The Technological Contributions of SFA International, Inc. to Combustion Catalyst Technology - 1996 to 2009

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SFA International began business in August, 1980 as a supplier of organo-metallic over-based magnesium compounds to owners and operators of combustion turbines, steam boilers and process heaters operating on fuels containing contaminant metals. These metals are oil-soluble compounds of vanadium, lead and nickel and water-soluble compounds of sodium, potassium and calcium. In the combustion process, these metals form oxides and sulfates with relatively low melting points in comparison to hot metal parts in turbines and boilers. Deposits stick to hot metal parts and reduce heat transfer at a minimum and cause catastrophic corrosion in the case of combustion turbines. SFA sold products that raised the melting points of these deposits so that they did no adhere to hot metal surfaces and cause corrosion. For the first sixteen years of SFA's existence, we concentrated on combustion turbines since these fuel additives were required for the operator to meet engine manufacturer warranty requirements.

SFA International did not vigorously pursue combustion catalyst business until 1996 as results were ephemeral. These types of additives were promoted for reducing smoke or particulate matter. Claims were sometimes grandiose and selling was based on testimonials and unqualified, largely hearsay evidence. Manganese was promoted for reduction of smoke allowing operation of boilers at minimal air to fuel ratios. This reduces exhaust volume and heat loss with the exhaust. Savings have been difficult to quantify and are highly dependent on consistent operation of the equipment. Quantifying advantages was also difficult due to the inherent nature of variables such as boiler type, age and condition. Unfortunately, this ambivalence promoted a "medicine man" aura and a huckster selling approach. SFA elected to stay out of this business and focused on the area where additives were required by engine manufacturers.

A significant book on fuel additives published in 1978 contains some of the best and most reliable data on combustion catalysts available until recently.[1] Experimental data are presented for distillates and residual oil containing 1% and 2% sulfur. Metals evaluated included iron, manganese, barium, cobalt, zinc and calcium. There was only

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[1] **Boiler Fuel Additives for Pollution Reduction and Energy Saving**, Ed. R. C. Eliot, Noyes Data Corp., Park Ridge, NJ, 1978. This book is out of print. The author has been informed that it is occasionally available on EBay and similar locations.

one case of a metal combination reducing particulate matter from 2% sulfur residual oil more than 50% (54% in this case) and that was with 35 ppm Ba and 14 ppm Mn. This concentration will take on more importance in later discussion and was high compared to most evaluations known at the time.

Westinghouse Combustion Turbines

In 1996, SFA was approached by Westinghouse to assist with a problem encountered in Korea.[2,3] Westinghouse was constructing a 1,800 MW power plant at Hanwha Energy, Ltd. in Inchon. The plant consisted of 12 Westinghouse 501 D5 turbines with ratings of 104 MW. Each turbines was equipped with a heat recovery steam generator (HRSG) yielding an additional 50 MW per turbine. The fuel for the power plant was low sulfur waxy residual (LSWR) originating from Indonesia and Malaysia. The fuel contained a nominal 2 ppm of vanadium and SFA supplied a magnesium additive to treat at a rate of 3 parts Mg to one part V by weight.

The Korean Ministry of Environment (MOE) required a maximum of 60 mg./M^3 particulate matter larger than 2 micrometers. They were measuring 120 – 160 mg./M^3. Westinghouse asked SFA for a fuel additive solution to suppress smoke or particulate matter in the exhausts. SFA undertook a study of the problem. The first metal considered was manganese as there are many data on the use of this metal in boilers. Manganese also forms low melting oxides and salts in ash from contaminant metals in the fuel. These compounds are lower melting than vanadium compounds.[4,5] As a result, manganese was ruled out as a candidate.

Other metals were considered. The most active was iron with up to 50% reduction of particulate matter in the exhaust. While this was at the limit of reducing from 120 to 60 mg./M^3, not even considering the higher readings up to 150, it was thought that by increasing metal level in the fuel, we could meet the MOE requirement.

A series of tests were carried out with an iron naphthenate containing 6% iron by weight. Measurements were made by Westinghouse, an outside laboratory hired by

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[2] Walter R. May, Ramu Ramdas, “Catalyst for Improving the Combustion Efficiency of Diesel Fuels”, Presented to IORS 2002 Oil Asia Symposium, Mumbai, India, Sept. 8, 2002. This paper is available on the SFA web site Library page.

[3] Walter R. May, “Catalyst for Improving the Combustion Efficiency of Petroleum Fuels”, Presented to the Technical Exchange Meeting, ARAMCO Research & Development Center, Dhahran, Saudi Arabia, April 28-30, 2003. This paper is available on the SFA web site Library page.

[4] Walter R. May, Michael J. Zetlmeisl, Robert R. Annand and David F. Laurence, “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. This paper is available by request from SFA International.

[5] Walter R. May, “The Effects of Manganese on Inhibition of Vanadium/Sodium Deposits and Corrosion in Gas Turbine and Diesel Engine Fuels”. Available on the Library Page of the SFA web site.

Hanwha Energy and MOE. Results were in the 50 – 60 mg./M^3 range. During the initial tests, magnesium was also injected into the fuel to control vanadium deposits. It was thought that there was no relationship between magnesium and iron on the catalysis of the combustion reaction by iron. After success was achieved and the operation was commercialized, Westinghouse asked SFA to combine the two products. Combining the two metals lowered the iron concentration to 5.5%. Because of additive pump limits, the maximum iron concentration was about 35 ppm. To be certain 6 ppm Mg was added, a ratio of 5 to 1 iron to magnesium was established for the product.

This plant continued to operate successfully from late 1996 through mid-1998 when the Korean MOE suspended use of all residual fuels in the province of Seoul.

During this time, Westinghouse installed four 501 F 150 MW combustion turbines at the Korean Electric Power Co. plant in Ulsan. These machines were designed to operate on natural gas that was not available when the machines were ready for commissioning. The machines were operating on distillate oil with major smoke during the start up period. The situation was so bad the turbines could not be started during daylight hours. Kerosene was provided as alternative fuel but it did not sufficiently solve the problem. Westinghouse asked SFA to supply the iron based catalyst for the Ulsan turbines. The catalyst was added to the kerosene fuel and the result was an outstanding success. Smoke during start-up was eliminated and the turbines could be started at any time of the day. Unfortunately for SFA, the gas lines were completed to the Ulsan plant and use of liquid fuels ended.

Westinghouse installed four 501 D5 104 MW turbines with HRSG units at the Hyundai Daeson Refinery Power Plant. This plant is outside the province of Seoul and uses the same LSWR fuel as at the Hanwha plant. A competitor, Turbotech, Ltd., initially won the business with a 15% iron – 2% magnesium product.

We developed a comparable product based on a colloidal dispersion iron product with up to 20% concentration iron. This product was tested extensively at the Hyundai Daeson Refinery Power Plant and the results are shown in Figure 1 below. We found that our product yielded an asymptotic curve relating particulate matter and iron level in parts per million in the fuel. The curve levels off around 50 ppm Fe. This is much higher than the general experience of the industry, but there are examples of this level of metal concentration in Eliot's book referenced above.[1]

More significantly, the Turbotect product yielded minimums and maximum. The plant found that if they treated with their product at 55 ppm, reasonably good results were obtained. If the level went to 50 or 60 ppm, regulatory limits were exceeded. This raised some interesting points. The Laws of Catalysis state that the change in reaction rate is proportional to the catalysis concentration and that the reaction kinetics follows calculations at one less order of reaction. It is obvious from these data that the

Turbotect product did not follow classical laws of catalysis. In this figure, SFA's FuelSpec 118-1502 is the lower blue line and Turbotect 703 is the higher yellow line.

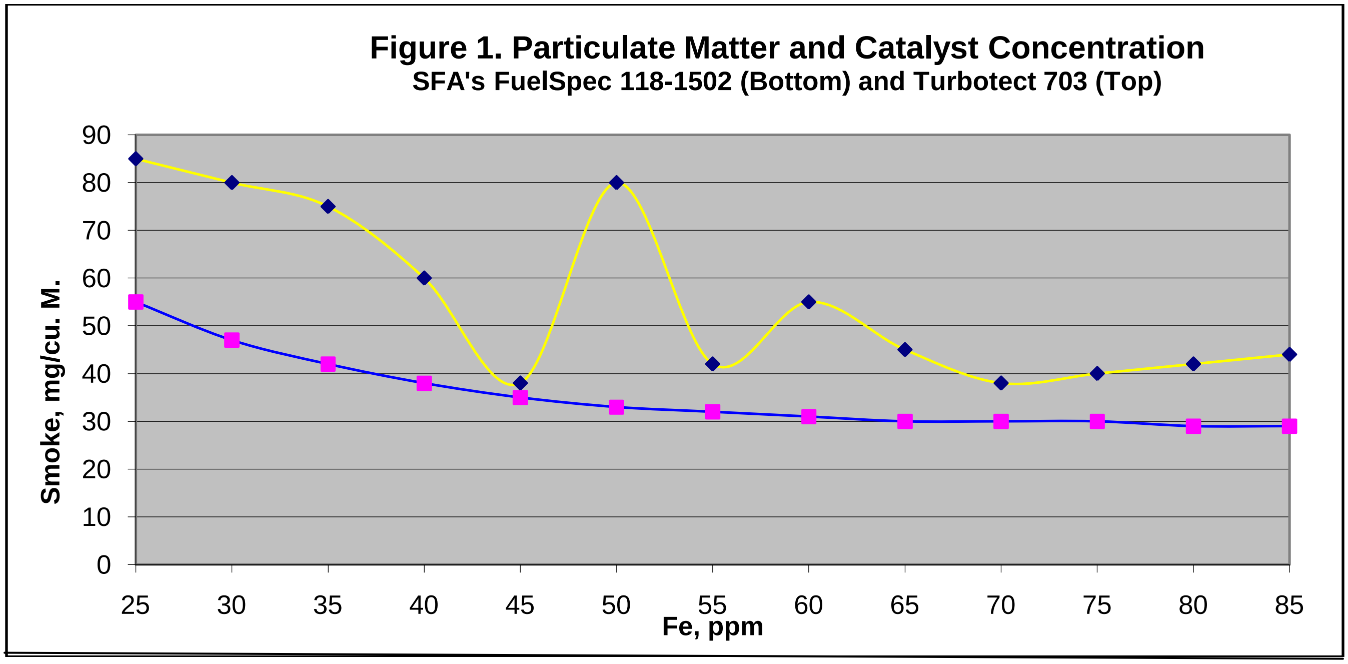

Figure 1. Particulate Matter and Catalyst Concentration
SFA's FuelSpec 118-1502 (Bottom) and Turbotect 703 (Top)

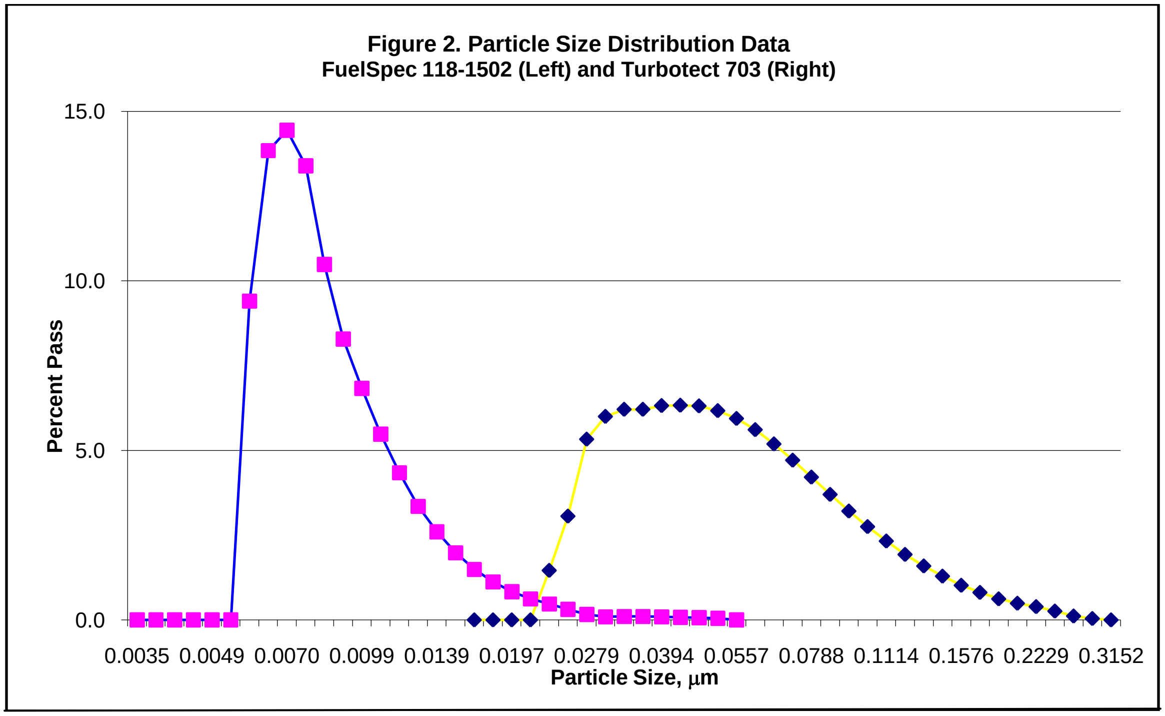

Figure 2. Particle Size Distribution Data
FuelSpec 118-1502 (Left) and Turbotect 703 (Right)

We undertook an evaluation of the Turbotect product to try to understand these observations. A particle size analysis resulted in the data presented in Figure 2.

This figure shows a significant difference in particle size. Turbotect 703 has an average particle size of 0.05 µ meters. SFA's FuelSpec® 118-1502 has an average particle size of 0.007 µ meters. Following these observations, both products were tested by the Korean Institute of Energy Research in a small test boiler. LSWR fuel from the Daeson Refinery Power Plant was used in the test. The results demonstrated that while the two products gave almost identical results at 75% load, FuelSpec® 118-1502 was significantly better at 50% load.

Table 1. KIER Test Data From a Small Boiler

Additive	Catalyst ppm Fe	50% Load Mg./M^3	75% Load Mg./M^3	0_2 Exhaust Gas
SFA International, Inc.	0	215	270.5	2.5%
FuelSpec 118-1502	50	32.2	34.4	1.6%
Reduction		84.3%	89.1%	
Turbotect Ltd.	0	222.7	221.4	6.0%
T-703	50	77.8	21.9	6.0%
Reduction		65.1%	90.1%	

Following these tests, FuelSpec® 118-1502 became the combustion catalyst of choice for the Daeson Refinery Power Plant. Data are given in Table 2 demonstrating the sum of results in two turbines in 2003 and four turbines in 2004. The results were reduction in particulate matter in excess of 90%, **a level never before seen in commercial practice**.

By the end of 2003, we had demonstrated the following discoveries in combustion catalyst technology:

1. A combination of iron and magnesium gives improved catalyst performance compared with iron alone.

2. For combustion turbines, steam boilers and process heaters, an optimum performance was found at 50 ppm iron, much higher than had been previously expected from the literature and field experience.

3. Particle size of the additive is critical. A significant difference was found in performance between SFA's FuelSpec® 118-1502 catalyst with a median particle size of 0.007 µ meters compared with Turbotect 703 with a median particle size of 0.05 µ meters.

4. SFA developed a stable colloidal dispersion of iron oxide in a hydrocarbon solvent with up to 20% iron content.

Table 2. HHI Daeson Refinery Power Plant Summary Results Reduction of Particulate Matter 2003 & 2004

Turbines	Westinghouse 501 D5 104 MW
Fuel	Low Sulfur Waxy Residual (LSWR) Oil
Korean Government Requirement	< 40 mg./M^3
Particulate Level without Catalyst	>160 mg./M^3
Particulate Level with Catalyst	

Turbine	**1**	**2**	**3**	**4**
2003				
High	38.6	25.9		
Low	11.2	12.3		
Average	24.1	17.4		
2004				
High	18.1	18.2	22.7	22.0
Low	10.3	8.1	5.4	9.2
Average	13.8	12.4	13.4	14.4

Compression-Ignited and Spark-Ignited Reciprocating Engines

The first application of our combustion catalyst technology in reciprocating engines began in 2002. Samples were given to an SFA distributor, Emission Control Products wll, for use in a Bahrain truck. This truck was in poor maintenance and could not pass inspection to renew registration. The truck not only passed inspection, but the driver reported more power. This led us to conduct our first trials in six school buses in Bahrain. Records provided in the resultant tests indicated fuel savings ranging from 2% to 20%. This work led to more testing and the Automobile Research Association of India tests. SFA received a grant from the Texas Commission on Environmental Quality and a test was carried out at Southwest Research Institute (SWRI). We conducted a number of tests in railroad engines and power generator sets. The result was many tests with widely varying results.[6]

SFA studied these data and found a correlation of catalyst performance with the level of sulfur in fuel. There were six tests where sulfur levels in the fuel were well defined. These data are given in Table III below.

Table I. Catalyst Performance and Fuel Sulfur Content

2000 or Older Engine

Data Source	SwRI	EcoMission	TGS Locomotive	L&P RR	ARAI	Bus Trial
Fuel Source	Chevron-Phillips	Tx-LED	Off-Road Diesel	Kerosene	India	Bahrain
% Sulfur	0.00006%	0.00100%	0.00270%	0.30000%	1.12000%	2.00000%
Sulfur, ppm	1	10	27	3,000	11,200	20,000
Sulfur, Log ppm	(0.22)	1.00	1.43	3.48	4.05	4.30
Fuel Efficiency	1.89	5.30	9.54	12.40	13.50	13.87

An asymptotic relationship was discovered between fuel savings and sulfur level. That indicated a logarithmic relationship existed between the values. The result is shown in Figure 3.

Linear regression analysis yielded the following mathematical relationship between Log Sulfur PPM and Fuel Savings:

Fuel Savings = 2.70 x log ppm S + 2.59

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[6] These tests are summarized in papers available on the SFA web site "Library" page.

An analysis was carried out on data to develop a mechanism to explain the observations. These data were evaluated with 1st and 2nd order kinetics equations. This resulted in a hypothesized mechanism where it was possible to postulate two distinctly different combustion reactions for simple aliphatic molecules and condensed high molecular weight polycyclic molecules. This led to two separate combustion reactions with rates of reaction differing by a factor of 10^2.

A paper on this work was presented to the American Chemical Society and at the August 2008 Fall Meeting in Philadelphia, PA.[7]

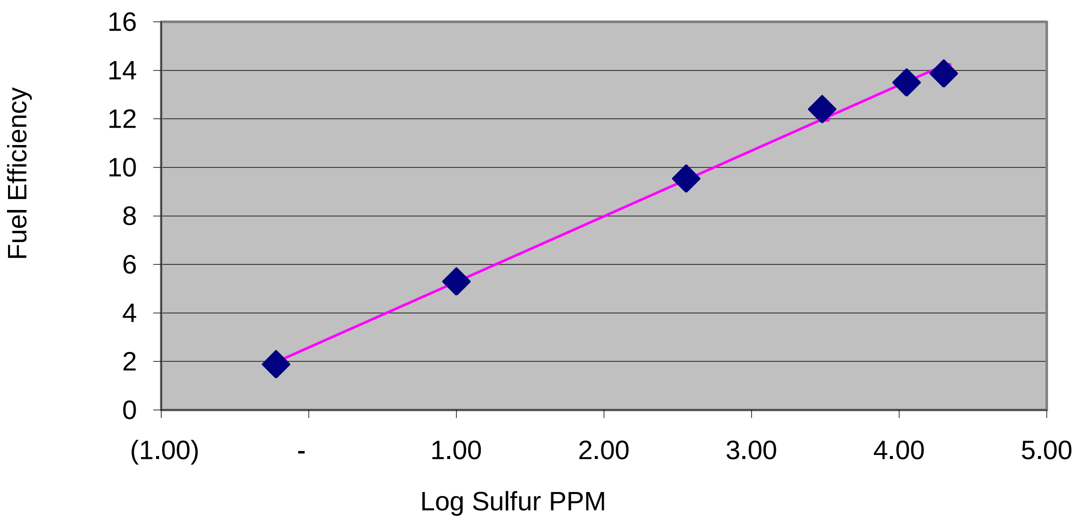

Figure 3. Fuel Efficiency and Sulfur

Several major breakthroughs in application of the catalysts in Diesel engines were discovered at Jerry Lang Combustion Consultants in Lindale, TX. We discovered that the optimum level for iron is 10 ppm. This led to rethinking the economics of fuel treatment and development of new product formulations.

The second major discovery was that in low sulfur “Low Emission Diesel” (LED) fuels, addition of a lubricity agent to the additive yielded much improved results. In comparison with iron catalysts that did not contain magnesium, we found that our iron-magnesium catalyst will yield 6% fuels savings in LED fuel compared with 4% for iron

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[7] W. R. May, “Hydrocarbon Fuel Chemistry: Effects of Sulfur on Combustion Reaction Rates”, American Chemical Society, Fall Meeting, Philadelphia, PA, August 2008, Paper No. 1207537.

alone. With addition of a lubricity agent, iron alone yields 6% savings and iron-magnesium yields 9% fuel savings.

The next discovery was that the product worked equally well in spark-ignited reciprocating engines operating on gasoline. Research found that the iron-magnesium catalyst reduced NO_x in engine exhausts by as much as 75% in both compression-ignited and spark-ignited engines. With this information, we realized that combustion catalysts reduce NO_x and particulate matter and save more than enough fuel to pay for them. SFA is currently using its technology to ensure commercial shipping is in compliance with government regulations through a major reduction in $NO_{x.}$.

We have discovered:

1. A mechanism based on quantum chemistry that explains how combustion catalysts function.

2. The effectiveness of combustion catalysts is directly related to asphaltenes in fuel. Fuel savings in reciprocating engines from use of a combustion catalyst can be predicted from sulfur in the fuel.

3. The optimum iron level in fuel for reciprocating engines is 10 ppm. This is 20% of the effective level for turbines and boilers. Higher levels of iron will result in reduced results. Lower dosage levels result in an increased time between the start of using catalyst and achieving best results.

4. Lubricity agents enhance combustion catalyst effectiveness in low sulfur aliphatic fuels. They increase fuel savings by about 50% for both iron and iron-magnesium catalysts.

5. Combustion catalysts are equally effective in Diesel and gasoline engines.

6. Combustion catalysts reduce NO_x significantly. SFA has been successful in reducing NOx in every fuel it has tested.

Additive Formulations, Dosing and Testing

Combustion catalysts depend on high quality components. Development of the 20% iron colloidal dispersion was discussed earlier. We developed a 12% iron salt of from a carboxylic acid. This product is totally soluble in fuels and will not precipitate or settle out with time. We developed a 30% magnesium sulfonate that gives superior solubility and formulation stability.

SFA has developed additive dosing systems and test protocols to insure that proper addition and mixing occurs in the fuel. A customer plant is surveyed by SFA engineers to understand the equipment and find the optimum place for additive injection. There is no substitute for customer service. Combustion catalyst can function only if the product is in the fuel. SFA engineers visit customers on a routine basis to assist customers with proper use of the products for maximum results.

SFA has worked diligently to teach proper use of combustion catalyst technology. There are companies that sell solid ferrocene. Adding ferrocene in solid form to a fuel tank will yield sporadic results at best. We teach customers to avoid these forms of catalysts. SFA has dissolved ferrocene in its product line for special applications where it is most effective. Dissolved ferrocene will provide beneficial catalytic effects if added properly. There are limitations to the amount of ferrocene that can be added to solution due to limited solubility of the compound in hydrocarbon fuels.

SFA will continue its effort to advance catalyst technology. The company is focused on:

1. Development of high quality and high-concentration oil-soluble iron and magnesium compounds for use in lighter fuels and in systems with minimum agitation and mixing.

2. Development of dosing systems and methods of surveying plant sites or equipment to yield optimum application and benefits.

3. Education to teach the proper use of combustion catalysts in all applications.

Conclusion

SFA is proud of its effort to develop the highest quality products with strong technical support. The company has made a significant contribution to combustion catalyst technology over the past 13 years.

We believe that we are on the cutting edge of new developments that will reduce harmful emission and pollution, fuel use and associated carbon footprint, and save customers money through actual fuel savings by using combustions catalysts as a solution vs. the alternative high capital engineering proposals to these problems.

SFA plans significant advancement in exhaust emissions monitoring and real time capture of exhaust emissions data to demonstrate to regulatory authorities that regulatory requirements are met. While we have made significant advances over the past thirteen years, the company expects this to only be the beginning of further developments in these areas.