6 to 7 : 1, for blast furnace gas 7 to 7½ : 1, and for coke oven gas which frequently contains over 50% of hydrogen the safe compression ratio is little if any greater than 5 : 1. Lucke is even more specific in respect of the role played by hydrogen. He states (12, p. 33), "gases rich in hydrogen generally preignite easily; approximately one atmosphere should be deducted from the compression allowable with no hydrogen for each 5 per cent of hydrogen present". The "safe" compression pressure given accordingly in Kent (4, 12-11) is 90 to 100 lb. per sq. in. gauge for coke oven gas which contains hydrogen in greater concentration than is found in other fuel gases. The views mentioned in respect of hydrogen appear to be confirmed by the experiments of Ricardo (16) and A. F. Burstall (2). Their experiments are discussed at some length

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by Pye (14, pp. 188-190) who after describing the operation of the E 35 engine on extremely weak hydrogen-air mixtures concludes, "the same faculty of rapid flame propagation which makes burning possible on the weak side, makes it impossible to work at the rich end of the scale of fuel-air ratios even up as far as the correct mixture. Whenever running was attempted with a hydrogen-air ratio more than about 95 per cent of that giving complete combustion, violent preignition set in, accompanied by firing back through the carburetor. This happened even when the compression ratio was lowered to 3.5 : 1 while at higher ratios smooth running was limited to even weaker mixtures."

The experimental results for engine trials with hydrogen and town gas, described in Parts V (10), VI (11), XII (6) and XIII (7), are completely at variance with those presently accepted as a basis for the authoritative conclusions mentioned above. Hydrogen has been used at compression ratios extending to 10 : 1 at any mixture strength and without preignition (10); town gas containing hydrogen in a concentration nearly as great as in coke oven gas has been used similarly at a compression ratio of 12 : 1 (7), the compression pressure then being 390 lb. per sq. in. gauge as compared with the "safe" value of 80 to 100 lb. given in "Kent". Moreover, the performance in respect of power and thermal efficiency was commensurate with the unusually high values of the compression ratio which at 12 : 1 was just within the Diesel engine range. It is indicated accordingly, and is illustrated by the experiments of Part XIII (7), that the spark ignition Otto cycle engine may be made to surpass the Diesel in respect of both power and thermal efficiency. It is thermodynamically possible because both types now use the Otto cycle, and combustion characteristics are the better for the carburetor spark ignition type.

The great increase in power and thermal efficiency obtainable by using fuel gases at Diesel engine compression ratios would be of economic importance if it could be realized in practice. It may be considered, therefore, that the object of the investigation presently in hand is in part to discover why it has been necessary to operate the spark ignition gas engine at the relatively low compression ratios for which power and thermal efficiency are necessarily inferior. The experimental results described in earlier Parts provide a partial explanation only. The experiments of this Part were planned in the hope of completing the explanation.

It was shown by the experiments with hydrogen alone, Part V (10), that preignition accompanied by firing back through the carburetor was due to ignition of the hydrogen-air mixture by finely divided carbon derived from the decomposition and oxidation of the lubricating oil, but starting with a clean engine some hours running was required for the necessary accumulation of carbon. On the other hand, the decomposition and oxidation of the lubricating oil did not yield finely divided carbon to the same extent when Toronto town gas was used as engine fuel, as noted in Part XIII (7). It

seemed that the engine would run for an indefinite period without preignition if a normal jacket temperature were maintained. Such a result, according to experience in practice, would be an impossibility if coke oven gas were used although the proportion of hydrogen in it is not substantially greater than in Toronto town gas. The gases differ mainly in respect of sulphur concentration. Toronto town gas is nearly free of hydrogen sulphide and contains organic sulphur in the extremely small concentration of 10 to 15 grains per 100 cu. ft., as mentioned in Part XIII (7), whereas the concentration in coke oven gas may be as great as several hundred grains per 100 cu. ft. and may extend to several thousand in refinery gases from sulphur crudes and in natural gases from sulphur bearing regions (13, p. 2362).

It appears, therefore, that hydrogen sulphide is the chief sulphur impurity in fuel gases. It is known that the substance promotes preignition, and the experiments of this Part were made to determine the extent and cause of the effect.

Experimental Arrangements and Results

The experimental arrangements were as described in Part XIII (7) plus means for adding hydrogen sulphide at a measured rate to the air-gas mixture. The hydrogen sulphide was obtained from the Matheson Co. in a high pressure steel cylinder from which it was drawn as required through a special pressure regulator. It was supplied at atmospheric pressure at the rate of 4.8 cu. ft. per hr. to the air-gas mixture used by the engine. The rate was the minimum that could be measured accurately by the available dry gas meter and is approximately 5.0% by volume of the rate of town gas required for maximum power.

The hydrogen sulphide was taken to have the higher calorific value of 630 B.t.u. per cu. ft. at 60° F. and 30 in. of mercury as given in works of reference. The lower calorific value was then 581 B.t.u. per cu. ft. in the standard conditions of temperature and pressure and was used for calculations of thermal efficiency.

The engine trials were run at 12 : 1 compression ratio, an engine speed of 900 r.p.m. and with the jacket coolant at 212° F. Although data were available for a trial made earlier when using town gas in the conditions mentioned, there was some uncertainty about the condition of surfaces in the combustion space, the engine not having been dismantled for cleaning since the beginning, some three months earlier, of the trials with town gas described in Part XIII (7). It was planned, therefore, to run a new trial with town gas, after cleaning the combustion space by means of a brush and scraper inserted through the spark plug and bouncing pin holes; a great deal of surface area could not be reached in this way. The trial was then to be followed by one with the addition of hydrogen sulphide to the gas-air mixture.

The trial with town gas alone was begun on Sept. 8, 1949, but was discontinued because dust from concrete work in progress nearby the engine induced

knocking combustion. A similar proknock effect had been obtained from concrete dust a year earlier when hydrogen was being used as the fuel for the same engine (9).

The work was resumed the next day, the dust concentration in the laboratory atmosphere having become normal, and the two trials were completed during the period 7 a.m. to 11 p.m. Measurements were made of brake and indicated horsepower and of rates of air and gas supply. Optimum spark advance as determined by prior experiments was always used. The experimental results are given by the graphs of Figs. 1 to 3.

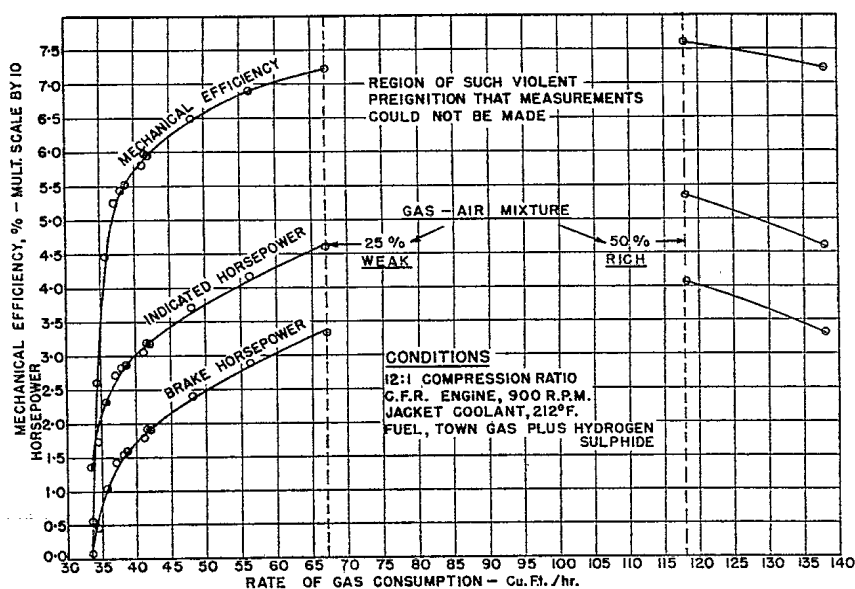


FIG. 1. Observed values of indicated horsepower and mechanical efficiency corresponding to rate of gas consumption.

Brake horsepower, indicated horsepower, and mechanical efficiency plotted on a base of rate of supply of town gas plus hydrogen sulphide are given by the graphs of Fig. 1. It will be noted that at rates of gas supply from 67 to 117 cu. ft. per hr. preignition was so violent that measurements of power could not be made, and it was unsafe to try to continue running the engine. Measurements were possible only at very weak or very rich gas-air mixtures as shown by the graphs.

Horsepower and mechanical efficiency measurements plotted on a base of air-to-gas ratio by volume and mixture strength percentages are shown by the graphs of Fig. 2. The value of the correct air-gas ratio shown on the figure as approximately 4.25 is the mean of values with and without hydrogen sulphide, which possesses a higher calorific value than the town gas. It will be noted that the mixture strength region over which operation of the engine

was prevented by preignition was from 25% weak to 50% rich. Preignition was pronounced even with the mixture 25% weak but was not sufficiently severe to prevent measurement.

It is not necessary to give in detail the results of the trial made when using town gas alone. They confirmed those obtained earlier in the same conditions which are shown by the graphs of Figs. 3 and 3, A, Part XIII (7), except

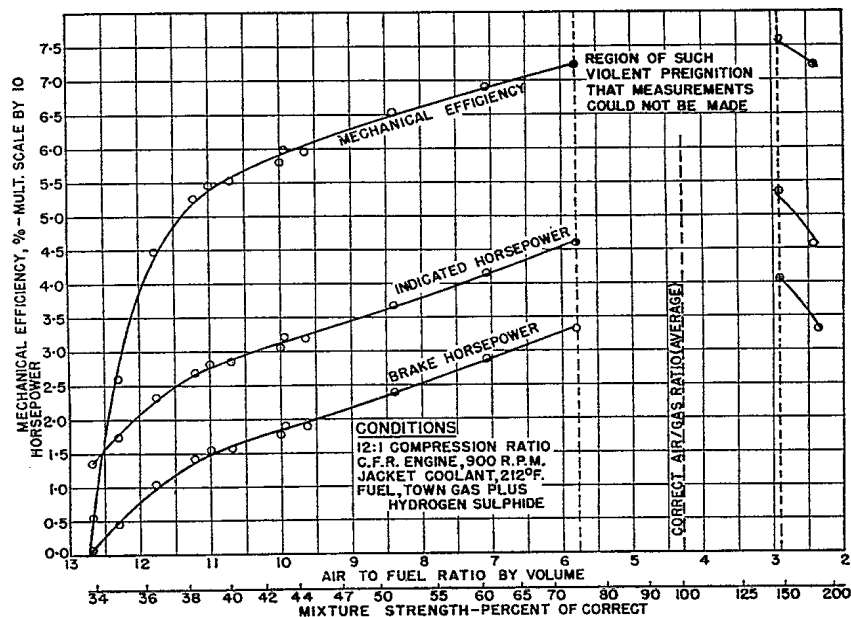


FIG. 2. Observed values of indicated horsepower and mechanical efficiency corresponding to air-to-gas ratio or percentage mixture strength.

that a slightly higher value of 43% was obtained for maximum indicated thermal efficiency as compared with the 42% of the earlier trial. The essential data for a comparison of the results of the two trials are given by the graphs of Fig. 3 for indicated thermal efficiencies plotted on a base of indicated mean effective pressure.

It will be seen by reference to the graphs that a maximum value of 44% was obtained for indicated thermal efficiency when the gas-air mixture contained hydrogen sulphide. This is an increase of 2.3% on the value obtained without hydrogen sulphide during the trial made earlier the same day and an increase of 4.8% on the value obtained for the trial described in Part XIII (7) when using a jacket coolant at 212° F. Maximum indicated thermal efficiency was obtained at about half power with a gas-air mixture 50% weak. On going to still weaker mixtures the value was progressively less affected by the hydrogen sulphide.

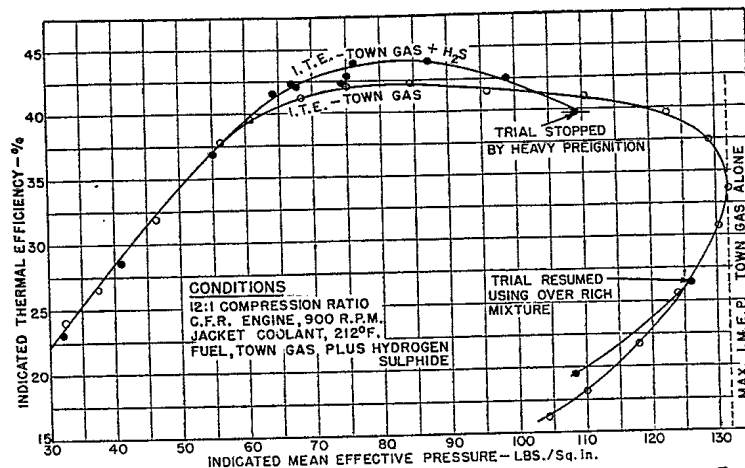


FIG. 3. Relation between indicated thermal efficiency and indicated mean effective pressure with and without hydrogen sulphide in gas-air mixture.

Preignition developed almost immediately on going to richer mixtures. Thermal efficiency diminished at a relatively high rate and preignition became so violent when values of the I.M.E.P. exceeded 109 lb. per sq. in. that measurements could not be made. The mixture strength was then increased to be 50% rich. Preignition did not occur and measurements could again be made.

The Residual Sulphur Effect

The experiments made with sulphur added to liquid fuels, described in Part III (5), disclosed the existence of a marked residual effect. It persisted even after the usual thorough cleaning of the combustion chamber surfaces with the engine dismantled and caused knocking combustion even when benzene was used at moderate compression ratios. The knocking combustion did not stop until after the engine had again been dismantled and the combustion chamber surfaces given a second and more drastic cleaning.

It was expected accordingly that a similar residual effect might exist after using town gas plus hydrogen sulphide even for the relatively short time of about five hours taken for the experiments described in this Part. The existence of the effect was verified by experiments. The engine was then dismantled and the combustion chamber surfaces drastically cleaned, special attention being given to the piston crown and the exhaust valve. Some residual effect was observed on again using the engine, and a period of 70 hr. running on a weak pentane-air mixture was required before the standard knock intensity corresponding to a particular octane-heptane mixture was regained.

Discussion

It was shown by experiments described in Part III (5, pp. 137-139) that a pentane-air mixture in combining proportions, passing through a red hot, 670° C., 1238° F., steel combustion tube would not ignite and explode because

of the reduction of its inflammability by dilution with the steam and carbon dioxide formed by surface oxidation. If, however, hydrogen sulphide were added to the pentane-air mixture, ignition and explosion occurred at 580°C ., a temperature corresponding to less than a dull red heat. It is well known that in the circumstances the effect of the hydrogen sulphide is to convert the surface of the steel tube to iron sulphide which is inactive to oxidize hydrocarbons to steam and carbon dioxide or hydrogen to steam.

It was shown further by experiments described in the reference quoted that the surface effect to inhibit oxidation to steam and carbon dioxide remained when the hydrogen sulphide was no longer added to the pentane-air mixture, explosion then occurring at a temperature 10°C . only higher than when the hydrogen sulphide was present in the mixture. The residual effect supports the view that neither the inhibitory action of hydrogen sulphide on the reaction to steam and carbon dioxide nor the reaction itself is other than a surface effect. Furthermore, it may be concluded that the degree of the inhibitory effect depends on time of exposure of the steel surface to the action of hydrogen sulphide as well as to the concentration of that "catalytic poison" in the combustible mixture.

The effect of steam formed by the oxidation of *hydrogen* in mixtures with air, on a surface of iron oxide to raise the ignition temperature, is shown by experiments also described in Part III (5, p. 128). Thus on passing the mixture through a silica tube, rate of oxidation of the hydrogen to steam was just measurable at 550°C . and explosion occurred at 587°C . When, however, the surface of the tube became partly coated with iron oxide, the hydrogen oxidized to steam with great rapidity and a temperature of 667°C . was required for ignition.

It will be noted that the igniting temperature of 587°C . for hydrogen in contact with an inactive silica surface is nearly the same as that of 590°C . for a pentane-air mixture on a steel surface made inactive by the poisoning effect of hydrogen sulphide.

The effect of surface reactions occurring when town gas is used in an engine can now be described. The principal constituents of the gas are hydrogen, carbon monoxide, and methane, and in the Toronto variety the approximate percentage concentrations are 50, 22, and 12 respectively. The average igniting temperatures of the gases in mixtures with air, given by Coward (3) as having been determined by H. B. Dixon when using a combustion tube having an inactive, porcelain, surface are, hydrogen 585°C ., carbon monoxide 650°C ., and methane 700°C . Therefore hydrogen, having the lowest surface ignition temperature and forming by far the largest constituent of town gas, would be expected to be responsible for preignition when it occurs in gas engines, a view in accordance with statements made in textbooks. The view is correct solely if the surfaces in the combustion space are *inactive* to oxidize the hydrogen to steam. *Active* surfaces can be raised to temperatures

higher than a red heat without igniting hydrogen-air mixtures in contact with them as illustrated by the graphs of Fig. 4. The graphs give the igniting temperatures for hydrogen-air mixtures passing through silica and stainless steel combustion tubes and are selected from experimental results obtained by King and Mole (8). Ignition occurred in the silica tube at a temperature as low as 565° C. It was not greatly affected by the concentration of hydrogen in the mixture which in the conditions was inflammable for contractions varying from 5 to 90%. The minimum igniting temperature of the mixture in contact with the steel surface was 630° and mixtures containing hydrogen in concentrations less than 20% or greater than 30% could not be ignited even at the measurable maximum of 750°C.

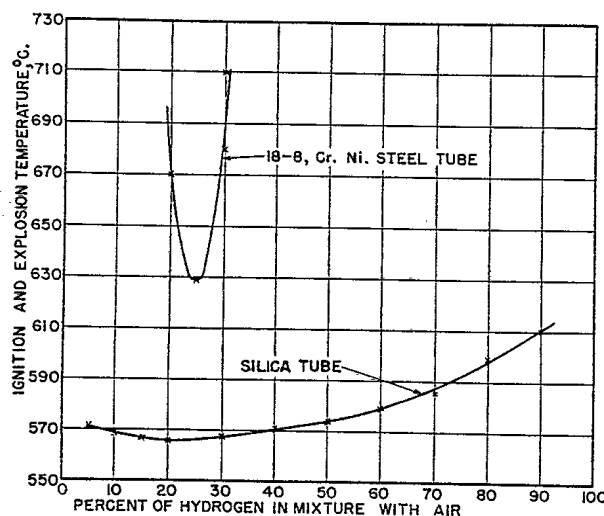


FIG. 4. Igniting temperatures and range of inflammability of hydrogen-air mixtures passing through open combustion tubes 1 in. internal diameter. Mixtures supplied at the rate of 150 cc. per min.

The conclusion is that the hydrogen constituent of a fuel gas is of useful effect to prevent preignition but of evil effect if the combustion chamber surfaces are such that oxidation thereon of the gas to steam cannot occur. Initially clean steel or iron surfaces in the combustion space become coated with metallic oxide almost immediately on running the engine under power. Steam is formed on the reduction of the oxide by the hydrogen, and compression ratio can be raised to values even higher than the 12 : 1 used for the trials of this Part, without the occurrence of preignition or detonation. The steam not only prevents preignition by hot surfaces but by reducing the inflammability of the end gas counteracts the igniting effect of finely divided carbon derived from pyrolysis of the lubricating oil to promote detonation. The steam forming reaction is continuous because in equilibrium conditions the rate of reduction of the oxide by hydrogen is equal to the rate of oxide formation by the oxygen in the gas-air mixture. The evil effect of hydrogen

becomes apparent when the surface reaction to form steam is inhibited by hydrogen sulphide because the surface ignition temperature of hydrogen then becomes lower than that of the other gases present in appreciable proportion in town gas.

All of the above mentioned effects are exemplified by the experiments of this Part made with combustion chamber surface temperature rising from that corresponding to zero brake horsepower to that attained at maximum power and then decreasing as power decreases with the use of overrich mixtures. Refer now to Fig. 3, and follow the graphs beginning with the minimum I.M.E.P. of 30 lb. per sq. in. for which brake horsepower is zero. It will be seen that indicated thermal efficiency values remain the same with and without hydrogen sulphide in the gaseous mixture until I.M.E.P. exceeds 60 lb. per sq. in. That is, the heat developed over the low power range is insufficient to raise surface temperature to the degree required for the oxidation of hydrogen to steam at an appreciable rate. There is then no reaction to be inhibited by the hydrogen sulphide and it provides merely part of the heat value of the combustible mixture, taken into account in calculating thermal efficiency.

The graphs diverge at the surface temperature attained when power exceeds 60 lb. per sq. in. I.M.E.P., indicating that rate of surface oxidation of the hydrogen to steam has become appreciable because thermal efficiency rises when the reaction is inhibited by the poisoning effect of the hydrogen sulphide.

The maximum value of the thermal efficiency attained on inhibiting the steam forming reaction is 44% as compared with the average maximum of 42.5% obtained otherwise. The maximum values were however always obtained for mixtures 50% weak and at corresponding surface temperatures. On using richer mixtures to increase power and consequently surface temperature, preignition became noticeable for the mixtures containing hydrogen sulphide and so heavy when I.M.E.P. exceeded 109 lb. per sq. in. that it was necessary to stop the engine. It was possible, however, to resume the trial at the lower surface temperature corresponding to a mixture 50% rich and to obtain then a slight increase of indicated thermal efficiency with hydrogen sulphide in the gaseous mixture, presumably because then the beneficial effect of inhibiting steam formation can be realized without the incidence of preignition, just as occurred when weak mixtures were used.

Concluding Comment

The experiments of this Part and those of Parts XII (6) and XIII (7) demonstrate that the hydrogen content of fuel gas free of sulphur renders it possible to run a gas engine at Diesel engine compression ratios, but at the expense of some slight loss of possible thermal efficiency. Thus the maximum thermal efficiency obtained at 10 : 1 compression ratio, Part XII, was 41% which is 68.5% of the air standard value of 59.8%. The maximum value

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