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A mitigação de emissões de navios através do uso de sonoquímica para o condicionamento do combustível

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Resumo

Este artigo apresenta os resultados de uma investigação experimental sobre o condicionamento de HFO (*Heavy Fuel Oil*) usando efeitos sonoquímicos em hidrocarbonetos e água para melhorar a combustão e mitigar as emissões de motores diesel. A tecnologia de sonoquímica é introduzida e os resultados práticos de campo obtidos são explicados, não apenas na redução de NOx e PM, mas também no consumo de SOx e do combustível específico. Além disso, o artigo apresenta o trabalho de pesquisa e desenvolvimento realizado sobre a aplicabilidade da tecnologia de sonoquímica na dessulfuração de HFO com alto teor de enxofre e a sua aplicabilidade na dessulfurização a bordo.

Keywords: Emissões, NOx, SOx, Ultrasons, Decomposição da água , Sonoquímica, HFO, redução de enxofre, redução de NOx.

Introduction

The motivation for this research, initiated in 2008 was based on the need to mitigate exhaust gas emissions of NOx. It is well known that Nitrogen Oxides (NOx) – Regulation 13 need imposed limits difficult to be achieved by most diesel engines.

Table 1 - Nitrogen Oxides (NOx) – IMO Regulation 13

Tier	Ship Construction date on or after	Total weighted cycle emission limit (g/kWh) n = engine's rated speed (rpm)		
		n < 130	n = 130 -1999	n ≥ 2000
I	1 January 2000	17.0	45·n(-0.2) e.g., 720 rpm -12.1	9.8
II	1 January 2011	14.4	44·n(-0.23) e.g., 720 rpm - 9.7	7.7
III	1 January 2016	3.4	9·n(-0.23) e.g., 720 rpm - 2.4	2.0

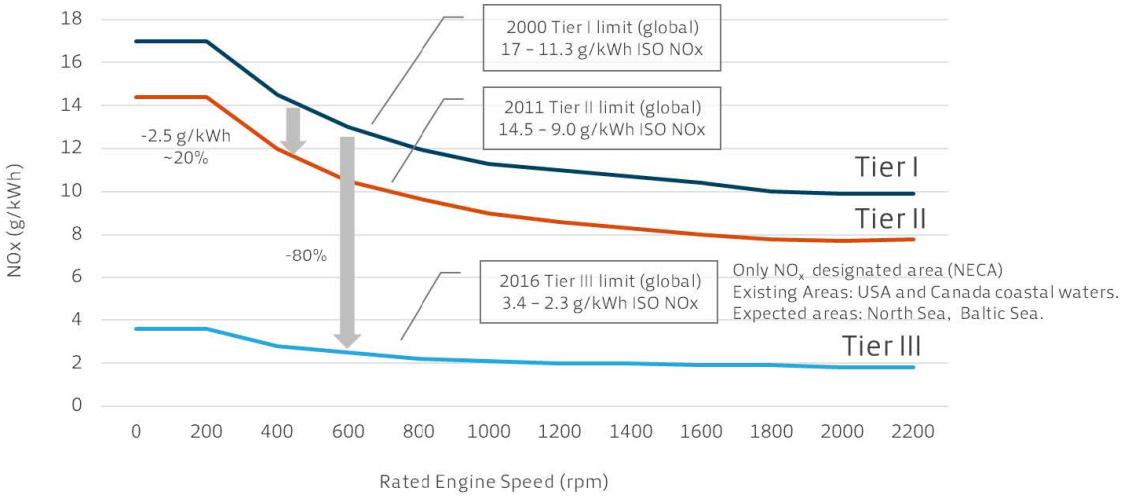


Figure 1 - Nitrogen Oxides (NOx) – IMO Regulation 13 in graphical form.

NOx formation mechanism

It is also well known, that the mechanism of the thermal NOx formation, also known as Zeldovich mechanism (3) is activated for combustion temperatures above 2200K, therefore is highly dependent on the engine load. Therefore, the production of NOx may be frozen if the combustion temperature is limited bellow such temperature.

A natural way of keeping the combustion temperatures below the threshold temperature of 2200K would be the addition of water to fuel, in such a way that, the heat of vaporization would keep the temperature under control.

The formation of thermal NOx is determined by a set of highly temperature-dependent chemical reactions known as the extended Zeldovich mechanism. The principal reactions governing the formation of thermal NOx from molecular nitrogen are as follows:

$$O + N_2 \overset{k+1}{\longleftrightarrow} N + NO \qquad (1)$$

$$N + O_2 \overset{k+2}{\longleftrightarrow} O + NO \qquad (2)$$

For near stoichiometric condition and for fuel rich combustions a third Zeldovich reaction plays an important role on the NOx formation.

$$N + OH \overset{k+3}{\longleftrightarrow} H + NO \qquad (3)$$

The net rate of formation of NO via Reactions (1), (2) and (3) is given by:

$$\frac{d[NO]}{dt} = k_1[O][N_2] + k_2[N][O_2] + k_3[N][OH] - k_{-1}[NO][N] - k_{-2}[NO][O] - k_{-3}[NO][H] \qquad (4)$$

In the above expressions, k_1, k_2 and k_3 are the rate constants for the forward reactions (1), (2) respectively, and k_{-1}, k_{-2}, and k_{-3} are the corresponding reverse rates. All of these rates have units of m^3/gmol s. All concentrations units are in gmol/m^3, and the values of k's are given in the Annex 1.

The Quasi-Steady Assumption for (N)

The rate of formation of NOx is significant only at high temperatures (3) (greater than 1800K) because fixation of nitrogen requires the breaking of the strong N_2 triple bond (dissociation energy of 941 kJ/gmol). This effect is represented by the high activation energy of reaction (1), which makes it the rate-limiting step of the extended Zeldovich mechanism. However, the activation energy for oxidation of N atoms is small. When there is sufficient oxygen, as in a fuel-lean flame like on diesel engine combustion, the rate of consumption of free nitrogen atoms becomes equal to the rate of its formation and therefore a quasi-steady state can be established. This assumption is valid for most combustion cases except in extremely fuel-rich combustion conditions (typical of gas or petrol engines). Hence, the NO formation rate becomes:

$$\frac{d[NO]}{dt} = 2k_1[O][N_2]\frac{\left(1 - \frac{k_{-1}k_{-2}[NO]^2}{k_1[N_2]k_2[O_2]}\right)}{\left(1 + \frac{k_{-1}[NO]}{k_2[O_2] + k_3[OH]}\right)} \quad (gmol/m^3 - s) \qquad (5)$$

As it can be seen from equation (4), the rate of formation of NO increases with the oxygen concentration, which is in fact a characteristic of turbocharged diesel engines, they operate with a great excess of air, that in fact only provide the oxygen required for a complete combustion, but also the cooling fluid of the combustion

chamber parts. The two radicals are rather different in chemical nature, however. Thus, the OH radical is known to initiate a number of reactions in solution; by contrast, the H radical can be rapidly captured by molecular oxygen or hydrocarbon molecules that are not electronically in equilibrium, to reach such equilibrium.

The Chaderton's effect

A strong reduction in particulate matter emission was observed, and the mechanism is associated to a better combustion, and necessarily associated to a better atomisation. The basic explanation for the reduced particulate formation is attributed to a phenomenon known Chaderton effect. The effect is characterised by an instantaneous water expansion, when highly compressed water and fuel are atomised into the combustion chamber at temperatures above 1000K. Due to the difference in densities, these droplets have enclosed water, that expand suddenly as they change state from superheated water (before injection) to superheated steam after injection, increasing its volume about 600 times. This instantaneous breaking the droplet into smaller droplets, results in a more complete vaporization and turbulent mixing of the fuel with oxygen.

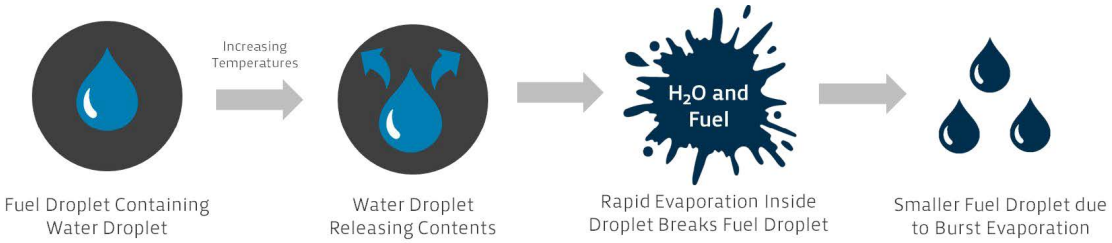


Figure 2 - Chadertton's effect of fuel droplet expansion.

The thermionic effect

It is known that water molecule can be thermionically (thermolysis) decomposed into hydrogen, oxygen and many other compounds namely peroxides. For example, at 2200°C about 3% of all H_2O are dissociated into various combinations of hydrogen and oxygen atoms, mostly H, H_2, O, O_2, and OH. Other reaction products [1] like H_2O_2 or HO_2 remain minor. At the very high temperature of 3000°C more than half of the water molecules are decomposed, but at ambient temperatures only one molecule in 100 trillion dissociates by the effect of heat. The high temperatures and material constraints have limited the applications of this approach.

Sonochemistry and the ultrasounds

The sonochemistry of liquids depends mainly on physical effects of the quick heating and cooling caused by cavity implosion. For instance, when Peter Riesz [2] and his colleagues at the National Cancer Institute irradiated water with ultrasound, they proved that the heat from cavity implosion decomposes water (H_2O) into extremely reactive hydrogen atoms (H^+) and hydroxyl radicals (OH^-).

During the quick cooling phase, hydrogen atoms and hydroxyl radicals recombine to form hydrogen peroxide (H_2O_2) and molecular hydrogen (H_2).

$H_2O \rightarrow OH\cdot + H\cdot$
$OH\cdot + H\cdot \rightarrow H_2O$
$2OH\cdot \rightarrow H_2O_2$
$OH\cdot + OH\cdot \rightarrow H_2 + O_2$
$2H\cdot \rightarrow H_2$
$2OH\cdot \rightleftarrows O + H_2O$
$2O\cdot \rightleftarrows O_2$
$H_2O\cdot + 2H\cdot \longrightarrow H_2O + H_2$
$H_2O\cdot + H_2O\cdot + O_2 \longrightarrow 2H_2O_2$
$HO\cdot + H_2O \longrightarrow H_2O_2 + H\cdot$

Additional reactions in the presence of oxygen
$O_2 \rightarrow 2O\cdot$
$O_2 + O\cdot \rightarrow O_3$
$O_2 + H\cdot \rightarrow OOH\cdot (or\ OH\cdot + O)$
$O\cdot + OOH\cdot \rightleftarrows OH\cdot + O_2$
$O\cdot + H_2O \rightarrow 2OH\cdot$
$2OHH\cdot \rightarrow H_2O_2 + O_2$

If other compounds are added to water irradiated with ultrasound, a wide range of secondary reactions can occur. Organic compounds are highly degraded in this environment, and inorganic compounds can be oxidized or reduced. To calculate the formation rates of NO and N, the concentrations of O, H, and OH are required. OH radicals are potential pollutant destruction agents on the grounds of their extremely high redox potentials (e.g. P =+ 2.8 V for OH radicals).

Other organic liquids also yield interesting reactions when they are irradiated with ultrasound. For example, alkanes, major components of crude oil, can be "cracked" into smaller, desirable fragments, such as gasoline.

Crude oil is normally cracked by heating the entire mixture to temperatures above 500ºC, irradiating alkanes with ultrasound, however, makes cracking possible at room temperature and produces acetylene, which cannot be produced through simple heating.

The chemical effects of ultrasound arise from the physical processes that create, enlarge and implode gaseous and vaporous cavities in a liquid. Ultrasound waves, like all sound waves, consists of cycles of compression and expansion. Compression cycles exert a positive pressure on the liquid, pushing the molecules together; expansion cycles exert a negative pressure, pulling the molecules away from one another.

During the expansion cycle, a sound wave of sufficient intensity can generate cavities. A liquid is held together by attractive forces, which determine the tensile strength of a liquid. In order for a cavity to form, a large negative pressure associated with the expansion cycle of the sound wave is needed to overcome the liquid's tensile strength.

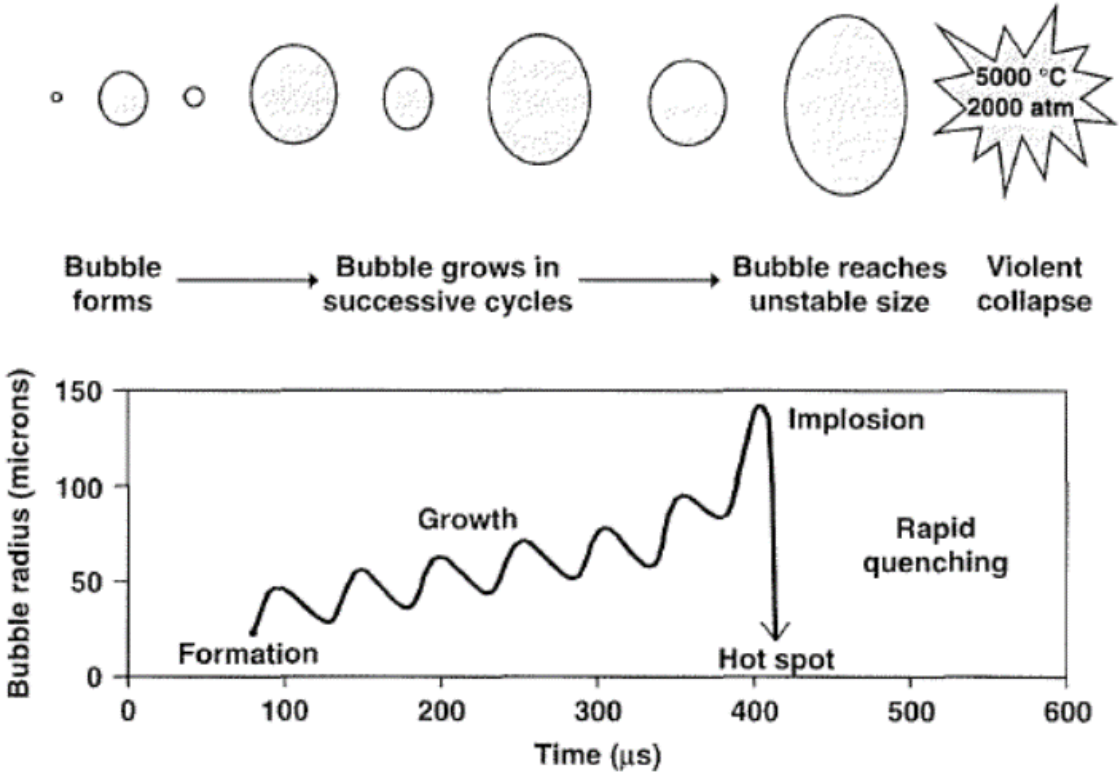


Figure 3 -Imploding Cavity time history in a liquid, from formation to the implosion. At a usual frequency of 20 kilohertz, the critical size is a cavity roughly 170 microns in diameter. At this point, the cavity grows rapidly in the course of a single cycle of sound. Once a cavity has experienced a very rapid growth caused by either low or high-intensity ultrasound, it can no longer absorb energy as efficiently from the sound waves. Without this energy, input the cavity can no longer sustain itself. The liquid rushes in and the cavity and implodes.

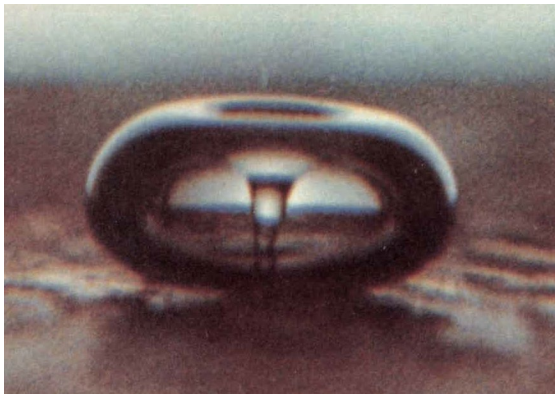


Figure 4 - Imploding Cavity in a liquid irradiated with ultrasound is captured in a high-speed flash photomicrograph (above). The implosion heats the gases inside the cavity to 5,500 degrees Celsius. Since this cavity formed near a solid surface, the implosion is asymmetric, expelling a jet of liquid at roughly 400 kilometres per hour. Both the heat and the jet contribute to a unique chemical environment in the liquid. The diameter of the cavity is about 150 microns.

The Enermulsion system

Enermulsion is the commercial name of the in-line fuel conditioning system developed by TecnoVeritas. The system, is composed by a number of cavitation chambers as in Figure 5 [3], varying in number and ultrasonic power, as a function of the fuel oil flow rate to be processed typically 4 kW/ton/h.

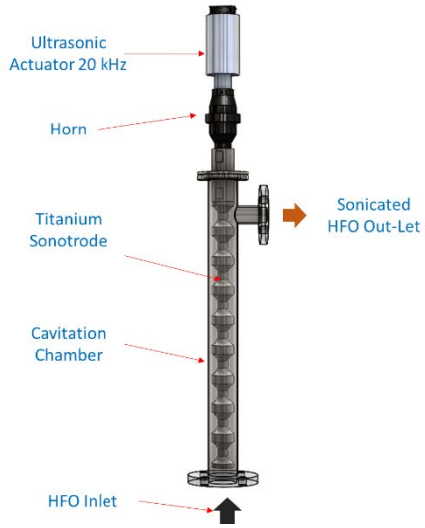


Figure 5 - Sonotrode, actuator and cavitation chamber arrangement

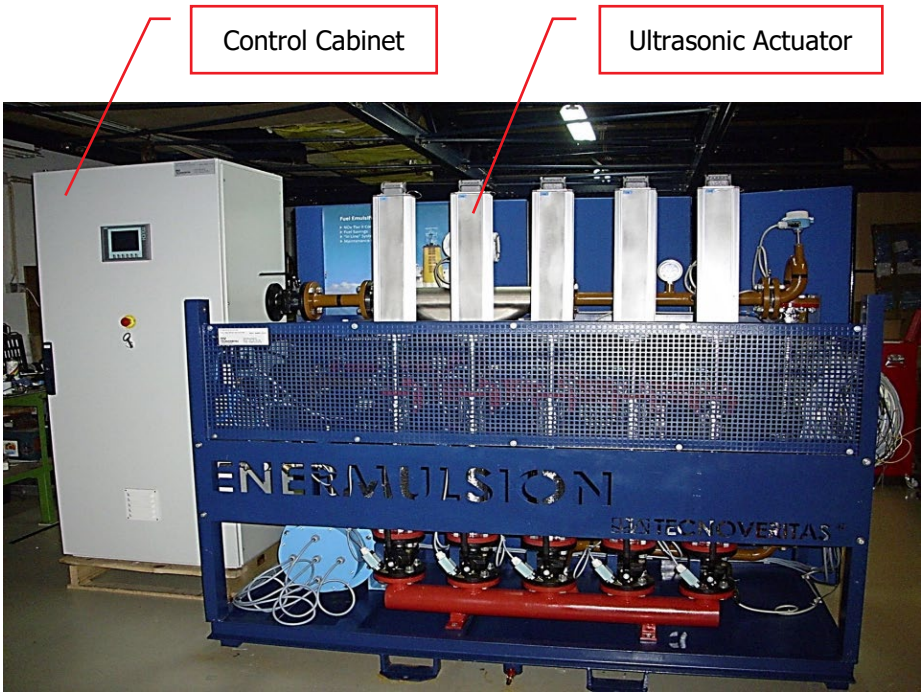


Figure 6 - The image of one ENERMULSION system with a capacity of HFO treatment of 6Ton/h. The ultrasonic actuators, the control system cabinet.

The system is installed in line on the fuel supply piping, just before the fuel mixing column, via two normally open valves and one normally closed valve, to ensure fail safe operation. A Process Logic Computer (PLC) reads off the engine load through a shaft torque meter like Optipower TM, and adjusts the quantity of water to be dissociated to the engine load fuel flow rate. This way, an optimised fuel processing is always achieved, either for optimised fuel consumption or for optimised emissions, without the need of dedicate tanks.

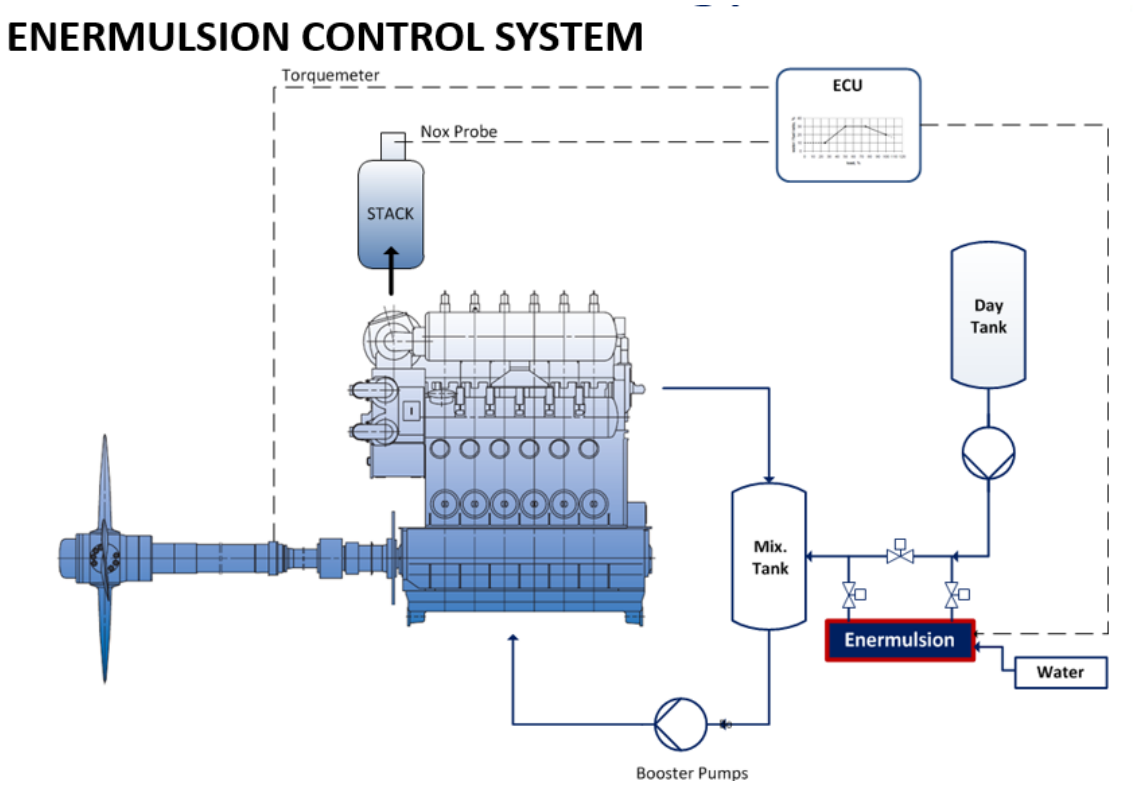


Figure 7 - ENERMULSION control system onboard

Figure 8 - Titanium sonotrode as new.

Figure 9 - Titanium sonotrode aspect after 6000 hours of operation. Cavitation marks on the working surfaces, evidencing material loss.

Field Results

Enermulsion system has been fitted to many marine diesel engines, Wartsila 32 and 46, MAN 40-60 equipped with conventional fuel injection system as well as with common rail injection systems. A great deal of field tests were carried out in a cogeneration plant equipped with a Wartsila 6V32D. This plant was considered ideal for testing, as engine load, energy produced and fuel consumption were readily available from the engine monitoring system, and therefore the variations of load were minimum and emissions were easy to be taken.

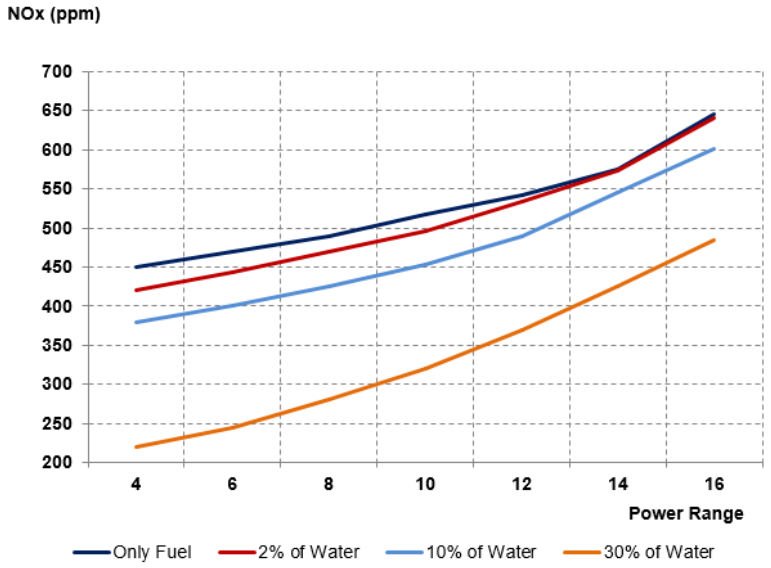


Figure 10 - NOx reduction as a function of engine load and emulsion water content. It can be said, that for the same engine load, the higher is the water content the bigger is the NOx reduction that can be achieved.

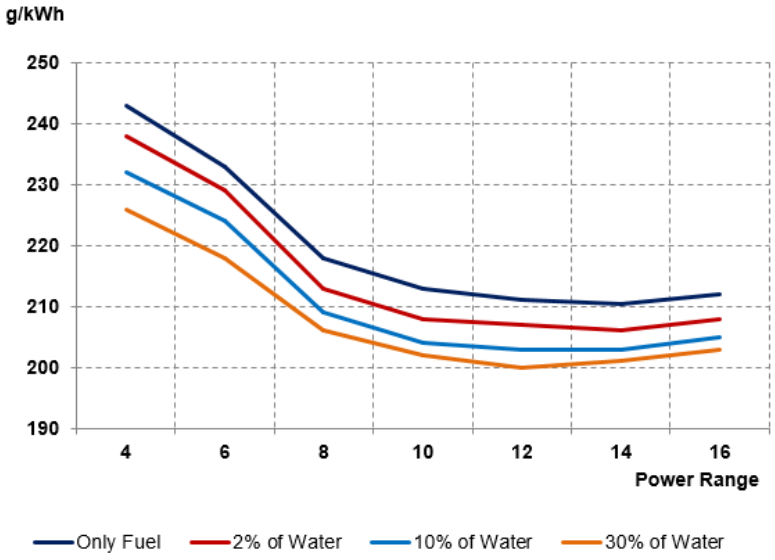


Figure 11 - Graph showing the specific fuel oil consumption as a function of engine load and emulsion water content. It can be seen, that the lower specific fuel oil consumption may be achieve for the higher emulsion water content in this case 10%.

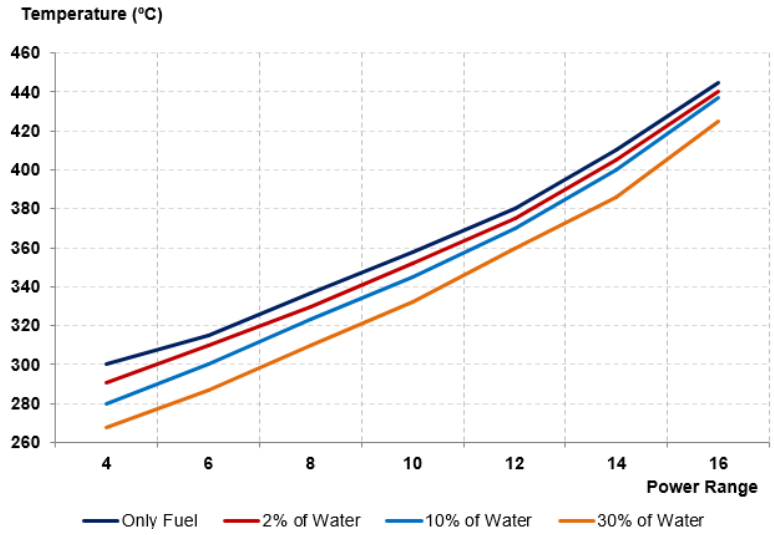


Figure 12 - Exhaust gas temperature as a function of engine load and emulsion water content. The higher the water content for the same engine load (power) the lower are he Exhaust gas temperatures, therefore contributing for less exhaust valves problems.

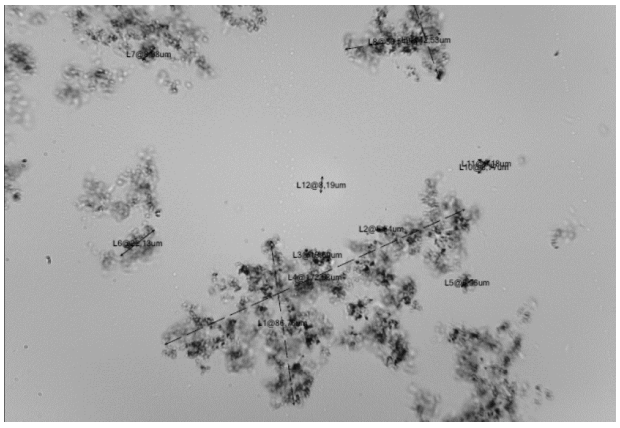


Figure 14 - Before Cavitation - Long chain hydrocarbon molecules (asphaltenes) responsible for filter clogging, deficient atomisation, smoke, nozzle ring clogging. Microscope image.

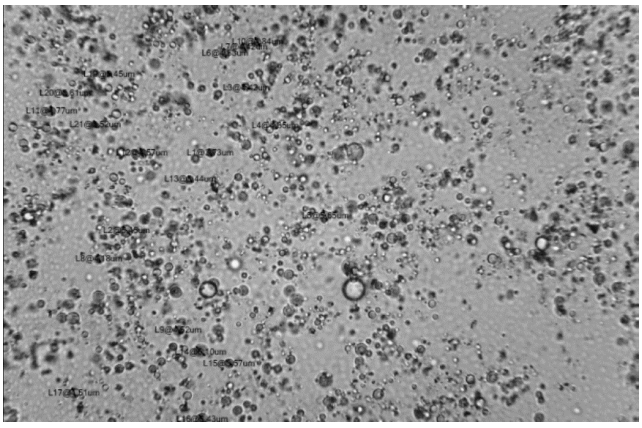


Figure 13 - After Cavitation - Cracked long chain hydrocarbon molecules. Microscope image.

Combustion improvement and specific fuel oil consumption

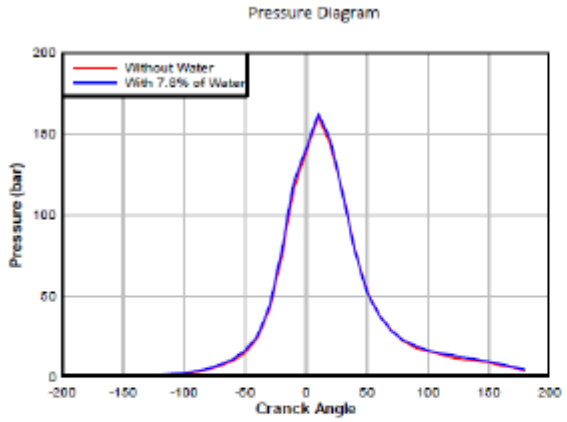
It was observed a reduction of consumption in all the Enermulsion applications under certain conditions. In order to better understand the effect of the conditioned HFO, open diagrams were taken as per Figure 15.

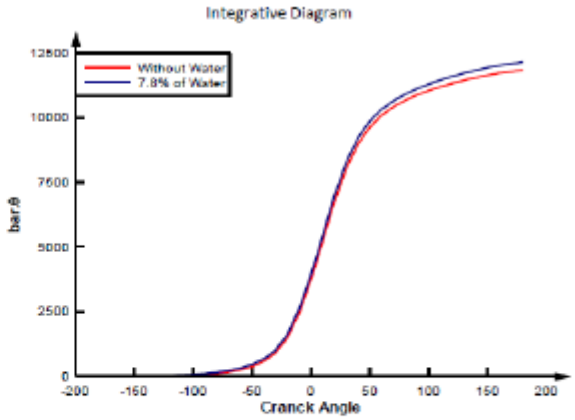
Table 2 - Characteristics of test engine MAN 40/60 Common Rail.

MAN 40/60 Common Rail Engine data	
Bore	0.4 m
Area	0.3 m^2
Stroke	0.6 m
Volume	0.075 m^3
Speed (N)	8.3 rev/s

As it can be seen on the figures below, the IMEP is higher with conditioned fuel than with non-conditioned fuel, resulting in a 2.6% more power per cycle for the decomposition of water equivalent to 7.8% of the fuel mass flow rate. The NOx reduction was reduced by 8% and PM reduction 60% [3]. Also it was noticed that for each engine load, there is an optimum water decomposition, above or below which the fuel consumption may vary.

Apparently, when too much water is added and decomposed, part of it recombines back to water, and this will remove too much heat from the combustion chamber, counteracting the effect of the fuel improvement, and therefore increasing the Specific Fuel Oil Consumption.





$$IMEP = \frac{\sum_{180}^{-180} P}{361}$$

$$CylPower = \frac{IMEP\ (Pa) \times V(m^3) \times N(\frac{rev}{s})}{nr}$$

	without	with	
IMEP	32,917	33,799	bar
	3291667	3379919	Pascal

Figure 15 - Comparison of Open cycle diagrams, with and without Enermulsion conditioned HFO.

Emissions control regarding

NOx (Nitrogen Dioxides): It was observed in all the Enermulsion applications that the bigger the decomposition of water in terms of the fuel mass flowrate, the bigger the reduction in NOx, but this needs to be adjusted to the engine load. It was possible to run the engines up to 40% water, if the fuel pumps, allow such volume. The observed reduction on NOx emissions is mainly attributable to Zeldovich mechanism freezing.

PM (Particulate matter): In terms of other emissions, it was observed Particulate matter reduction up to 80% again for optimised water decomposition flowrates. In particular, black carbon due to low load operation disappeared, making the process interesting for slow steaming vessels. The observed reduction is attributable to the more complete combustion as the free OH radicals, as well as other combustible gases like free hydrogen and alcohols.

SOx (Sulphur Dioxides): It was observed an interesting reduction of the sulphur dioxides, in the range of 1% to 1.5%. This is in fact due to the following effects: i) possible dilution of the original sulphur content; ii) reduction of sulphur oxides by OH radicals, originating other sulphur compounds not detectable by the gas emissions analyser equipment (SO, SO_2 and H_2S) but eventually not so noxious.

CO (Carbon Monoxide): As expected, in parallel with the reduction of SFOC, a reduction of Carbon Monoxide was observed, indicating a better a more complete combustion, i.e., a better burning. This fact is due to the better fuel atomisation, but also to the presence of hydrogen and peroxides, both species work as combustion improvers.

Maintenance

In terms of engine operation and maintenance [3], the results were outstanding, as the exhaust gas temperatures became more even when the engines are operated with processed HFO as it can be observed on Figure 16.

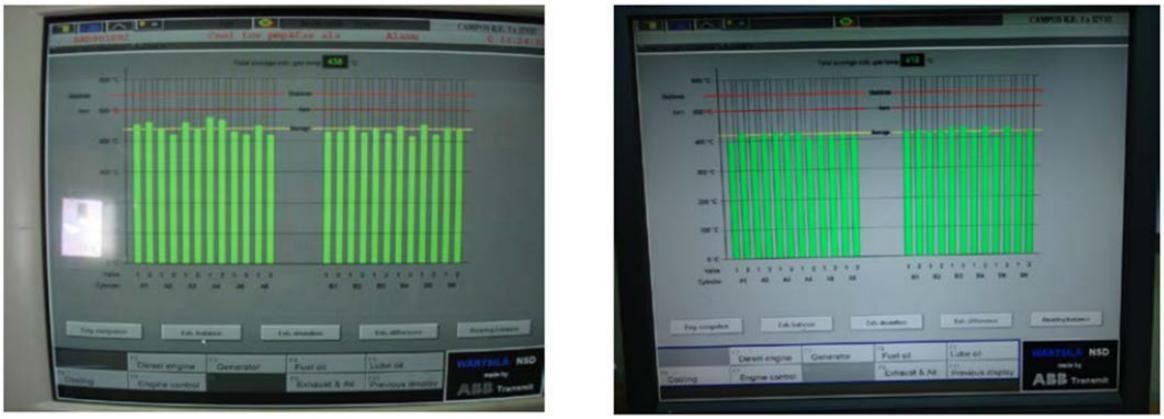


Figure 16 - Wartsila 16V32D Engine monitoring system screen. Left hand exhaust gas screen exhaust gas temperatures without processed fuel. Right hand side screen exhaust gas temperatures with processed fuel.

It could be observed that engine was operated at full power without the need of derating due to excessive exhaust gas temperature.

Injector nozzles last longer [3], about the double of the time as without unprocessed HFO, and filter clogging did not happen during the two years of tests.

Turbocharger rotor blades, nozzle rings, exhaust piping and economiser ran much cleaner, without deposits. Turbocharger ran at slightly higher speed, due to the turbine cleanliness and slightly higher mass flowrate, and economiser produces the same as the somehow lower exhaust gas temperatures, are compensated by cleaner tubes.

Turbocharger turbine 7,000h operation with HFO 380 cSt @ 50ºC with fuel conditioning evidencing the cleanliness.

Turbocharger turbine 6,000h operation with HFO 380 cSt @ 50ºC without fuel conditioning evidencing carbon deposits.

Figure 17 - Comparative photos of the turbocharger turbine blades.

Further work: Treatment of high sulphur HFO to meet future requirements

After many considerations and learnings about the positive effect of the sonication of HFO and water decomposition, it was investigated why the reduction of SOx. As a result, TecnoVeritas developed a new system, the Desul®, which the purpose is the removal of the sulphur onboard the vessels. The system originally developed to be operated onboard, produces a stronger reduction of the sulphur content on the HFO, obtaining values down to 0.1%. As the Enermulsion, it used sonochemistry technology, extracting the sulphur from the HFO as disposable sulphones and water.

This way, ships can bunker high sulphur content fuels, which are then treated onboard to meet the sulphur limits. The systems are now available as a prototype.

Conclusions

The technique here presented, serves the objective of mitigation of exhaust gas emissions in all aspects, particularly, NOx, CO_2, SOx, CO, VOC and PM, while simultaneously improves the fuel consumption, provided the water molecule decomposition is optimised for each engine load.

The technique is extremely promising to remove sulphur from regular HFO (no matter the sulphur content), making this a serious alternative to scrubbers and low sulphur fuels.

The power, pressures and temperatures, are extremely low, making the system suitable to install on board.

For non-optimised water decomposition regarding the engine load, some penalties may occur, if any. The technique is particularly interesting for slow steaming diesel engines, as it keeps the engines cleaner and kills the black smoke.

The sonochemical effect of ultrasounds, has strong effects on the improvement of the HFO quality, producing a cracking effect on the long chain hydrocarbon molecules.

As a result, lighter hydrocarbons are produced, which associated to the ions produce by the thermionic decomposition of water molecule, namely OH- and H+ result in improved combustion fuel molecules.

The effect of water molecule re-composition, results in a better atomization of fuel, increasing its air fuel mixture.

References

[1] R. Chang, "Chemistry," *J. Chem. Educ.*, vol. 66, no. 3, 1989.

[2] K. S. Suslick, "The Chemical Effects of Ultrasound," *Sci. Am.*, 1989.

[3] "Notes of field tests on the ENERMULSION commissioning." .

Annex 1

$$
\begin{aligned}
k_1 &= 1.8 \times 10^8 e^{-38370/T} \\
k_{-1} &= 3.8 \times 10^7 e^{-425/T} \\
k_2 &= 1.8 \times 10^4 T e^{-4680/T} \\
k_{-2} &= 3.8 \times 10^3 T e^{-20820/T} \\
k_3 &= 7.1 \times 10^7 e^{-450/T} \\
k_{-3} &= 1.7 \times 10^8 e^{-24560/T}
\end{aligned}
$$