

Catalyst for Reducing Particulate Emissions in Combustion Turbine Engine Exhaust

Walter R. May, Ph.D., SFA International, Inc., Houston, Texas, U.S.A.

Abstract

In 1996 an oil-soluble organo-metallic iron containing combustion catalyst was developed for use in Siemens-Westinghouse 501 D-5 104 MW combustion turbine engines. The product included magnesium to reduce vanadium deposits and corrosion. The product resulted in significant reduction of smoke in the exhaust of the engines in steady state and non-equilibrium start-up conditions. The effects were greater than predicted from the literature. The product was used in four power plants in varying size turbine engines and fuels ranging from distillate to residual oil. This paper presents field data and proposes a mechanism for the catalysis.

Introduction

Liquid petroleum fuels, especially high boiling vacuum distillate cuts and residual oil, can contain high molecular weight molecules that do not burn completely to carbon dioxide and water in the combustion process, resulting in carbon particulate matter or smoke in the exhaust. Modern combustion turbine combustion systems known as "high-swirl low-NOx" rapidly quench the flame to reduce temperature and slow formation of NOx. Combining this system with low-sulfur fuel yields environmentally safe exhaust. However, this can increase smoke in the exhaust because of incomplete combustion.

There are several methods of improving combustion. These include reduction of fuel viscosity by dilution with distillate fuel or viscosity improvers. Water and/or steam at the fuel injection will help break up fuel droplets. Optimized operation such as maximum power output will reduce smoke. Metal containing fuel additives will catalytically improve combustion and reduce smoke.

Several metals are known to catalyze combustion of hydrocarbon fuels. These metals include manganese, iron, copper, barium, cerium, calcium and platinum. Reports in the literature indicate that 50% reduction in carbonaceous matter in the exhaust is the limit of effectiveness of these catalysts (1). There are positives and negatives to using these various metals. Manganese, while an effective catalyst, interferes with inhibition of vanadium by magnesium (2). Iron is thought to catalyze formation of sulfur trioxide leading to increased sulfuric acid in the exhaust (acid rain) limiting use to low sulfur fuels. Copper, barium and calcium are less effective (1). Cerium and platinum are very expensive. Iron was the best choice for the catalyst in LSWR fuel.

Hanwha Energy Ltd. Inchon Power Plant

Hanwha's Inchon Plant is located adjacent to their refinery in Inchon, Korea. It consisted of 12 Siemens-Westinghouse 501 D5 104 MW combustion turbine engines fitted with Heat Recovery Steam Generators (HRSG). The HRSG's boosted the output to 150+ MW per engine with 55% heat recovery efficiency.

The plant was built in three stages, three engines, three engines and six engines. The economics of the plant was based on using low sulfur waxy residual (LSWR) oil from the refinery. The crude oil came from Indonesia and China. The LSWR fuel had <2 ppm vanadium, minimal lead and about 15 ppm Ni. The sulfur level was <0.5%. The fuel contained up to 50 ppm Na + K and was washed in an Alfa Laval centrifuge fuel treatment system to <1.0 ppm Na + K.

The exhaust from these engines contained up to 150 mg./M³ particulate matter. This exceeded the 60 mg./M³ requirement at the time that was later reduced to 40 mg./M³ in 1998. Siemens-Westinghouse asked SFA International to evaluate the situation to determine if it could produce a fuel additive that would reduce particulates below 40 mg./M³.

An oil-soluble iron carboxylate was developed that could be combined with oil-soluble over-based magnesium to inhibit vanadium in the fuel. The iron component was limited to 6% iron by weight of metal due to the high molecular weight of the carboxylic acid used to manufacture the product.

Exhaust particulate matter data were measured by Siemens-Westinghouse using EPA Method 5, Hanwha Energy using a Korean firm and a Continuous Emission Monitor (CEM). Examples of these data are given in Table 1. The data were taken with the following variables: power, Fe ppm in the fuel, load and distillate vs. residual content in the fuel. We believed at the time that optimum iron concentration should be about 30 ppm.

It was found that particulate matter was minimized at maximum power output. Particulate matter reduced asymptotically with iron concentration and up to 20% distillate blended into the LSWR significantly reduced particulates. These results were reported by Rising in December 1997 (3).

The fuel additive was formulated to contain 5.5% Fe and 1.1% Mg. This allowed treatment of the fuel at 30 ppm Fe and 6 ppm Mg to treat up to 2 ppm V.

The Hanwha Inchon plant continued to use LSWR fuel with the Fe – Mg combustion catalyst from October 1996 through August 1998. Particulate matter measurements varied to as low as 20 mg./M³. The LSWR use ceased when the Korean Ministry of Environment forbid use of LSWR fuel in the Seoul Province. The plant has since been converted to LNG.

Hyundai Heavy Industries, Ltd.
Hyundai Petroleum Company
Daeson Refinery Power Plant

During 1996-97, Siemens-Westinghouse built a power plant adjacent to the HPC Daeson refinery. This plant contains four 501 D5 104 MW combustion turbines. It is designed to operate three engines full time to primarily supply power to the refinery. Excess power is sold to Korean Electric Power Co. (KEPCO). This plant also has HRSG units to increase efficiency. The fuel is LSWR similar to that used at Hanwha. The fuel treatment system has Westphalia centrifuges to water-wash the fuel and remove water-soluble salts. Because of low fuel cost, this plant operates at high load – an average of 2.7 turbines 8,800 hours per year.

Two products were initially tested in these turbines, SFA International's FuelSpec® 115-6064-21 5.5% Fe – 1.1% Mg oil-soluble product and Turbotect Ltd.'s 703 15% Fe – 2% Mg colloidal dispersion. Extensive evaluations were carried out by HHI to reduce particulate matter below 40 mg/M³. It was found that greater than 30 ppm Fe was required to reach minimum particulate matter levels. To achieve these higher levels of iron, Turbotect's 703 with the higher concentration of iron was selected.

Turbotect 703 was tested over a wide range of iron levels in the fuel with unusual results as shown in Figure 1. These data are averages of a number of measurements and the overall trend has been replicated several times. They illustrate an unexpected and unusual effect. The product shows a minimum at 45 ppm and a second minimum in the 60 ppm range. There is no simple explanation for these observations as they do not follow the usual laws of catalysis.

SFA International developed a new colloidal iron product available in up to 24% iron concentration. FuelSpec® 118-1502 – containing 15% Fe and 2% Mg - has been tested over a range of iron levels and shows the expected asymptotic curve illustrated in Figure 2. It has a distinctly lower smaller median particle size as illustrated in Figures 3 and 4 – 0.0076 micrometer for FuelSpec® 118-1502 compared with 0.0484 micrometer for Turbotect 703. As will be demonstrated in the discussion on mechanism below, this product follows the laws of catalysis.

Hyundai Heavy Industries
Hyundai Electronics Industries Company
Ichon Power Plant

The HEIC Ichon Power Plant is similar in function to the Daeson Refinery Power Plant. However, it has three Siemens-Westinghouse 251 D12 44 MW machines equipped with HRSG's and a Westphalia fuel washing system. This plant was also tested with SFA International's oil-soluble FuelSpec® 115-6064-21 and Turbotect 703. Because of the higher dosage requirement, Turbotect 703 has been used at this plant.

Korean Electric Power Company Ulsan Power Plant

Siemens Westinghouse installed four 501 F 150 MW combustion turbines at this plant. They are dual fuel machines equipped with HRSG's. They were designed for LNG use which was not available during plant commissioning. During this period, they were operated on distillate fuel.

These engines are equipped with high-swirl low-NO_x combustors. During the forty-five minute start-up sequence, full fuel pressure is not achieved until full load is achieved leading to poor atomization of the fuel. With excess air introduced into the combustor to cool the flame and reduce NO_x, poor combustion occurs during start-up resulting in excess smoke when operating on liquid fuel. During plant commissioning phase, the turbines were started during dark hours to avoid disturbing neighbors.

Kerosene was substituted as a start-up fuel. This reduced the smoke somewhat but not sufficient for daylight start-up. Siemens-Westinghouse asked SFA International to develop an additive for testing in the start-up kerosene fuel. SFA devised a product with density and viscosity similar to kerosene so that it would disperse into the fuel with mixing from thermal convection and tank recirculation.

With the additive, the turbines were started during daylight hours with minimal but acceptable smoke levels. As a result, the start-up phase of the plant continued and the turbines were operated with additive until the plant was converted to LNG.

Emission Testing

Siemens-Westinghouse has done extensive testing on exhausts for the effect of the catalyst on SO_x, NO_x and CO. There have been no observations that the catalyst has any effect on these species in the exhaust.

Summary of Field Experiences.

The following observations were made from these experiences.

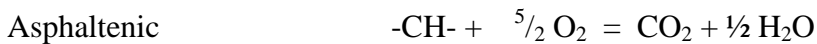
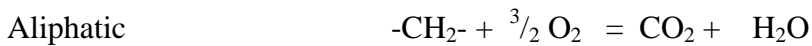
1. The particulate matter in the engine exhaust was considerably lower than predicted from the literature – up to 90% reduction compared with previously observed 50% with oil soluble iron compounds.
2. The treatment system was effective in distilled fuel (kerosene) and residual oil (LSWR).
3. The additive was effective in 44, 104 and 150 MW engines. Size of engine did not affect results.
4. Some distillate added to LSWR improved results.
5. Best results were obtained with full engine load.

6. The catalyst system does not have any effect on other species in the exhaust including nitrogen oxides, sulfur oxides and carbon monoxide. In fact, the effect on nitrogen oxide is beneficial in that the catalyst allows increased quenching of the hot gasses to reduce NO_x formation while eliminating unburned hydrocarbon.

The improved results compared the literature is attributed to the unexpected synergistic combination of iron with magnesium. Magnesium does not have combustion catalyst activity. The combination of magnesium with iron gives much improved results.

Observations of Catalysis

Hydrocarbon fuels contain a mixture of molecules with varying hydrogen to carbon ratio. Three examples of combustion reactions are:



The exact chemical reaction in the combustion process depends on the molecular structure and distribution of the fuel. In a combustion turbine engine, fuel and air are close to stoichiometric as combustion commences. To consider the order of reaction, one must think of discreet packets of fuel and air traveling through the combustion zone.

The activation energy and temperature relationship is defined by the equation (4,5):

$$K = s e^{-\Delta H_a/RT}$$

Where s is a constant and ΔH_a is the heat of activation. Set in logarithmic form, the equation becomes:

$$\ln k = \frac{-\Delta H_a}{R T} + \ln c$$

Differentiating this equation and integrating between limits yields:

$$\ln k_1 / k_2 = \frac{\Delta H_a (T_2 - T_1)}{R T} + \ln c$$

The Heat of Activation (ΔH_a) is the slope of the plot of $\ln k$ versus $1/T$ ($^{\circ}\text{K}$). The slope of the line for the combustion reaction is very steep indicating high activation energy is required to ignite the fuel. With the catalyst, the reaction appears to continue at lower

temperatures. This leads to an apparent lower slope of the line indicating that the catalyst lowers the activation energy for the reaction. This is illustrated in Figure 5.

The next problem is the ramifications of reducing the reaction order by one. The rate expression for a classic second order reaction is:

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

The integrated form of this equation is:

$$k_2t = 1/(a - b) \ln (b(a - x)) / a(b - x))$$

The reaction rate will follow a logarithmic decay as the reactants are consumed. The combustion process has a high activation energy indicated by the temperature required to cause combustion. The immediate reaction of fuel and oxygen results in an increase in temperature of the gaseous phase reactants and products. High pressure in the combustion chamber resulting from the heat of combustion is converted to kinetic energy as the hot gasses expand, reduce temperature and provide work that causes the power vanes to move transferring kinetic energy to the shaft. This is followed by an immediate reduction in temperature in the power section of the turbine. To further complicate matters, immediately following combustion, air is introduced into the gas phase increasing pressure and reducing temperature quickly to 1,000° to 1,200° C.

If the chemical reactants are of sufficient molecular weight and structural complexity to reduce the rate of reaction, the temperature can drop below the level for the activation energy allow reaction to continue before all the fuel is consumed. The result is unreacted hydrocarbon in the exhaust stream resulting in smoke.

Catalytic controlled reactions follow two laws. (1) The order of the reaction is reduced by an order of one and; (2) The rate of reaction is proportional to the concentration of the catalyst.

The rate expression for a classic first order reaction is:

$$-d(a - x) / dt = k_1(a - x)$$

The integrated form of this equation is:

$$k_1t = \ln (a / (a - x))$$

Therefore, with catalysis the reaction will follow the decay of the concentration limiting reactant, generally the fuel in steady state conditions. Combustion immediately stops indicating that fuel is the limiting reactant.

The second law of catalysis requires that the effect is proportional to concentration of the catalyst. We found that the effect is directly proportional to the catalyst concentration.

The smoke reduction follows an asymptotic curve up to 50 ppm catalyst. This follows the same observation as seen with combustion turbines illustrated in Figure 2. Above that level, the effect appears to be minimal.

Mechanism of Catalysis

The fuel additive used in these tests was designed to treat vanadium at 2 ppm and provide combustion catalysis at 30 ppm in the fuel. The product is bimetallic containing a solution of iron naphthenate and over-based magnesium carboxylate and sulfonate mixture. The combination yield far more activity than has been predicted from the literature. Magnesium has no catalytic effect on combustion and iron is known to reduce carbon matter in exhausts by about 50% (1).

We believe that the catalytic effect of iron and magnesium comes about from excitement of outer shell electrons into higher energy states. As these electrons decay to degeneracy, energy is released that maintains the activation energy for reaction even though the temperature is below that required to maintain reaction from that source. Two factors should be considered. The catalyst, while in solution in the fuel and considered homogeneous in that state, is a heterogeneous catalyst in the combustion phase. The bimetallic catalyst converts to metal oxides that are intimate with the fuel and oxygen reactants but not homogeneous. The second is that the catalyst does not reduce the activation energy of the reaction. The more likely effect is that the catalyst releases energy to maintain the activation energy during reducing ambient temperature conditions in the combustion system so that the reaction continues to completion. Therefore, the apparent reduction in Arrhenius Activation Energy illustrated in Figure 2 does not actually occur. We believe that energy released by the catalyst during as electrons decay to the degenerate state replaces that lost by quenching continuing the reaction along the same Arrhenius Activation Energy path as without catalyst.

Iron has the electron structure $1S^2, 2S^2, 2P^6, 3S^2, 4S^2, 3D^6$. Iron is found in three valence states, Fe^0 , Fe^{+2} and Fe^{+3} . Under conditions of the combustion reaction and minimal excess oxygen, the ferric ion is the only likely species to be available. The most likely degenerate electron configuration of the ferric ion is $1S^2, 2S^2, 2P^6, 3S^2, 4S^0, 3D^5$. There are a large number of electron orbitals available as electrons move to higher energy levels. The result is a large number of emission spectra lines with relative low energies.

Magnesium in the +2 valence state has a much simpler electron structure, $1S^2, 2S^2, 2P^6, 3S^0$ and much less complicated emission spectra. On the other hand, the peaks are much stronger than the iron peaks indicating that the electron energy adsorptions are between principal quantum numbers rather than orbital quantum numbers.

Major peaks in the emission spectra of magnesium and iron (III) are given in Table 2. It is noted that the five major peaks of magnesium fall in areas where iron does not have spectra lines. It is also noted that the magnesium lines are stronger by a factor of 10 to 100 than the iron lines. We suggest that the synergistic effect of magnesium on iron is

caused by a small number of complimentary spectra lines of magnesium combined with the many more numerous iron lines over a much wider frequency range.

Conclusion

Observations over the past six years of the use of combustion catalysts in combustion turbine engines present a strong case for the efficacy of reducing particulate matter in engine exhausts. The catalysts function under a variety of situation and do not appear to be dependent on fuel type or engine design.

Initial evaluation indicates that the catalyst does not contribute to emissions in a material manner and the ash produced from these metals is benign. Iron oxide is in the environment as rust and magnesium oxide is ingested into the body as a treatment for stomach acid.

Significant reductions in emissions and the simultaneous increase in fuel efficiency have obvious implications for environmental conditions and fuel economy. We hope that this paper stimulates interest in pursuing further evaluations of this system.

References

1. Eliot, R. C., ed., Boiler Fuel Additives for Pollution Reduction and Energy Saving, Noyes Data Corp., Park Ridge, NJ, 1978.
2. May, Walter R., et.al., "High-Temperature Corrosion in Gas Turbines and Steam Boilers by Fuel Impurities. Part VIII. Evaluation of the Effects of Manganese, Calcium and Several Heavy Metals on Corrosion and Slag Formation", Presented to the American Chemical Society Division of Fuel Chemistry, Inc., Symposium on Heavy Fuel Oil Additives, New York, NY, April 5, 1976.
3. Rising, B., "Particulate Emission Reduction Using Additives, Power-Gen '97 International Exhibition, Dallas, Texas, Dec. 1997.
4. Dykstra, C. E., Physical Chemistry, Prentice Hall, Upper Saddle River, NJ 07458, 1997.
5. E. A. Moelwyn-Hughes, Physical Chemistry, Pergamon Press, New York, 1957.

August 27, 2002