

Marine Emissions Abatement

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There are 46,340 ocean going ships with an average main engine size of 5.6 MW and three auxiliaries of 750 kW each. These engines run 300 days per year while the auxiliaries are operated 365 days per year. In the United States, 4% of petroleum liquids go into marine transportation, or 2,900 tons/day. The U.S. uses about 25% of total world petroleum consumption. Based on that statistic, marine consumption of petroleum liquids is approximately 12,000 tons/day or 4,320,000 tons/year.

There are four pollutants in the exhaust of engines operating on hydrocarbon fuels that are of primary concern to environmentalists and governmental regulatory agencies: carbon dioxide, particulate matter, nitrogen oxides and sulfur oxides. There are other materials in lesser quantities that will be addressed as well. The purpose of this paper is to evaluate available technology for abating these compounds.

Table I contains a summary of Marine Emission Abatement Technology. This gives the primary methods of reducing each category of emissions with positives and negatives.

Carbon Dioxide and Fuel Consumption

The reaction of a hydrocarbon fuel with oxygen in the combustion process releases carbon dioxide, water and energy. There is no alternative in the process of releasing the energy from a hydrocarbon fuel. Carbon dioxide released is directly proportional to the amount of energy released. The amount of carbon dioxide released by hydrocarbon fuels depends a great deal on the molecular structure of the fuel. Natural gas releases the least amount of carbon dioxide for a fixed amount of energy due to the fact that the ratio of hydrogen to carbon in the average molecule of methane is highest of all hydrocarbon fuels. Liquid petroleum fuels release more carbon dioxide for the same amount of energy because of the lower hydrogen to carbon ratio followed by coal with the most carbon dioxide because it approaches pure carbon. The chemistry of these reactions is illustrated in Table II.

While there is ongoing discussion about the effect of carbon dioxide on global climate change, carbon dioxide in the upper atmosphere has almost doubled from 250 ppm in 1750 to 450 ppm today. It is not the purpose of this paper to take sides on the issue. Our position is that reducing fuel consumption and protecting the environment is good for world economies regardless of the direct effect of carbon dioxide levels in the upper atmosphere on climate change.

The theoretical efficiency of energy release in a chemical reaction can be calculated from the following equation:

$$\text{Energy Efficiency} = \frac{T_{\text{Combustion}} - T_{\text{Exhaust}}}{T_{\text{Combustion}}}$$

T is in degrees on the Absolute temperature scale. In this scale, 0° absolute = -273.16° C. or -459.69° F. At 2,500° Abs. combustion temperature and 500° Abs. exhaust temperature, the theoretical efficiency would be 80%.

In practice, the efficiency of energy in fuel into an engine compared with power out is much different. The practical limit of the most efficient field-erected steam boiler or combustion turbine equipped with a heat recovery steam generator in the exhaust is about 55%. Ultra low-speed Diesel engines reach 50% efficiency. A medium- or high-speed compression-ignited reciprocating engine (Diesel) is in the 30 – 35% range and a spark-ignited reciprocating engine (gasoline) is in the 20 – 25% range. Steam railroad locomotives were in the 5% range as they did not condense used steam and recycle the water.

There are ways to reduce fuel consumption. These are:

- Engine design which is moving toward more efficient engines. The new Wärtsillä RTflex engines approach 50% efficiency. These engines operate at 100 rpm and produce in some models more than 100,000 HP.
- Higher quality fuels. MDO (medium Diesel oil) is a distilled fuel with higher quality than HFO (heavy fuel oil). MDO burns more cleanly producing more energy and lower total fuel consumption. This is reflected in the energy value of the fuel measured in BTU's/lb. or Joules/Kg.
- Combustion catalysts result in more efficient combustion of the fuel. The catalyst causes the fuel to burn more rapidly and completely yielding more energy from the fuel and higher pressure on the piston at the optimum crank angle in reciprocating engines.

Reduced fuel consumption leads to a smaller carbon footprint even though the amount of carbon dioxide produced is the same. The difference is in particulate matter, unburned hydrocarbons and carbon monoxide. The result is lower emissions and reduced impact on the environment.

Particulate Matter

Particulate matter (PM) is smoke or soot emanating from the exhaust. Particulate matter is partially burned hydrocarbon material that is in the condensed aromatic form. It is similar to graphite and resembles sheets of carbon joined in a hexagonal form. These molecules have unsaturated bonds that result in sharing of electrons. These types of molecules cause free radical formation and are highly carcinogenic. Mice on verges of highways have high incidences of pulmonary tumors caused by PM's.

In actual practice on a ship, high levels of soot result in oily material on the ship with a low pH from entrained sulfuric acid. It is not only a health hazard, but is difficult to clean and remove. It is highly corrosive to metal. Ship personnel complain that the material is tracked all through the ship.

PM's can be measured quantitatively by passing a measured sample of exhaust gases through a filter for a period of time and weighing the retained material. Filters are limited to 2 micrometer (micron) size range. The resulting measurement is only for particulate matter of greater than 2 micron in size. The human eye can see light in the 0.4 to 0.7 micron wavelength. As a result, we can see particles down to 0.4 microns in size. Therefore, the actual level of P.M. is a multiple of the measured amount by this method. PM measurements range from a few milligrams to 2,000 milligrams per cubic meter of exhaust gas. The latter would be typical of a truck Diesel smoking heavily under load.

There are several ways to alleviate particulate matter.

- Distilled, clean fuels will burn more completely reducing particulate matter formation.
- Maintaining engines in good repair will reduce PM's.
- Operating at reduced loads and higher air to fuel ratios reduce PM's. However, this approach reduces engine efficiency.
- Combustion catalysts cause more efficient burning of the higher molecular weight compounds in the fuel leading to much reduced PM's. We have seen 90% reduction in PM's in engine exhausts. Fuel savings from use of the catalyst will more than pay for the catalyst cost.

Nitrogen Oxides (NO_x)

Nitrogen oxides form at combustion temperatures through reaction of the naturally occurring nitrogen (N₂) with oxygen (O₂). NO_x is highly toxic; the LD₅₀ concentration is only 10 times greater than for hydrogen cyanide. NO_x goes to the upper atmosphere

where it combines with oxygen and carbon dioxide to form smog, a highly dangerous form of pollution.

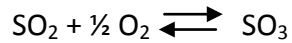
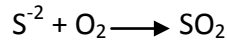
There are two ways to reduce or eliminate NO_x . The first is reduction of combustion temperature, or time at combustion temperature. The second method is reaction of nitrogen in NO_x with ammonia or urea to form atmospheric nitrogen (N_2). The following is a discussion of different methods.

- Reduction of combustion temperature. This is commonly carried out by either reducing engine load or adding water to the fuel. In the former case, the engine is operated at lower loads and under less efficient conditions. The result is less NO_x but higher fuel consumption. In the second case, water is emulsified into the fuel. The water must be heated to the boiling point, converted into steam by adding the heat of vaporization, and raised to the combustion temperature. This absorbs energy increasing fuel use and reducing engine efficiency. The resulting trade off is less than desirable.
- Selective Catalytic Reduction. Exhaust gases are passed over a catalyst bed containing heavy and expensive metals such as molybdenum and tungsten. Ammonia or urea is injected into the exhaust stream to reduce the nitrogen in NO_x to atmospheric nitrogen. While the process is efficient when operated properly, it is expensive to install and requires manpower and attention to operate. Urea must be constantly injected into the exhaust stream. The catalyst bed must be maintained in a clean condition. The result is an expensive system for the operator.
- Combustion Catalysts. Catalysts reduce the time at maximum combustion temperature resulting in significantly reduced NO_x formation. An iron containing catalyst will reduce NO_x by as much as 30%. An iron-magnesium combination catalyst has demonstrated 75% and higher reduction. Use of a combustion catalyst requires continuous injection with good mixing of the product into the fuel stream before it enters the engine. A supply of catalyst must be maintained on board. The positives are that the catalyst is much easier to add to the fuel than urea in the SCR approach. There is a minimum investment in equipment to add the catalyst and, lastly, fuel savings from use of the catalyst will more than pay for the system.

Sulfur Oxides (SO_x)

Sulfur is a naturally occurring element in hydrocarbon fuels. It is associated with asphaltenic fuels and correlated with vanadium content. Sulfur generally occurs in large aromatic molecules. Because of this, it is concentrated in residual oils or HFO.

In the combustion process, sulfur forms sulfur dioxide (SO₂). This compound is relatively benign. However, it enters an equilibrium reaction with oxygen to form SO₃ which combines with water to form sulfuric acid (H₂SO₄). The chemical reactions are as follows:

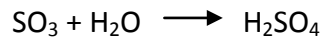


This equilibrium is the key to controlling sulfuric acid formulation. The mathematical expression for the equilibrium is:

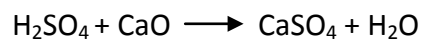
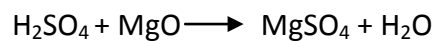
$$K = \frac{[SO_3]}{[SO_2] [O_2]^{1/2}}$$

K equals about 0.1 in most cases. Iron surfaces catalyze the formation of SO₃ increasing the value of K. Magnesium oxide reduces the value of K, perhaps by coating iron surfaces or by catalyzing the formation of SO₂. Formation of SO₃ requires oxygen. Operation under reduced excess air conditions will reduce sulfur trioxide formation.

Once SO₃ is formed, it will react with water to form sulfuric acid as follows:



If magnesium oxide or calcium oxide are present in the exhaust stream, they will react with sulfuric acid to form neutral calcium and magnesium sulfate salts.



There is a strong effort being made to remove sulfur from fuel. The current limit for ships operating within Emission Control Areas is 1.5% sulfur. Examples of these areas are a proposed 200 mile nautical limit around the U.S. and Canada, and the North Sea. These limits are expected to fall to 1.0% in July 2010 and 0.10% in January 2015. The latter level is the same as Low Emission Diesel (LED) currently available at the pump in the United States.

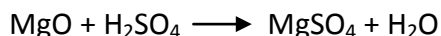
Sulfur can be removed by hydrodesulfurization in refineries. This process involves passing the fuel over catalyst beds containing heavy metals (similar to SCR beds for NO_x removal discussed above). Hydrogen is added to break up condensed aromatic molecules containing sulfur.

There are currently two approaches to removing sulfur from ship exhausts. The first is to burn higher quality fuels at 50% and higher costs. In addition to the cost issue, there is a problem with fuel availability. If all ocean going ships were to convert to these fuels (MDO or Middle Distillate Oil), enormous refinery expansions and increase in crude oil consumption would be required. It would also result in a glut of residual oil on the market.

The second approach is seawater scrubbing. The exhaust is scrubbed with seawater that removes the sulfuric acid and particulate matter. The low pH scrubber water is reacted with calcium oxide (lime) to form calcium sulfate. The sludge is disposed of when the ship is in port. This approach has three major problems:

- Cost of the scrubber system as well as time and availability of equipment and manpower to install the equipment. Cost per scrubber is more than \$1 million. As many as four per ship are required.
- Cost of operation and maintenance.
- Cost of lime and disposal of sludge in port.
- Problems with system failures when a ship is at sea and penalties for entering Emission Control Areas.

A third approach is to add a magnesium carboxylate additive to fuel. The magnesium carboxylate forms MgO in the combustion process and reacts with sulfuric acid to form magnesium sulfate, a neutral compound.



Magnesium oxides formed from the additive coat metal parts reducing the formation of sulfur trioxide in the equilibrium reaction. As a result, it is known that 16 ppm magnesium per one percent sulfur will eliminate sulfuric acid in the exhausts. While this eliminates most of the acid rain problem, sulfur dioxide gases remain in the exhaust. The cost of using oil-soluble magnesium carboxylate fuel additives would be a small fraction of the cost of fuel.

It is theoretically possible to add much higher levels of magnesium to the fuel via the fuel additive and remove most sulfur oxides. This can be promoted through iron catalysis of sulfur trioxide formation leading to capture as magnesium sulfate.

Another proven approach is to add calcium additives to the fuel or exhaust. Calcium effectively removes sulfur dioxide. However, calcium leads to deposit problems in combustion turbines and in some boiler situations. This leads to the possibility of adding a combination of magnesium and calcium. The magnesium will remove sulfuric

acid and prevent calcium deposits from forming. The calcium will remove sulfur dioxide. This type of approach will require development of low cost calcium additives and methods of adding the material to the fuel or exhaust.

SFA International and associates will study this problem to develop a more economical solution.

Summary

In all these cases, combustion catalysts are a logical approach to decreasing carbon footprint and reducing particulate matter and nitrogen oxides emissions. The costs for equipment and manpower to maintain and operate the equipment as well as chemicals needed in their operation indicate combustion catalysts are not only better on a cost basis, but are more reliable.

Additive approaches to the elimination of sulfur dioxide and trioxide species in the exhaust may represent a more economical solution than substitution of higher cost fuels or seawater scrubber technology. SFA International is committed to finding better solutions and will look for opportunities to develop this technology.

Acknowledgements

Sindee Gillespie, President of G.O.A. Enterprises strongly encouraged me to write this paper. She worked tirelessly to find the latest information in the press for the current situation in the industry and where it is headed.

Thanks are due Ken Koch of Liquid Minerals, Inc. for discussions on the effects of magnesium on the sulfur dioxide – trioxide equilibrium reaction as well as the latest information on magnesium dosage levels for controlling sulfuric acid.

Lastly, thanks are due Jerry Radway of EnerChem, Inc. for information on calcium reaction with sulfur dioxide as well as sulfur trioxide. He postulated the possibility of using the iron catalyst to form sulfur trioxide and remove it with higher levels of magnesium.

Information Sources

There was not an attempt to footnote each piece of information given in this paper. Information was summarized from a number of sources. Most of these are given below:

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Table I. Marine Emission Abatement Technology

Cause	Methods of Reduction	Advantages	Disadvantages
Carbon Dioxide			
By Product of Combustion	Reduce use of hydrocarbon fuels	Reduces carbon dioxide.	Energy required for task.
	Fuels that produce less carbon dioxide	Natural gas available, low cost.	May not be possible to substitute NG in equipment or at site.
	Combustion Catalysts	Reduces total fuel consumption and other emissions, cost offset by fuel savings. Lower total carbon footprint.	Total carbon dioxide production the same.
Particulate Matter, Unburned Hydrocarbons, Carbon Monoxide			
By Product of Incomplete Combustion	Increase air to fuel ratio in engine	Reduce particulate matter.	Heat loss and reduces power output.
	Better quality fuel	Fuels generally available, easy to use.	Higher cost of fuel, especially marine.
	Combustion Catalysts	More complete combustion, cost offset by fuel savings.	Product must be mixed into fuel, accurate dosage required.

Table II. Emission Abatement (Continued)

Cause	Methods of Reduction	Advantages	Disadvantages
Nitrogen Oxides (NO_x)			
Extended time at high combustion temperatures	Emulsify water into fuel to reduce combustion temperature	Reduces NO _x by up to 100%.	Lost of efficiency through evaporation of water. Cost of equipment, emulsifier and labor.
	Selective Catalytic Reduction	Reduces NO _x approaching 100%.	Cost of catalyst bed (>\$1,000,000), installation and maintenance. Urea or ammonia injected into exhaust steam, cost and manpower.
	Iron Combustion Catalysts	Reduces NO _x up to 30%. Cost of catalyst offset by fuel savings.	Product must be mixed into fuel, accurate dosage required.
	Iron-Magnesium Combustion Catalysts	Reduces NO _x up to 75% depending on engine condition and fuel. Cost of catalyst offset by fuel savings.	Product must be mixed into fuel, accurate dosage required.

Table I. Emission Abatement (Continued)

Cause	Methods of Reduction	Advantages	Disadvantages
Sulfur Oxides (SO_x)			
Result of reacting sulfur in fuel with oxygen.	Remove sulfur from fuel	Eliminates SO _x from exhausts.	Hydrodesulfurization of fuel required at refinery. Increased cost of fuel, refinery capacity.
	Seawater Scrubbers	Eliminates SO _x from exhausts.	Cost of scrubbers (>\$1,000,000), lime required for treatment, disposal of sludge. Manpower, size, weight, installation time.
	Magnesium Fuel Additives - low levels	Removes sulfuric acid. Lower cost.	Does not remove SO ₂ .
	Calcium Fuel Additives	Removes all SO _x . Lower cost.	High dosage rate of additive, possible deposit problems in engines.
	Magnesium Fuel Additives - high levels	Removes all SO _x . Lower cost.	Stoichiometric level of Mg, technology not proven.
	Magnesium - Calcium Fuel Additive	Removes all SO _x . Lower cost. Expected to be more efficient than Ca alone.	Stoichiometric level required, technology not proven.

Table II. Hydrocarbon Combustion Reactions

		Excess Air = 10%													
Methane	1	CH ₄ + 16.043	2.0	O ₂ + 64.000	7.47	Air + 209.384	0.95	Excess Air 27.34	→	1	CO ₂ + 44.011	2	H ₂ O + 36.032	8.41	Air 236.7
Aliphatic	1	CH ₂ + 14.027	1.5	O ₂ + 24.000	5.60	Air + 157.038	0.71	Excess Air 20.50	→	1	CO ₂ + 44.011	1	H ₂ O + 18.016	6.31	Air 177.5
Aromatic	1	CH + 13.019	1.25	O ₂ + 20.000	4.67	Air + 130.865	0.59	Excess Air 17.09	→	1	CO ₂ + 44.011	0.5	H ₂ O + 9.008	5.26	Air 148.0
Carbon	1	C + 12.011	1	O ₂ + 32.000	3.73	Air + 104.692	0.47	Excess Air 13.67	→	1	CO ₂ 44.011	0	H ₂ O +	4.21	Air 118.4

Fuel Type		Natural Gas <i>Methane</i>	Tx-LED <i>Aliphatic</i>	Kerosene <i>Aromatic</i>	Coal <i>Carbon</i>
Engine Horsepower		1,341			
Engine Kilowatts =		1,000			
BTU/Lb.		22,000	19,665	18,900	15,500
Engine efficiency		52%			
BTU/Kw Hr.		6,558			
BTU/Hr		6.56E+06			
Fuel/Hr	Lbs./Hr	298	333	347	423
	Kg./Hr	135	151	157	192
	Cu. Ft.	6,803			
Percent Compound		93%	100%	100%	75%
Gram Moles Fuel/Hr		7,838	10,784	12,089	11,983
Exhaust	Lbs./Hr	5,885	5,695	5,356	5,719
	Kg./Hr	2,670	2,583	2,429	2,594
	BTU/Hr.	1,034,816	1,001,395	941,730	1,005,622
	Heat Loss	0	0	0	0
Exhaust	Volume/Hour				
	Liters	3,064,564	2,231,305	1,814,676	1,398,047
	Cu. Meters	3,065	2,231	1,815	1,398
Exhaust Temp.	250 ° C.				
	482 ° F.				
Exhaust Vol./Hr.	Cu. M.	5,869	4,273	3,475	2,678
Lbs. CO ₂ per Hour		760	1,046	1,173	1,163
Increased ratio of carbon dioxide over Natural Gas			1.38	1.54	1.53