

FUEL OIL QUALITY & UNDERSTANDING THE SOURCE OF TODAY'S STABILITY PROBLEMS

Catalytic Cracking and Fuel Stability

Today's refineries produce more higher yielding products while the life of many stored fuels has dropped from years to months.

Fuel and heating oil service professionals with many years of experience remember a time when fuel seemed to last longer. They claim a dramatic increase in unscheduled service calls due to dirty filters and clogged nozzle and fuel injection system failures. Increasingly, we're realizing that the increasing fuel-related service calls can be traced to changes in the refining process.



Increasing incidences of sludge in today's heating systems is a direct result of changes in the refining process.

Until the 1970's, most heating oil was produced using the traditional distillation process. This process yielded 60% light and middle distillates and 40% heavy products. The oil crisis of the 70's pressured refiners to look for ways to increase yields of middle distillates as a way of keeping their costs lower and the Clean Air Act of 1990 added

Prior to the 1970's, most heating oil was produced by a simple distillation process. This fuel sample is almost 35 years old and has produced virtually no sediment.

Shortages and pressure to be produce more high value product from the same quantity of crude oil caused refiners to catalytic cracking, a process by which long chain (heavy) oils are "cracked" into shorter chains.

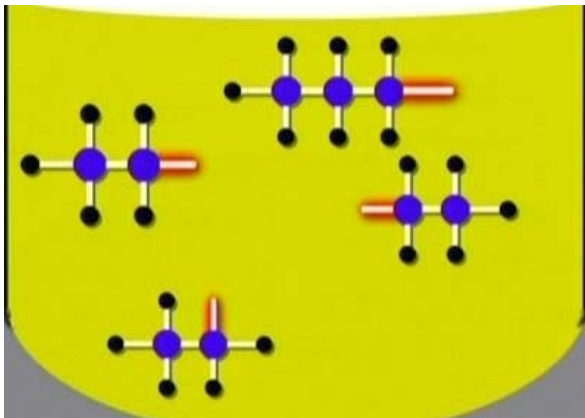
The results increased yields of lighter and more valuable fuels such as gasoline, kerosene and heating oil at lower costs. But cracking has been a mixed blessing for fuel oil dealers and users. It increased the supply, helping to moderate prices. However, the "new" blended fuel with its artificially broken chains is much more instable.



Re-polymerization: A Word Every Fuel Oil Dealer Should Understand

During the catalytic cracking process long chain hydrocarbon molecules are broken into shorter chains which are refined and blended into additional gasoline, kerosene, on and off road diesel fuels and heating oil. Unlike their natural counterparts, the artificially cracked chains have “active ends” – (bonds) which have been broken and which are susceptible to recombining with other unstable molecules. When cracked and or blended fuels are stored, these molecules begin recombining, in a process known as **re-polymerization**.

This process results in increasing the size and mass of the fuel particle. Often the re-polymerized chains, join with other chains (agglomerate) eventually into visible particles. These organic compounds that first form insipient solids continue to grow, turning into black particles (tank sludge) that settle in tanks, clog filters and damage system components.

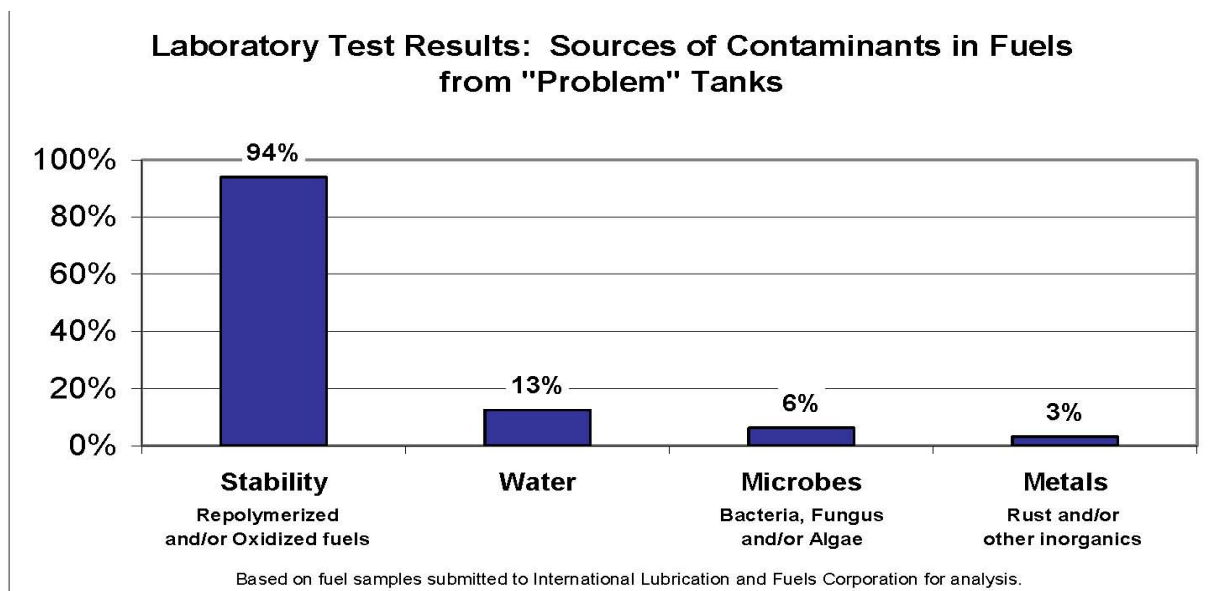


Active ends (shown in red) of artificially cracked hydrocarbon chains are the source of instability in today's fuels. Over time, these ends recombine, forming agglomerations of long chain molecules in stored fuel.



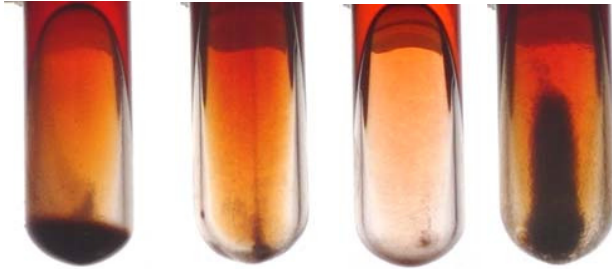
Although re-polymerization begins at a sub-microscopic level, as long-chain hydrocarbons begin to re-form they agglomerate and form visible sediment. The sample on the right shows the result of this process. The sample on the left was treated with a stabilizer and dispersant to inhibit re-polymerization.

The extent of fuel problems is illustrated in the graph below. Water, biological contaminants and rust continue to create fuel storage problems work as catalysts in the process. Their impact has been dwarfed by problems caused by re-polymerization.



The One Constant is Variation

Fuel oil samples from customers' tanks around the country for testing shown below.



These test tubes contain untreated four months old fuel that was “aged” by a heating process. These samples from around the county, show variation in fuel stability.

One thing is certain. There is a great deal of variety in the susceptibility of fuel to sediment formation. Unfortunately, we know that much of today's cracked fuel breaks down quickly unless it is treated. Some fuels seem to have a head start. Studies show that “barged” fuel causes more service problems than pipeline fuel.

Based on customers' reports, we also strongly suspect that periodically “bad batches” are introduced into the fuel stream. Frequently, by the time clogged system components prompt a service call, the fuel has passed through the system making it difficult to trace the problem to its source.

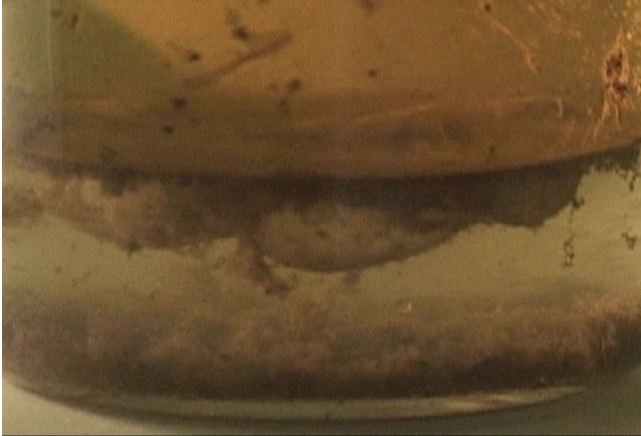
Traditional Problems Still Exist

Although re-polymerization is by far the most significant threat to stored fuel, other more traditional problems remain.

Oxidation.

When exposed to air or water, fuel combines with oxygen. In many cases, the result is harmless darkening in color. Oxidation can also result in sediment formation. Many older fuel stability tests still use oxidation as a key indicator. Make certain you understand the capability of any lab you use for fuel testing.

Bacteria and Fungus. Biological contaminants will grow in fuel tanks, particularly if water is present. Bacterial or fungal contamination as a primary cause of operational problems is much rarer than commonly believed.



Bacterial, fungal or algae growth may occur. Even though performance problems due to microbial activity are less common than those resulting from re-polymerized fuels.

Water & Rust: The presence of water and sulfate reducing bacteria cause H₂S-hydrogen sulfide, leading to rust, corrosion seen as pitting. Water is a necessity for microbial activity, that in turn leads to ionization of the water, making it more corrosive. This phenomenon is known as microbially induced corrosion (MIC). **Microbial contamination is one of the accelerating factors in “fuel quality degradation”.**

An Industry Priority

A very large percentage of unscheduled service calls are caused by fuel related problems such as: “clogged filters, nozzles, pumps and strainers”

Biofuels and Low-Sulfur Fuels

Bio-diesel B-5, the likely standard for the near-term contains only 5% bio-fuel and 95% of today's cracked petroleum-based fuel.

Low-sulfur fuels hold a great deal of promise to keep e.g. heating systems cleaner downstream of the nozzle. Questions remain about low-sulfur fuels' stability in storage and consequently it's impact on system components “upstream” of the nozzle.

Low sulfur fuels will continue to be cracked, as they are today and ultra-low sulfur fuels are more susceptible to breakdown due to the formation of peroxides. However, part of the process that removes sulfur includes the introduction of hydrogen. In other words, more research needs to be done.

Additives

Good housekeeping, proper tank maintenance, fuel conditioning and filtration practices and the selective implementation of premium broad spectrum additive packages provide a solution to problems created by fuel in-stability.

List of terms to assist in evaluating the many additives on the market

Solvents Solvents are part of many fuel additives used as carriers for other chemicals; or, as the primary active ingredient. They break up sludge, but generally do so too rapidly, creating a rash of service problems when they are first used. It is recommended to avoid solvents as the tool to break up sludge.

Stabilizers: Stabilizers reduce the formation of in-soluble materials due to oxidation.

Dispersants: Dispersant is used to prevent particulate to agglomerate and separate existing agglomerated particles. They do this chemically and are consumed by the process.

Antioxidants: Antioxidants slow the oxidation process lead to sediment formation.

Biocides: Biocides are designed for use in either fuel or water or both. They are not the cure-all that they are generally believed to be and have no effect on the process of re-polymerization, nor do they deal with the problem of tank sludge. Some biocide-additives will form solids in fuel aggravating the problems they were intended to solve.

Biocides vary widely in effectiveness and are generally based on a variety of toxic ingredients that are often trans-dermal. These toxic chemicals are potentially very harmful to people. One has to be very careful in selecting and applying a biocide. Generally, biocides are meant to stop and/or prevent microbial activity. (the reproduction of bacteria, fungus, yeast and mould)

Rust inhibitors: Rust inhibitors slow down the rust forming process by forming films or by chemically neutralizing one of the rust forming chemical mechanisms.

De-emulsifiers: De-emulsifiers are meant to change the surface tension of fuel and/or water causing a clear separation of water and fuel.

Cold-flow improvers: Products that reduce gelling and keep oil flowing when cold meet a tremendous need in the oil heating industry. However, they are an entirely separate class of products from additives that prevent sludge formation. Cold-flow improvers do not extend the storage life of fuel.