Preprint
UCRL-JC-137099

The Inevitability of Engine-Out Nox Emissions from Spark-Ignition and Diesel Engines

P.F. Flynn, G.L. Hunter, L.A. Farrell, R.P. Durrett, O.C. Akinyemi, C.K. Westbrook, W.J. Pitz

This article was submitted to Twenty Eighth International Symposium on Combustion, Edinburgh, Scotland, July 30 – August 4, 2000

U.S. Department of Energy

Lawrence Livermore National Laboratory

January 11, 2000

Approved for public release; further dissemination unlimited

Introduction

Internal combustion engines, both spark ignition and Diesel, are dominant types of vehicle power sources and also provide power for other important stationary applications. Overall, these engines are a central part of power generation in modern society. However, these engines, burning hydrocarbon fuels from natural gas to gasoline and Diesel fuel, are also responsible for a great deal of pollutant emissions to the environment, especially oxides of nitrogen (NO_x) and unburned hydrocarbons (UHC).

In recent years, pollutant species emissions from internal combustion engines have been the object of steadily more stringent limitations from various governmental agencies. Engine designers have responded by developing engines that reduce emissions to accommodate these tighter limitations. However, as these limits become ever more stringent, the ability of engine design modifications to meet those limits must be questioned.

Production of NO_x in internal combustion engines is primarily due to the high temperature extended Zeldovich reaction mechanism:

$$O + N_2 = NO + N \qquad (1)$$

$$N + O_2 = NO + O \qquad (2)$$

$$N + OH = NO + H \qquad (3)$$

The rates of these reactions become significant when combustion temperatures reach or exceed about 2000K. This large temperature dependence, characterized by large activation energies for the rates of the reactions listed here, is a direct result of the need to break apart the tightly bonded oxygen and nitrogen

molecules. The strongest bond is the triple bond in the $N \equiv N$ molecule, resulting in an activation energy of about 75 kcal/mole for Reaction (1), which is the principal cause for the large temperature dependence of the extended Zeldovich NO_x mechanism. In most engines, NO_x is therefore produced primarily in the high temperature combustion product gases. Using a reliable kinetic model for NO_x production such as the GRI Mechanism [1] or the Miller-Bowman model [2] with hydrocarbon products at temperatures from 1500K through 2500K, the amounts of NO_x produced at a given residence time in an engine can easily be computed, as shown in Figure 1. Figure 1 depicts how temperatures such as those existing in the combustion zones of heavy-duty engines would produce NO_x emissions. This figure was created assuming that a fuel/air equivalence ratio ϕ of 0.65 was used to heat the combustion air. This equivalence ratio would be similar to that of a heavy-duty lean-burn spark-ignition or diesel engine. At temperatures in the neighborhood of 2000K and residence times between 1-5 milliseconds, which are typical of residence times at these temperatures in engines, the production of NO_x increases dramatically. It is evident from Fig. 1 that product temperatures must remain below approximately 2100K to achieve extremely low NO_x production levels in engines. This conclusion led to a combined experimental and modeling study of product gas temperatures in engine combustion and their influence on emission levels.

Experimental results

A range of engine experiments in Diesel and spark-ignition engines were carried out over a number of years, studying the conditions that affect product temperatures.

Spark-ignition engine experiments

Two families of engine experiments were carried out under spark-ignition conditions to change the product gas temperatures at the end of combustion, measuring the levels of unburned hydrocarbons in the exhaust gases. Experiments were carried out for fuels including natural gas, propane, and indolene, with very similar qualitative results for all three fuels.

While exploring the limits for lean-burn spark-ignition combustion, the results portrayed in Figures 2 and 3 were encountered. These figures portray some critical attributes that must exist in order to have a reliable spark-ignition combustion process. The focus of these experiments was to determine how lean an engine could be operated so as to minimize NO_x production while still maintaining reasonable fuel economy. In addition to controlling the level of NO_x emissions, it was important to complete combustion and minimize exhaust unburned hydrocarbons. As fuel/air ratios were leaned or as combustion timing was retarded by delaying the spark, circumstances were encountered where unburned hydrocarbons rose drastically even though the engine continued to run steadily and NO_x emissions were being lowered. Since these tests were being performed with engines running on natural gas, which is difficult to

oxidize in the exhaust stream, it was decided to explore the fundamental makeup of this limit. The hypothesis was that flame propagation near the end of combustion was weakened in those cases with large unburned hydrocarbon emissions, and that weak flame propagation was due to inadequate temperature rise in those flame such that the chemical reactions could not be completed.

Figure 2 presents these circumstances. Plotted in this diagram are the unburned hydrocarbon emissions of the engine on a fuel-specific basis against the end-of-combustion flame temperatures. These are "engine-out" values prior to any aftertreatment. Note that at 100 g/kg, the unburned hydrocarbons represent 10% of the entire fuel in the engine. These end-of-combustion flame temperatures were deduced from flame temperature rise in the adiabatically compressed end gases at the a range of fuel/air ratios. The analysis was completed at 95% of total heat release.

This diagram shows that if the flame temperatures are allowed to fall too low during the combustion process, a very substantial fraction of the total fuel is not burned and the combustion process will not be completed. The limiting end-of-combustion flame temperature was determined to be approximately 1920K, as illustrated in Fig. 2. This was the first data in this study that suggested that there might be a possible temperature limit for the combustion of hydrocarbons inside engines.

Some years ago, Smith et al. [3] studied essentially the same problem of flame quenching in an expanding combustion chamber. At lean values of equivalence ratio ($\phi \sim 0.6$), they determined that when the combustion chamber had expanded to reduce the adiabatic flame temperature below about 1606K, the flame would be quenched. The pressure ranges for the experiments of Smith et

al. were only slightly greater than atmospheric and considerably lower than the approximately 50 atmospheres of the present study, indicating an increase in flame quenching temperature with increasing pressure. As noted below, Law and Egolfopoulos [4] computed a quench temperature of about 1460K at one atmosphere pressure, consistent with the present results. Smith et al. commented that bulk quenching became increasingly important as the ignition timing is retarded, also consistent with the evidence from the experiments described above. The same type of flame quenching phenomenon was observed by Quader [5], with a similar explanation.

These experiments show that engine expansion leads to a condition in which the product temperature falls below a critical value, effectively quenching further combustion, and that all the fuel remaining unburned at this time would be observed as UHC emissions. At lower values of the equivalence ratio, the flame speed is further reduced and combustion takes even longer to complete, so a smaller amount of expansion and cooling is needed to extinguish the flame.

On exploring the circumstances portrayed in Fig. 2 in more detail, it was concluded that if such a minimum temperature limit did exist, its ramifications would be observable under other kinds of circumstances. If 1920K is a real minimum temperature for flame propagation, it ought to be impossible to start a flame before circumstances were created that would give a flame temperature above 1920K.

Figure 3 depicts the results of a series of experiments designed to test this premise. In these experiments, a variety of typical and high energy ignition systems were installed on an engine with spark timings set at unrealistic advanced circumstances. Again, the focus of the experiments was to see if there

was a discernable limit in terms of flame temperatures required for combustion to be initiated. The "burned zone" temperature was determined by adding the adiabatic flame temperature rise for the existing equivalence ratio to the adiabatically compressed end gas temperature when the first significant heat release was observed.

As indicated in Fig. 3, no flames were observed with a post-reaction burned zone temperature less than about 1920K. These experiments were run with several ignition systems. One of the peculiar circumstances observed was that with very high energy ignition systems and very early spark timings, the spark could be set off early under circumstances such that flame propagation did not occur immediately; however, flame propagation would then be initiated later in the compression stroke once the lean reactants had been compressed to the point where the burned zone temperature had reached the 1920K threshold. That is, the total heat release and associated temperature increase of the reactants hadn't changed, but now the gases had been compressed enough that the sum of the temperature rise from reaction and the temperature increase due to compression had reached 1920K. .

Similar circumstances were observed in engines running on propane, natural gas, and indolene. The limiting temperatures observed over this wide range in fuels have been nearly invariant. These observations are consistent with those of Badr [6], Hertzberg [7] and others. This similarity of quench temperature with different hydrocarbon fuels is evidently caused by the fact that the final energy release from any alkane hydrocarbon fuel comes from the oxidation of similar small fuel fragments.

Both series of spark-ignition engine studies provide a consistent picture of a flammability limit where the combustion temperature must exceed 1920K for flame propagation to be possible. The important new feature of the present study is that these results were all obtained at engine pressures considerably greater than atmospheric pressure, sometimes approaching 50 atmospheres.

Diesel engine experiments

Additional experiments to assess the operational characteristics of practical engines near limits of flammability were carried out in a conventional Diesel engine to which progressively more and more cooled exhaust gas recirculation (EGR) was added to the air intake manifold. The engine operated with 75 psi bmep and at constant fuel injection rate and injection timing.

The addition of inert diluent has several effects on combustion, including a gradually lower average temperature, longer duration of combustion, lower total heat release, lower NO_x production, and finally rapid rises in unburned hydrocarbons, CO and soot production. An attempt was made to determine if it was possible to interpret these results in a manner similar to those obtained above from the spark-ignition engine results.

In a Diesel engine, it is difficult to define a combustion temperature that is comparable to that in a premixed environment. In the Diesel, most of the combustion takes place in a diffusion flame where the temperature is considerably greater than elsewhere in the combustion chamber. Extracting the peak combustion temperatures from experimental data is dependent on modeling the diffusion flame as well as identifying a way to calibrate

experimental measurements from the combustion. For this study, experimental data on radiation from the Diesel flame, combined with a simple model of a diffusion flame [8], was used to compute a peak flame temperature for the interpretation of the engine data. However, the values for the flame temperatures computed in this way should be interpreted as only approximate, due to the many simplifications involved in the simple model.

The results of a complete series of nine experiments with varying EGR are shown in Figures 4 and 5, in which the fuel-specific NO_x production is plotted against peak flame temperature and brake-specific fuel consumption. As expected, the NO_x falls almost to zero as the peak flame temperature is decreased to about 2000K, but the fuel consumption increases rapidly as theNO_x is reduced. Although not shown in Fig. 5, the increases in fuel consumption for the last three, lowest NO_x points translated almost totally into increased soot and UHC emissions. Thus these experiments show that as the peak flame temperature in the Diesel engine falls below about 2150K and the NO_x levels continue to decrease, hydrocarbon and soot emissions grow very rapidly. These temperatures are not greatly different from the values developed above for spark-ignition combustion. It should not be expected that exactly the same critical flame temperature for premixed flame propagation should be the same as that for diffusion flames, and the estimation of the flame temperatures in theDiesel experiments are more uncertain than those in the spark-ignition engine. The main point is that both types of flame propagation seem to have

critical combustion temperatures that are reasonably similar and are quite close to temperatures where NO_x production would be expected to proceed at a significant rate.

All of these experimental results for spark-ignition and Diesel engine combustion were interpreted in terms of a flammability limit to combustion. In the next section, recent theoretical and modeling studies of lean flammability limits are used to examine these experimental results and their implications for pollutant emissions from these engines.

Lean flammability limits

Law and Egolfopoulos [4,9] studied the lean limit of flame propagation for laminar flames of hydrogen, mixtures of hydrogen and CO, and a variety of small hydrocarbon species in air at atmospheric pressure and room temperature. They found that this limit was characterized by a competition between the primary chain branching reaction

$$H + O_2 = O + OH \qquad (1)$$

and the related reaction

$$H + O_2 + M = HO_2 + M \qquad (2)$$

At lean conditions approaching the flammability limit, reaction (2) not only suppresses chain branching, but it effectively provides chain termination, since the HO_2 produced then often reacts with OH

$$HO_2 + OH = H_2O + O_2 \qquad (3)$$

to make stable, unreactive species. Reaction (1) provides chain branching because it consumes one H atom radical and produces two new radical species. In contrast reaction (2) consumes the same H atom radical and produces one HO_2 radical, making it a chain propagation reaction. When reaction (3) follows reaction (2) the overall path consumes one radical and produces none, making it a chain termination sequence.

The rate expressions for reactions 1 and 2 are:

$$k_1 = 5 \times 10^{16} \; T^{-0.82} \; \exp(-16500/RT)$$

$$k_2 = 1.65 \times 10^{15} \exp(+1000/RT)$$

Because of the large difference in activation energies for these two reactions, the relative rate of the quenching reaction (2) will increase relative to the rate of reaction (1) as temperature is reduced. Flame temperatures decrease monotonically with decreasing equivalence ratios for lean fuel/air mixtures. Therefore, for laminar flames at atmospheric pressure, Law and Egolfopoulos showed that, as the equivalence ratio is decreased, reaction (2) steadily begins to compete with the chain branching reaction (1), and at the lean limit, the rate of reaction (2) actually equals the peak rate of reaction (1) in the flame. This occurs at an equivalence ratio of $\phi \cong 0.48 \pm 0.02$ for methane/air, in good agreement with experimental observations [10,11] that the lean limit is found at approximately $\phi = 0.5$. For even lower values of the equivalance ratio, the excess chain termination due to reaction (2) effectively quenches the flame. Law and Egolfopoulos also noted that at the lean limit of $\phi \cong 0.48 \pm 0.02$ the adiabatic flame temperature was about 1460K for methane/air at atmospheric pressure.

Approximately the same lean limit flame temperature was noted for other hydrocarbon fuels at atmospheric pressure, although the lean limit flame temperature for hydrogen/air was found to be about 1000K for hydrogen/air, also at atmospheric pressure. Law and Egolfopolous also noted that the lean limit flame temperature increased rapidly for flames with significant heat losses included in the model calculations.

We have repeated the same type of laminar flame calculations as those of Law and Egolfopoulos but at the compressed gas temperatures and pressures that we expect to see under engine conditions. Specifically, we selected conditions with pressure of 50 atm and corresponding unburned gas temperature of 650K. This is a slightly higher compression than most spark-ignition engine combustion and a moderately lower compression than most Diesel engine combustion, but it provides an illustrative set of conditions. We carried out model calculations for methane and propane; the experimental results suggest that results for other hydrocarbon fuels would be very similar.

A return to the discussion above of the rates of reactions (1) and (2) shows that reaction (1) is bimolecular while reaction (2) is termolecular, meaning that the rate of reaction (2) increases with pressure relative to the increase in the rate of reaction (1), at a constant temperature. Thus one would expect that at elevated pressure, reaction (2) will compete with reaction (1) at higher temperatures and correspondingly greater equivalence ratio. Calculations of laminar flames at elevated pressure were then carried out to test this assumption and to predict the magnitude of the effect of increased pressure on the lean limit.

The Chemkin laminar flame model was used to compute the flame speed and spatial variations in species concentrations and temperature through the

flame. A chemical kinetic reaction mechanism was used that had been developed for and tested by comparisons with a wide variety of experimental combustion data [12-14]. At 650K and 50 atm, using exactly the same basis for the properties of the lean flammability limit as used by Law and Egolfopoulos, we found that the peak rate of reaction (2) reached the rate of reaction (1) at the center of the flame when the equivalence ratio ϕ reached a value of about 0.6. At these conditions, the adiabatic flame temperature was about 1900K. Both of these values are subject to some uncertainty, depending on details of the chemical kinetic reaction mechanism, the specific rate expressions for reactions (1) and (2), and other details of the laminar flame model. However, the results clearly indicate that the lean flammability limit at elevated pressures occurs at an adiabatic flame temperature much higher than that at atmospheric pressure, and the flammability limit at elevated pressure can be associated with flame temperatures in the vicinity of 1900K.

These changes in the adiabatic flame temperature and the limiting equivalence ratio with pressure and temperature are shown to be directly related to the competition between the rates of reactions (1) and (2). The pressure dependence of the rate of reaction (2) makes it compete with the rate of reaction (1) at higher temperatures as the pressure is increased.

The rate of reaction (2) does not increase strictly proportionately with pressure over the pressure range from 1 to 50 atm. Like many such reactions, eventually increases in pressure are not fully reflected in an increased reaction rate. Kineticists refer to this effect as "pressure falloff" and results in a somewhat slower response of the reaction rate to pressure increase than might initially be expected. We have included the pressure dependent rate of reaction (2) due to

pressure falloff in our computations. If we had not included the falloff effects in the reaction rate, the changes in lean limit equivalence ratio and adiabatic flame temperature with pressure would have been even greater than those reported here.

The combination of the experimental observations and the computed lean limit laminar flame conditions show that at elevated pressures, the requirements of flame propagation ensure that adiabatic flame temperatures must exceed values that are of the order of 1900K or greater. In fact, if the flame temperatures at the beginning and end of combustion are equal or greater than 1900K, it is clear that during the remainder of the engine combustion cycle, temperatures will be considerably greater than 1900K for normal operation. Typical variations in temperatures during the combustion period suggest that maximum temperatures would be expected to be higher than the minimum values by about 300 – 400 K during the combustion period. At such temperatures, the rate of production of oxides of nitrogen (NO_x) will be significant, as shown in Fig. 1.

The implications of these computations are important. These computations have shown that if the adiabatic flame temperature of the combustible mixture is less than about 1920K at typical engine conditions, then the mixture will not burn. However, at and above such temperatures, the rate of NO_x production is significant and will lead unavoidably to appreciable production of NO_x. Modifications in combustion processes cannot reduce NO_x production below this level without serious misfire or other production of even more significant hydrocarbon emissions. Thus the engine designer is faced with

a choice. The only way to reduce NO_x emissions is to reduce flame temperatures below about 2000K, but that will result in significant emissions of unburned hydrocarbons. Consumption of the hydrocarbons requires temperatures high enough to lead to significant production of NO_x. If environmental regulations insist on NO_x emissions below some especially demanding level, the only way to respond would be to provide aftertreatment to reduce the resulting production of unburned hydrocarbons that is the inevitable result of the low combustion temperatures.

Conclusions

The chemical kinetic analysis and empirical results described in this paper clearly indicate that a limiting, minimum temperature exists for sustaining viable combustion for both lean-burn spark-ignition and diesel engine configurations presently used in heavy-duty applications. At the pressures typical of both spark-ignition and diesel engines (i.e., 50 – 100 bars), the limiting temperature is of the order of 1900K. Above this flame temperature, NO_x production is significant, while below this limit, huge emissions of unburned hydrocarbons are the result. This limiting temperature for combustion viability leads directly to a limit in the potential for in-cylinder NO_x reductions. Since regulators are proposing NO_x emissions levels significantly below these limiting in-cylinder values, all such regulations will force combinations of in-cylinder combustion

management plus the adoption of very effective, long lived NO_x and hydrocarbon removal engine aftertreatment systems. To date none of these aftertreatment systems has demonstrated the capabilities for high efficiency, long life and broad range operation that will be demanded in the future.

In the present work, engines were run under pathological conditions, far from normal operations, to see what characteristics were observed that might be common to limits of combustion. Spark ignition engines were operated under conditions where late spark and piston expansion produced flame quench. In addition, spark ignition engines were operated with too lean a mixture to complete combustion in time, and spark ignition engines were operated with too much spark advance before the mixture was flammable. Diesel engines were operated with too much EGR to maintain stable operation. For all of these problems, the one common feature was that all had 1900-1920K in common as the limit to flame propagation.

Both types of engines require that a flame must exist to convert fuel and oxidizer into combustion products, so they are constrained by the requirements for flammability. By examining the conditions for flammability, it was found that the high pressures encountered in conventional engine combustion chambers requires a flame temperature significantly higher than 1900K, where significant amounts of NO_x will inevitably be produced.

ACKNOWLEDGMENTS

This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

References

1. Bowman, C. T., Hanson, R. K., Davidson, D. F., Gardiner, Jr., W. C., Lissianski, V., Smith, G. P., Golden, D. M., Frenklach, M., and Goldenberg, M., *http://www.me.berkeley.edu/gri_mech/*,1995.
2. Miller, J. A., and Bowman, C. T., Prog. Energy Combust. Sci. 15, 287-338 (1989).
3. Smith, O. I., Sawyer, R. F., and Westbrook, C. K., Seventeenth Symposium (International) on Combustion, pp. 1305-1313, The Combustion Institute, Pittsburgh, 1978..
4. Law, C. K., and Egolfopoulos, F. N., Twenty-Fourth Symposium (International) on Combustion, pp. 137-144, The Combustion Institute, Pittsburgh, 1992.
5. Quader, A. A., "What Limits Lean Operation in Spark Ignition Engines: Flame Initiation or Propagation?" Society of Automotive Engineers publication SAE-760760, 1976.
6 O.A. Badr, N. Elsayed and G.A. Karim, Journal of Energy Resources Technology, Transactions of the ASME, Vol. 118, pp. 159-163 (1996).
7 Martin Hertzberg, The Flammability Limits of Gases, Vapors and Dusts: Theory and Experiment, Proceedings of the International Conference on Fuel-Air Explosions, University of Waterloo Press, Waterloo, Ontario (1982).
8. Primus, R. J., unpublished engine model, 1990.
9. Law, C. K., and Egolfopoulos, F. N., Twenty-Third Symposium (International) on Combustion, pp. 413-421, The Combustion Institute, Pittsburgh, 1990.

10. Andrews, G. E., and Bradley, D., **Combustion and Flame** 18, 133 (1972).

11. Coward, H. F., and Jones, G. W., "Limits of Flammability of Gases and Vapors", Bureau of Mines Bulletin 503 (1952).

12. Westbrook, C. K., and Pitz, W. J. **Combustion Science and Technology** 37, 117-152 (1984).

13. Curran, H. J., Gaffuri, P., Pitz, W. J., and Westbrook, C. K. **Combustion and Flame** 114, 149-177 (1998).

14. Curran, H.J., Pitz, W.J., Westbrook, C.K., Callahan, C.V., and Dryer, F.L., **Twenty-Seventh Symposium (International) on Combustion**, pp. 379-387, The Combustion Institute, Pittsburgh, 1998.

Figure captions

1. Computed production rates of NO_x at different residence times in a typical engine environment.
2. Hydrocarbon emissions as functions of flame temperatures, for spark ignition engines.
3. Correlation of flame temperature with spark timing, for spark ignition engines.
4. NO_x emissions as functions of peak flame temperatures.
5. Correlation of NO_x emissions with fuel consumption.

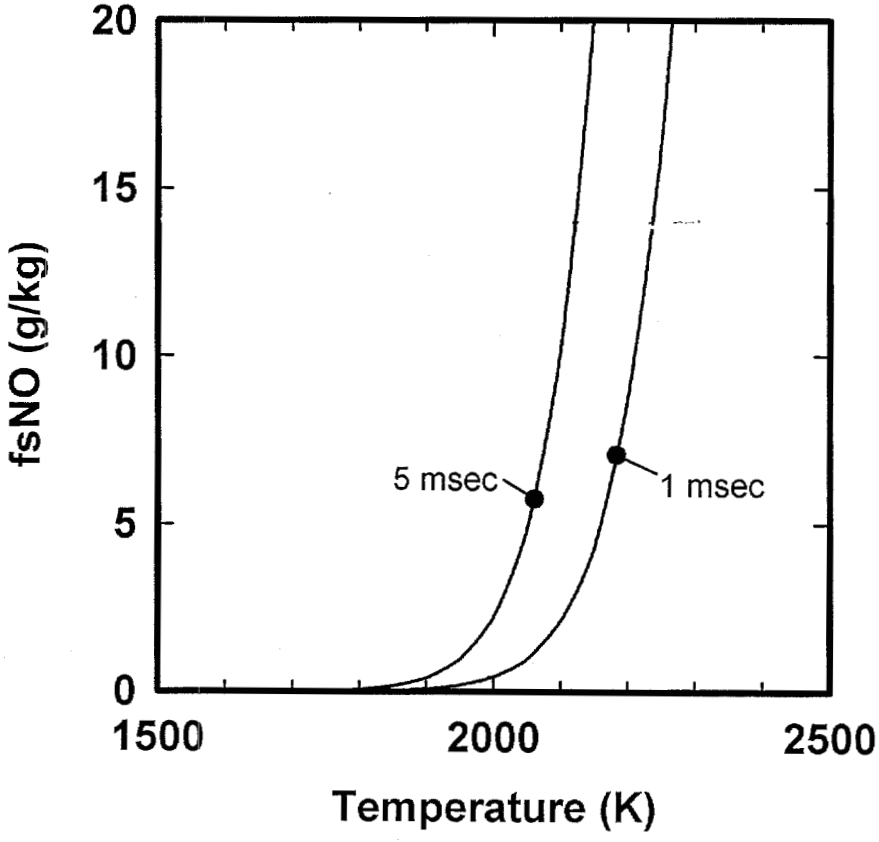

Fig 1

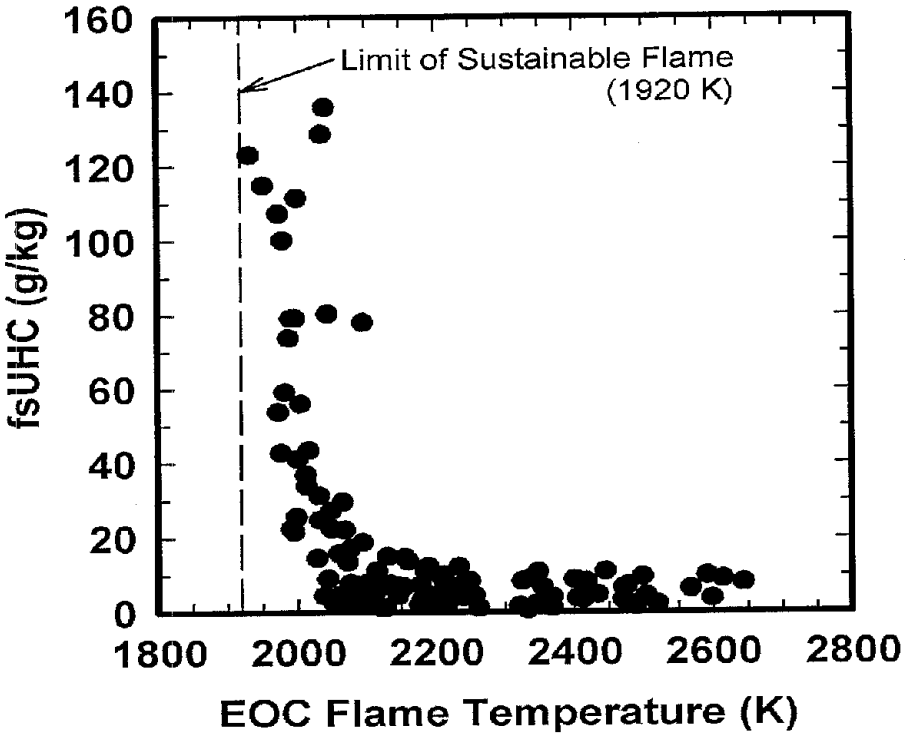
160
140
120
100
80
60
40
20
0
fsUHC (g/kg)
Limit of Sustainable Flame
(1920 K)
1800
2000
2200
2400
2600
2800
EOC Flame Temperature (K)

Fig 1

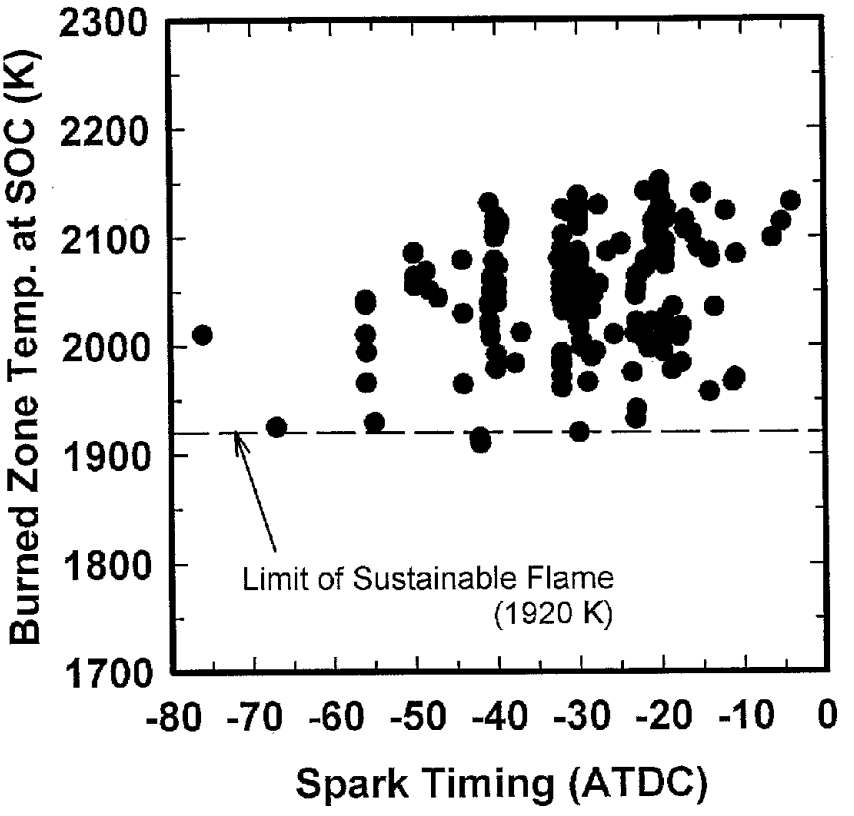
Burned Zone Temp. at SOC (K)
2300
2200
2100
2000
1900
1800
1700
-80
-70
-60
-50
-40
-30
-20
-10
0
Spark Timing (ATDC)
Limit of Sustainable Flame
(1920 K)

Fig. 3

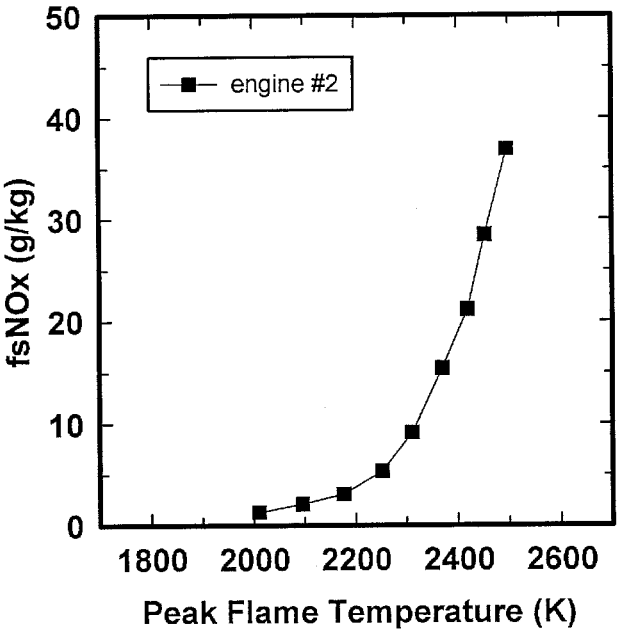
50
40
30
20
10
0
fsNOx (g/kg)
engine #2
1800
2000
2200
2400
2600
Peak Flame Temperature (K)

Fig 4

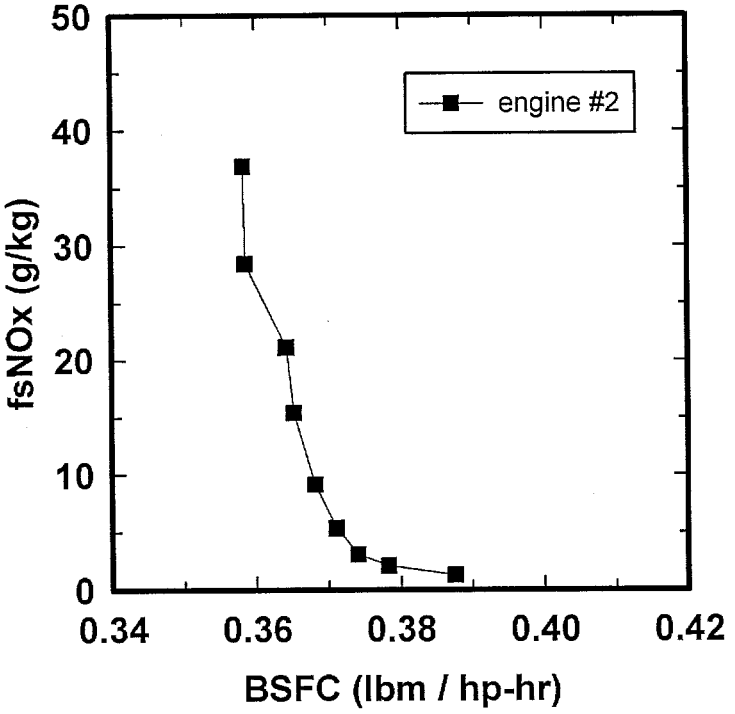
50
40
30
20
10
0
fsNOx (g/kg)
engine #2
0.34
0.36
0.38
0.40
0.42
BSFC (lbm / hp-hr)

Fig. 5