# THE GREENING OF MARINE FUELS

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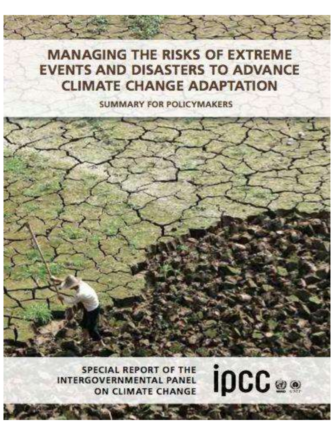
## Introduction

In some circles, carbon dioxide ($CO_2$) is really a good thing. Ask any greenhouse owner operating $CO_2$ generators to accelerate plant growth, or sparkling water manufacturers looking for the perfect fizz. In fact, were it not for $CO_2$, planet Earth would be but another barren ice rock? We should be grateful!

Yet $CO_2$ has suffered some bad marks on its otherwise sterling reputation in recent years – a new, ominous dark side. Although the flora of our delicate green and blue ball thrives from its presence – the increased atmospheric presence of $CO_2$ since the dawn of the Industrial Age has been blamed for a 0.8-degree Celsius hike in global temperature.

## $CO_2$: the beginning of the discussion




Modern concerns began in 1990 when the Intergovernmental Panel on Climate Change (IPCC) – created by the United Nations in 1988 – issued its first report regarding the effect of $CO_2$ atmospheric warming.

Warning that unless measures were soon taken to reduce manmade $CO_2$ emissions – the IPCC report unreservedly stated that over the next several decades, we could expect rising sea levels, weather pattern changes and an irreversible disruption of agricultural production.

Some of the alarm initially focused on early climate change computer modeling which, in some cases, projected horrific scenarios only a few decades hence. Even today a handful of doomsayers have warned we have but ten years – maybe less – to set things right.

Pre-Industrial Age levels of $CO_2$ were about 280 ppm, and today content has risen more than 40 percent to 415 ppm. Not good. As even some of the more conservative modeling has suggested, a continued upward trend would indeed have severe long-term consequences.

There is some good news. Nature may be bestowing a temporary reprieve – buying the world some time for the development of technological solutions.

We see a cooling trend," said Martin Mlynczak of NASA's Langley Research Center. "High above Earth's surface, near the edge of space, our atmosphere is losing heat energy. If current trends continue, it could soon set a Space Age record for cold." The reason? A long period of reduced solar activity.

Recent studies by the University of California at San Diego and Northumbria in the UK are predicting a "Grand Solar Minimum" over the next several decades – similar in length and effect as the Maunder Minimum which contributed in part to the Little Ice Age in Europe from 1645 to 1715 – an extended time of much lower temperatures.

## IMO contribution

Regardless, the Marine Environment Protection Committee (MPEC) of the International Maritime Organization (IMO) found it prudent to heed the conclusions of the 1990 IPPC report and subsequent warnings, moving forward with measures to reduce marine emissions of $CO_2$, thought to account for about two percent of global $CO_2$ emissions.

In 2018 MPEC issued an extremely ambitious goal – a 50 percent reduction of $CO_2$ emissions from ships by the year 2050.

The IMO proposed amendments as a path to that goal in November 2020 – articles that will be put forward for formal adoption at the MEPC session sometime this year.

Given the ambitious target, this path appears to be a practical and conservative one - buying time until advanced technology is developed to truly revolutionize marine propulsion systems. Rather than calling for any wholesale conversion to the days of sail – or perhaps a reconsideration of nuclear-powered vessels, these measures simply find better ways to improve efficiencies on existing vessels by implementing a new Energy Efficiency Ship Index (EEXI) program.

This, in turn, generates a new reporting system, dubbed the carbon intensity indicator (CII), which will be determined and reported annually for each vessel and incorporated into the Ship Energy Efficiency Management Plant (SEEMP).

Under this plan, a vessel will be rated annually – graded on a scale from A to E. Should a vessel suffer three consecutive years of a D or E rating, a corrective action plan must be submitted. Once implemented, this scheme would require the IMO to review the effectiveness of the program no later than January 2020.

## Fuel treatments to help reducing $CO_2$?

Not surprisingly, vendors are already excited about cashing in on this proposed program – from software development companies to, yes, even manufacturers of marine fuel treatments, who are touting fuel additives as one way to reduce $CO_2$.

But wait. How can that be? Claiming combustion improvement with a chemical fuel treatment to reduce Greenhouse Gas emissions ($CO_2$) ignores once simple rule of combustion physics that provides a direct contradiction of the stated goal - a simple case of combustion physics 101.

For optimum combustion to occur in a modern marine diesel engine, the fuel injection system must be in perfect working condition to properly meter the fuel into the engine for the required output. Then, of course, is timing. The fuel must be injected as an atomized spray at the precise moment during the compression stroke. This spray must go far enough into the cylinder to ensure even distribution.

Simple. But in time systems can be compromised. If the fuel lacks sufficient lubricity, injector wear can accelerate, affecting injector efficiency. Fuels with a high carbon content as measured by mcr (micro carbon residue) testing – or fuels that have suffered some degree of degradation from blending and storage may also cause an accumulation of unburned petroleum coke on injector apertures, impinging spray patterns and inhibiting full combustion.

While an excellent preventative maintenance program can minimize and even eliminate most factors that contribute to compromised combustion – the one wild card remaining is fuel. The IMO has made a valiant effort to implement some measure of remedy over the years by mandating fuel formula changes – the most recent being the global marine fuel sulfur cap of 0.5 percent which took effect in January 2020.

## Major issues with IMO-2020 fuel grade (VLSFO)

Yet here the law of unintended consequences has taken effect. Since this mandate, vessel operators and testing laboratories have seen a substantial increase in problematic fuels – mostly issues with excessive sludge production, fouled fuel delivery systems and compromised ignition quality. Some cite two major contributing factors.

First of these is chemical incompatibility. No refiner produces a straight run 0.5 percent sulfur fuel. So, to achieve the sulfur target – fuels must be blended – typically a mix of onshore automotive distillate product with a sulfur cap of 15 ppm (0.015 % sulfur) with somewhat heavier hydrotreated distillates - a light measure of heavier fuel oil thrown in for good measure.

The problem arises because each of the separate fuels has its own set of chemical precursors that are often different than those in the fuel into which it is mixed. When these different precursors are blended – reactions are set up between them which result in the formation of unwanted decomposition products consisting of gum, resin, high carbon weight polymeric structures and asphaltenic residue.

Even a straight run fuel will suffer some measure of similar degradation over time, the rate of deterioration dependent on exposure to heat and oxygen during long storage periods.
Extended storage time is the second major contributing factor, and in recent months this has been extremely aggravated thanks to the global Covid 19 pandemic, resulting in record storage levels of fuels at all major global ports.

To summarize – modern marine fuels are subject to issues of chemical and physical stability. It is the degradation of these properties that result in compromised ignition quality and excessive unburned hydrocarbon and particulate emissions.

## False claims and risky fuel treatments

In recent weeks, a handful of marine fuel treatment manufacturers have rushed forth claiming their products can help vessel operators improve efficiencies under the new MEPC guidelines. One company produces an excellent sludge dispersant chemistry – an organic tall oil fatty acid (TOFA) which is capable of penetrating sludge on a molecular level – separating heavier asphaltenic components and distributing the material evenly throughout the fuel mixture.

In turn, this effect helps maintain proper fuel droplet size following injection – keeping the rate of combustion consistent and even. That is a good thing. Yet does this effect reduce $CO_2$ emissions? Not really. Rather, it simply maintains the desired design parameters of the fuel delivery system – maintaining some measure of proper combustion appropriate for that engine design.

A second manufacturer is touting a "new" product which embraces a not so new technology - one that long-ago lost favor in the onshore automotive industry and among refiners. This product is formulated with ferrocene (dicyclopentadienyl iron) – a reason why it is critically important for technical personnel to carefully review the safety data sheets of products they are considering using.

In the steam turbine days almost all marine fuel treatment manufacturers formulated with ferrocene, most abandoning the approach with the dawn of the motor ship era. Indeed, ferrocene is an effective catalyst in accelerating the combustion process. In steam turbine operations, ferrocene application to the fuel did result in reduced visible smoke. But a notable byproduct of ferrocene combustion is iron (ferric) oxide.


Ferrocene

Accumulation of iron oxide in a traditional marine boiler – essentially devoid of moving parts – was hardly problematic. For internal combustion engines, it is an entirely different story.
In sanctions against the late 1930s German regime, the U.S. government cut off supplies of tetraethyl lead (TEL) to German refineries – the octane boost additive used in fuels at that time. Germans then turned to ferrocene as a replacement. In short order engine wear rates accelerated owing to the abrasive nature of iron oxide on components.

With its fine abrasive qualities, iron oxide is an excellent polishing agent – the primary component of "jeweler's rouge" - the residue wiped clean after each job. Not so easy to do on the exhaust valve surfaces of a modern marine diesel engine.

Today the Worldwide Fuel Charter – an international body of onshore engine makers – has banned the use of ferrocene in onshore fuels. So has every major global refiner. The engine maker Wartsila refuses to issue any "No Objection" letter for any marine additive containing the material.

And there is one specific downside when the cetane number of fuels is elevated with the use of a metal catalyst. Contrary to any implication that such products reduce global greenhouse gases – the opposite is true.

## Back to basics: notions of mechanical engineering

Simply, the laws of combustion physics are inviolable. When the ignition quality of any hydrocarbon fuel is improved, a tiny bit more of the fuel is consumed of the amount injected. Provided the air/fuel ratio and fuel injection timing factor is optimum, carbon monoxide (CO) emissions are slightly reduced, and carbon dioxide ($CO_2$) emissions are increased.

How can that be good? This increase is somewhat offset by the fact that it takes slightly less fuel – an exceedingly small amount – to produce the same unit of energy – measured in brake specific horsepower.

How small? A rule of thumb is for every bar increase in peak firing pressure (pmax), approximately 0.25 percent less fuel is required for the same output. So, if a two bar pmax increase is attained, 0.5 percent less fuel is required to produce the same amount of energy.

But increasing cetane more than just a couple of points can have an adverse effect on particulate emissions, as some research studies have shown. The reason is simple. With a higher cetane number – the fuel in the combustion chamber reaches higher temperatures which in turn increases the formation of less burnable, higher carbon weight structures in the phase of combustion known as the "afterburning" stage.

This material is formed from the cracking of what are known as "unsaturated" structures – typically olefinic components of the fuel. These structures have double electron bonds. When they initially split or crack in the early stage of combustion, they tend to share bonds with one another, causing them to recombine into much longer chain polymeric structures with much higher carbon weight than before.

This is where the notion of "thermal stability" come into play. Petroleum chemists have long sought ways to improve thermal stability by limiting or preventing the formation of these polymeric structures – the primary cause of particulate emission and carbon deposits on engine components. Over the years this has been a critical objective in the production of aviation fuels.

After all, the turbine blades of a jet aircraft flying at 30,000 feet must not be subject to abrasive, unburned hydrocarbon deposits.


The same holds true for modern automotive fuels – now subject to rigorous clean air standards. Engines and fuel systems must remain clean. So, in addition to improvements in fuel formulations and refining, a major contributing factor to the cleaner burning of these fuels has been the application of amine-based additives designed to greatly improve fuel thermal stability.

Some of these additives for petrol have been given trade names by refiners – Shell's V.Power, Chevron's Techron, BP's Ultimate. Today the same concept developed by refiners for aviation and automotive fuels has been developed and refined by Newport Fuel Solutions for all grades of commercial marine fuel – heaviest to lightest. Here again, the key is greatly improved thermal stability – the result being greatly reduced carbon deposits on engine components and reduced unburned hydrocarbon and particulate emissions.

### The right solution is the best solution

To achieve an exceptional level of chemical and thermal stability, Newport formulates with a very specialized amine complex at a high concentration – the same proven chemistry applied by refiners globally in the production of industrial fuels. This is combined with a tall oil fatty dispersant which provides exceptional physical stability – necessary to break down heavy asphaltene components and contaminates in fuels which are then evenly dispersed throughout the mixture into a colloidal state.

This flagship product, NP-HFO, is appropriate for all marine fuel grades, protecting against incompatibility issues while providing extremely effective deposit control for fuel delivery systems and engine components at an economic dose rate of one liter per 20 mt. A 100 percent active, refinery-grade product, NP-HFO contains no cheap petroleum solvent "fillers" or dangerous metallic catalysts. NP-HFO is also classified "non-hazardous" for safe onboard storage and handling by personnel.

Newport also manufacturers a stand-alone fuel oil treatment dispersant chemistry, NP-FOT. With a treatment rate of one liter per 30 mt. NP-FOT is 100 percent active concentration, organic, non-toxic, and non-dangerous.

To complement these products and provide added value and additional protection, Newport manufacturers refinery grade, highly concentrated lubricity additives at exceptionally low cost. After all, the thinking goes, vessel owners should enjoy the same low cost as that benefitting global refiners.

Newport clients are given a certificate of proof of application to be included in a vessel's SEEMP plan – yet another weapon in the green arsenal for responsible corporate compliance in meeting IMO objectives. For more information, please contact your local Newport representative and visit Newport at newportfuelsolutions.com.