

Nitrogen Oxide Suppression with Combustion Catalysts

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Nitrogen oxides, specifically NO and NO₂, known collectively as NO_x are highly toxic and contribute to upper atmospheric pollution through formation of ozone¹. Efforts are being made world wide to curtail NO_x pollution from all users of hydrocarbon fuels. SFA International has discovered that combustion catalysts containing iron and magnesium will not only increase combustion efficiency leading to reduced fuel consumption but will also reduce particulate matter and NO_x. The purpose of this paper is to present data and offer a mechanism to explain the phenomena.

Nitrogen

Nitrogen is the first element in Group V of the periodic table². 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. 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.

Nitrogen's interesting 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

¹ Kenneth Wark, Cecil Warner and Wayne Davis, **Air Pollution, Its Origin and Control**, Addison Wessley Longman, Inc., Menlo Park, CA, 1998.

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

Dinitrogen tetroxide (N₂O₄), nitrogen (IV) oxide
Dinitrogen pentoxide (N₂O₅), nitrogen (V) oxide

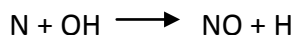
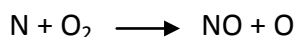
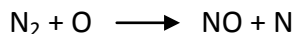
The latter three oxides are unstable and convert to NO or NO₂. NO and NO₂ are highly toxic. Human limits in air are presented below with comparison for some other well known toxic materials:³

| 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):



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

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.

forms free N_2 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.

Prompt NO_x is the third source attributed to the reaction of atmospheric nitrogen, N_2 , with radicals such as C, CH, and CH_2 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), H_2CN (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.

Health Effects

The toxicity of nitrogen oxides were presented above. They have surprisingly high levels of toxicity compared with better known poisonous gasses such as hydrogen cyanide. NO_x reacts with ammonia, moisture and other compounds to form nitric acid vapor and related particles. Small particles can penetrate deeply into sensitive lung tissue causing damage and death in extreme cases. Inhalation of such particles may cause or worsen respiratory diseases such as emphysema and bronchitis; and it can aggravate existing heart disease.

NO_x reacts with volatile organic compounds in the presence of heat and sunlight to form ozone (O_3). Ozone is highly oxidative and can cause adverse effects such as damage to lung tissue and reduction in lung function mostly in susceptible populations (children, elderly, asthmatics) through formation of free radicals in tissue. Ozone can be transported by wind currents and cause health impacts far from the original sources. The American Lung Association estimates that nearly 50% of United States inhabitants live in counties that are not in ozone compliance.

Removal of NO_x from Combustion Gasses

There are only two basic methods of reducing NO_x; reduction of combustion temperature and reaction with lower valence state nitrogen compounds to form N₂. Reduction of combustion temperature can be done by de-rating or reducing power output of an engine. The disadvantage of this is that less power is produced with reduced fuel efficiency and there may not be sufficient power for the requirements of an application. Another approach to reducing combustion temperature is to add water to the fuel. The disadvantage of this process is that the raising the temperature of water to the boiling point, the heat of vaporization and heating steam to combustion temperatures absorbs energy.

A third approach in the area of reducing combustion temperature is to add a fuel borne combustion catalyst. The catalyst causes the fuel to burn faster resulting in a shorter time at combustion temperature. This method not only significantly reduces NO_x, fuel savings accompanying use of the catalyst will more than pay the cost of the catalyst.

The second basic method for removing NO_x is by reaction with ammonia, NH₃, or urea, H₂NCONH₂. With Selective Non-Catalytic Reduction, the reaction occurs in the 870° to 1,150° range. With the Selective Catalytic Reduction process, the reaction occurs over a substrate of base metal catalysts such as titanium and vanadium oxides and other expensive elements such as molybdenum and tungsten. Zeolite catalysts can be used at higher temperatures.

The catalyst is an expensive add-on device in the exhaust system and requires continuous injection of reducing agents.

Iron-Magnesium Combustion Catalysts

The use of iron containing fuel borne catalysts to reduce NO_x has been known for some time. Lissianski, et al.,⁵ published a paper based on work at the General Electric Energy and Environmental Research Corporation, Irvine, CA showing a 20 – 25% reduction of NO_x.

Several years ago SFA International discovered that a combination of iron and magnesium is much more effective than any known metal in reducing particulate matter or smoke. The best known metal in the literature was iron and reduces particulate matter in boiler and combustion turbine exhausts by 50%.⁶ Iron combined with

⁵ V. V. Lissianski, P. M. Maly and V. M. Zamansky, "Utilization of Iron Additives for Advanced Control of NO_x Emissions from Stationary Combustion Sources, *Ind. Eng. Chem. Res.*, **40** (15), 3287, 2001.

⁶ "Boiler Fuel Additives for Pollution Reduction and Energy Saving," Ed. by R. C. Eliot, Noyes Data Corp., Park Ridge, NJ, 1978.

magnesium reduces particulate matter up to 90%.^{7,8} We have found significant reductions in fuel consumption with these catalysts correlated with sulfur content.⁹ A mechanism was presented based on two reaction rates for 2nd order reactions. The first reaction rate was an average for combustion of lower molecular weight aliphatic molecules. The second was the average for the combustion of higher molecular weight condensed polycyclic aromatic molecules that are present in asphaltenes and contain sulfur. We found that a difference in these combustion rates by a factor of one hundred yielded theoretical results for non-catalyzed combustion that correlated with observed fuel consumption. The iron-magnesium catalyst increases the rate of reaction of the more complex molecules improving fuel consumption. We found that the requirements for asphaltenes in fuels for testing specified by the Texas Commission on Environmental Quality correlated very well with these theoretical calculations.

Reduction of NO_x with Fuel Borne Combustion Catalysts

SFA's fuel borne combustion catalyst has been tested by several recognized independent institutions and companies. These include:

Automobile Research Institute of India
Southwest Research Institute
University of Houston, Engine Testing Laboratory
Korea Institute of Energy Research
Siemens-Westinghouse Corporation
Hyundai Heavy Industries

All of these tests were for the purpose of evaluating particulate matter and fuel savings. While our focus was not on NO_x reduction during this testing, the small amount of data collected indicated a reduction of NO_x.

We have carried out testing at Jerry Lang Combustion Consultants in Lindale, TX. The test equipment in the laboratory is described in Table I. It includes two gasoline and one Diesel test rigs. Exhaust gases are tested by a Testo 335 analyzer that yields NO_x, NO and CO data. A summary of data on the Diesel test rig is given in Table II. These tests were run between 05-Jun-08 and 17-Oct-08. Baseline measurements on nitrogen oxides were between 238 and 286 ppm. With 41.6 ppm Fe, the nitrogen oxides dropped to 103 ppm or about 40% of the baseline value.

⁷ Walter R. May, Ramu Ramdas, "Catalyst for Improving the Combustion Efficiency of Diesel Fuels," 9th Annual India Oil & Gas Review Symposium, Mumbai, India, Sept. 9-10, 2002.

⁸ Walter R. May, "Catalysts for Improving the Combustion Efficiency of Petroleum Fuels," 2003 Technical Exchange Meeting, Engineering Services, R&D Center, Aramco, Dhahran, Saudi Arabia, April 28-30, 2003.

⁹ Walter R. May, "Hydrocarbon Fuel Chemistry: Effects of Sulfur on Combustion Reaction Rates," Available on the SFA International web site at www.SFAInternational.com. A redacted version of this paper was presented at the American Chemical Society Fall Meeting, Philadelphia, PA, August 21, 2008.

There were several nitrogen oxide readings made on the gasoline test stand. On 02-Oct-08, nitrogen oxide dropped from 197 to 42 ppm with 41 ppm Fe. On 17-Oct-08, NO_x dropped from 242 to 113 ppm and then returned to 196 ppm in the absence of Fe in the fuel. On 29-Oct the nitrogen oxides were 224 and dropped to 101 ppm on 04-Nov with 8 ppm Fe. They returned to 204 ppm on 12-Nov with no catalyst.

The main thrust of this testing was to find the optimum iron (combined with magnesium) level in the fuel and the effects of fuel lubricity agents on combustion catalyst performance. While the best treatment rate in boilers, process heaters and combustion turbines has consistently been 50 ppm Fe, we found that 10 ppm Fe in reciprocating engines was the optimum level. We also found 60 to 70% reduction of NO_x at this level of iron.

Another significant observation was that the exhaust temperature reduced from 475° to 425° F. This observation confirms that combustion takes place at a faster rate in the presence of the catalyst.

At the time of writing this paper (early July, 2009), Esilanna Marine, SFA International distributor, has a test in progress on the *Andenes Havfiskelskap*, a fishing vessel. This ship is powered by a medium speed V46 Wärtsilä Diesel engine. Fuel is treated with SFA's FuelSpec® 116-4509 iron-magnesium combustion catalyst at a rate of 10 ppm Fe. Nitrogen oxide measurements with catalyst have ranged between 30 and 60% less than NO_x levels without catalyst in the fuel under similar power and load conditions.

Mechanism of NO_x Reduction with a Combustion Catalyst

The formation of nitrogen oxides is a high energy reaction occurring at combustion temperatures. Examples of bond energies are given below:

| | |
|-------|------------------|
| N - N | 225.94 Kcal/Mole |
| N - O | 150.71 |
| O - O | 119.02 |
| C - O | 257.3 |
| C - C | 145 |
| C - H | 81 |

The naturally occurring nitrogen dimer (N₂) has a triple bond; the nitrogen atoms share three electrons in order to complete their octets. This is an unusually strong bond and takes considerable energy to break. It is interesting to note that at the accepted combustion temperature of 2,500° C., only a few hundred ppm of nitrogen oxides are formed.

We have demonstrated in earlier cited papers that several percent of the fuel burns incompletely (particulate matter and carbon monoxide) or exhausts as unburned

hydrocarbon. The combustion process is continuing at the end of the power stroke indicated by higher exhaust temperatures as compared with catalyst use.

The combustion reaction activation energy is very high approaching levels of explosives. Based on 2nd order reaction rates required for the fuel to complete combustion during the time of the power stroke, we estimate that the rate of reaction is 35,000 moles⁻¹ second⁻¹ at 2,500° C. With an estimate that the reaction rate has decreased to 5,000 at 2,450°, the Heat of Activation is 2.58 x 10⁵ calories per mole. Figure 1 shows the exceptionally steep curve for this reaction.

We postulate that the mechanism for the combustion catalyst to reduce NO_x formation is based on cooling, or to put it more succinctly, the time the reaction mixture is at combustion temperature. The combustion catalyst causes the reaction to take place at a faster rate, more energy is absorbed by the mechanical cycle of the piston moving, expanding the chamber and reducing the temperature, leading to less time at elevated temperatures.

Conclusion

Laboratory and field observations have demonstrated that SFA International's iron-magnesium combustion catalyst results in a significant reduction of nitrogen oxides in reciprocating engine exhausts. We have observed this phenomenon in fuels ranging from low molecular weight aliphatic fuels to those containing high molecular weight condensed aromatic compounds.

The observations from mathematical models developed from 1st and 2nd order kinetics equations applied to simultaneous combustion reactions for low molecular weight aliphatic compounds and high-molecular weight aromatic species support the hypotheses put forth. The activation energy for the combustion reaction is very high, as expected. By increasing the reaction rate for all species in the fuel with the combustion catalyst, the combustion reaction is at a high temperature for a shorter length of time reducing the opportunity for formation of nitrogen oxides.

Significant advantages of the fuel borne combustion catalyst are that

- Energy is not lost by addition of water to the fuel.
- The engine is not de-rated or operated at lower load resulting in rated power and operating efficiency.
- Expensive catalyst systems and injection systems for nitrogen compounds such as ammonia or urea into the exhaust stream are not required.
- The fuel borne combustion catalyst reduces fuel consumption resulting in savings to the operator and reduction of particulate matter while meeting NO_x requirements.

Acknowledgements

The work carried out at Jerry Lang Combustion Consultants by the principal investigator, Jerry Lang is acknowledged. The results have been very informative and helpful in designing dosage rates and improving product formulations.

The efforts of Timothy Hill, Managing Director of Esilanna Marine, Ltd., to work with the owners of the ***Andenes Havfiskelskap*** to test the catalyst and gathering of data under difficult conditions is most appreciated.

Table I. Test Equipment

Test Engines

| Manufacturer | Model | Cycle | Cylinders | Fuel | Watts | Fuel Tank | Comments |
|-----------------------------|--------------|--------------|------------------|-------------|--------------|------------------|------------------|
| Kohler | CH 235 | 4 | 2 | Gasoline | 11 KW | 12 Gal. | Air Cooled |
| Kubota | V 1505 | 4 | 4 | Diesel | 22 HP | 15 Gal. | Water Cooled |
| GM | Buick V8 | 4 | 8 | Gasoline | | | 5.2 Liter |
| Exhaust Gas Analyzer | | | | | | | |
| Testo | 335 | | | | | | Engine Kit Probe |

Table II. Diesel Test Engine Data

| Estimated Fuel Density | | 7.50 Lbs./Gal. | | 0.900 Grams/CC | | | | | | | |
|------------------------|-----------|----------------|-------------|----------------|--------|--------|----------------------|----------------|-----|----|----|
| Date | Time | | Product | Oz./15 Gal. | ppm Fe | Inches | Fuel Use Gal. / Hour | Percent Change | NOx | NO | CO |
| | Beginning | End | | | | | | | | | |
| 5-Jun-08 | 11:20 AM | 3:20 PM | None | Baseline | | 2.42 | 1.21 | | | | |
| 10-Jun-08 | 8:20 AM | 2:20 PM | FS 116-4509 | 1.00 | 25.0 | 3.32 | 1.11 | -8.5% | | | |
| 11-Jun-08 | 8:15 AM | 2:15 PM | FS 116-4509 | 1.66 | 41.5 | 3.34 | 1.11 | -8.0% | | | |
| 12-Jun-08 | 8:10 AM | 12:10 PM | FS 116-4509 | 2.10 | 52.5 | 2.29 | 1.14 | -5.5% | | | |
| 17-Jun-08 | 8:10 AM | 2:10 PM | FS 116-4509 | 1.40 | 35.0 | 3.43 | 1.14 | -5.5% | | | |
| 18-Jun-08 | 8:10 AM | 2:10 PM | FS 116-4509 | 0.93 | 23.3 | 3.32 | 1.11 | -8.5% | | | |
| 19-Jun-08 | 8:35 AM | 2:35 PM | FS 116-4509 | 0.62 | 15.5 | 3.54 | 1.18 | -2.5% | | | |
| 21-Jun-08 | 8:30 AM | 2:30 PM | | Baseline | | 3.63 | 1.21 | | | | |
| 22-Jun-08 | 9:55 AM | 2:55 PM | FS 118-1502 | 1.08 | 90.0 | 3.00 | 1.20 | -0.8% | | | |
| 23-Jun-08 | 8:15 AM | 2:20 PM | FS 118-1502 | 1.00 | 83.3 | 3.35 | 1.10 | -9.0% | | | |
| 24-Jun-08 | 8:30 AM | 2:30 PM | FS 118-1502 | 0.66 | 55.0 | 3.41 | 1.14 | -6.1% | | | |
| 1-Jul-08 | 9:20 AM | 3:20 PM | FS 118-1502 | 0.45 | 37.5 | 3.39 | 1.13 | -6.6% | | | |
| 2-Jul-08 | 8:20 AM | 2:20 PM | FS 116-1002 | 1.00 | 5.6 | 3.25 | 1.08 | -10.5% | | | |
| 3-Jul-08 | 8:15 AM | 2:15 PM | FS 116-1002 | 1.00 | 5.6 | 3.25 | 1.08 | -10.5% | | | |
| 8-Jul-08 | 10:25 AM | 2:25 PM | SFX | 0.50 | 5.0 | 2.36 | 1.18 | -2.5% | | | |
| 9-Jul-08 | 8:15 AM | 12:15 PM | SFX | 0.50 | 5.0 | 2.01 | 1.01 | -16.9% | | | |

| Date | Time | | Product | Oz./15 Gal. | ppm Fe | Inches | Fuel Use Gal. / Hour | Percent Change | NOx | NO | CO |
|-----------|-----------|----------|----------|-------------|--------|--------|-------------------------|-------------------|-----|-----|-----|
| | Beginning | End | | | | | | | | | |
| 10-Jul-08 | 8:15 AM | 12:15 PM | SFX | 0.50 | 5.0 | 1.97 | 0.99 | -18.6% | | | |
| 30-Jul-08 | 11:28 AM | 2:28 PM | ML 333U | 0.50 | 4.2 | 1.73 | 1.15 | -4.7% | | | |
| 31-Jul-08 | 8:15 AM | 2:15 PM | ML 333U | 0.75 | 6.2 | 3.49 | 1.16 | -3.9% | | | |
| 5-Aug-08 | 8:25 AM | 2:25 PM | ML 333U | 0.50 | 4.2 | 3.22 | 1.07 | -11.3% | | | |
| 7-Aug-08 | 10:00 AM | 2:00 PM | ML 333U | 0.50 | 4.2 | 2.16 | 1.08 | -10.7% | | | |
| 12-Aug-08 | 8:30 AM | 2:30 PM | None | | | 3.25 | 1.08 | -10.5% | | | |
| 13-Aug-08 | 8:40 AM | 2:40 PM | ML 333X | 1.00 | 8.3 | 3.40 | 1.13 | -6.3% | | | |
| 14-Aug-08 | 8:20 AM | 1:20 PM | ML 333X | 0.75 | 6.2 | 3.05 | 1.22 | 0.8% | | | |
| 2-Sep-08 | 8:20 AM | 2:20 PM | None | New Fuel | | 3.41 | 1.14 | | 229 | 227 | 113 |
| 3-Sep-08 | 9:05 AM | 3:05 PM | Korean | 1 Tablet | | 3.37 | 1.12 | -1.2% | 238 | 236 | 111 |
| 4-Sep-08 | 8:15 AM | 2:15 PM | Korean | 1 Tablet | | 3.24 | 1.08 | -5.0% | | | |
| 9-Sep-08 | 9:00 AM | 3:00 PM | Korean | 1 Tablet | | 3.13 | 1.04 | -8.2% | | | |
| 10-Sep-08 | 8:30 AM | 2:30 PM | Korean | 0.5 Tablet | | 3.42 | 1.14 | 0.3% | | | |
| 11-Sep-08 | 8:20 AM | 2:20 PM | None | | | 3.39 | 1.13 | -0.6% | | | |
| 12-Sep-08 | 8:10 AM | 2:10 PM | Korean | 1 Tablet | | 3.42 | 1.14 | 0.3% | 238 | 236 | 115 |
| 16-Sep-08 | 8:10 AM | 2:10 PM | Korean | 2 Tablet | | 3.46 | 1.15 | 1.5% | | | |
| 2-Oct-08 | 8:20 AM | | Baseline | | | 3.41 | 1.14 | | 286 | 283 | 112 |
| | 8:20 AM | 2:20 PM | ML 333X | 5.00 | 41.6 | 3.07 | 1.02 | -10.0% | 103 | 102 | 310 |
| 6-Oct-08 | 8:20 AM | 2:20 PM | ML 333X | 5.00 | 41.6 | 3.61 | 1.20 | 5.9% | | | |

| Date | Time | | Product | Oz./15 Gal. | ppm Fe | Inches | Fuel Use Gal. / Hour | Percent Change | NOx | NO | CO |
|-----------|-----------|----------|----------|----------------|--------|--------|-------------------------|-------------------|-----|----|----|
| | Beginning | End | | | | | | | | | |
| 8-Oct-08 | 9:35 AM | 3:35 PM | ML 333X | 3.75 | 31.2 | 3.40 | 1.13 | -0.3% | | | |
| 9-Oct-08 | 8:50 AM | 2:50 PM | ML 333X | 2.81 | 23.4 | 3.48 | 1.16 | 2.1% | | | |
| 15-Oct-08 | 9:30 AM | 11:35 AM | None | 5 ml / 15 gal. | | 0.997 | 1.00 | -12.3% | | | |
| | 11:57 AM | 2:02 PM | ML 333SX | 0.18 | 1.5 | 1.31 | 1.26 | 10.6% | | | |
| 16-Oct-08 | 10:20 AM | 12:25 PM | ML 333SX | 0.18 | 1.5 | 1.52 | 1.46 | 28.4% | | | |
| | 12:44 PM | 2:49 PM | ML 333SX | - | | 1.06 | 1.02 | -10.5% | | | |
| 17-Oct-08 | 8:50 AM | 10:55 AM | None | | | 1.07 | 1.02 | -10.1% | | | |
| | 12:02 PM | 2:07 PM | ML 333X | 0.53 | 4.4 | 0.99 | 0.95 | -16.7% | | | |

Table III. Gasoline Test Engine Data

| Estimated Fuel Density | | 8.00 Lbs./Gal. | | 0.960 Grams/CC | | | | | | | | |
|------------------------|----------------|----------------|-------------|----------------|-------------|--------|--------|----------|----------------|-----|-----|--------|
| Date | Time Beginning | Time End | Time | Product | Oz./20 Gal. | ppm Fe | Inches | Fuel Use | Percent Change | NOx | NO | CO |
| 3-Jul-08 | 10:40 AM | | | | 0 | | | | | | | |
| | 1:40 PM | | | | 0 | | 2.416 | 0.805 | | | | |
| | 2:40 PM | | | | 0 | | 3.217 | 0.801 | | | | |
| | 4:40 PM | | | | 0 | | 4.82 | 0.802 | | | | |
| | Average | | | | Baseline | | | 3.424 | | | | |
| | | | Hrs. | | | | | | | | | |
| 8-Jul-08 | 9:25 AM | 1:25 PM | 4.00 | SulfurX | 1 | | 3.05 | 3.253 | -5.00% | | | |
| 9-Jul-08 | 8:15 AM | 12:15 PM | 4.00 | SulfurX | 1 | | 3.12 | 3.328 | -2.82% | | | |
| 10-Jul-08 | 8:20 AM | 2:20 PM | 6.00 | SulfurX | 0.5 | | 4.63 | 3.292 | -3.86% | | | |
| 24-Jul-08 | 8:30 AM | 12:30 PM | 4.00 | May/Lang | 1 | 5.85 | 3.125 | 3.333 | -2.66% | | | |
| 13-Aug-08 | 10:05 AM | 2:05 PM | 4.00 | May/Lang | 1 | 5.85 | 3.18 | 3.392 | -0.95% | | | |
| 25-Aug-08 | 9:30 AM | 3:30 PM | 6.00 | May/Lang | 1 | 5.85 | 4.57 | 3.250 | -5.10% | | | |
| 26-Aug-08 | 8:05 AM | 12:05 PM | 4.00 | ML 333X | 1 | 5.85 | 3.04 | 3.243 | -5.31% | | | |
| 27-Aug-08 | 9:05 AM | 2:05 PM | 5.00 | FS 116-450 | 1 | 17.58 | 4.37 | 3.729 | 8.89% | | | |
| 2-Oct-08 | 8:15 AM | 10:15 AM | 2.00 | Baseline | | | 1.61 | 3.428 | 0.09% | 197 | 195 | 25,269 |
| 2-Oct-08 | 10:25 AM | 2:25 PM | 4.00 | ML 333X | 7 | 40.97 | 2.88 | 3.072 | -10.29% | 42 | 42 | 5,676 |

| Date | Time | | Time | Product | Oz./20 Gal. | ppm Fe | Inches | Fuel Use | Percent Change | NOx | NO | CO |
|-----------|-----------|----------|--------------------|----------|-------------|--------|--------|----------|----------------|-----|-----|--------|
| | Beginning | End | | | | | | | | | | |
| 6-Oct-08 | 8:15 AM | 12:25 PM | 4.17 | ML 333X | 7 | 40.97 | 3.32 | 3.400 | -0.72% | | | |
| 8-Oct-08 | 10:45 AM | 2:45 PM | Min. 240 | | Baseline | | 602 | 2.508 | | 242 | 240 | 27,981 |
| 14-Oct-08 | 9:54 AM | 12:41 PM | 167 | | 5 | 6.88 | 384 | 2.299 | -8.33% | | | |
| 15-Oct-08 | 11:47 AM | 2:28 PM | 161 | | 5 | 6.88 | 384 | 2.385 | -4.91% | | | |
| 16-Oct-08 | 8:38 AM | 11:17 AM | 159 | ML 333SX | 5 | 6.88 | 384 | 2.415 | -3.72% | | | |
| | 11:31 AM | 2:12 PM | 161 | ML 333SX | 10 | 13.76 | 384 | 2.385 | -4.91% | | | |
| 17-Oct-08 | 8:42 AM | 11:34 AM | 172 | ML 333SX | 15 | 20.65 | 384 | 2.233 | -10.99% | 113 | 112 | 34,427 |
| | 11:48 AM | 2:30 PM | 162 | ML 333X | 15 | 20.65 | 384 | 2.370 | -5.50% | | | |
| 21-Oct-08 | 8:40 AM | 11:31 AM | 171 | ML 333X | 20 | 27.53 | 384 | 2.246 | -10.47% | | | |
| 22-Oct-08 | 9:14 AM | 11:55 AM | 161 | | | | 384 | 2.385 | -4.91% | 196 | 194 | 30,067 |
| | 12:37 PM | 3:29 PM | 172 | | | | 384 | 2.233 | -10.99% | | | |
| 23-Oct-08 | 8:07 AM | 10:52 AM | 165 | | | | 384 | 2.327 | -7.22% | | | |
| | 11:01 AM | 1:41 PM | 160 | ML 333SX | 5 | 6.88 | 384 | 2.400 | -4.32% | | | |
| 27-Oct-08 | 8:15 AM | 11:06 AM | 171 | ML 333SX | 5 | 6.88 | 384 | 2.246 | -10.47% | | | |
| | 11:13 AM | 1:55 PM | 162 | ML 333SX | 5 | 6.88 | 384 | 2.370 | -5.50% | | | |
| 28-Oct-08 | 8:23 AM | 11:06 AM | 163 | ML 333SX | 5 | 6.88 | 384 | 2.356 | -6.08% | | | |
| | 11:17 AM | 2:01 PM | 164 | ML 333SX | 5 | 6.88 | 384 | 2.341 | -6.65% | | | |
| 29-Oct-08 | 8:18 AM | 11:08 AM | 170 | ML 333SX | 5 | 6.88 | 384 | 2.259 | -9.95% | 224 | 222 | 27,243 |
| | 11:15 AM | 2:14 PM | 179 | ML 333SX | 5 | 6.88 | 384 | 2.145 | -14.48% | | | |

| Date | Time | | Time | Product | Oz./20 Gal. | ppm Fe | Inches | Fuel Use | Percent Change | NOx | NO | CO |
|-----------|-----------|----------|------|----------|-------------|--------|--------|----------|----------------|-----|-----|--------|
| | Beginning | End | | | | | | | | | | |
| 4-Nov-08 | 8:16 AM | 11:17 AM | 181 | ML 333SX | 8 | 11.01 | 384 | 2.122 | -15.42% | 101 | 100 | 42,816 |
| 5-Nov-08 | 8:33 AM | 11:28 AM | 175 | ML 333SX | 5 | 6.88 | 384 | 2.194 | -12.52% | | | |
| | 11:44 AM | 2:38 PM | 174 | ML 333SX | 5 | 6.88 | 384 | 2.207 | -12.02% | | | |
| 6-Nov-08 | 7:55 AM | 10:50 AM | 175 | | | - | 384 | 2.194 | -12.52% | | | |
| | 10:59 AM | 1:47 PM | 168 | | | - | 384 | 2.286 | -8.88% | | | |
| 11-Nov-08 | 8:26 AM | 11:15 AM | 169 | | | - | 384 | 2.272 | -9.41% | | | |
| | 1:11 PM | 3:56 PM | 165 | | | - | 384 | 2.327 | -7.22% | | | |
| 12-Nov-08 | 8:33 AM | 11:29 AM | 176 | CESFX #1 | | - | 384 | 2.182 | -13.02% | 204 | 202 | 27,571 |
| | 11:39 AM | 2:23 PM | 164 | CESFX #1 | | - | 384 | 2.341 | -6.65% | | | |

Table IV. Activation Energy for Combustion

| °C | Temp | | 1/T x 10 ⁴ | Reaction Rate | |
|------|---------|----------|--------------------------|---------------|--------|
| | °A | 1/T | | k | ln k |
| 2350 | 2623.16 | 0.000381 | 3.812196 | 50 | 3.912 |
| 2400 | 2673.16 | 0.000374 | 3.740891 | 500 | 6.215 |
| 2450 | 2723.16 | 0.000367 | 3.672204 | 5000 | 8.517 |
| 2500 | 2773.16 | 0.000361 | 3.605995 | 35000 | 10.463 |

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

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

$$\Delta H_a = 258,459 \text{ cal/mole}$$

Figure 1. Reaction Rates vs. Temperature

