

The Function of Fuel Borne Metallic Catalysts in the Reduction of Thermal and Prompt NO_x In Exhausts of Natural Gas Fuel Engines

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We have observed a number of effects in the combustion of hydrocarbon fuels in reciprocating engines when metallic catalysts are added to the fuel. Some of these are:

- Reduced NO_x formation
- Reduced fuel consumption – or put another way, reduced carbon footprint
- Reduced particulate matter in exhaust gases

We have also observed the following:

- Iron and magnesium combinations perform better than iron alone
- Metallic catalysts perform better with a lubricity agent added when sulfur levels in the fuel are <1,000 ppm
- Extended life of engine oil
- Less knocking in compression ignited engines
- A time delay is generally observed in the action of the metallic catalyst for fuel savings but not for NO_x reduction
- The catalyst effect can be reduced by overdosing, i.e., there are optimal dosing levels for various fuels

We have seen these effects in all liquid hydrocarbon fuels from ASTM No. 1 naphtha (gasoline feedstock) to No. 6 residual oil. Some of these effects have also been observed in natural gas fuels. While these effects can be rationalized in heavier fuels such as residual oil, it is more difficult to explain in No. 1 naphtha and especially in natural gas.

This paper presents data demonstrating that the catalyst promotes combustion at extreme lean burn ratios allowing reduction of thermal NO_x while permitting the engine to operate at full power. Data are also presented demonstrating that the catalyst reduces prompt NO_x without a reduction in excess air. Mechanisms for the catalyst action are presented. Fuel savings from use of the catalyst result in a net zero cost to the engine operator while reaching regulatory compliance for NO_x emissions.

Field Observations

Over the past few years, reciprocating engines used in natural gas compression and pumping stations have come under increasingly stringent regulations for NO_x and other emissions by the

Environmental Protection Agency at the Federal level and state agencies such as Texas Commission on Environmental Quality. There are a large number of these engines in each of the natural gas producing states; it is estimated that Texas has as many as 12,000. These engines are often located in isolated areas and difficult to access. These power sources can be both spark-ignited and compression-ignited reciprocating engines and range from a few hundred to 8,000 HP or more. They are generally equipped with emissions sensors and can be operated under conditions to control specific emissions such as NO_x.

During 2009, experiments carried out on natural gas fueled reciprocating engines indicated combustion catalysts reduced NO_x measured in engine exhausts as much if not more than observations in liquid fuel engines. Application of this technology to natural gas engines presented a number of challenges. Each of these was solved with engineering and chemical solutions. Problems encountered were:

- A fuel borne catalyst cannot be mixed into the natural gas fuel in the same manner as with liquid fuels. It must be injected into the fuel stream in such a manner that it is uniformly mixed at all times on a consistent and continuous basis. It was also observed that the treating rates were significantly lower than for liquid fuels.
- The injection rate for the product is very low: about 1 ounce of product per hour for a 1,340 HP engine. Achieving this required inventing an injection pump that can inject less than a milliliter per minute on a continuous, uniform basis.
- A product is required that will immediately vaporize into the fuel stream. This required research into product formulation and design that will achieve this and simultaneously support a stable product with no precipitation of components.
- Identification of an injection point for the catalyst into the fuel stream that is consistent with engine design with no deleterious effects on the engines.
- Delivery of dosing systems, products and service to engines is required in remote locations. This required designing a business model that will deliver high quality product with superior sales and technical support.

Initial field tests in the 2nd quarter of 2009 led to research and development that yielded technology that supported field applications during the 4th quarter of 2009. One of the initial applications was at a compressor station in the Barnett Shale production area near Fort Worth, TX.¹ The engine is a Caterpillar 3516 1,340 HP spark-ignited unit equipped with emissions sensors. Excess air can be controlled to meet emissions requirements.

¹ Because of Confidentiality Agreements, we are unable identify the engines discussed in this paper more than as indicated. Data from these engines are in the possession of the authors.

A problem with controlling NO_x with excess air is that while excess air (or lean burn) will reduce NO_x to acceptable levels, the engine cannot produce maximum required power output. Under these lean burn conditions, the engine will shut down at higher loads. We discovered that SFA's FuelSpec® patented combustion catalyst administered with JLCC Catalyst's patent pending pump system will allow the engine to operate at required maximum load under lean burn conditions that will reduce NO_x production by >75%.

Field data presented in Table 1 illustrate the results of using the combustion catalyst. The engine was generating about 300 ppm NO_x (2 gms./bhp-hr) under normal operating conditions. Catalyst was introduced into the engine. Initially, oxygen levels were manually increased to reduce NO_x. There is generally a delay of a few days from the time the catalyst is first introduced until the full effect is seen. With reduction in oxygen to more lean burn conditions, the NO_x reduced from 300 to 120 the first day. After about one week, the oxygen-fuel ratio was controlled by the NO_x sensor to achieve 70 ppm or less NO_x levels (0.5 gms./bhp-hr). Without use of the catalyst, this is a lean-burn condition where the engine will fail at high power requirements. The engine performed at high load conditions under these lean burn conditions demonstrating the effects of the catalyst.

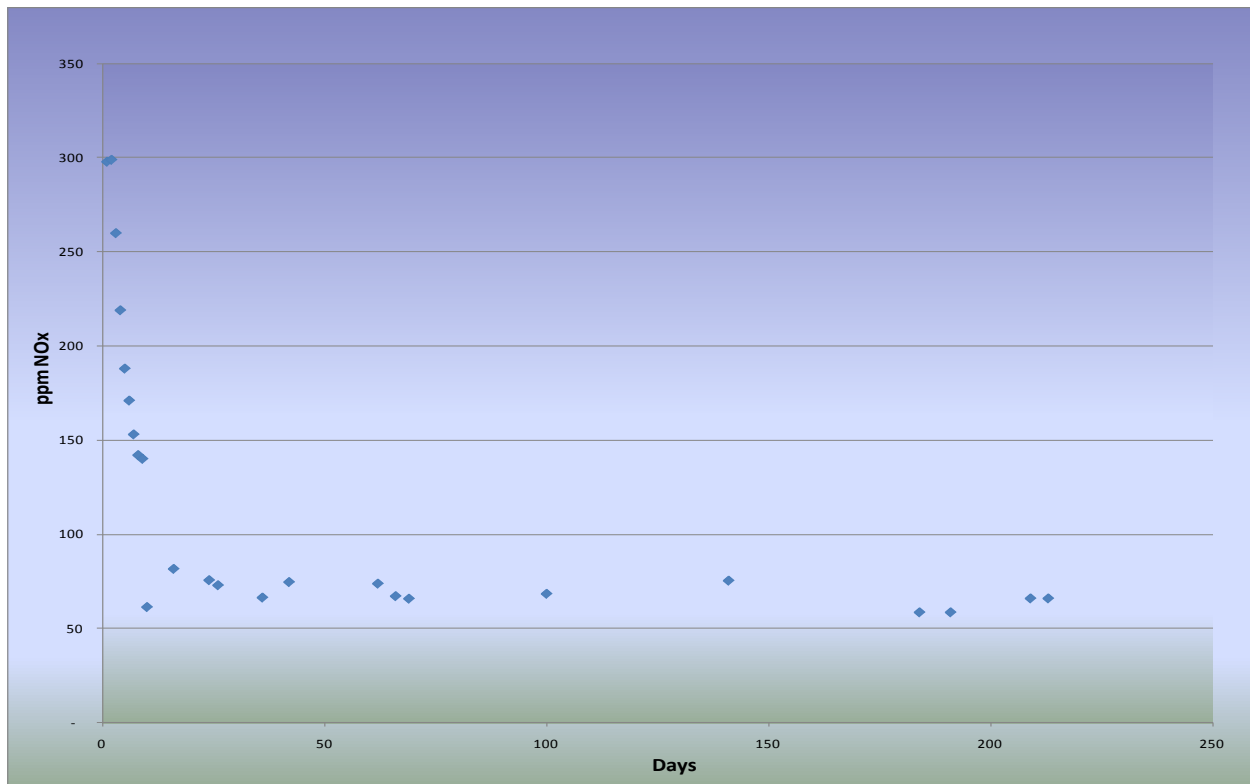


Figure 1. Barnett Shale Unit 5, NO_x ppm

Table 1 presents data taken over an approximate six month period. Figure 1 presents a plot of ppm NO_x with days of use. Data from the first day were expanded on the time scale to present the immediate reduction of NO_x. The result has been more than 75% reduction of NO_x from

300 ppm to 70 ppm or less. This level of NO_x is in compliance with anticipated regulations from the Texas Commission on Environmental Quality.

Figure 2 presents a plot of oxygen levels with time; again data from the first day were expanded on the time scale to illustrate the initial increase in oxygen in the exhaust. Oxygen levels stabilized at about 1% higher than before catalyst use.

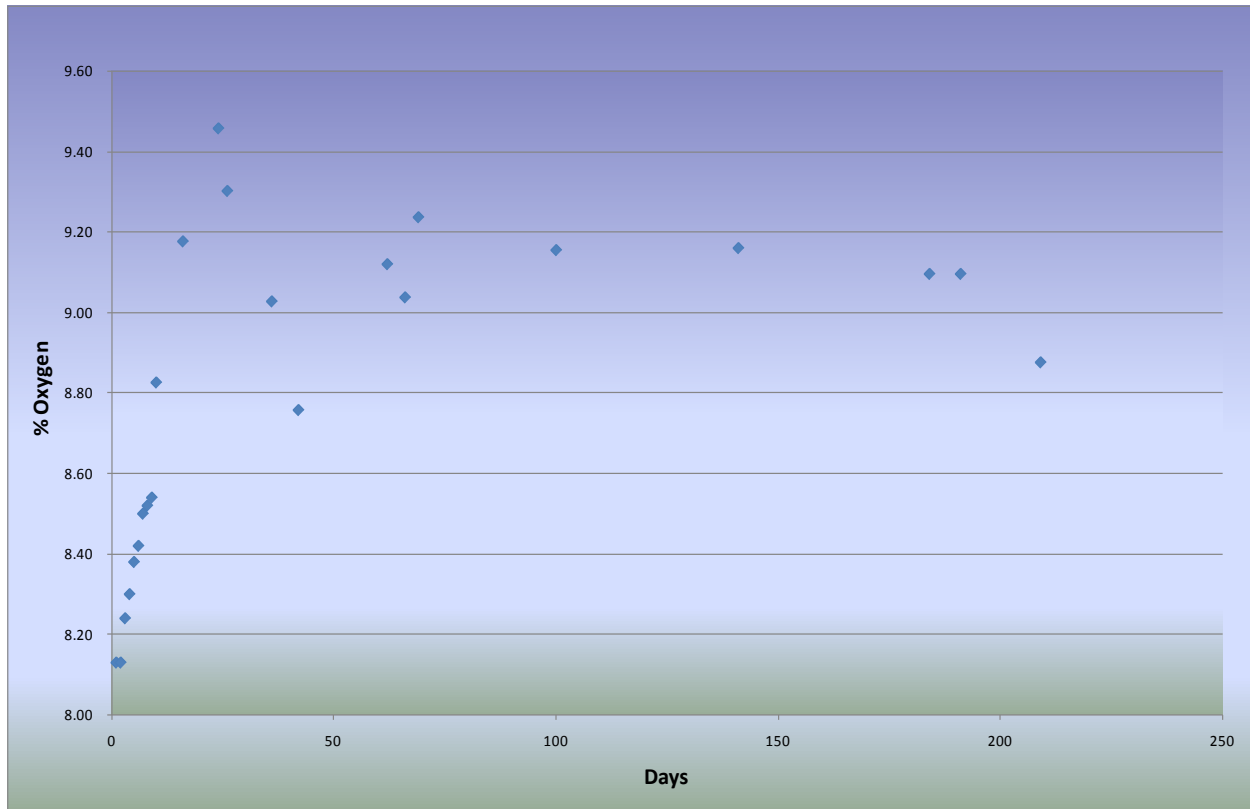


Figure 2. Barnett Shale Unit 5, % Oxygen

This engine can produce the same horsepower at higher oxygen levels (lean burn conditions) with catalyst use as with rich burn conditions. This raises the question as to how the catalyst produces this effect. Note that with improvements with the catalyst formulation, we were able to reduce oxygen to 8.9% compared with 8.1% before catalyst use was begun.

Table II presents data from a more recent application where we followed closely the events at the start of the application. The engine is the same as in the Barnett Shale Unit 5 with an oxygen sensor in the exhaust and excess air control based on oxygen level in the exhaust. At the beginning of the test, the oxygen level was set at 7.5 for stable power at maximum load. The catalyst dosing system was connected to the intake manifold. Four measurements were taken to establish baseline conditions on the 9th of June, 2010. NO_x was in the 171 to 181 ppm range leading to 0.94 to 1.00 gm./bhp-hr levels. Catalyst addition was started following the last reading on the 9th.

The next morning measurements indicated that the NO_x levels had dropped with no changes in the oxygen control settings. It was observed that the oxygen level in the exhaust had risen from the 7.80 – 7.95% range to 7.91 – 8.09% range. This was not sufficient to cause a significant change in the NO_x level in the exhaust. However, NO_x had reduced to the 78 – 91 ppm range or 0.43 – 0.67 gm./bhp-hr.

The oxygen was increased to an 8.2% setting. NO_x measurements taken one hour later were in the 55 – 57 ppm range or 0.31 gm/bhp-hr. The engine operated normally at full power loads with this high excess air or oxygen level.

Both of these sets of field data illustrate that use of a combustion catalyst combined with increase of excess air will yield exceptional reduction in NO_x levels. In the second set, we were able to examine more closely events at the beginning of catalyst use. In this case, we observed a significant reduction of NO_x without increasing excess air.

We have observed reductions in NO_x levels compared with baseline conditions (although not as large) in liquid fuel engines carried out in engine laboratories without changes in oxygen level in the exhaust. Examples are given below:

Southwest Research Institute	5%
University of Houston (biodiesel)	8%
Norwegian Testing Laboratory	6%

There is no logical reason to expect the combustion catalyst to reduce temperature in the piston chamber. Therefore, this reduction must be attributed to an effect of the catalyst on the formation of prompt NO_x.

Nitrogen Oxides

Nitrogen is the first element in Group V of the periodic table.² It has an atomic number of 7 and molecular weight of 14.007. The nucleus consists of 7 protons and 7 neutrons. The electron structure is 1s², 2s², 2p³. There are two major isotopes of nitrogen, ¹⁴N and ¹⁵N, the former comprising 99.64% of all nitrogen. Nitrogen makes up 78.084% of the atmosphere followed by 20.946% oxygen, 0.934% argon and 0.033% carbon dioxide by volume.

In the periodic table, nitrogen is surrounded by lithium, beryllium, boron, carbon, oxygen, fluorine and neon in the second row. Below nitrogen are the other members of Group V: phosphorus, arsenic, antimony and bismuth. The chemistry of nitrogen is sufficiently interesting that it is generally studied apart from the remainder of the Group V elements.

² E. S. Gould, **Inorganic Reactions and Structure**, Henry Holt and Company, New York, 1955.

Nitrogen's unusual chemistry comes from the fact that it can either be reduced and gain three electron to complete the octet or it can oxidize losing up to five electrons. As a result, nitrogen exhibits valence states from -3 to +5. Few other elements have such a large range of valence states and compounds.

There are six nitrogen oxide compounds. These are:

Nitric oxide (NO), Nitrogen(II) oxide
Nitrogen dioxide (NO₂), nitrogen(IV) oxide
Nitrous oxide (N₂O), nitrogen (I) oxide
Dinitrogen trioxide (N₂O₃), Nitrogen (II, IV) oxide
Dinitrogen tetroxide (N₂O₄), nitrogen (IV) oxide
Dinitrogen pentoxide (N₂O₅), nitrogen (V) oxide

The latter three oxides are unstable and convert to NO or NO₂. NO and NO₂ are highly toxic. Human limits in air are presented below with comparison for some other well known toxic materials:³

Toxic Agent	ppm	
Nitric Oxide	25	
Nitrogen Dioxide	5	
Hydrogen Cyanide	10	(Skin)
Carbon Monoxide	50	

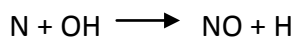
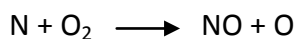
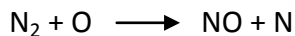
These are surprisingly low threshold numbers for gases that are so common. NO and NO₂, together known as NO_x react in sunlight with volatile organic compounds to form photochemical smog, a significant form of air pollution.⁴ Children, people with asthma and people who work or exercise outside are susceptible to adverse effects of smog such as damage to lung tissue and reduction in lung function. NO_x also reacts with oxygen to form ozone.

There are three primary industrial sources of NO_x, thermal, fuel and prompt.

Thermal NO_x refers to NO_x formed through high temperature oxidation of diatomic nitrogen found in the atmosphere. The formation rate is primarily a function of temperature and the residence time of nitrogen at that temperature. At high temperatures, usually above 1,600° C. (2,900° F.), molecular nitrogen (N₂) and oxygen (O₂) in the combustion air disassociate into their atomic states and participate in a series of reactions. N₂ is highly stable with the two nitrogen atoms attached by a triple bond. Extreme heat causes these bonds to break leading reaction with elemental oxygen as follows (Zeldovich mechanism):

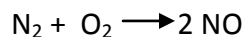
³ R. C. Weast, ed., **Handbook of Chemistry and Physics**, CRC Press, Inc., Boca Raton, FL, 1984.

⁴ Nitrogen Oxide, http://en.wikipedia.org/wiki/Nitrogen_oxide.

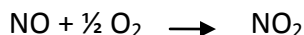


NO_x Formation Temperature Dependence

The following calculations and charts show the effect of temperature on reaction rate and the equilibrium constant for the following reaction.



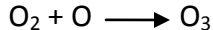
This reaction is followed by:



In the presence of sunlight, NO₂ breaks down to yield an oxygen atom in the monatomic state.



This reacts with O₂ to produce ozone, the precursor to smog.



The enthalpy (ΔH) for the formation of NO is 22 kcal/mole and the entropy (ΔS) is -50 cal/mole °K.⁵ From the equation

$$\Delta H = \Delta G + T \Delta S$$

the Free Energy (ΔG) is 42 kcal at 298° K. At 2,400° C., the Free Energy is 32 kcal. This process is highly temperature dependent and not spontaneous.^{6,7}

With knowledge of the thermodynamic parameters for the reaction, we can calculate the reaction rates for various temperatures.

⁵ W. Kovarik and M. Hermes, "Fuels and Society. The NO_x and Tropospheric Ozone Problem," <http://www.chemcases.com/tel/tel-e.htm>.

⁶ An understanding of this basic equation of thermodynamics requires knowledge of the Laws of Thermodynamics. According to the first law, enthalpy or total energy of a system cannot be gained or lost. The second law describes entropy or disorder which will always go to the maximum. The third law relates free energy to enthalpy and energy, and with the consequence that at absolute zero temperature all electronic motion in an atom will cease.

⁷ F. Daniels and R. Alberty, Physical Chemistry, John Wiley & Sons, New York, First Edition, 1955, pages 341ff.

Arrhenius proposed that the relationship between a reaction rate and temperature can be expressed by the equation

$$K = se^{-\Delta H/RT}$$

Rearranged in logarithmic form, this becomes

$$\ln k = \frac{-\Delta H}{R} \frac{1}{T} + \log s$$

Differentiation yields

$$\frac{d \ln k}{d T} = \frac{\Delta H}{RT^2}$$

and integrating between limits yields

$$\log \frac{k_2}{k_1} = \frac{\Delta H_a}{2.303 R} \left(\frac{T_2 - T_1}{T_2 T_1} \right)$$

$$\Delta H_a = \log \frac{k_2}{k_1} \frac{T_2 T_1}{(T_2 - T_1)} \times 2.303 R$$

$$\Delta H_a = 32.0 \text{ kcal/mole}$$

From this equation, we can calculate reaction rates at various temperatures.

°C	Temp			Reaction Rate	
	°A	1/T	1/T x 10 ⁴	k	ln k
1500	1,773	0.000564	5.64	1	-
2000	2,273	0.000440	4.40	132.4	4.886
2500	2,773	0.000361	3.61	3000	8.006
3000	3,273	0.000306	3.06	25000	10.127

The results in Figure 3 are based on Free Energy (ΔG) = 32 kcal. The formation of NO is highly endothermic and far from a spontaneous process (from reference 5 above).

The formation of NO is less than negligible at room temperature with an equilibrium constant of 1×10^{-15} . At 2,400° C., the equilibrium constant is

$$K = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = 5 \times 10^{-2}$$

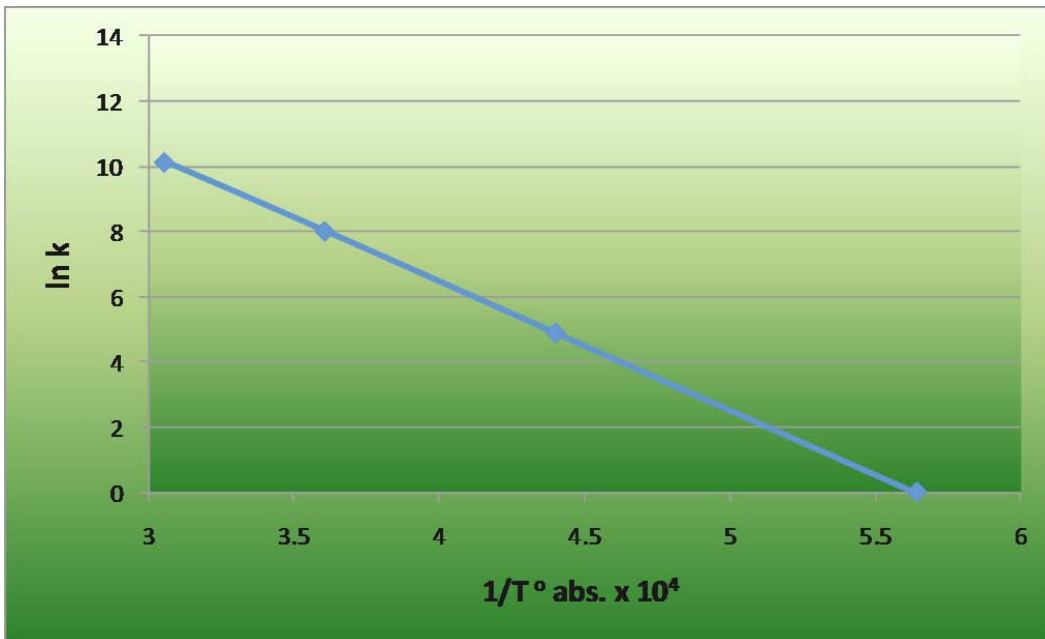


Figure 3. Reaction Rate and Temperature

Similar mathematical arguments can be made for the relationship between equilibrium constants and temperature as for the relationship of reaction rate and temperatures given above. From this, we can calculate equilibrium constants at various temperatures.

°C	Temp		Equilibrium Constant		
	°A	1/T	1/T x 10 ⁴	k	log k
25	298.16	0.003354	33.53904	1E-15	-15
2400	2673.16	0.000374	3.740891	0.05	-1.30

$$\Delta H_e = 15.76 \text{ kcal/mole}$$

Figure 4 demonstrates the highly temperature dependent nature of the equilibrium constant with temperature. When NO is formed, the gas mixture quickly cools and the composition is “frozen” at the NO concentration at the combustion temperature.

The only logical mechanism for the metallic fuel borne catalyst to reduce thermal NO and, subsequently NO₂, is to allow the engine to operate under stable conditions at increased excess oxygen levels in the exhaust. The catalyst must increase the rate and cause more uniform combustion of the fuel. This is accomplished by elimination of hot spots in the combustion area. This leads to reduced unburned fuel, un-reacted hydrocarbons (UHC's) and soot or particulate matter (condensed carbon) in the exhaust.

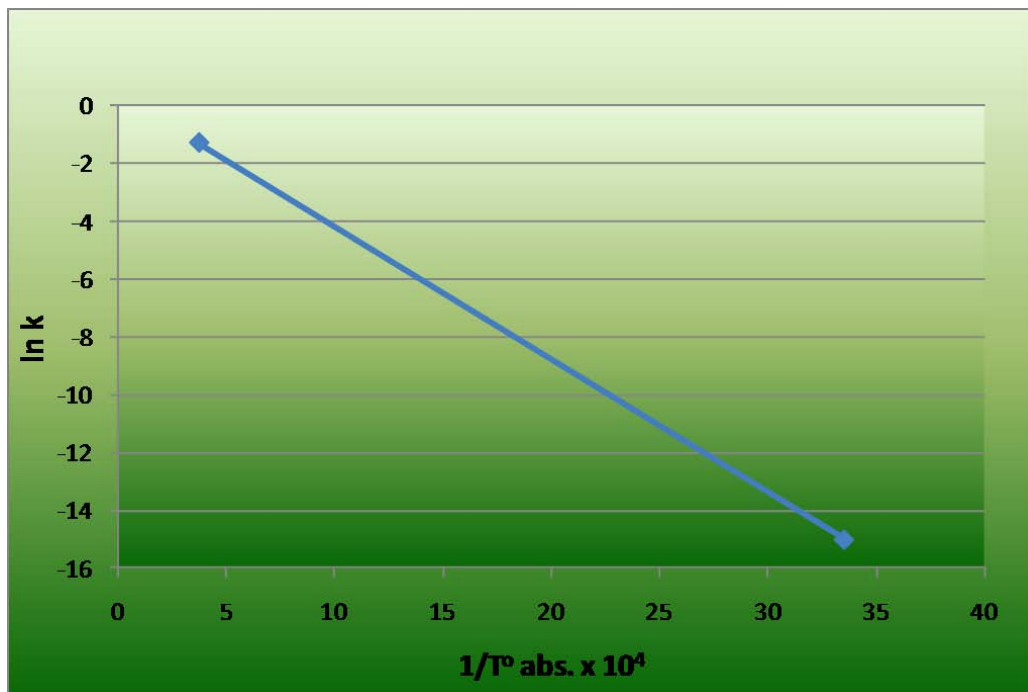


Figure 4. Equilibrium Constants and Temperature

This conclusion is consistent with a conditioning period seen in engines as carbon deposits are burned out, reduced exhaust temperatures, more efficient combustion of the fuel leading to lower fuel consumption, reduced particulate matter in the exhaust and reduced NO_x. In liquid fuel engines, we consistently see an increase in CO (carbon monoxide) in the exhaust with initial use of the catalyst. We attribute this to burning out carbon deposits which can be incomplete combustion resulting in an increase in CO. As fuel consumption reduces, CO will also reduce consistent with removal of carbon deposits in the engine. We rarely see an initial rise in CO in engines operated on natural gas. This is attributed to less carbon deposits in natural gas fueled engines. In these engines, we generally see an immediate reduction in CO following reduction in NO_x.

Fuel NO_x is the conversion of fuel bound nitrogen to NO_x during combustion. This occurs in nitrogen-bearing fuels such as certain sources of coal and oil. During combustion, the nitrogen bound in the fuel is released as a free radical and ultimately forms free N₂ or NO. Fuel NO_x can contribute as much as 50% of total emissions from oil and 80% from coal.

Although the complete mechanism is not fully understood, there are two primary paths of formation. The first involves the oxidation of volatile nitrogen species during the initial stages of combustion. During the release and prior to the oxidation of the volatiles, nitrogen reacts to form several intermediaries which are then oxidized into NO. If the volatiles evolve into a reducing atmosphere, the nitrogen evolved can be readily made to form nitrogen gas rather than NO_x. The second path involves the combustion of nitrogen contained in the char matrix during the combustion of the char portion of the fuel. This reaction occurs much more slowly than the volatile phase. Only around 20% of the char nitrogen is ultimately emitted as NO_x, since much of the NO_x that forms during this process is reduced to nitrogen by the char, which is nearly pure carbon.

Fuel NO_x is commonly observed in solid fuels. It is improbable in natural gas as there are no nitrogen compounds in this fuel.

Prompt NO_x is the third source attributed to the reaction of atmospheric nitrogen, N₂, with free radicals such as C, CH, and CH₂ fragments derived from fuel, where this cannot be explained by either the aforementioned thermal or fuel processes. Occurring in the earliest stage of combustion, this results in the formation of fixed species of nitrogen such as NH (nitrogen monohydride), HCN (hydrogen cyanide), H₂CN (dihydrogen cyanide) and CN⁻ (cyano radical) which can oxidize to NO. In fuels that contain nitrogen, the incidence of prompt NO_x is especially minimal.

Prompt NO_x can range from 10 to 100 ppm in the exhaust. While thermal NO_x generally presents most of the NO_x, the prompt NO_x can present a sufficient amount to prevent reaching regulatory compliance. The second set of data indicates that the initial reduction of NO_x came from prompt NO_x since there was no temperature reduction to yield less thermal NO_x or nitrogen in the fuel leading to fuel NO_x,

The data in Table 2 indicate a reduction of NO_x with catalyst and without increase in oxygen along with other observation cited above lead us to postulate that the catalyst increases the rate of combustion removing fuel available for prompt NO_x formation.

Catalyst Mechanism

The catalyst presents two phenomena. The first is the ability of the engine to produce full power at excessive oxygen levels that are below the lower flammability limit for natural gas and air. The second is reduction or elimination of free radical formation in the initial phases of the combustion process that lead to prompt NO_x formation. Both of these observations require that the catalyst causes the combustion process to proceed at a higher rate of reaction and more uniformly than without it.

We believe that metals function as a combustion catalyst by storing energy at high temperatures and releasing that energy as the system cools. The released energy causes the

combustion process to proceed uniformly. This can be understood by considering the physics of atomic emission spectra.

The emission spectra of a chemical element or chemical compound show the relative intensity of each frequency of electromagnetic radiation emitted by an element's electrons as they return to a ground state.⁸ Elemental emission spectra are unique. Therefore, emission spectroscopy can be used to identify elements in matter of unknown composition. Similarly, the emission spectra of molecules can be used in chemical analysis of substances.

Emission is the process by which energy in the form of a photon is released by a particle, for example, by an atom whose electrons make a transition between two electronic energy levels. The emitted energy is in the form of a photon with a specific frequency.

When the electrons in the atom are excited, for example by being heated, the additional energy causes an electron to move to higher energy orbits. This is not a continuous process; it occurs in discrete steps. When the electron returns to the ground or degenerate state, the same discrete amount of energy is re-emitted in the form of a photon. The wavelength (or equivalently, frequency) of the photon is determined by the difference in energy between the two states. These emitted photons form the element's emission spectra.

An understanding of this phenomenon requires a rudimentary knowledge of the structure of an atom. The basic building blocks of atoms are protons, neutrons and electrons. The atomic number of an element is equal to the number of protons and neutrons in the balanced charge (zero valence) state. The difference between the number of protons and the average atomic weight is made up of neutrons. The reason that elements have weights unequal to zero is that there can be several isotopes of an element with different numbers of neutrons, and therefore different atomic weights. The atomic weight is an average of the weight of the isotopes of the element.

Quantum chemistry teaches that electrons are found in orbital patterns. A study of the periodic table of elements reveals the pattern that has been proven both experimentally and mathematically. Electrons in atoms of the first row of the periodic table have a simple orbital containing up to two electrons – hydrogen and helium - called the “s” orbital. The second row has a second “s” orbital and another orbital called “p”. This orbital adds six electrons yielding the eight atoms in the second row. The third row has an “s” orbital and a “p” orbital and a third orbital called “d” with ten possible electrons. The fourth row adds an “f” orbital with fourteen possible electrons and this pattern continues for the entire periodic table.

Orbital geometries calculated from the solution of Schrödinger's Wave Equation are given in Figure 3. The “s” orbital is a simple sphere with probable electron density spread out on the surface of the sphere. The “p” orbital electron density probabilities are concentrated on the axes of a Cartesian coordinate projection. The “d” orbital electron density probabilities take on more complicated patterns lying between the axes of the projection.

⁸Wikipedia, “Emission Spectra,” http://en.wikipedia.org/wiki/Emission_spectra

The fact that only certain colors appear in an element's atomic emission spectra means that only certain frequencies of light are emitted. Each of these frequencies is related to the energy by the following formula developed in the late 19th century Ernst Planck. This relationship was fundamental to the development of quantum physics.

$$E_{\text{photon}} = h \nu = h / \lambda$$

where E is the energy of the photon, ν (Greek letter nu) is its frequency, λ (Greek letter lambda) is wavelength and h is Planck's constant. This concludes that only photons having

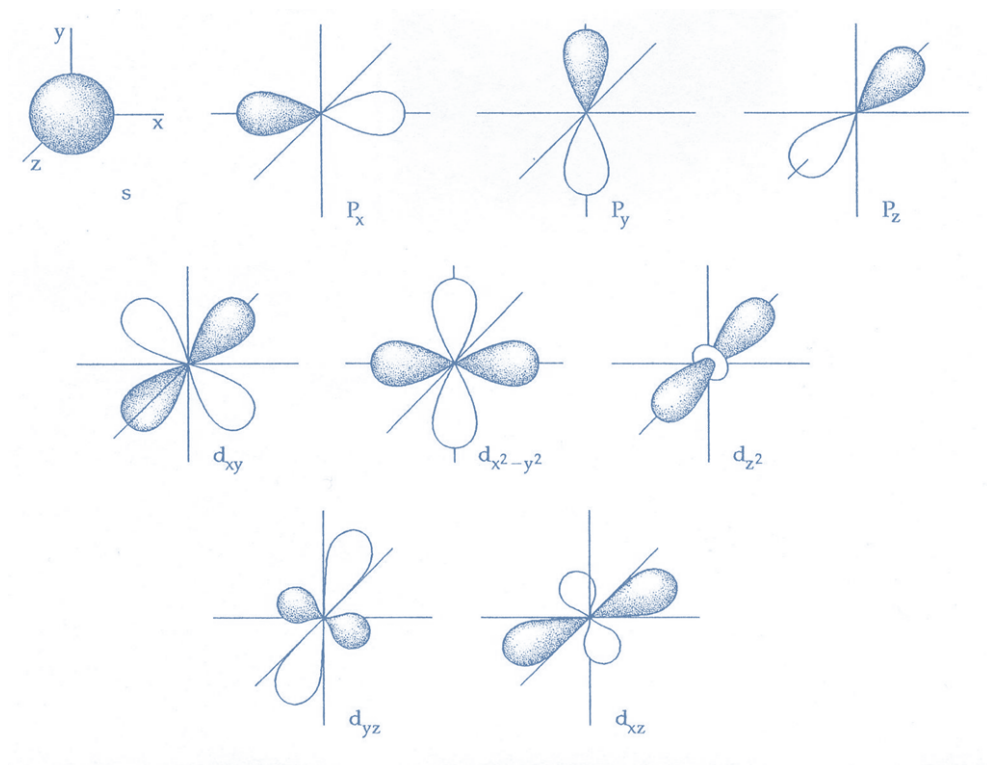


Figure 3. Atomic Electron Orbital Shapes

certain energies are emitted by the atom. The principle of the atomic emission spectra explains the varied colors in neon signs, as well as chemical flame test results mentioned above.

The frequencies of light that an atom can emit depend on the energy released when electrons moves to lower energy level. When excited, an electron moves to a higher energy level or orbital. When the electron falls back to its ground or degenerate level, light or energy is emitted. Explained another way, the decay of electrons from high energy levels to degeneracy is a discontinuous process and occurs in steps.

Hydrogen with one electron will have the smallest number of atomic spectrum. The spectra of elements increase in numbers of spectrum with higher numbers of electrons and available orbital's.

Iron is a third row element and contains 5 electrons in the 3d orbital. This is in addition to filled 1s, 2s, 2p, 3s, 3p and 4s orbital's. The emission spectra of iron in Figure 4 show a large number of lines from the ultraviolet to the infrared. Iron has 235 lines in the 4 000 A° to 7,000 A° range.

We believe that energy released in the cooling process as electrons drop to lower energy levels promotes continued reaction between oxygen and hydrocarbon species leading to uniform and more complete burning of the fuel.

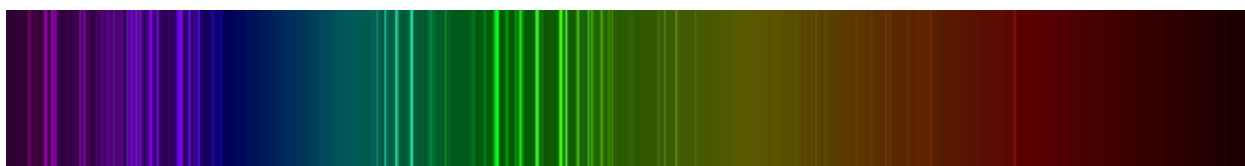


Figure 4. Iron Emission Spectra

Magnesium has no known fuel catalysis properties. However, it has been proven to improve the catalyst effect of iron in the combustion process.⁹ We believe that magnesium synergizes the iron effect by releasing energy that reactivates the iron atoms and continues the catalysis process.

Magnesium has an atomic number of twelve and falls in the third row of the Periodic Table. It has two electrons in the 3s orbital and filled 1s, 2s and 2p orbitals. The magnesium emission spectra in Figure 5 show a smaller number of higher energy lines than are seen with the iron spectra. Magnesium has 54 lines in the 4 000 A° to 7,000 A° range.¹⁰



Figure 5. Magnesium Emission Spectra

Since magnesium has no effect on the catalysis of the combustion reaction, we can surmise that none of the energy releases in the magnesium spectra promotes reaction of hydrocarbon with oxygen. We postulate that energy releases from the magnesium emission spectra reenergize

⁹ See papers on the "Library" page of the SFA International web site, www.sfainternational.com.

¹⁰ <http://laserstars.org/data/elements/>

iron which then releases energy and continues the combustion process. In other words, iron catalyzes combustion and magnesium catalyzes iron to continue the process when it would have otherwise lost energy and cooled.

An alternative explanation has been considered based on Lewis Acid-Base Theory. Lewis acids accept electrons and Lewis bases release electrons in reaction processes. This approach would require the iron atoms to release atoms in the combustion process to further reaction. While this explanation is viable for oxidation – reduction reactions, that type of reaction is not occurring in the combustion process. Therefore, we believe this explanation can be ruled out.

Combustion Kinetics

In an earlier paper by the author,¹¹ it was postulated that the combustion process continues over the entire volume expansion of the cylinder or rotation of the crankshaft 180°. We have since observed that the added pressure from combustion of the fuel in addition to pressure from compression reaches a peak at about 20° after maximum compression and fuel injection as shown in Figure 6.

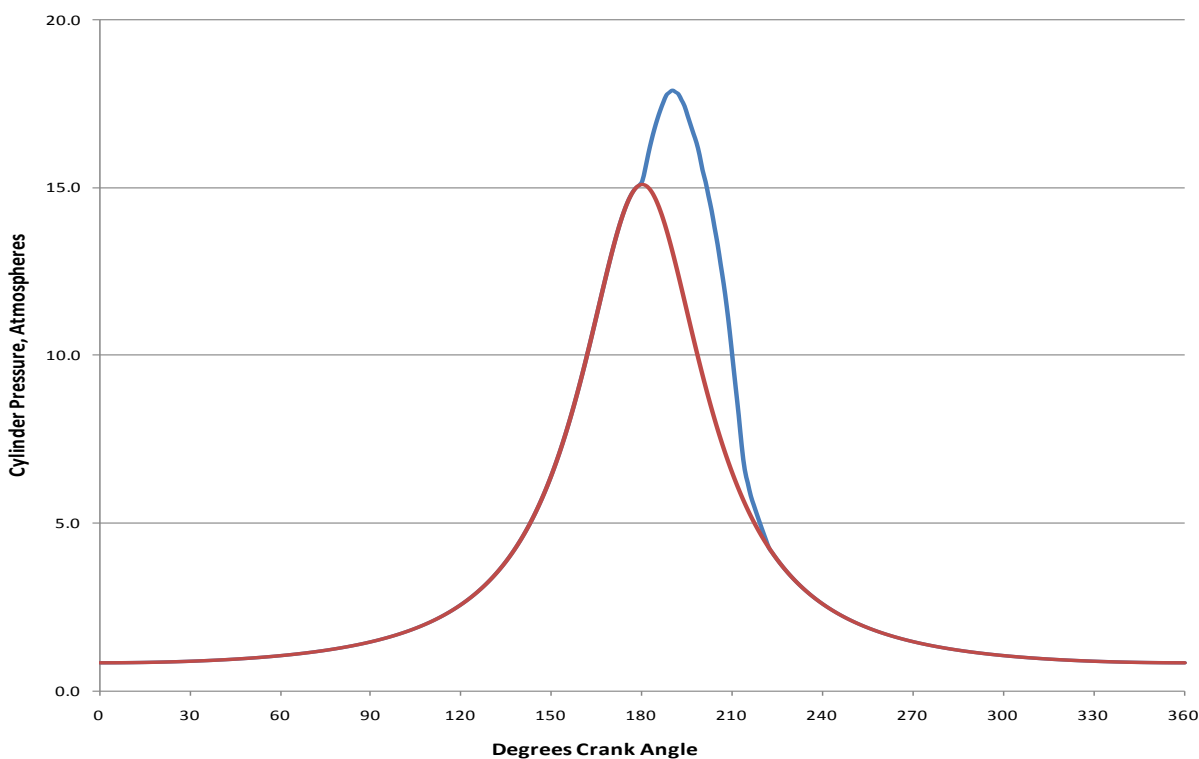


Figure 6. Typical Engine Cylinder Pressure with Fuel Combustion

¹¹ W. R. May, "Hydrocarbon Fuel Chemistry, Effects of Sulfur on Combustion Reaction Rates," American Chemical Society, Paper No. 1207537, Philadelphia, PA, Fall Meeting, 2008.

Mathematically, the area under the curve for compression and expansion in the absence of fuel will be equal (red line).

$$\int_{0^{\circ}}^{180^{\circ}} f(\text{compression}) = \int_{180^{\circ}}^{360^{\circ}} f(\text{expansion})$$

When fuel is introduced into the cylinder and burned, the increase in moles of combustion products and temperature will add the area corresponding to the power from combustion (blue line). The power is represented by the additional area under the curve above 180° crank angle.

$$\int_{180^{\circ}}^{360^{\circ}} f(\text{measured}) - \int_{0^{\circ}}^{180^{\circ}} f(\text{compression}) = \int_{180^{\circ}}^{360^{\circ}} f(\text{power})$$

Our earlier thinking on the increase in energy from the combustion process led us to postulate that more energy was transmitted from the piston to the crankshaft in the 45° to 135° range. This is not the case as it is obvious that the pressure effects of combustion have dissipated within 30 – 40° after piston apogee. It is further noted that there are no changes in this pressure curve with use of catalyst. This leads to the conclusion that the catalyst causes more uniform and complete burning of the fuel. This is consistent with the observations that the catalyst reduces the “knocking” sound in liquid fuel compression ignited engines.

When hydrocarbon fuels are consumed in the combustion process in a reciprocating engine, microscopic amounts of fuel remain in the piston chamber. Lower boiling fractions evaporate leaving behind higher boiling portions that proceed to partially burn. This results in carbon deposits. We believe that the delay seen in effect of the catalyst is due to burning away of carbon deposits. These deposits cause hot spots that lead to increase NO_x production. Reductions in fuel consumption are delayed, and we believe that this “conditioning” period is related to carbon deposits.

Reduction of carbon formation is consistent with less particulate matter in the exhaust and extended engine oil life. With less blow-by of carbon into the crank case, engine oil has a longer life.

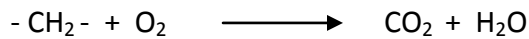
In natural gas fuels, the combustion process with catalyst takes place in a more complete manner at lean-burn air-fuel ratios enabling the engine to function at high power loads with full power from the fuel.

Prompt NO_x and Competing Reactions

Prompt NO_x results from free radicals derived from unburned hydrocarbons reacting with nitrogen to form nitrogen oxides. Reduction of prompt NO_x requires reducing free radical formation. We hypothesize that the combustion catalyst promotes reaction of carbon and carbon free radicals with oxygen.

To demonstrate this hypothesis mathematically, we assumed that aliphatic compounds in the fuel and free radicals react with oxygen in separate, competing reactions with different reaction rates. Examples of these reactions are:

Aliphatic Compounds



Free Radicals (for example)



Kinetics for 2nd order reactions are expressed as follows^{3,4}:

$$dx/dt = k_2 (a - x) (b - x)$$

Rearranging yields the following differential equation:

$$dx / [k_2 (a - x) (b - x)] = dt$$

This equation can be solved by integrating with partial fractions yielding:

$$k_2 t = [1 / (a - b)] \ln [b (a - x) / a (b - x)]$$

Conversion to exponential form yields:

$$e^{(a-b)k_2 t} = [b (a - x) / a (b - x)]$$

Solving for x, the finished product, results in the following expression:

$$x = [a (1 - e^{(a-b)k_2 t})] / [1 - (a/b) e^{(a-b)k_2 t}]$$

Table 3 presents calculations for second order competing reactions with a common reactant. We calculated yields of carbon dioxide at crank angles from 0° to 40°. We estimated reaction rates based on fuel reacting to 95.1% with oxygen by the end of the power stroke. This required a rate of 17,500 per mole – second. We based our competing reaction on NO_x

formation to produce 150 ppm based on exhaust weight at the end of the power stroke with a reaction rate of 1.51 per mole – second. This yielded a ratio between the two rates of 11,589.

We believe that the prompt NO_x is reduced with use of the catalyst due to increase in the rate of reaction of fuel with oxygen. This reduces the fuel available to react with nitrogen to form the precursor species to formation of prompt NO_x. The two laws of catalysis require that the rate of reaction is proportional to catalyst concentration and the reaction order is reduced by one. Because the prompt NO_x is not catalyzed, we chose to compare the two reaction rates with catalysis in the 2nd order form.

In Table 4, calculations are presented where the rate for the combustion reaction is increased until 99.6% of the fuel is consumed at the end of the power stroke. This corresponds to the observation in the Pampa data that the carbon dioxide was reduced by 5%. In order to reach the observed 50 ppm NO_x, the reaction rate for prompt NO_x formation was reduced to 0.60 per mole – second. This yielded a ratio of 58,333 for the two reaction rates.

While these reaction rates cannot be taken literally, the ratios indicate that the catalyst speeds the reaction of fuel with oxygen by a factor of 5 times compared with the prompt NO_x reaction. Catalysis of the combustion reaction removing free radicals from availability to react with nitrogen explains the reduction in the Pampa data case of NO_x reduction from 150 to 50 ppm without any change in excess air or reduction of thermal NO_x.

Fuel Efficiency

The observations for carbon dioxide in Table 2 indicate a reduction indicating less fuel is consumed. We corrected the carbon dioxide level for increased oxygen. The result was a 4 to 5% reduction in fuel consumption. This level of fuel consumption reduction is consistent with observations in ultra-low sulfur liquid fuels.

Other Observations on Use of Metallic Catalysts

We have observed that overdosing of catalyst will show an initial effect followed by a return to conditions consistent with reference fuel containing no catalyst. Removal of catalyst from the fuel following overdosing will yield conditions indicating the catalyst is present followed by a return to conditions with no catalyst present. We know that a small amount of the metallic oxides from the catalyst coat metal surfaces inside the piston chamber and reaches an equilibrium where sufficient catalyst is present on metal surfaces to prevent carbon deposits but insufficient to cause an overdose. This indicates that metallic iron alloy surfaces may yield better conditions for catalytic action than surfaces covered by iron (and magnesium) oxides.

We have observed that addition of a lubricity agent to the catalyst will improve performance in fuels containing <1,000 ppm sulfur. Hydro desulfurization during the refining process to remove sulfur from fuel also removes high molecular weight aromatic components that contribute a lubricating effect to the fuel. The result is galling of metal parts. We believe that

the lubricity agents cause better spray patterns in the fuel injection step. This leads to more uniform burning of the fuel.

As a general rule, we have observed the following fuel consumption savings in ultra low sulfur (10 ppm) liquid fuels with the following combinations of components:

4%	iron catalyst
6%	iron catalyst plus lubricity agent
6%	iron – magnesium catalyst
9%	iron – magnesium catalyst plus lubricity agent

Conclusion

Reduction of NO_x from exhausts of engines using natural gas fuel can be brought about by reducing temperatures in the piston chamber while operating at higher oxygen levels or lean burn conditions. Engines such as the Caterpillar 3516 are not designed for high load operation under these conditions. FuelSpec® combustion catalyst causes the fuel to burn in a more uniform and complete manner resulting in fuel efficiency and stable operation under lean burn conditions at high power loads.

We have also discovered that the FuelSpec® combustion catalyst reduces prompt NO_x without an increase in excess air. Our evaluation of the kinetics of the reactions indicate that the catalyst causes the fuel to burn at a higher reaction rate leading to removal of carbon free radicals before they can contribute to NO_x formation

JLCC Catalysts and SFA International have collaborated to develop new technology for additive injection into natural gas fuels in a uniform and consistent manner, and new catalyst formulations that yield good performance in natural gas fuels. The result is a consistent 75% and greater reduction in NO_x aiding owners and operators to meet new emission regulations. Exhaust catalyst systems are not required saving the cost of installation. The catalyst saves sufficient fuel to pay for the product leading to a net zero cost to the user.

Acknowledgements

The contributions of Jeff Myers, Don Corley, Chris Sosa and Michael Lang of JLCC Catalysts installing dosing equipment, delivering catalyst and gathering data is acknowledged. Without their dedication to the project, this paper would not have been possible.

Table 1. Barnett Shale Field, Unit 5

Engine	Caterpillar	Model	3516						
Date	Time	% O2	ppm CO	ppm NO	ppm NOx	Gms/BHP-Hr	Temp oF	% CO2	Remarks
5-Oct-09	9:13:05	8.13	391	265	298	2.06	59.80	7.13	Base Line
	9:18:39	8.13	391	266	299	2.07	59.80	7.13	Caterpillar Specs
	9:39:30	8.24	378	229	260	1.80	61.30	7.07	Adjusted Oxygen levels up
	9:42:40	8.30	370	190	219	1.52	61.40	7.04	Started catalyst addition
	9:44:56	8.38	361	160	188	1.30	61.80	6.99	
	9:47:57	8.42	354	144	171	1.18	61.60	6.97	
	9:51:31	8.50	346	127	153	1.06	61.20	6.93	
	9:53:19	8.52	345	116	142	0.98	61.40	6.91	
9:56:22	8.54	343	114	140	0.97	61.20	6.90		
5-Oct-09	Average	8.35	364	179	208		61.06	7.01	
6-Oct-09	14:58:27	8.93	326	32	74	0.51	72.50	6.69	Oxygen sensor regulating
	14:59:41	8.86	329	20	61	0.42	72.40	6.73	
	15:02:38	8.84	332	13	54	0.37	74.70	6.74	
	15:03:57	8.72	329	23	64	0.44	72.20	6.80	
	15:05:22	8.78	330	12	53	0.37	72.00	6.77	
6-Oct-09	Average	8.83	329	20	61	0.42	72.76	6.75	
12-Oct-09	12:39:02	8.83	333	65	88		61.31	6.74	NOx sensor regulating
	12:52:26	9.29	320	64	87		61.40	6.49	100 ppm NOx
	12:59:37	9.90	309	63	86		61.60	6.15	
	13:04:10	8.95	333	54	77		61.80	6.68	
	13:07:14	9.04	343	53	76		61.60	6.62	
	13:09:35	9.05	344	52	75		61.30	6.62	
12-Oct-09	Average	9.18	330	59	82	0.57	61.50	6.55	
20-Oct-09	9:54:03	9.53	316	53	76		69.50	6.35	NOx sensor regulating
	10:07:09	9.39	316	52	75		71.50	6.44	80 ppm NOx
20-Oct-09	Average	9.46	316	53	76	0.53	70.50	6.40	
22-Oct-09	10:49:02	9.37	306	45	67		59.80	6.44	
	10:50:40	9.06	317	61	84		58.30	6.62	
	10:51:04	9.31	312	47	69		59.70	6.48	
	10:53:34	9.08	313	47	69		64.60	6.60	
	10:57:29	9.69	304	52	75		61.40	6.26	
22-Oct-09	Average	9.30	310	50	73	0.51	60.76	6.48	
1-Nov-09	14:01:39	9.00	315	49	71		78.60	6.65	
	14:08:52	8.85	316	44	66		83.10	6.73	
	14:16:57	9.11	308	45	67		79.10	6.59	
	14:17:38	9.15	306	39	61		78.60	6.57	
1-Nov-09	Average	9.03	311	44	66	0.46	79.85	6.64	
7-Nov-09	11:20:38	8.98	321	57	80		68.40	6.66	
	11:22:48	8.74	327	51	74		69.00	6.79	
	11:24:40	8.67	326	50	72		67.50	6.83	
	11:30:17	8.64	325	50	72		68.20	6.85	
7-Nov-09	Average	8.76	325	52	75	0.52	68.28	6.78	

Table 1 Continued

Date	Time	% O2	ppm CO	ppm NO	ppm NOx	Temp oF	% CO2	Remarks
27-Nov-09	16:43:46	9.22	319	48	70		6.53	
	16:49:12	9.09	323	52	75		6.60	
	16:52:39	9.05	326	53	76		6.62	
27-Nov-09	Average	9.12	323	51	74		6.58	
1-Dec-09	15:37:02	9.15	320	46	68		6.57	
	15:38:32	9.01	323	45	67		6.64	
	15:41:14	8.95	324	49	71		6.68	
	15:46:55	9.04	323	40	62		6.63	
1-Dec-09	Average	9.04	323	45	67		6.63	
4-Dec-09	11:54:08	9.29	321	41	63		6.49	
	11:59:08	9.22	329	43	65		6.53	
	12:12:07	9.20	327	47	69		6.54	
4-Dec-09	Average	9.24	326	44	66		6.52	
4-Jan-10	10:19:41	9.21	342	47	69		6.53	
	10:22:19	9.15	347	45	67		6.56	
	10:28:32	9.12	350	47	69		6.58	
	10:30:57	9.14	349	46	68		6.57	
4-Jan-10	Average	9.16	347	46	68		6.56	
14-Feb-10	15:59:20	9.17	353	53	76		6.55	
	16:00:42	9.15	354	51	74		6.56	
	16:05:23	9.12	357	54	77		6.58	
	16:09:40	9.20	357	51	74		6.53	
14-Feb-10	Average	9.16	355	52	75		6.56	
29-Mar-10	8:50:14	9.15	339	34	56		6.54	
	8:56:00	9.10	345	34	56		6.59	
	9:00:18	9.06	343	39	61		6.61	
	9:02:36	9.08	342	35	57		6.60	
	9:06:44	9.09	344	40	62		6.60	
29-Mar-10	Average	9.10	343	36	58		6.59	
5-Apr-10	7:25:34	9.22	379	31	53		6.52	
	7:30:55	9.22	379	33	55		6.52	
	7:42:10	9.23	385	39	61		6.52	
	7:55:10	8.83	341	35	57		6.74	
5-Apr-10	Average	9.13	371	35	57		6.58	
23_Apr-10	13:47:58	8.98	351	38	60		6.66	
	13:52:12	8.92	354	40	62		6.69	
	13:57:30	8.81	358	49	71		6.75	
	14:06:11	8.86	358	46	68		6.72	
	14:15:00	8.81	353	46	68		6.75	
23_Apr-10	Average	8.88	355	44	66		6.71	
27-Apr-10	8:10:49	9.28	357	40	62		6.49	
	8:13:25	9.21	365	44	66		6.53	
	8:22:36	9.13	360	40	62		6.57	
	8:28:58	9.14	366	46	68		6.57	
	8:34:35	9.12	367	47	69		6.58	
27-Apr-10	Average	9.18	363	43	65		6.55	

Table 2
Caterpillar 3516
Pampa, TX

Date	Time	O ₂ Control Setting	% O ₂	CO	NO	NO _x	gm. NO _x bhp-hr	% CO ₂	CO ₂ Reduction	Corrected % CO ₂	Fuel Reduction
9-Jun-10	14:10:00	7.5	7.95	426	147	174	0.96	7.24		10.1	
	14:10:46		7.87	432	153	181	1.00	7.28		10.1	
	14:11:34		7.87	428	144	171	0.94	7.28		10.1	
	14:15:43		7.80	433	144	171	0.94	7.32		10.1	
10-Jun-10	8:38:31	8.20	8.10	370	68	91	0.50	7.16	1.6%	10.0	1.0%
	8:39:52		8.09	367	65	88	0.49	7.16	1.6%	10.0	1.0%
	8:45:18		8.06	359	63	86	0.67	7.18	1.4%	10.0	1.0%
	8:53:33		8.06	350	61	84	0.46	7.18	1.4%	10.0	1.0%
	9:01:36		8.03	337	55	78	0.43	7.20	1.1%	10.0	1.0%
	9:32:55		7.91	342	58	81	0.45	7.27	0.1%	10.0	1.0%
	10:37:10		8.29	328	42	64	0.35	7.06	3.0%	10.1	0.0%
	10:52:29		8.22	344	47	69	0.38	7.09	2.6%	9.9	2.0%
	11:35:22		8.57	293	35	57	0.31	6.90	5.2%	9.7	4.0%
	11:42:54		8.62	288	34	56	0.31	6.87	5.6%	9.6	5.0%
	11:44:10		8.63	287	35	57	0.31	6.87	5.6%	9.6	5.0%
	11:52:25		8.57	289	35	57	0.31	6.90	5.2%	9.7	4.0%
	11:55:07		8.57	287	33	55	0.30	6.90	5.2%	9.7	4.0%
11:58:04	8.58	289	34	56	0.30	6.90	5.2%	9.7	4.0%		

Table 3. Uncatalyzed Combustion Kinetics

Engine	Caterpillar 3516						
Cylinders	16			Reaction Rates	Fuel	Prompt NOx	Ratio of Rates
Rated Power	1,340	bhp at	1,200	rpm			
Fuel	225.44	Kg/Hr.		mole ⁻¹ sec ⁻¹	17,500	1.51	11,589
Fuel Consumption	14.09	Kg. / Hr Cylinder		0.391	gm fuel per power stroke		
rpm	1,200			a =	4.89E-02	moles oxygen	
rps	20			b =	2.45E-02	moles fuel per power stroke	
seconds/revolution	0.050			x =		moles carbon dioxide	
seconds/degree	0.000139			c =	1.60E-01	moles nitrogen	
				y =		moles NOx	

Degrees	Time	Fuel			Prompt NOx		
		(a-b)k2t	e	CO ₂	(a-b)k2t	e	NO _x
0.0	0.0000	-	1.000	-	-	1.00000000	0.00E+00
1.0	0.0001	0.06	1.061	0.00267	0.000029	1.00002893	8.36E-07
2.0	0.0003	0.12	1.126	0.00493	0.000059	1.00005881	1.70E-06
3.0	0.0004	0.18	1.195	0.00687	0.000089	1.00008943	2.58E-06
4.0	0.0006	0.24	1.268	0.00855	0.000121	1.00012065	3.48E-06
5.0	0.0007	0.30	1.346	0.01001	0.000152	1.00015235	4.40E-06
6.0	0.0008	0.36	1.429	0.01129	0.000184	1.00018444	5.33E-06
7.0	0.0010	0.42	1.516	0.01243	0.000217	1.00021685	6.26E-06
8.0	0.0011	0.48	1.609	0.01343	0.000249	1.00024952	7.21E-06
9.0	0.0013	0.54	1.708	0.01433	0.000282	1.00028242	8.15E-06
10.0	0.0014	0.59	1.812	0.01514	0.000315	1.00031550	9.11E-06
11.0	0.0015	0.65	1.923	0.01587	0.000349	1.00034873	1.01E-05
12.0	0.0017	0.71	2.041	0.01652	0.000382	1.00038209	1.10E-05
13.0	0.0018	0.77	2.166	0.01712	0.000415	1.00041556	1.20E-05
14.0	0.0019	0.83	2.299	0.01766	0.000449	1.00044913	1.30E-05
15.0	0.0021	0.89	2.440	0.01816	0.000483	1.00048277	1.39E-05
16.0	0.0022	0.95	2.589	0.01861	0.000516	1.00051648	1.49E-05
17.0	0.0024	1.01	2.748	0.01902	0.000550	1.00055024	1.59E-05
18.0	0.0025	1.07	2.916	0.01940	0.000584	1.00058405	1.69E-05
19.0	0.0026	1.13	3.095	0.01975	0.000618	1.00061789	1.78E-05
20.0	0.0028	1.19	3.284	0.02007	0.000652	1.00065177	1.88E-05
21.0	0.0029	1.25	3.485	0.02036	0.000685	1.00068568	1.98E-05
22.0	0.0031	1.31	3.699	0.02064	0.000719	1.00071960	2.08E-05
23.0	0.0032	1.37	3.925	0.02089	0.000753	1.00075355	2.17E-05
24.0	0.0033	1.43	4.166	0.02113	0.000787	1.00078750	2.27E-05
25.0	0.0035	1.49	4.421	0.02134	0.000821	1.00082147	2.37E-05
26.0	0.0036	1.55	4.692	0.02154	0.000855	1.00085544	2.47E-05
27.0	0.0038	1.61	4.979	0.02173	0.000889	1.00088942	2.57E-05
28.0	0.0039	1.66	5.284	0.02191	0.000923	1.00092340	2.66E-05
29.0	0.0040	1.72	5.608	0.02207	0.000957	1.00095738	2.76E-05
30.0	0.0042	1.78	5.952	0.02222	0.000991	1.00099136	2.86E-05

Table 3 Continued

Degrees	Time	Fuel			Prompt NOx		
		(a-b)k2t	e	CO ₂	(a-b)k2t	e	NO _x
31.0	0.0043	1.84	6.316	0.02236	0.001025	1.001025333	2.96E-05
32.0	0.0044	1.90	6.703	0.02249	0.001059	1.001059307	3.06E-05
33.0	0.0046	1.96	7.114	0.02261	0.001093	1.001093276	3.15E-05
34.0	0.0047	2.02	7.549	0.02273	0.001127	1.001127240	3.25E-05
35.0	0.0049	2.08	8.012	0.02283	0.001161	1.001161199	3.35E-05
36.0	0.0050	2.14	8.503	0.02293	0.001194	1.001195150	3.45E-05
37.0	0.0051	2.20	9.024	0.02303	0.001228	1.001229095	3.55E-05
38.0	0.0053	2.26	9.576	0.02311	0.001262	1.001263032	3.64E-05
39.0	0.0054	2.32	10.163	0.02320	0.001296	1.001296961	3.74E-05
40.0	0.0056	2.38	10.786	0.02327	0.001330	1.001330882	3.84E-05
				95.1%			0.1569%

Table 4. Catalyzed Combustion Kinetics

Engine		Caterpillar 3516					
Cylinders	16	Reaction Rates			Fuel	Prompt NOx	Ratio of Rates
Rated Power	1,340 bhp at	1,200 rpm					
Fuel	225.44 Kg/Hr.	sec-1			600	0.0001	6.00E+06
Fuel/Cylinder rpm	14.09 Kg. / Hr Cylinder	0.391 gm fuel per +			moles oxygen		
rps	1,200.00	a = 4.89E-02			moles fuel per power stroke		
seconds/revolution	20.00	b = 2.45E-02			moles carbon dioxide		
seconds/degree	0.05000	x =			moles NOx		
	1.39E-04	c =					
		Fuel			Prompt NOx		
Degrees	Time secs	k1t	k1t e	CO ₂	k1t	k1t e	NOx
0	0.00000						
1	0.00014	0.083	1.0869	0.00196	0.0000	1.000000014	3.3974E-10
2	0.00028	0.167	1.1814	0.00376	0.0000	1.000000028	6.7949E-10
3	0.00042	0.250	1.2840	0.00541	0.0000	1.000000042	1.0192E-09
4	0.00056	0.333	1.3956	0.00693	0.0000	1.000000056	1.3590E-09
5	0.00069	0.417	1.5169	0.00834	0.0000	1.000000069	1.6987E-09
6	0.00083	0.500	1.6487	0.00962	0.0000	1.000000083	2.0385E-09
7	0.00097	0.583	1.7920	0.01081	0.0000	1.000000097	2.3782E-09
8	0.00111	0.667	1.9477	0.01190	0.0000	1.000000111	2.7180E-09
9	0.00125	0.750	2.1170	0.01291	0.0000	1.000000125	3.0577E-09
10	0.00139	0.833	2.3010	0.01383	0.0000	1.000000139	3.3974E-09
11	0.00153	0.917	2.5009	0.01468	0.0000	1.000000153	3.7372E-09
12	0.00167	1.000	2.7183	0.01546	0.0000	1.000000167	4.0769E-09
13	0.00181	1.083	2.9545	0.01618	0.0000	1.000000181	4.4167E-09
14	0.00194	1.167	3.2113	0.01684	0.0000	1.000000194	4.7564E-09
15	0.00208	1.250	3.4903	0.01745	0.0000	1.000000208	5.0962E-09
16	0.00222	1.333	3.7937	0.01801	0.0000	1.000000222	5.4359E-09
17	0.00236	1.417	4.1234	0.01853	0.0000	1.000000236	5.7756E-09
18	0.00250	1.500	4.4817	0.01900	0.0000	1.000000250	6.1154E-09
19	0.00264	1.583	4.8712	0.01944	0.0000	1.000000264	6.4551E-09
20	0.00278	1.667	5.2945	0.01984	0.0000	1.000000278	6.7949E-09
21	0.00292	1.750	5.7546	0.02021	0.0000	1.000000292	7.1346E-09
22	0.00306	1.833	6.2547	0.02055	0.0000	1.000000306	7.4744E-09
23	0.00319	1.917	6.7983	0.02086	0.0000	1.000000319	7.8141E-09
24	0.00333	2.000	7.3891	0.02115	0.0000	1.000000333	8.1539E-09
25	0.00347	2.083	8.0312	0.02142	0.0000	1.000000347	8.4936E-09
26	0.00361	2.167	8.7291	0.02166	0.0000	1.000000361	8.8333E-09
27	0.00375	2.250	9.4877	0.02188	0.0000	1.000000375	9.1731E-09
28	0.00389	2.333	10.3123	0.02209	0.0000	1.000000389	9.5128E-09
29	0.00403	2.417	11.2084	0.02228	0.0000	1.000000403	9.8526E-09
30	0.00417	2.500	12.1825	0.02245	0.0000	1.000000417	1.0192E-08

Table 4. Continued

Degrees	Time secs	Fuel			Prompt NOx		
		k1t	k1t	CO ₂	k1t	k1t	NOx
31	0.00431	2.583	13.2412	0.02261	0.0000	1.000000431	1.0532E-08
32	0.00444	2.667	14.3919	0.02276	0.0000	1.000000444	1.0872E-08
33	0.00458	2.750	15.6426	0.02290	0.0000	1.000000458	1.1212E-08
34	0.00472	2.833	17.0020	0.02302	0.0000	1.000000472	1.1551E-08
35	0.00486	2.917	18.4796	0.02314	0.0000	1.000000486	1.1891E-08
36	0.00500	3.000	20.0855	0.02324	0.0000	1.000000500	1.2231E-08
37	0.00514	3.083	21.8311	0.02334	0.0000	1.000000514	1.2571E-08
38	0.00528	3.167	23.7283	0.02343	0.0000	1.000000528	1.2910E-08
39	0.00542	3.250	25.7903	0.02351	0.0000	1.000000542	1.3250E-08
40	0.00556	3.333	28.0316	0.02359	0.0000	1.000000556	1.3590E-08
				96.4%			0.000056%