

Catalyst for Improving the Combustion Efficiency of Petroleum Fuels

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Abstract

In 1996 an oil-soluble organo-metallic iron combustion catalyst was developed for use in Siemens-Westinghouse 501 D-5 104 MW combustion turbine engines. The product also included oil-soluble magnesium to reduce vanadium deposits and corrosion. This product resulted in significant reduction of smoke in the exhaust of engines operating in steady state and non-equilibrium start-up conditions. The overall effects were greater than predicted from the literature.

We extended this work to steam boilers and compression-ignited reciprocating engines. We have found that the iron-magnesium catalyst when added to Diesel and heavy fuel oil supplies, promotes complete and more efficient combustion in the engine, resulting in increased power, improved fuel economy and radically reduced smoke emission. Certain metals, including Mn, Fe, Cu, Ba, Ce and Pt, are known to have catalytic activity in combustion processes. The iron-magnesium combination acts synergistically to give greater activity than expected.

This paper presents data from tests conducted by a combustion turbine engine manufacturer and customer, a government testing laboratory and independent fleet tests. A mechanism for the catalysis is proposed.

Combustion Turbines – Hanwha Energy Ltd., Incheon, Korea

In 1996, Siemens Westinghouse began start-up of a new power plant at Hanwha Energy in Incheon, Korea. There were initially three model 501 D5 104 MW combustion turbines with nine more in process of installation. The economics of the plant were based on use of low sulfur waxy residual (LSWR) fuel oil from the Hanwha refinery adjacent to the power plant. Particulate matter in the exhaust was 120 – 150 mg./cu. M. exceeding the 60 mg./cu. M. requirement at the time. This requirement was reduced to 40 mg./cu. M. in 1998. Westinghouse began an investigation into the use of fuel additives containing combustion catalysts to solve the problem. This work was reported by Rising in 1997 (1). SFA International, Inc. was invited to participate in this work.

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 (2). There are positives and negatives to using these various metals. Manganese, while an effective catalyst, interferes with inhibition of

vanadium by magnesium (3). Iron is thought to catalyze formation of sulfur trioxide leading to sulfuric acid formation limiting use to low sulfur fuels. Copper, barium and calcium are less effective (2). Cerium and platinum are very expensive. It was decided that iron was the best choice for the catalyst.

An oil-soluble iron carboxylate was developed that was miscible in the fuel and could be combined with oil-soluble over-based magnesium used to inhibit vanadium in the fuel. This was a 6.0% oil-soluble iron-napthenate product. Initial work indicated reduction of particulate matter from 120-150 mg./cu. M. to 60 which met the initial Korean Ministry of Environment requirement in 1996-98. Westinghouse and Hanwha measured the data summarized in Table 1.

The second set of turbines came on line later in 1996 and testing continued with the catalyst in six units. Table 2 presents data taken between October 31 and Dec. 26, 1996 under varying loads and percents distillate oil in the LSWR fuel. These data demonstrated that $<60 \text{ mg./M.}^3$ could be achieved with 0% distillate oil and less than full load – see unit 3 data. The data remained above 40 mg./M.^3 in most cases.

This work demonstrated that (1) lower particulates are found at high load, (2) distillate fuel yielded significantly lower particulates than LSWR residual fuel, and blending small amounts of distillate into the LSWR significantly reduced particulates and (3) the reduction of particulates was proportional to the concentration of catalyst.

The remaining turbines came on line in 1997 raising the total to 12 units. Heat recovery steam generators (HRSG) units were installed and the plant capacity increased to 1,800 MW. Dust loadings as low as 20 mg./M.^3 at 40 ppm Fe were measured indicating more than 80% reduction in particulate loading. The Korean Ministry of Environment reduced the particulate level requirement to 40 mg./cu. M. in 1998. We were able to meet this requirement until mid-1998 when the Korean Ministry of Environment proscribed use of the fuel in the Province of Seoul. This plant now operates on liquefied natural gas.

Combustion Turbines – Hyundai Heavy Industries, Ltd., Daeson, Korea

Hyundai Heavy Industries Petroleum Subsidiary built a new refinery at Daeson. This refinery included an on-site power plant for the refinery and local area with four Westinghouse 501 D-5 104 MW combustion turbines similar to those at Hanwha's Inchon Plant. The fuel was a similar LSWR material although derived from Chinese crude oil rather than Indonesian in the case of Hanwha. Both SFA International, Inc. and a competitor competed for this business. The competitor introduced a dispersion type product with 15% iron and 2% Mg that was extensively tested. The results were unusual as indicated in Figure 1. The product shows a minimum at 45 ppm Fe with strong peaks on both sides. These data are not consistent with classical laws of catalysis.

SFA also developed a colloidal dispersion product with high iron concentration. We found a dosage curve similar to that at Hanwha Energy shown in Figure 1 that follows classical laws of catalysis. SFA's FuelSpec® 118-1502 has shown lower particulate

matter over the dosage range than competitor's product. SFA's FuelSpec® 118-1502 has an unusually small average particle size of 0.007 µm compared with average particle size of 0.05 µm for the competitor's product shown in Figure 2. We believe that the smaller particle size results in higher activity. We do not have an explanation for the fact that the competitor's product activity is not proportional to concentration other than the particle size.

Low Pressure Boiler Application

The Korean Ministry of Environment required that the additive was tested in a government operated laboratory at the Korean Institute for Energy Research (KIER) to verify that it would function as required and not create any additional environmental problems. This work was carried out in a low-pressure test boiler at 50% and 75% loads. LSWR fuel from the Hyundai Daeson Refinery was used in the test. The data are presented in Table 4. These data are averages of up to 10 tests under each condition. The data demonstrate that SFA's FuelSpec® 118-1502 combustion catalyst reduces emissions by 84.3 and 89.1% respectively at 50% and 75% loads. This compares with tests presented in Table 5 for the competitor's product one year earlier. We have no explanation as to why FuelSpec® 118-1502 performed better than the competitor's product at 50% load and compared similarly at 75% load. The tests were carried out eleven months apart on different fuel samples.

The reductions were similar to those observed in combustion turbine exhausts at Hanwha and Hyundai. There are no data in the literature that give similar reductions of particulate matter in boiler emissions (3).

Application in Reciprocating Engines

Reciprocating engines, whether spark-ignited or compression-ignited, represent a different set of problems from combustion turbines, steam boilers and industrial process heaters. Reciprocating engines have a more complex system of pistons and valves subject to abrasive wear and problems with deposit build-up and corrosion. SFA International has treated Wärtsilla V 32 18-cylinder 8 MW engines at the Coastal Power Plant at Nejapa, El Salvador. That experience indicated that over-based oil-soluble magnesium fuel additives could be used to inhibit vanadium deposits and prevent corrosion on piston crowns and valve seats. It also reduced corrosion and failure of turbocharger power rotors. There were no examples to our knowledge of iron-magnesium fuel additives used in automotive high-speed (4,000 rpm) compression-ignited engines used in transportation applications.

A KIA 1.6 liter Diesel truck used at the Emission Control Products WLL blend plant and warehouse in Bahrain had a severe emission problem. It would not pass inspection for annual renewal of registration. It was suggested that the oil-soluble iron combustion catalyst combined with oil-soluble over-based magnesium might alleviate the emission problem so that the vehicle would pass inspection. The product was introduced into fuel

at the rate of 30 ppm iron. A reduction of emissions was noted visually. The dosage level was increased 60 ppm. Emissions were visually eliminated and the vehicle passed inspection. More surprisingly, the driver of the vehicle reported that it had the power of a new truck.

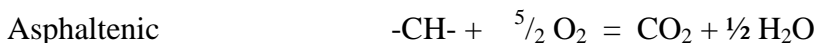
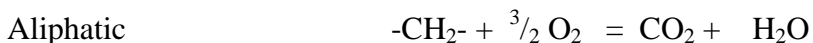
Following this observation, an owner of a bus fleet in Bahrain agreed to test in six vehicles over a period of about 8 weeks. We reformulated the fuel additive so that 500 ml. of additive achieved 50 ppm iron and 10 ppm magnesium in 100 liters fuel. This additive was a combination of iron salts of 200-240 molecular weight highly oil soluble carboxylic acid and over-based magnesium oxide suspended in a carboxylic acid and sulfonic acid surfactant system. The product concentration was adjusted with Solvent 150, a highly aromatic solvent with a flash point $>60^{\circ}$ C. The fuel additive closely duplicated density and viscosity of the fuel so that mixing and distribution of the metals in the fuel in a homogeneous manner could be easily attained by agitation caused during normal driving conditions. This additive has been named MNK® 1221, a registered trademark of Emission Control Products WLL.

There was no attempt to control driving conditions or duplicate traffic conditions. The results of this test are given in Table 6. The six vehicles gave a range of 2.9% to +19.7 % reduction in fuel consumption. The vehicle with the lowest result was badly in need of major engine maintenance and was using oil heavily. The other vehicles had 200,000 km or more on the odometer. All drivers with positive results reported a noted increase in power from the engine.

Further tests were carried out on a single vehicle under the auspices of the Automotive Research Association of India (ARAI). The vehicle was a small Padmini Premier 137D sedan. The fuel line was attached to a calibrated measuring device so that the fuel use could be accurately measured. In a relatively short test, a total of some 1,500 km., fuel consumption was decreased 16.1% and 18.7% under city and highway conditions respectively. These data are presented in Table 7. The driver also noted an increase in power from the engine.

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 the combustion-ignited reciprocating engine, oxygen present in air is compressed to ignition temperature and fuel is injected. While

the air is in slight excess, it can be safely assumed that a discreet 2nd order reaction is occurring with two distinct reactants, hydrocarbon fuel and oxygen.

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

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

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 a lower slope of the line indicating that the catalyst lowers the activation energy for the reaction. This is illustrated in Figure 3.

The next problem is the ramification 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 piston 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 piston to move transferring kinetic energy to the crankshaft. This is followed by an immediate reduction in temperature in the piston chamber.

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 reaction is complete. The result is unreacted hydrocarbon in the exhaust stream resulting in smoke.

Catalytic controlled reactions follow two laws. The order of the reaction is reduced by an order of one, and the rate of reaction is proportional to the concentration of the catalyst. Our field observations indicate a catalytic effect on emissions and energy from the fuel as indicated from increased “power” and fuel efficiency.

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. Under accelerating conditions the reaction will follow the oxygen level when excess fuel is injected into the piston chamber. This is observed as smoke not entirely eliminated during acceleration.

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. Since the catalytic effect (under steady state conditions) is the only observation beyond the fact that fuel and oxygen remain in “infinite” supply in the combustion chamber, the system appears to have reduced to a pseudo zero-order reaction.

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%.

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 Activation Energy illustrated in Figure 5 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 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 8. 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

The results presented in this paper are those that have been carried out by sources independent from SFA International to demonstrate unbiased evaluation of the catalyst. SFA has carried out a number of other tests with customers under proprietary conditions that have given similar results. The product has been in commercial use in combustion turbines since 1996 and in boilers since 2002. We have yet to find a case in which emissions have not been reduced and/or power increases from the equipment observed.

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. 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.

Reductions in emissions have been well beyond anything seen in the literature and indicate an unusual and unexpected catalytic effect.

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Figure 1
Particulate Matter and Catalyst Concentration
SFA's FuelSpec 118-1502 (Blue) and Competitive Product A (Red)

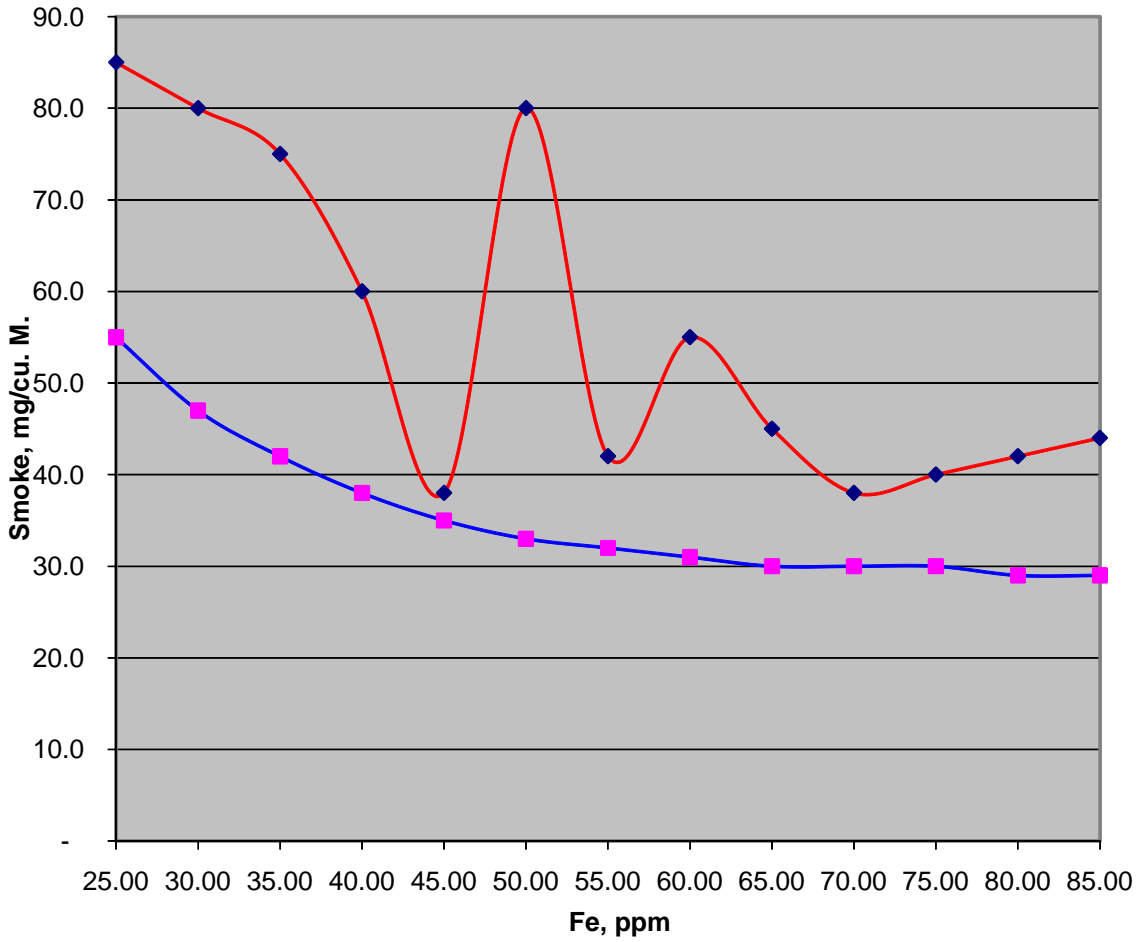


Figure 2
SFA's FuelSpec 118-1502 (Red) and Competitive Product A (Yellow)

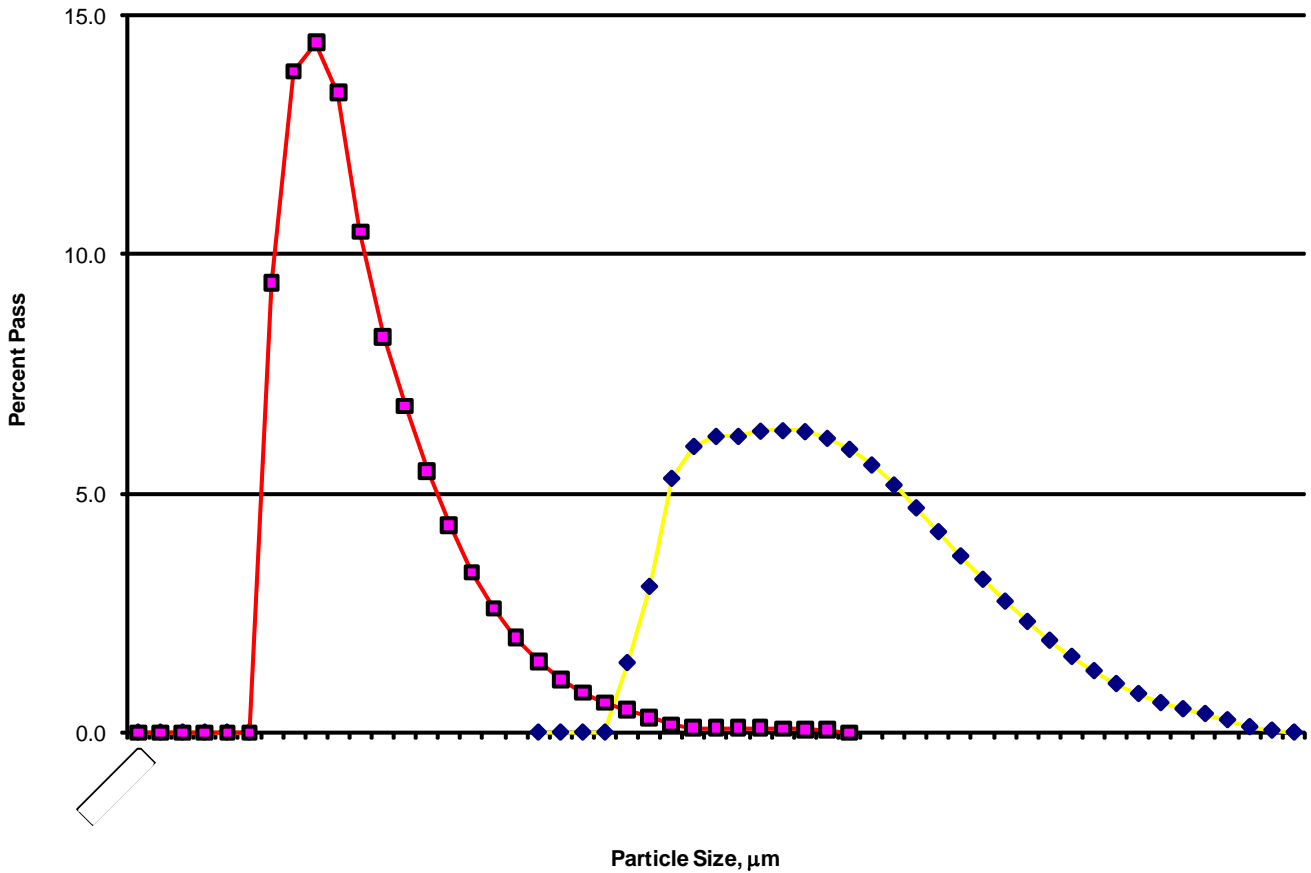


Figure 3.
Activation Energy for Combustion Catalysis Reaction

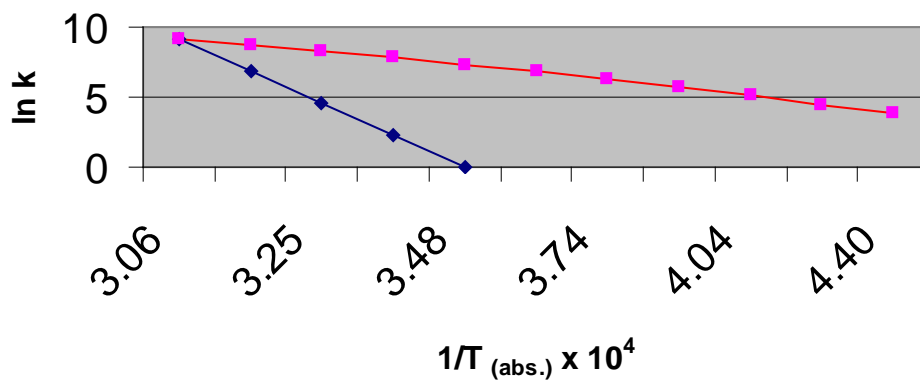


Table 1

Hanwha Energy Ltd. Inchon Plant

Westinghouse 501 D-5 104 MW Combustion Turbines

Unit	Load MW	Fe ppm	Exhaust O ₂ , %		Particulates 4% O ₂		Fuel
			M-5	HEC	M-5	HEC	
1	90	0.0	15.6	15.3	122.4	108.2	LSWR
2	87	0.0	15.6	15.3	93.9	92.4	
2	88	7.5			123.7		
2	85	14.9	15.6	15.2	76.7	79.2	
1	87	14.9	15.4	15.6	80.5	87.1	
1	88	29.9	15.6	15.6	62.9	78.6	
2	84	31.3	15.8	15.2	61.1	73.9	
1	88	35.8	15.6	15.6	61.1	76.7	
2	88	44.87	15.8	15.1		74.2	
1	89	29.9	15.8		61.1		
2	90	29.9	15.8		54.2		
1	88	0.0	18.8		58.2		DO Only
2	85	29.9	15.6		29.1		

M-5 EPA Method 5 (Westinghouse Measurements)

HEC Hanwha Energy Corporation

Data received from Westinghouse Electric Corporation Sept. 23, 1996.

Table 2
Hanwha Particulate Emission Data
Operating Data from Units 1 – 6

Unit	Load MW	Date	% DO	Dust Mg./M. ³	Fe ppm
1	90	18-Dec-96	0	94	30
2	105	16-Dec-96	5	51	30
3	95	31-Oct-96	5	37	30
3	95	31-Oct-96	5	38	30
3	100	06-Nov-96	5	49	30
3	99	20-Dec-96	0	74	30
3	99	20-Dec-96	0	49	36
3	80	24-Dec-96	0	57	36
3	80	24-Dec-96	0	62	36
3	95	26-Dec-96	15	51	36
3	95	26-Dec-96	15	40	36
3	90	26-Dec-96	15	46	36
4	100	02-Nov-96	5	46	30
4	100	02-Nov-96	5	49	30.3
5	97	04-Nov-96	5	63	27.6
5	100	04-Nov-96	5	50	27.6
5	60	16-Dec-96	5	79	30
5	100	20-Dec-96	0	73	30
5	100	20-Dec-96	0	60	36
6	100	06-Nov-96	5	50	30
6	90	18-Dec-96	5	58	30

Table 3

Hyundai Heavy Industries Daeson Refinery Power Plant

Combustion Catalyst Tests

Ppm Fe	July 10-11, 2002		July 18, 2002	
	Product A Mg./M ³	SFA 118 Mg./M ³	Product A Mg./M ³	SFA 118 Mg./M ³
30		21.7 46.2 52.3		
Average		34.0		
35				31.1 41.2 42.2 42.6
Average				39.3
40	114.4 154.7 174.4 199.0			
Average	160.6			
45	31.6 32.7 47.3			31.6 33.4 33.5 36.6 37.1
Average	37.2			34.5
50	64.1 70.5 58.3 51.1	25.6 38.5 47.6 48.1		
Average	61.3	40.0		
55				23.8 30.6 38.8 39.5
Average				33.2

Table 4

Korean Institute of Energy Research

Low Pressure Boiler Tests – Low Sulfur Waxy Residual Fuel

Load		75%	75%	Difference
Catalyst, ppm Fe		0	50	
Date		10-Oct-02	10-Oct-02	
Smoke No.	Bach. No.	3.1	2.1	-1.1
Dust	Mg./M ³	306.2	33.4	-272.9
Dust, O ₂ , 4%	Mg./M ³	268.8	29.3	-239.6
Improvement				89.1%

Table 5

Korean Institute of Energy Research

Comparison of Results with Two Combustion Catalysts

Additive	Catalyst ppm Fe	50% Load Mg./M ³	75% Load Mg./M ³	O ₂ Exhaust Gas
SFA International, Inc.	0	215	270.5	2.5%
FuelSpec® 118-1502	50	32.2	34.4	1.6%
October, 2002		84.3%	89.1%	
Competitive Product	0	222.7	221.4	6.0
November, 2001	50	77.8	21.9	6.0
		65.1%	90.1%	

Table 6
Emission Control Products WLL
Bahrain Fleet Tests

Manufacturer	Ashok Leyland	Ashok Leyland	Ashok Leyland	Mitsubishi	Mitsubishi	Toyoto
Year	1991	1996	1997	1996	1997	1995
Vehicle No.	4059	4394	4402	4038	4068	4374
Without Catalyst						
Kilometers	3,267	3,488	3,281	3,615	5,034	3,201
Km./Lit	3.209	3.566	3.249	6.537	6.000	5.041
With Catalyst						
Kilometers	3,521	3,913	4,607	2,710	5,311	3,528
Km./Lit.	3.510	4.005	3.888	6.725	6.445	6.010
Improvement	9.38%	12.31%	19.67%	2.88%	7.42%	19.22%

Table 7

Automotive Research Association of India (ARAI)

Calibrated Fuel Measurement Test

Premier Padmini 137D 1.6 Liter Diesel Engine

Conditions	Km	Without Catalyst		Improvement
		Liters	Km/Liter	
City	256	26	9.85	
Highway	389	28	13.89	
		With Catalyst		
City	480	42	11.43	16.1%
Highway	531	32.2	16.49	18.7%

Table 8

Major Atomic Spectra Lines for Iron(III) and Magnesium(II)

Iron		Magnesium	
Wavelength	Intensity	Wavelength	Intensity
2,151.78	15		
2,174.66	15		
		2,795.53	1,000
		2,825.70	600
		2,852.13	6,000
3,013.17	15		
		3,832.30	300
		3,838.29	50
3,954.33	16		
4,164.73	18		
4,296.85	16		
4,304.78	18		
4,310.36	20		
4,372.81	18		
5,243.31	18		
5,276.48	15		
5,282.30	16		
5,833.93	18		
5,891.91	15		
5,929.69	18		
5,999.54	18		
6,032.59	16		