TECNOVERITAS®

Dedicated to innovation

DESulphur

A disruptive solution

White Paper

July 2017

1 | Current Contex and Challenges

We are currently suffering the effects of environmental pollution caused by the emission of several key pollutants (CO_2, CO, particulate matter, Hydrocarbons (HC), NO_X, SO_X) to the atmosphere. The pollution can have both a shore or sea origin, but generally come from the incomplete combustion of fuel, the thermal splitting of HC, the high temperature of combustion in the engines cylinder or the oxidation of Sulphur in the fuel composition.

Maritime transport has an impact on the global climate and on air quality, as a result of the carbon dioxide (CO_2) emissions and other emissions that it generates, such as nitrogen oxides (NO_x), sulphur oxides (SO_x), methane (CH_4), particulate matter (PM) and black carbon (BC).

Until few years ago, International maritime shipping remained the only means of transportation not included in the Union's commitment to reduce greenhouse gas emissions.

Although more recently some restricted regulations were created. One of them related more to the CO_2 emissions (EU 757/2015 and EU 2072/2016 Regulation) - MRV Regulation), and stipulated the obligation of shipowners since January 2018, to Monitor, Report and Verify the carbon dioxide (CO_2) emissions. In terms of NO_x emissions, MARPOL set limits to emissions for Diesel engines with a power output of more than 130 kW starting on January 2000.

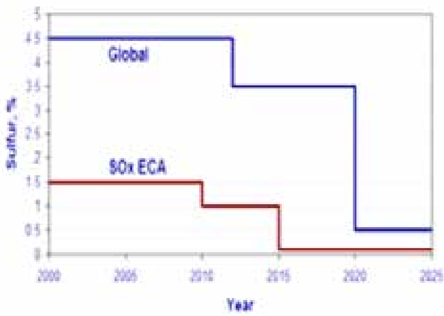
But what about Sulphur emissions?
Sulfur in any of its forms reacts with the oxygen in the air (spontaneously or upon burning), producing oxides (called SO_x, of which sulfur dioxide (SO_2) is the most known). These Sulphur oxides in the presence of humidity from the combustion processes turn into acids such as Sulfuric acid (H_2SO_4) and Hydrogen sulfide (H_2S) that can originate environmental problems such as Acid Rain.

Acid Rain are harmful to agriculture (damaging soils), wildlife (causing deflorestations, oceans acidity), damage monuments as being well as extremely harmful to human health being associated with diseases of the respiratory, cardiovascular and even cancer. Sulphur is also responsible for the emission of particulates (soot) as the filters used in the means of transportation are rapidly degraded by fuels with a high sulfur content.

Figure 1- Acid rain effect

In this specific case, MARPOL stipulated Limits on Sulphur content in Marine Fuel Oil (HFO) as it can be seen on Figure 2. This limits are even more restricted in ECA areas:

Outside ECA		Inside ECA	
4.50 wt %	Prior to 1 Jan 2012	1.50 wt %	Prior to 1 July 2010
3.50 wt %	After 1 Jan 2012	1.00 wt %	After 1 July 2010
0.50 wt %	After 1 Jan 2020 *	0.10 wt %	After 1 Jan 2015



Limits of sulphur content in oil fuels according to Annex VI to MARPOL.
http://www.dieselnet.com/standards/inter/imo.php

Figure 2 - Comparison between the Sulphur limits imposed inside and outside ECA along the different years.

When considering other types of fuel for example, US regulations (CCR) defined specific limits on S content in marine gas oils (MGO) and marine diesel oils (MDO).

In **Auxiliary Diesel Engines**:

i) Until 30th December 2011, MGO: maximum content of 1.5% and MDO a maximum of 0.5%;
ii) From 1st Jan 2012, MDO with a maximum sulphur content 0.1%.

In **Main Diesel engines and Auxiliary Boilers**:
MGO and MDO

i) From 1st July 2009, MGO: maximum content of 1.5% and MDO a maximum of 0.5% may be used;
ii) From 1st Jan 2012, MGO or MDO with a maximum sulphur content 0.1% may be use.

With that said we could conclude that Shipowners are currently sinking under a big green wave! For that reason some measures should be implemented.

2 | Different Techniques to use Low-Sulphur Fuel

There are several technologies that can be used in order to prevent the effects of SO_X emissions: the use of low-sulphur fuel (low-sulphur HFO), the use of Flue Gas Desulphurisation (FGD) techniques or Desulphurisation itself.

Relatively to the first option, the use of low-sulphur fuels have an economic impact related to their higher costs (Low-sulphur heavy fuel has a somewhat higher price than the high sulphur heavy fuel, due to increasing demand and the cost of the desulphurisation process - Figure 3)

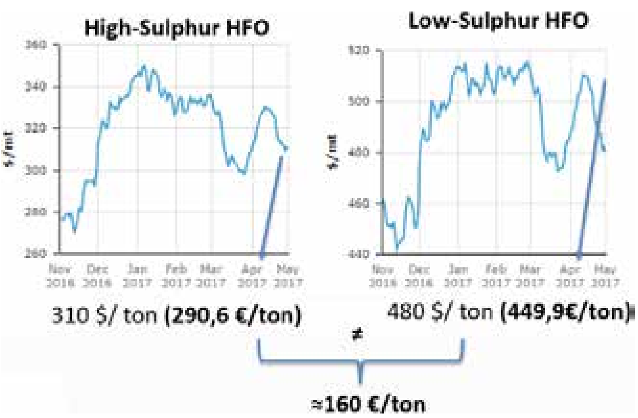


Figure 3 - Comparison of prices on High Sulphur-HFO and Low-Sulphur HFO.

If it is considered for example a ship that processes 4 ton of HFO per hour, it corresponds to a consumption of 35040 ton/year of HFO. That corresponds to a significant investment that represents 15,77 M €/ year. With such savings in perspective wouldn't it be more reasonable to invest in an effective Desulphurization Technique?

Another important aspect is the fact that HFO with low-Sulphur content have a limited availability in the recent future. It is foressen that only HFO with high sulphur levels would be available in few years time. In that way shipowhners must pay for that fuel high emissions.

Also there are operative problems in considering low-sulphur alternatives to HFO such as Low Sulphur Distillate Oils (LSDO) since shipowners and manufacturers of marine engines have limited experience using such types of fuel. Furthermore, modifications of the installations are necessary due to the requirement to use such fuels. Regarding operational safety and the ship itself, engines, pumps, boilers and boiler burners should be properly adjusted for the maintenance and burning of LSDO.

With so many operative problems associated, wouldn't it be reasonable to search for a method that allows shipowners to continue to use HFO with lower Sulphur content?
As mentioned above another interesting technique that can be used to remove So_x is the Flue-gas desulfurization (FGD). It is a set of technologies used to remove Sulphur oxides from exhaust flue gases of fossil-fuel power plants, and from the emissions of other sulfur oxide emitting processes). Although this technologies have several disadvantages, namely:

- High operating costs;
- Increase in power consumption;
- Increase in dust emissions ;
- Cannot be used for waste gas SO_2 concentrations grater then 2000 ppm;
- Disposal of waste products with significant costs.

An ultimate alternative would be to resort on Desulphurisation Techniques.

Desulphurisation have been commonly used, although many different techniques have been implemented industrially.

Among the different techniques, the most classic of them all is the Hydrodesulphurisation (HDS).

This classical process have been implemented in refineries and require extreme operational conditions, such as high pressures (30-130 atm), high temperatures (300-400 ºC) and require considerable amount of thermal energy. Another risk of the process is associated with the use of Hydrogen and the possibility of leakage through the walls of the reactor. The reaction takes place in a Fixed-Bed reactor, used an expensive solid or metallic catalyst such as Co/Mo or Ni/Mo.

The Hydrodesulphurisation (HDS) has some limitations to be pointed out, namely the fact that only enables the conversion of limited sulphur organic compounds present in fuel (Thiols, Thiophenes, Mercaptans, Thioethers and Disulfides). Relatively to other sulphur compounds like Aromatic and cyclic (Benzothiophenes (BT) or dibenzothiophenes (DBT)), they can hardly be removed by this technique.

Another aspect that limits the use of HDS is the fact that it can only be applied for high production capacity factories - Large refineries (requiring high reactors and high reaction times).

After HDS other technique have been developed, namely the Oxidative Desulphurisation (ODS). ODS is based on the use of a chemical with High Oxidative Potential: Hydroperoxide (in most cases H_2O_2 - 50% V/V), that will oxidize free and molecular sulphur to its oxide form (Sulphones and Sulphoxides), easier to remove from fuel (substantially more polar than sulfides).

The oxidant used although it is not pollutant or harmful to the environment, is expensive and also potentially dangerous. This technique allows to remove suphur compounds resistent to HDS, due to the oxidation step. It allows to work with more reasonable operatory conditions (lower temperatures and pressures), don't requiring as much termal energy as HDS, being in that way compatible with smaller processing units in terms of capacity.

More recently some studies considered the advantage of combining the oxidant step with the effect promoted by Ultrasound (Ultrasound-Assisted Oxidative Desulphurisation - UAOD).

The fundamentals consist in combining the fuel with the oxidizing agent (hydroperoxide) in the presence of an aqueous fluid (for example water), being applied ultrasound to increase the reactivity of the species in the blend. As ODS it ables its users to operate at ambient temperature and atmospheric pressure to selectively remove sulfur compounds from hydrocarbons.

In the other hand UAOD requires the use of a solid catalyst (Tungstate: $CuSO_4$ or Fe (II)) to regulate the activity of the OH radical. It also requires a Phase transfer agent (PTA) to accelerate the conversion of sulfides to sulfones. A final separation step of the technique involves a step of S/L extraction or L/L extraction to separate the sulfones from the fuel. UAOD permits to remove sulphur compounds from fuel with a yield of 99,90%.

3 | DESulphur, TecnoVeritas disruptive solution

3.1 | The fundamentals

TecnoVeritas has recently developed a Desulphurisation technique that can overcome some of the limitations of classical processes consisting of an effective and cleaner way to remove sulphur compounds from fuels.

DESulphur is a newly and innovative Desulphurisation Process developed by TecnoVeritas that can be applied to installations (at shore and at sea) that require the use of Fuel Oil , Heavy Fuel Oil (HFO), Marine Gas Oil or Marine Diesel Oil.

Due to the restrictive regulation on Sulphur content imposed recently to Maritime Transportation (especially in the ECA areas), to the lack of fuel with low Sulphur in the market (which prices increased) and to the need of restricting the SO_x emissions caused by the oxidation of sulphur in fuel (also verified in shore industries), it was urgent to find a solution to this problem.

With this innovative solution, users can reduce the Sulphur content of their fuels to levels allowed by the regulations at same time that it remains its desirable characteristics (thermal, Physical and Chemical).

The process is based in some of the principles and advantages of UAOD but uses a compound with a higher oxidative potential, which is produced on-site and is cleaner (non-polluant) than hydroperoxides. The produced oxidant prometes a more efficient oxidation of the sulphur compounds present in liquid fuels.

The production of the oxidant specie combined with the ultrassound system will convert more efficientely the sulphur compounds into oxides and peroxides (due to the increase of reactivity), which are easier to remove.

DESulphur is easy to install, requiring no modifications to the installations, since it can be installed “In-Line”. It is also easily adapted to different production capacities and flow rates.

It is able to be implemented aboard ships, allowing them to burn fuel with the appropriate Sulphur content. By-products can be treated as oily waste by dedicated on-board systems and dispensed in the usual way.

The process requires the addition of only a few components to the fuel (cheap, easy to obtain and recoverable in the process), and operate at reasonable operatory conditions (Low Temperatures and Atmospheric Pressure).

The process takes into account the oxidation of sulphur species presented in fuel to oxides and peroxides that are easier to remove. The oxidation process occurs efficiently due to the presence of an oxidant produced in situ and do the effect of ultrasound system that create cavitation and promote the thermal ionic dissociation of the water presented in the fuel.

The Phase separation step allows the remove the undesirable components from fuel (Sulphones, that are Sulphur oxides and peroxides), obtaining in the end a treated fuel with low Sulphur content.

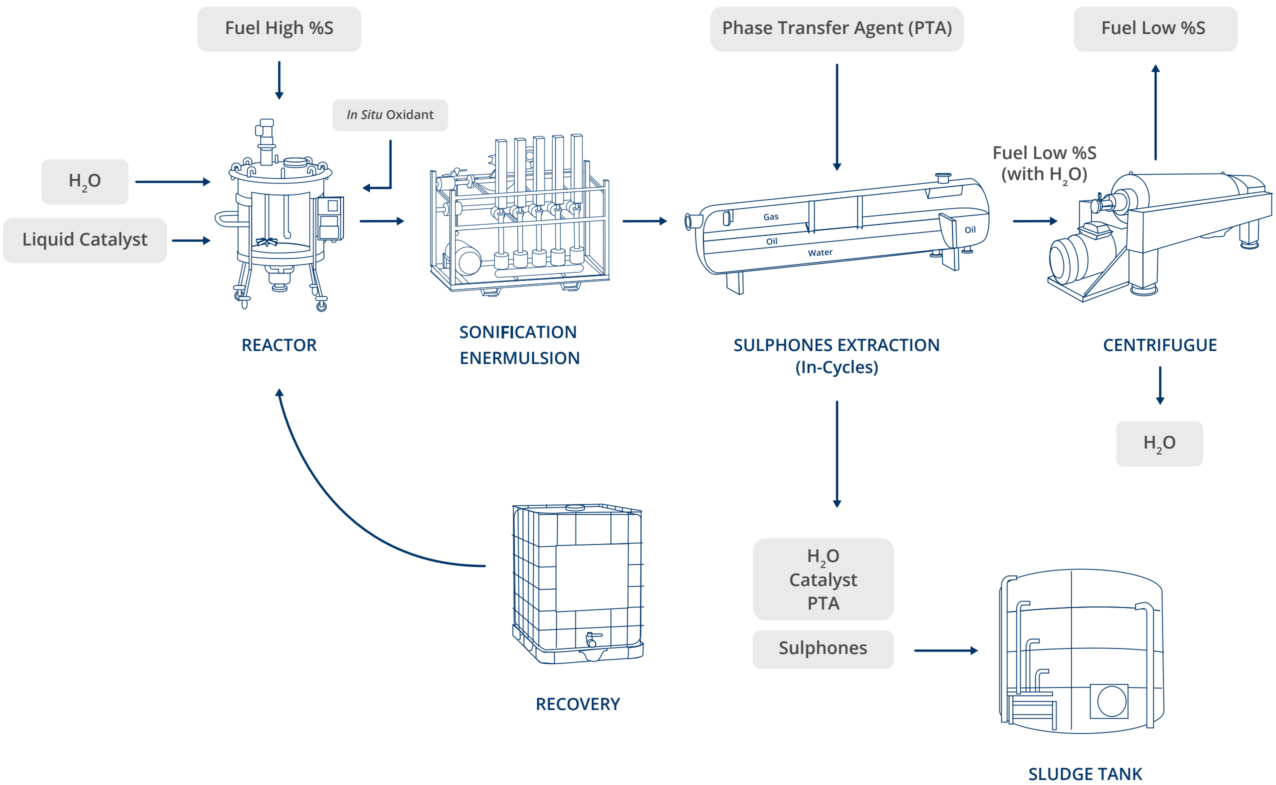


Figure 4 - DESulphur Process Description

3.2 | DESulphur Advantages

Desulphur has several advantages, namely: economical, security and environmental.

In terms of **economical** advantages we can name the following:

- The Oxidant Agent is produced *in situ*, therefore there is no need to add external compounds to the process;
- The process doesn't require significant amounts of energy, presenting low production costs;
- All reagents used are not expensive and are relatively easy to obtain. These reagents can be recovered in the process with higher yields;
- DESulphur uses low temperatures and low pressures (which involve lower costs), comparing to HDS for example.

In terms of **security** advantages:

- The process doesn't present any harm in terms of storage and handling, and all operative conditions are reasonable.

Desulphur brings also an **environmental** advantage:

- Process compatible with low flow rates, it can be implemented aboard ships allowing them to burn fuel with the appropriate content of sulphur. By-products can be treated as oil residues by dedicated on-board systems and dispensed in the usual way.

This TecnoVeritas Desulphurisation technique is disruptive relatively to the other classic techniques due to the fact that it uses a higher oxidative potential agent which is produced in-situ and cleaner. The produce oxidant guarantees in combination with the ultrasound effect a more efficient oxidation of the Sulphur species, allowing an easier removal.

The purified (with lower Sulphur content) fuel maintain its desirable properties and can be used for maritime aplications, but it is not limited to it.

3.3 | Market and Applications

In terms of the Market and Applications for this technology, we could say that it can be used on a global scale (within maritime and industrial sectors), with special interest in countries with seaports delivering greater economic, energetic, operational/safety and environmental advantages. An example of the sectors in which it could be used are: Petroleum Industry, Waste treatment and recovery of fuels, fuel producers, global industries that use Heavy Fuel in their activities or Naval sector.

3.4 | Conclusions

A brief economical evolution of the process was made to establish its viability. For instance, considering an installation that processes 4 tons of fuel per hour, (with an utilization factor of 80%) the estimate investment is supposed to be recovered in about 184 days. According to the calculations made, about 52.2% of the Payback corresponds to the Operating Expenses index.

Summarizing Tecnoveritas developed a revolutionary product that could be a solution to solve a global problem of harmful emissions to the environment. It can offer numerous advantages comparing to conventional desulphurisation techniques. Its applications would be at worldwide level, considering a diversity of customers that would go from industrial to maritime sector.