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FLAME-PROPAGATION RATES IN AMMONIA–AIR COMBUSTION AT HIGH PRESSURE

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The reluctance of ammonia to be ignited easily and the necessity to advance the spark for optimum performance in combustion engines led to this investigation. Ionization gap techniques showed that long induction times and slow flame speed were both contributors to the observed phenomena.

The most important factor in determining combustion characteristics of ammonia was found to be the extent of predissociation prior to attempted ignition.

There was evidence from combustion gas analysis that NO^+ was the probable most abundant ion contributing to successful application of the ionization gap techniques, and that the NO^+ was probably produced in the pyrolysis of ammonia rather than by equilibrium reactions.

Introduction

This work is related to the proposed utilization of ammonia as an engine fuel.[1] Such an application is not new,[2] but little information is available for rational application in such an unusual way. In turn, the renewed interest results from a proposed emergency or specialized use of ammonia, which might be possible through successful development of means for synthesizing anhydrous ammonia in nuclear-powered energy depots.[3]

Experiences in the related investigation[1] showed how ammonia could be used successfully as a spark-ignition engine fuel, and the level of performance which results. Performance was very nearly that which was predicted theoretically. It was necessary, however, to advance the time of ignition as compared to hydrocarbon. Also, an increase in spark-discharge energy enhanced the capability for successful ignition of the mixture. The latter observations created the interest which resulted in the work reported here.

For successful engine operation at normal operating conditions and compression ratios, it was found necessary to either add a more reactive fuel than ammonia to the mixture or to decompose part of the ammonia to hydrogen and nitrogen. For this investigation, it was decided to decompose the ammonia partially before engine induction, thereby providing hydrogen as the pilot fuel in the mixture of gases. The minimum amount of hydrogen necessary varied with engine speed and compression ratio. Experience showed that 3% to 5% by weight of hydrogen in the fuel was a satisfactory concentration, requiring the corresponding dissociation of 17% to 28.3% of the ammonia.

Dissociation was accomplished by directing the ammonia through a high-temperature (400°C) iron oxide catalyst chamber. By contrast to a simple addition of hydrogen gas to the fuel stream (or even hydrogen and nitrogen), the procedure adopted inherently retained—and in a simple manner—the atomic ratios of the ammonia–air mixture itself.

Of course, it is obvious that combustion was not purely of ammonia, but of a mixture of ammonia and hydrogen. Furthermore, it is obvious that the ammonia undergoes further decomposition in the compression process. Thus, the concentration of hydrogen at the time of ignition may be somewhat greater than at induction. In addition, there are undoubtedly intermediate species from the thermal decomposition (which ammonia undergoes during compression) that are present, which enhance the ignition and the combustion process. The concentrations of these intermediate species were not determined, being beyond the scope of this investigation and difficult either to sample or to retain in frozen equilibrium. In any event, it is proposed that ammonia combustion in any system is successfully accomplished only when sufficient thermal or ignition energy is supplied, such that the ammonia becomes partly dissociated thereby. Thus, the predissociation of ammonia in this investigation is felt to be an entirely rational approach to the measurement of ammonia-combustion characteristics.

While this study is highly empirical, it does embody implicitly and explicitly a broad range of experimental parameters. Hopefully, the results will not only be applied directly but will also be useful in allowing others to confirm future analytical approaches relating to ignition and flame speeds in ammonia-air systems at high pressures and temperatures.

Experimental Equipment and Techniques

The principal objective of the study was to establish the combustion characteristics of ammonia in a spark-ignition engine, and to compare the results to a hydrocarbon fuel in the same system. Specific items of interest were flame-kernel-development time and the velocity of the fully developed flame. Ionization gap techniques were selected for the study. Other previous investigations[4–7] showed that the ionization gap method is relatively simple and reliable when hydrocarbon fuels were being studied.

It was suspected at the outset that some difficulty might be experienced in detecting ammonia–air flamefronts with ionization gap techniques. This was because of the relatively low temperatures, 2000° to 2500°K, and high pressures, 10 to 40 atm, involved. However, other investigators had identified NO^+ and NH_4^+ (Ref. 8) in ammonia–oxygen flames.

Even so, equilibrium calculation[9] showed that the maximum concentrations of NO to be expected at peak temperature and pressure should be between 500 and 5000 ppm. Further, application of the Saha equation[10] for ionized species indicated an order of 10^{-12} to 10^{-16} concentration of NO^+. Thus, there was not much hope anticipated for strong signals from ionization gaps as a means for detecting flamefronts. Contrary to expectation, and for reasons which are developed later, NO^+ is suspected to be the most abundant ion and that which was most responsible for the substantial ionization signals observed.

A standard CFR engine[11] was used for the experimental work. It was fitted with a seven-hole cylinder head, allowing the placement of five ionization gaps, a spark plug, and a pressure transducer. Champion N–8, 14-mm extended-reach spark plugs were used for the ionization gaps, due to their compatibility with the construction of the head. The ground electrodes were removed to avoid potential pre-ignition hot spots and to provide a symmetrical target for the approaching flamefront. Ion gap distance was 3 mm. A Champion UD–16 spark plug was used for ignition of hydrocarbons and an RJ11 for ammonia. Spark energies were on the order of 10^{-3} Joules. Figure 1 shows the configuration of the cylinder head.

The bore of the cylinder was 3.25 in. and the stroke 4.5 in. The resulting engine displacement was 37.4 in.^{3}. The engine was connected to a Sprague dynamometer. It was possible to hold the speed of the engine to ±2%.

Ammonia was maintained under equilibrium pressure in a constant-temperature bath, and withdrawn and metered in the vapor phase.

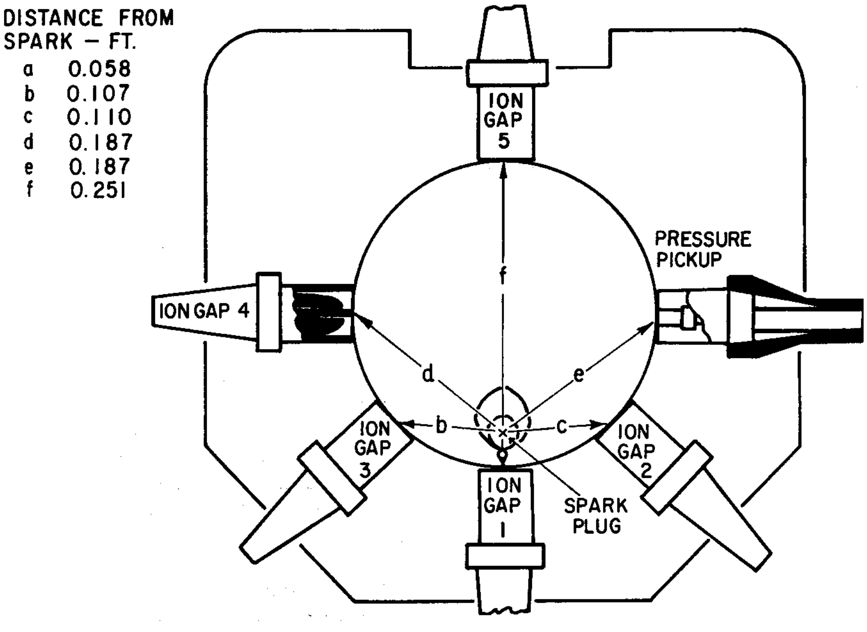

FIG. 1. Ionization gap location.

Iso-octane was used for comparison purposes and as a representative hydrocarbon fuel. Air was furnished from the laboratory compressed-air system, heated to 125°F for metering, and delivered to the engine at 100°F and a controlled manifold pressure, usually 1 atm. The engine cooling system was maintained at 154°F for the iso-octane runs (by the evaporation and condensation of methanol), and at 360°F for ammonia (using an ethylene glycol–water mixture). The elevated jacket temperature with ammonia aided in accomplishing successful combustion, probably as a consequence of the decomposition which took place on the hot iron surface during the compression process.

Simultaneous display was made of the ion gaps and pressure-pickup signals on a single multi-channel oscilloscope, and photographed for further analysis. Amplification and shaping of the ionization signals was considered, using a circuit developed by Dahm.[5] However, a lesser number of ion gaps and the availability of a multi-channel oscilloscope made this unnecessary for the purpose of identification, even though it might have clarified the display and eliminated a ragged ionization signal.

Because of the high-voltage potential imposed on the ionization gap (1200 V d.c.), it was not advisable to locate the oscilloscope input directly across the gap. The final circuit design allowed the input signal to be drawn off at a lower potential, across a resistance in parallel with the ionization gap. All five gaps were connected in parallel with respect to the 1200-V source.

A Kistler crystal pressure transducer (Type 601A) and Type S/N 1455 charge amplifier were used for the pressure history. A typical photographic record of the oscilloscope traces is shown in Fig. 2. A significant cycle-to-cycle variation in signal amplitude (Fig. 3) existed, as well as a difference in electrical output between the two fuels being studied. It was determined that iso-octane created approximately a threefold greater signal than ammonia under similar operating conditions.

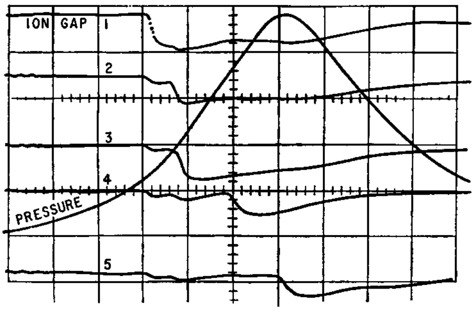

Fig. 2. Typical oscilloscope record.

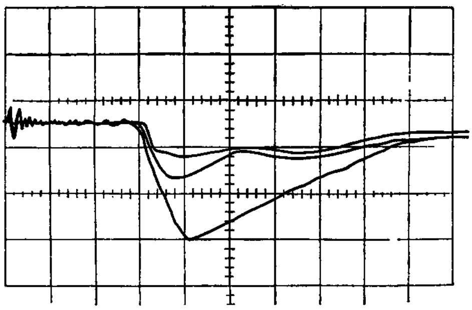

Fig. 3. Ionization signal cyclic variation.

Experimental Procedure

The controlled variables in this study were the air- and fuel-flow rates, compression ratio, speed, manifold pressure, and amount of ammonia dissociated. Gas chromatography was used to determine hydrogen concentration. For each set of conditions, ten single-sweep records were taken of the five ionization signals and the one pressure display. Noise was sometimes encountered within the first graduation. This was a result of spark discharge, which initiated the sweep. Some of the ionization signals also can be seen in Fig. 2 to reflect responses from other channels. This is easily interpreted, however, since the signal due to ionization was of much greater intensity.

Data Treatment

Because of the cycle-to-cycle variation in pressure and flame travel, statistical methods were enlisted. As indicated, ten representative pictures for each operating point were used in this process. This number was principally determined by the time and effort involved in reading.

The pictures were read on a Lehner–Benson Oscar N-2 analyzer, which printed directly onto IBM cards the coordinate points from magnified oscilloscope photographs. A computer program was formulated to treat the flamefront data statistically and produce results appropriate to the propagation study. The card output of the Oscar greatly facilitated the computer data reduction process. More than 80 engine conditions were investigated and 1100 oscilloscope records treated.

Interpretation of the Results

Flame Speed

Typical results obtained from a single operating condition and the ten recorded sets of statistically treated data showed that the flamefront, as indicated by the ionization gaps, proceeds linearly with time, after the initial period of induction or kernel development.

Kernel Development

If the flame history is extrapolated to zero distance, a finite time intercept would be indicated. In previous[4,5,7] as well as this study, it was observed that the time of flamefront arrival at the first ionization gap did not align with the arrival time at those further distant. This was interpreted as an indication that the reaction was not yet fully developed at this first gap. Arbitrarily, therefore, it was decided that the kernel-development time should be taken as that time when the reaction front passed the 0.05-ft (or 15.25-mm) point. This is graphically illustrated in Fig. 4.

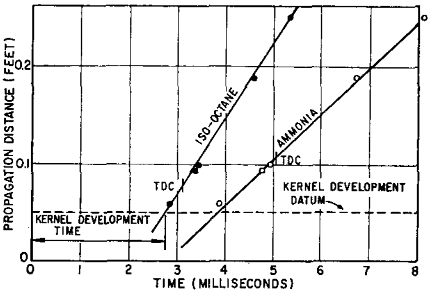

FIG. 4. Reduced data interpretation.

This arbitrary choice of a "datum" distance for interpretation of the establishment of a fully developed reaction in no way changes the relative values to be reported. It was decided that this was the only rational way to treat the data, in view of cycle-to-cycle variability in kernel-development time and the necessity for statistical treatment of the data.

Experimental Results and Discussion

Figure 4 is typical of comparative reduced data for ammonia and iso-octane at one operating condition. The fully developed reaction not only takes more time to become established, but also travels more slowly with ammonia than with iso-octane.

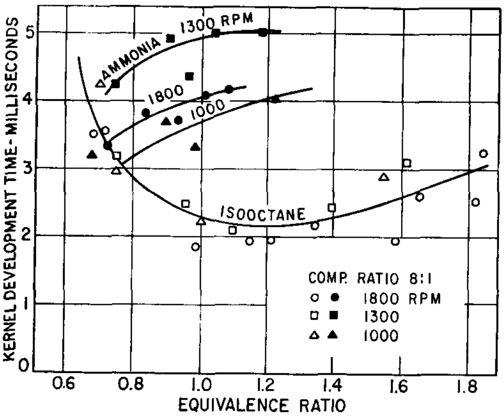

FIG. 5. Influence on engine speed on flame development.

It was possible, both with ammonia and iso-octane, to obtain regular and continuous relationships between flame-propagation rate and such variables as equivalence ratio, compression ratio, engine speed, and extent of ammonia predecomposition. Unfortunately, such was not always the case for kernel-development time.

Flame-Kernel-Development Time

With ammonia, there seemed to be anomalies in the relationship between the time until development of the fully established flames and most other variables (except for hydrogen concentration in the fuel–air mixture). As is shown, this is generally contrary to experience with hydrocarbons, where the correlations are more regular and consistent. Figures 5, 6, and 7 illustrate these observations.

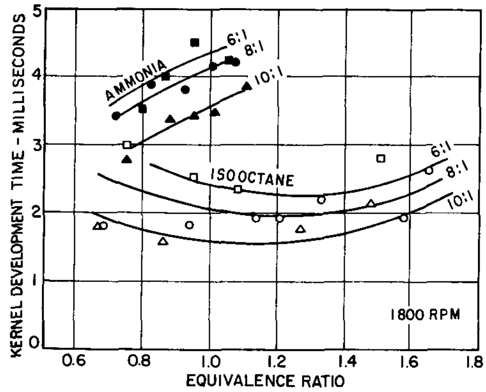

FIG. 6. Effect of compression ratio on flame development.

Figure 5 presents the effect of engine speed on kernel-development time. It can be seen that the data for ammonia are beyond simple interpretation with respect to the influence of speed. The iso-octane results, by contrast, can be related reasonably well by one simple line. There is no question, however, that the kernel-development time for ammonia combustion is always greater than that for iso-octane in the range of realistic mixture strengths (0.8 to 1.0 equivalence ratio for ammonia and 0.8 to 1.4 for iso-octane).

Figure 6 shows a more-regular relationship between compression ratio and the time for establishment of a fully developed flame in ammonia. The results can be explained by the influence which the change in compression ratio has on dissociation of the ammonia during the compression process. This is in accordance with all other observations made in this work with respect to the ignition of ammonia.

Figure 7 illustrates how strongly kernel-development time depends upon the extent to which the ammonia has been decomposed prior to engine entry. Ammonia decomposition was only regulated reasonably well enough to yield a concentration of between 3% and 5% by weight of hydrogen in the data points shown on Figs. 5 and 6. This helps to explain the scatter in those two representations.

Of course, the hydrogen concentrations indicated in Figs. 5, 6, and 7 are those at introduction to the engine and, thus, the start of the compression process. With the increase in temperature occurring during the compression process, further decomposition undoubtedly occurs. As an example, for the condition shown in Fig. 7, 1800 rpm and a compression ratio of 8:1, the pressure increases to about 12 atm and the temperature to about 500°F in the 11 msec before spark ignition. Even further compression takes place during the kernel development time. Thus, there can be a higher concentration of hydrogen (and of other species resulting from the decomposition of ammonia) not only at the time of ignition, but even more so at the time the fully developed flame is established.

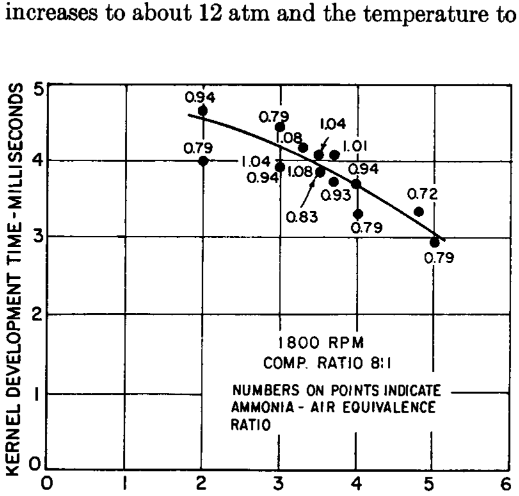

FIG. 7. Dependence of flame development on ammonia predissociation.

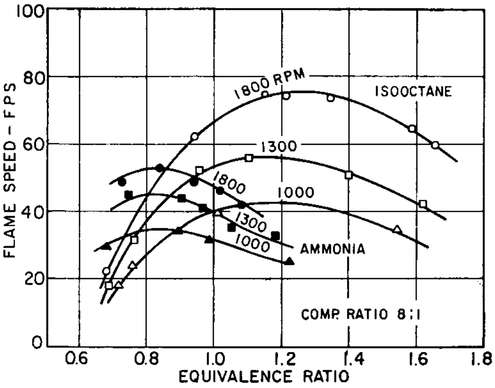

FIG. 8. Influence of engine speed on flame speed.

In the course of the investigation, it was noted that an increase in the compression ratio, cylinder-wall and intake-charge temperatures, or a decrease in the engine speed, facilitated ignition. This was interpreted as evidence that dissociation was taking place during the compression process and was enhancing the initiation of the reaction. At the time of this writing, no attempt had as yet been made to determine the further extent of dissociation, or the species which may be produced intermediately in this process of ammonia decomposition to hydrogen and nitrogen. These are items which are scheduled for near-future research.

It must be pointed out that the extent of ammonia decomposition, or hydrogen concentration, is even more important up to that amount (above 3%) that permits positive establishment of the flame. Beyond that amount, the influence of further decomposition is still significant, both with respect to kernel-development time and flame speed. However, excessive decomposition can lead to combustion difficulties, due to the resulting hydrogen-rich mixture.

Flame Speed

Influence of Engine Speed

Figure 8 shows how flame speed is influenced by mixture strength and engine speed. The

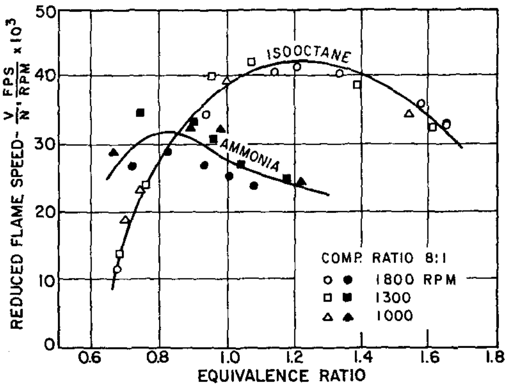

Fig. 9. Flame-speed correlation.

equivalence-ratio ranges investigated were limited by misfire for iso-octane and power loss for ammonia. The data for iso-octane are characteristic for hydrocarbons. The influence of engine speed shown in Fig. 8 can generally be attributed to a corresponding change in mixture turbulence, as is shown here.

Figure 8 also illustrates implicitly the comparative flame speeds for ammonia and iso-octane. Note that maximum flame-propagation rates for ammonia occur at about a 20% lean mixture. For hydrocarbons, as exemplified by iso-octane, the maximum flame speed takes place at about a 20% rich mixture. The maximum flame speed for ammonia at any given engine speed was always less than that experienced with iso-octane. The comparable flame speeds for ammonia were 70% to 80% of that for iso-octane.

The data plotted in Fig. 8 were subjected to the simple relationship of Damkohler,[12] in the form

$$V = f\,(\mathrm{Re}),$$

where V is turbulent fleme speed and Re is Reynolds number. Since the only effect on Reynolds number that results from engine speed change should be speed, *per se*, the flame speeds of Fig. 8 were divided by respective engine speeds and replotted as shown in Fig. 9. The correlation for iso-octane is obviously quite good, while that for ammonia shows more scatter. The 1000- and 1300-rpm data seem to fall close to the same line, but the 1800-rpm data are significantly lower.

The reason for this particular lack of correlation is again most likely associated with the decomposition reactions which the ammonia undergoes during the precombustion process. The time available for, and thus the extent of, decomposition undoubtedly also decrease as engine speed is increased. It is only logical to assume that the products of ammonia decomposition—whether hydrogen, as such, or intermediate species—should enhance flame speed.

It was previously pointed out in Fig. 7 that the influence of ammonia predissociation, measured as hydrogen, was greater at lean than rich mixtures. The same appears to be true in Fig. 9, where rich-mixture data correlate better than lean.

Effect of Compression Ratio

Figure 10 shows how flame speed is influenced by compression ratio at 1800-rpm engine speed. Exhibited, among other factors, are the concurrent effects of changes in mixture temperature and density, turbulence, dilution fraction remaining in the cylinder, and extent of precombustion reaction which accompany changes in compression ratio. All of the factors taken together result in an increase in ammonia flame speed of about 30% for a change in compression ratio from 6:1 to 10:1. For iso-octane, the change in flame speed is correspondingly about 25%.

Influence of Induction Pressure

A simple determination was made of the effect of mixture density on flame speed. This was done by reducing the mixture-supply pressure by about one-third, from 30 to 21 in. Hg (abs.). It was rationalized that this should produce an approximately corresponding influence on pressure histories in the cylinder. The results are shown in Fig. 11.

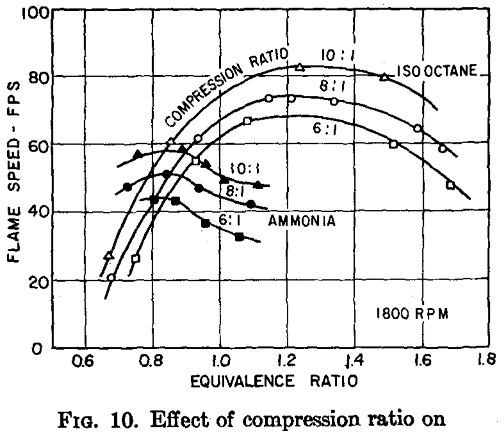

Fig. 10. Effect of compression ratio on flame speed.

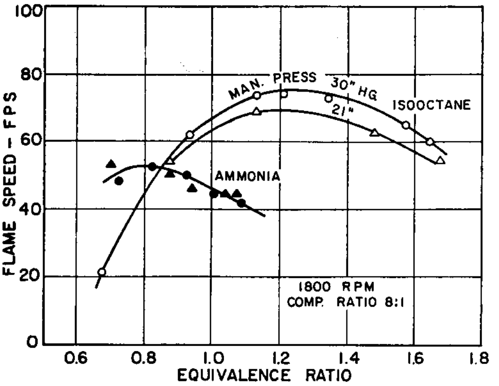

FIG. 11. Influence of pressure level on flame speed.

The influence of this change in pressure level was less than the normal data dispersion for ammonia, but it did result in a corresponding change of 12% flame speed for iso-octane. If there was an influence of pressure level on ammonia flame speed, it was much less than that effected by any of the other variables investigated.

Identification of Nitric Oxide

A companion investigation to that reported here was concerned with exhaust-gas composition when burning ammonia. Typical results are shown in Fig. 12. The concentrations labeled "Equilibrium at Peak Temperature" were calculated by utilization of measured pressures and inference of temperature from the other known state properties. The exhaust concentrations were measured by an ultraviolet absorption technique.[13]

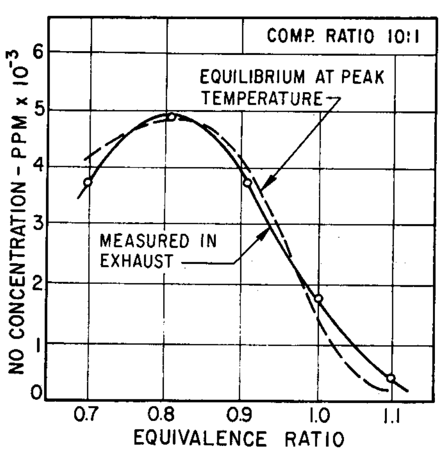

FIG. 12. Observed nitric oxide concentration and prediction from frozen equilibrium.

It can be observed that NO concentration at equivalence ratios greater than 0.8 were equal to or exceeded those calculated for peak temperature equilibrium. Obviously, the concentrations were even more disproportionately high, when compared to equilibrium at exhaust temperature.

It was to be expected that concentrations of nitric oxide found in the exhaust would be greater than those calculated for equilibrium at exhaust temperature. This reflects previous experience with hydrocarbon combustion and the demonstrated failure for the kinetics of the NO decomposition to follow rapid expansion processes.[14] However, the data presented in Fig. 12 implies that there must be another factor in addition to the kinetics of the NO-decomposition process. The super-equilibrium concentration encountered indicates that the NO is being generated by other mechanisms than equilibrium. In view of this observation, and of the unexpectedly strong ionization experienced in the study presented here, it is suggested that the NO is produced principally as a consequence of ammonia flame reactions. This corresponds to the observation of De Jaegere, Deckers, and van Tiggelen.[8]

Conclusions

1. Ammonia is characterized by a flame propagation rate about 30% slower, and an average kernel-development time 40% longer than for iso-octane.
2. The extent to which ammonia is decomposed prior to ignition is the most important variable in determining successful ignition, flame-development time, and flame speed. At the start of compression, 3% to 5% by weight of hydrogen seems to be the lower limit for reliable ignition at representative compression ratios.
3. Flame speed and engine speed correlate very well for iso-octane, but only reasonably well for ammonia.
4. An increase in compression ratio from 6:1 to 10:1 increased maximum flame speed of iso-octane about 25%, but that of ammonia 30%.
5. A decrease in pressure reduced the flame speed of iso-octane slightly. For ammonia, however, the flame speed appeared uneffected.
6. Slower flame propagation and longer time for development both are responsible for the necessity to advance the spark for ammonia over that required for iso-octane.
7. NO^+, probably formed in the combustion

reaction, would account for the ionization signals and the relatively high concentrations of NO found in the exhaust gas when burning ammonia.

ACKNOWLEDGMENTS

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COMMENTS

Mr. M. L. Brown (Caterpillar Tractor Company, Peoria): In the calculation of the peak concentration of nitrogen oxide in the cycle, was an attempt made to estimate a time peak temperature or merely a maximum mass average temperature? This could be important because the gas temperature in spark-ignition engines is far from homogeneous. The part of the fuel–air mixture that is first burned is compressed after burning, and at the peak pressure point these initial products are much hotter than the calculated maximum mass average temperature. This is the most likely reason for nitrogen oxide concentration greater than the theoretical maximum.

Prof. E. S. Starkman: Mr. Brown's comment regarding nonhomogeneity of temperature is important and well taken. The nitric oxide concentrations in this work were calculated on the basis of a mass average temperature. Thus, there is no reflection of concentration gradients resulting from peak temperature variations with respect to position and time. The influence of such variations on the calculated concentrations of nitric oxide would, of course, depend on the magnitude of the temperature variation, the character of the variation, and the influence of temperature on concentration. Obviously, this is beyond the limit of the presently available instrumentation for sensing combustion temperatures and was not attempted.

◆

Dr. J. L. Lauer (Sun Oil Company): Have the authors corrected the data showing trends with compression ratio for the increase in surface-to-volume ratio in the combustion chamber? As this latter ratio increases, more ammonia would be expected to dissociate catalytically, thereby increasing the hydrogen concentration, which exerts a very significant influence on the combustion process.

Prof. E. S. Starkman: It is impossible, at the present level of understanding of the ammonia decomposition process, to assess the separate effects of compression ratio and surface-to-volume ratio on the results obtained. However, the change in surface-to-volume ratio in the range under investigation is felt to be a relative minor factor in determining the experimental results.

◆

Mr. F. Verkamp (Allison Division, General Motors Corporation): What were the comparative analytical and experimental values for nitric oxide concentration in iso-octane and ammonia exhaust gases?

Prof. E. S. Starkman: For hydrocarbons, measured nitric oxide concentrations in this work usually approximated 50 per cent or more of the calculated peak temperature equilibrium value. For ammonia the concentration were more nearly 100 per cent.

◆

Mr. W. Cornelius (General Motors Research Laboratory): Information on the comparative rates of emission of oxides of nitrogen from a spark-ignited reciprocating engine when burning ammonia and gasoline was obtained on a spark-ignited single-cylinder engine at the General Motors Research Laboratories during 1963, while evaluating ammonia as an alternate fuel for certain military applications.[1]

During one phase of the study, exhaust-gas samples were collected while running the single-cylinder engine on ammonia at maximum power conditions and at several different engine speeds. A standard spectrophotometric procedure was used to determine the concentration of the oxides of nitrogen in each gas sample. It was found that the concentration of the oxides of nitrogen increased with increasing indicated thermal efficiency of the engine and ranged from a concentration of about 200 ppm for a thermal efficiency of 15 per cent to 1200 ppm for a thermal efficiency of 30 per cent. If gasoline were to be burned in the engine at similar operating conditions, similar concentrations of oxides of nitrogen in the engine exhaust gas would be expected.

This single-cylinder engine had a displacement of 27 cubic inches and was run at a nominal compression ratio of 9.4:1 when these measurements were made. A conventional automotive-type ignition system and a special fuel–air mixing chamber to insure adequate mixing of gaseous ammonia and air were employed.

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