ImproChem

# Capabilities Profile
## Refining and Fuel Additives

ImproChem

A business of AECI Water & Process ™

# CRUDE OIL

Crude oil refining is the terminology used to describe a field of engineering that takes "unprocessed" crude oil and converts it into useful petroleum products. Crude oil is a fossil fuel, which means that it was made naturally from decaying plants and animals living in ancient seas millions of years ago. Crude oils vary in colour, from translucent to black, and in viscosity, from free-flowing liquids to semi-solid tarry substances.

Crude oils are a useful starting point for so many different substances because they contain hydrocarbons. Hydrocarbons are molecules that contain hydrogen and carbon which vary in lengths and structures, including straight chains, branched chains, cyclic compounds and aromatic rings.

Hydrocarbons are energy rich molecules. Many of the petroleum products derived from crude oil like petrol, diesel, jet fuel and paraffin wax, take advantage of this energy.

The major classes and characteristics of hydrocarbons in crude oils include:

**Paraffins**

- general formula: $C_nH_{2n+2}$ (n is a whole number, usually from 1 to 20)
- straight- or branched-chain molecules
- can be gasses or liquids at room temperature depending upon the molecule
- examples: methane, ethane, propane, butane, isobutane, pentane, hexane

**Aromatics**

- general formula: $C_6H_5$ - Y (Y is a longer, straight molecule that connects to the benzene ring)
- ringed structures with one or more rings
- rings contain six carbon atoms, with alternating double and single bonds between the carbons
- typically liquids
- examples: benzene, napthalene

**Napthenes or Cycloalkanes**

- general formula: $C_nH_{2n}$ (n is a whole number usually from 1 to 20)
- ringed structures with one or more rings
- rings contain only single bonds between the carbon atoms
- typically liquids at room temperature
- examples: cyclohexane, methyl cyclopentane

Other hydrocarbons:

**Alkenes**

- general formula: $C_nH_{2n}$ (n is a whole number, usually from 1 to 20)
- linear or branched chain molecules containing one carbon-carbon double-bond
- can be liquid or gas
- examples: ethylene, butene, isobutene

### Dienes and Alkynes

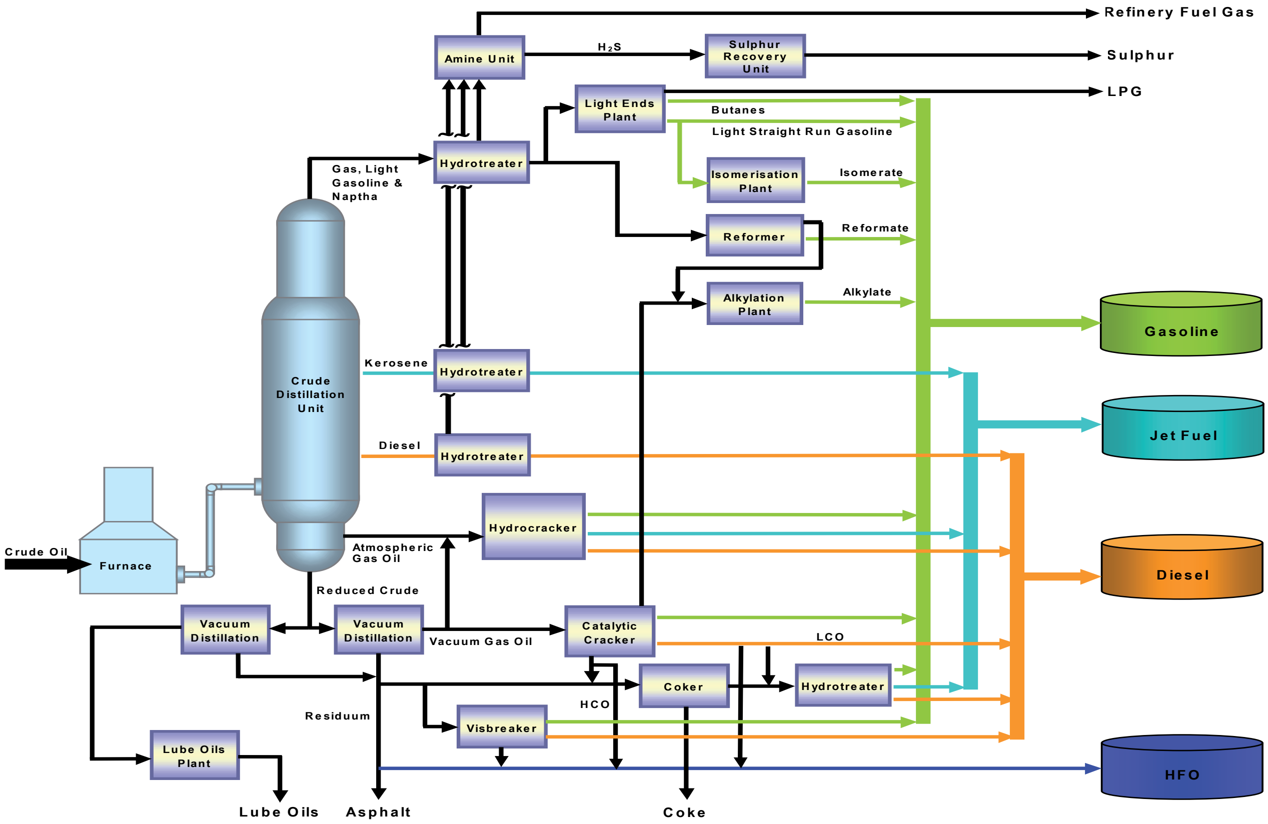
- general formula: $C_nH_{2n-2}$ (n is a whole number, usually from 1 to 20)
- linear or branched chain molecules containing two carbon-carbon double-bonds
- can be liquid or gas
- examples: acetylene, butadienes

On average, crude oils are made of the following elements or compounds:

- Carbon - 84%
- Hydrogen - 14%
- Sulphur - 1 to 3% (hydrogen sulphide, sulphides, disulphides, elemental sulphur)
- Nitrogen - less than 1% (basic compounds with amine groups)
- Oxygen - less than 1% (found in organic compounds such as carbon dioxide, phenols, ketones, carboxylic acids)
- Metals - less than 0.1% (nickel, iron, vanadium, copper, arsenic)
- Salts - less than 0.1% (sodium chloride, magnesium chloride, calcium chloride)

## CRUDE OIL PROCESSING IN THE REFINERY

Most refineries, regardless of complexity, perform a few basic steps in the refining process: **DISTILLATION**, **CRACKING, COMBINING, TREATING, REFORMING and BLENDING**.



## 1. Distillation

The oil refinery's refining process begins when desalted and heated crude oil is distilled in a Crude Distillation Unit (CDU). Modern refineries often have more than one distillation column, one that operates at near atmospheric pressure (atmospheric column), and one or more that operate at less than atmospheric pressure (vacuum column).

During this distillation process, the lightest materials, like propane, butane and gasoline, vaporise and rise to the top of the first distillation column. Medium weight materials, including, jet and diesel fuels, condense in the middle section of the distillation column. Heavy materials, called gas oils, condense in the lower portion of the distillation column. The heaviest tar-like material, called residuum, is referred to as the "bottom of the barrel" because it never really rises.

This distillation process is repeated in many other plants as the oil is further refined to make various products.

In some cases, distillation columns are operated at less than atmospheric pressure (vacuum) to lower the temperature at which a hydrocarbon mixture boils. This "vacuum distillation" (VDU) reduces the chance of thermal decomposition (cracking) due to over heating of the mixture.

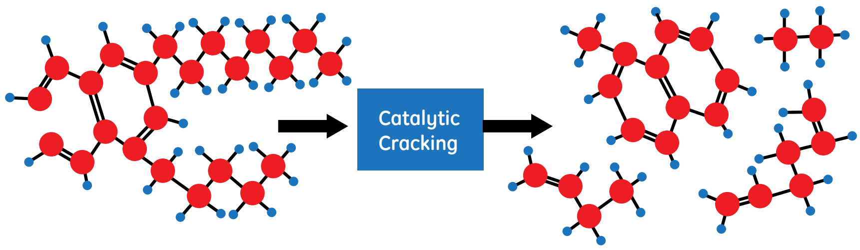
Using highly sophisticated computer control systems, refinery operators precisely control the temperatures in the distillation columns which are designed with pipes to withdraw the various types of products where they condense. Products from the top, middle and bottom of the column travel through these pipes to different plants for further refining.

## 2. Cracking

Since the marketplace establishes product value, a refinery's competitive edge depends on how efficiently it can convert middle distillate, gas oil and residuum into the highest value products.

At most modern refineries, middle distillate, gas oil and residuum is converted into primarily petrol, jet and diesel fuels by using a series of processing plants that literally "crack" large, heavy molecules into smaller, lighter ones.

Heat and catalysts are used to convert the heavier oils to lighter products using three "cracking" methods: Fluid Catalytic Cracking (FCC), Hydrocracking (Isomax), and Thermal Cracking (Delayed Coking or Visbreaking).




The Fluid Catalytic Cracker (FCC) uses high temperature and catalyst to crack heavy gas oil mostly into petrol and diesel. Hydrocracking uses catalysts to react gas oil and hydrogen under high pressure and high temperature to make both jet fuel and petrol.

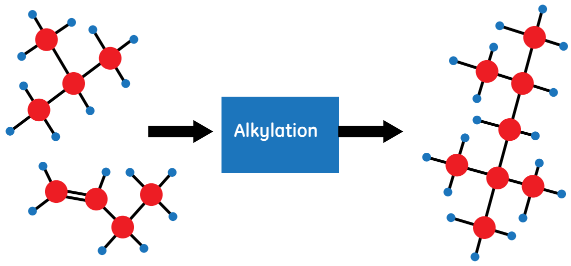
In some modern refineries, lighter gas oil is converted in Isomax Units, using this hydrocracking process. Most of the products from the FCC and the Isomaxes are blended directly into transportation fuels, i.e. petrol, diesel and jet fuel. The lightest molecules are burned as fuel gas in the refinery's furnaces, thus conserving natural gas and minimizing waste.

In a Delayed Coking Unit (Coker), low-value residuum is converted (using a thermal-cracking process) to high-value light products (petrol and diesel), producing petroleum coke as a by-product. The large residuum molecules are cracked into smaller molecules when the residuum is held in a coke drum at a high temperature for a period of time. Only solid coke remains and must be drilled from the coke drums. Petroleum coke is typically sold for use as anode coke, or as fuel in cement manufacturing.

In a Visbreaker, low value residuum is also converted (using a thermal cracking process) to high-value light products and fuel oil during production runs. Any coke that is formed during these processes is removed from furnace tubes, heat exchangers and other equipment during scheduled shutdowns between production runs.

## 3. Combining

While the cracking processes break most of the gas oil into petrol and jet fuel, they also break off some pieces that are lighter than petrol. Since most refineries' primary focus is on making transportation fuels, lighter components are recombined in Alkylation Units. This process takes the small molecules and recombines them in the presence of hydrofluoric (predominantly) or sulphuric acid catalyst to convert them into high octane petrol.




## 4. Treating (Removing Impurities)

The products from a CDU and the feeds to other units contain some natural impurities, such as sulphur and nitrogen. Using a process called hydrotreating, these impurities are converted into hydrogen sulphide and ammonia and removed from the fuels to reduce air pollution when the fuels are used.

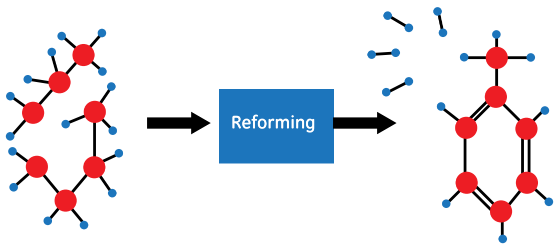
The RDS Unit's main product, low sulphur vacuum gas oil, is fed to the FCC unit which then cracks it into high value products such as petrol and diesel.

## 5. Reforming

Octane rating is a key measurement of how well a petrol performs in an automobile engine. Much of the petrol that comes from the CDU or from the Cracking Units does not have enough octane to burn well in cars.

The petrol process streams in the refinery that have a fairly low octane rating are sent to a Catalytic Reforming Unit where their octane levels are boosted. These reforming units employ precious-metal catalysts - platinum and rhenium – and thereby get the name "Platformers", "Rheniformers" or just "Reformers". In the reforming process, low octane paraffins are "reformed" or converted into higher octane iso-paraffins, napthenes and aromatics for blending into petrol. For example, methyl cyclohexane is reformed into toluene.

The reforming process actually removes hydrogen from low-octane petrol. This hydrogen is captured for use throughout the refinery in various cracking (hydrocracking) and treating (hydrotreating) units.




## 6. Blending

A final and critical step is the blending of fuel products. Petrol, for example, is blended from treated components made in several processing units. Blending and Shipping Area operators precisely combine these to ensure that the blend has the right octane level, vapour pressure rating and other important specifications. All finished refinery products are blended in a similar fashion.

# CRUDE PROCESSING PROBLEMS AND THE USE OF REFINERY PROCESS CHEMICALS

Crude oil refining is predominantly a number of thermal processes. Heating and cooling and reheating, recooling are basic ingredients. Since there is no known material that can withstand extreme variations, instability is generally the cause of major problems. These problems exemplify themselves as corrosion and/or deposits, both of which have an economic bearing upon the operating cost of the refinery.

Crude oil contains a considerable amount of impurities, termed Bottom Sediment and Water (BS&W), but also includes salt, metals and sulphur. These impurities should be removed prior to crude processing to prevent damage to refinery equipment through corrosion and fouling. Salts are removed through a purification step called desalting. Calcium and magnesium chlorides must be removed because under the temperatures reached in the crude processing units, these salts convert to hydrogen chloride (HCl) which will cause extensive corrosion in the crude tower overhead. Sodium also causes exchanger fouling and is a precursor to coke formation in furnace tubes.

Desalting is the intimate contact of water and oil such that the salt is washed from the oil and dissolved in the water. The water and oil are subsequently separated and the desalted crude is ready for processing in the initial distillation step. Water-in-oil emulsions are the biggest problem associated with desalting operations. This emulsion must be broken to separate the crude oil from the water. Normally heat and an electrical charge is employed to dehydrate the crude using a device called an electrostatic desalter.

Crude dehydration is critical because excessive water will:

- Increase the differential pressure between the desalter and the furnace outlet line, which will decrease the crude throughput rate.
- Increase the energy requirements to maintain a constant furnace outlet temperature. Fuel is consumed to vaporise (boil) the water contained in the desalted crude.
- Increase the tendency for foaming in the preflash tower and distillation columns. Excessive water can cause erratic crude flows due to pump cavitation and level control difficulties. These foaming induced mechanical problems will cause poor distillation efficiency; and result in off-specification products being produced. In extreme cases, the rapid expansion of water to steam (1 to 1600 volume increase) will be violent enough to displace distillation trays in the distillation column, which will reduce crude throughput and distillation efficiency.

As the crude leaves the desalter, it still contains some salt; however, it is low compared to the original crude. This residual salt will partially distill overhead in the atmospheric distillation tower along with $H_2S$ and organic acids to cause corrosion problems in the crude column and overhead cooling exchangers.

The crude prior to the atmospheric distillation tower must be elevated in temperature to provide distillation. Part of this heat is provided by heat exchangers which transfer heat from a process stream that needs to be cooled. Additional heat is supplied through direct fired heaters or furnaces. As the crude is heated up to 343 – 360 $^{o}$C, it becomes unstable, and deposits will form in the exchangers and furnaces thus impairing heat transfer and restricting throughput.

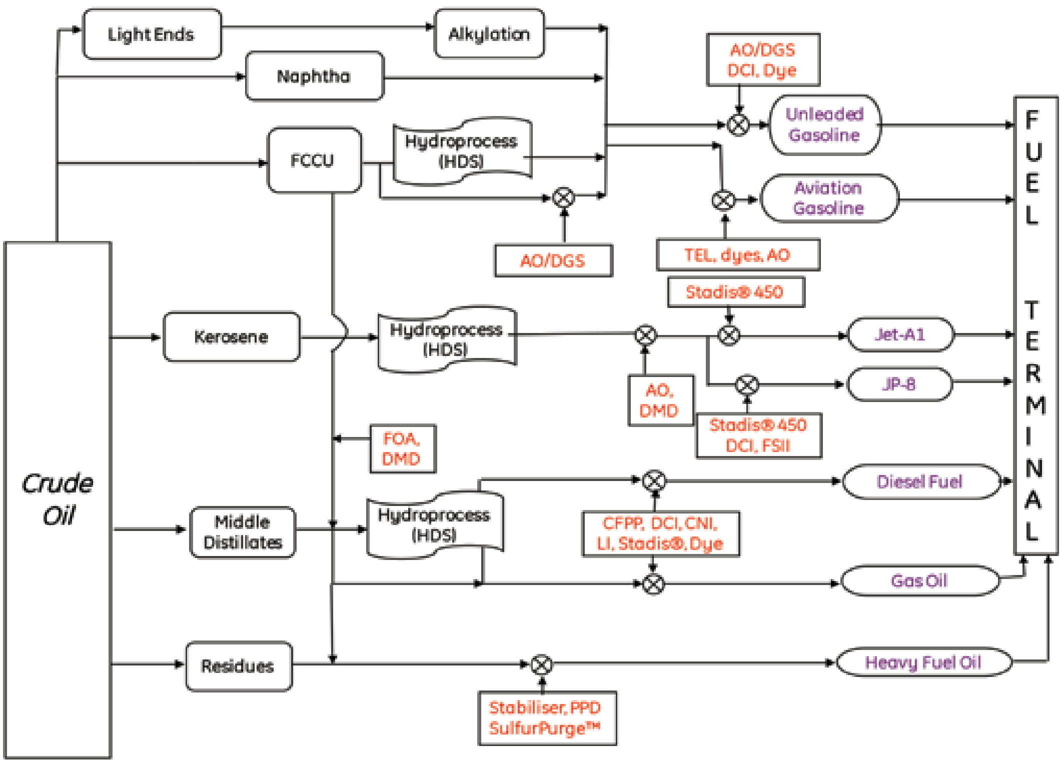
Other problem areas within the refining process include:

- Reboiler fouling and corrosion
- Coker foaming
- Vacuum column fouling
- Vacuum tower overhead corrosion
- Visbreaker furnace coking
- Visbreaker column foaming
- Reformer preheat fouling
- Catalytic cracker fractionator overhead corrosion
- Sour water stripper corrosion
- Unwanted side reactions
- And many more

Refinery process treatment chemicals help to improve plant integrity, operational efficiency and production capacity by performing the following functions:

- **Foam Control:** Antifoams are used in the refinery process to suppress foam formation in various unit operations, thereby improving operational control and allowing increased unit throughput.
- **Corrosion Control:** Corrosion inhibitors are used to control corrosion in the refining process, thereby protecting the integrity of plant and equipment. Corrosion inhibitors work by many different mechanisms, including acid neutralisation, protective film formation, metal passivation and oxygen removal.
- **Desalting Aids:** Crude oil entering the refinery contains water, salts and other contaminants. Crude oil is desalted to reduce corrosion and fouling in downstream processing units, maximise plant throughput, extend run length and reduce heating energy costs. Desalting chemicals can make the removal of crude oil contaminants easier and more complete, thereby improving plant integrity, capacity and operational efficiency.
- **Emulsion Breaking:** Emulsion breakers and solids wetting agents are used to aid in the removal of suspended solids and/or emulsified water from crude oil (desalting) and other refinery process streams.
- **Fouling Control:** Fouling is the formation of deposits in process equipment which impedes the transfer of heat, increases the resistance to fluid flow and could lead to under-deposit corrosion. At refineries, crude oil is distilled and converted into many different products during which a large amount of energy is consumed. Anti-foulant chemicals are added to the process stream to help reduce the build up of insulating deposits on heat exchangers and furnaces, thereby improving heat transfer, conserving energy, protecting system integrity and producing economies of scale for the refiner.
- **Passivation:** Passivation chemicals are used to deactivate competitive catalysts and unwanted side-reactions in fluid catalytic cracking units. For example, Nickel and Vanadium are the most common metal contaminants which compete with the FCC catalyst to react with the hydrocarbon feed. As they contact feed hydrocarbon, the metals cause production of excessive hydrogen and contaminant coke, at the expense of liquid product yields.
- **Lube Dewaxing Aids:** Lube dewaxing aids are wax crystal modifiers designed to affect the structure of the wax crystal formed in a refinery dewaxing unit. Dewaxing aids convert normally poor filtering wax crystals into more desirable shapes that filter easier for improved oil/wax separation.
- **Microbial control:** Microbial contamination is controlled through the use of biocides and single function bio-dispersants.

## REFINERY PRODUCTS AND FINISHED FUEL ADDITIVES



After separation, conversion and purification the various refinery process streams are blended into useful products. Some of the major products produced at a complex crude oil refinery are as follows:

- Petroleum gas - used for heating, cooking, making plastics
  - small alkanes (1 to 4 carbon atoms)
  - commonly known by the names methane, ethane, propane, butane
  - boiling range = less than 40 degrees Celsius
  - often liquefied under pressure to create LPG (liquefied petroleum gas)

- Petrol - motor fuel
  - liquid
  - mix of alkanes and cycloalkanes (5 to 12 carbon atoms)
  - boiling range = 32 to 104 degrees Celsius

- Naphtha - intermediate that will be further processed to make petrol
  - mix of 5 to 9 carbon atom alkanes
  - boiling range = 104 to 157 degrees Celsius

- Kerosene - fuel for jet engines and tractors; starting material for making other products
  - liquid
  - mix of alkanes (10 to 18 carbons) and aromatics
  - boiling range = 157 to 232 degrees Celsius

- Gas oil or Diesel distillate - used for diesel fuel and heating oil; starting material for making other products
  - liquid
  - alkanes containing 12 or more carbon atoms
  - boiling range = 232 to 343 degrees Celsius

- Lubricating oil - used for motor oil, grease, other lubricants
  - liquid
  - long chain (20 to 50 carbon atoms) alkanes, cycloalkanes, aromatics
  - boiling range = 300 to 370 degrees Celsius

- Heavy gas oil or fuel oil - used for industrial fuel; starting material for making other products
  - liquid
  - long chain (20 to 70 carbon atoms) alkanes, cycloalkanes, aromatics
  - boiling range = 343 to 427 degrees Celsius

- Residuals - coke, asphalt, tar, waxes; starting material for making other products
  - solid
  - multiple-ringed compounds with 70 or more carbon atoms
  - boiling range = greater than 427 degrees Celsius

After components are blended back to make finished products, there generally is a need for further stability and quality improvement through the use of finished fuel additives.

Fuel additives help refiners to meet finished fuel quality specifications whilst maximising the yield of high value transport fuels. Almost all fuels are bought and sold using industry standards based on recognized performance testing. In the US, ASTM specifications and test methods are used to assure quality of products. In Europe and South Africa, IP specifications and test methods are used.

Fuel additives are used inside and outside the refinery gate for blending and shipping of fuels. Fuel additives can be used continuously to help meet fuel specifications or as once-off treatments to fix problem blends and cargoes.

Fuel additives are created to meet the refiner's requirements for fuel performance and for improving handling and storage properties. These additives include:

- **Antioxidants:** which block chemical reactions involved in fuel oxidation, thereby improving fuel stability
- **Metal Deactivators:** which chemically isolate copper and other dissolved organo-metallic compounds that catalyse fuel oxidation processes and harm fuel stability.
- **Stabilizers:** which improve the storage stability of the fuel by minimizing fuel oxidation, preventing corrosion, deactivating metals and/or dispersing insoluble components. Stabilisers help prevent colour degradation and sediment formation of stored fuel.
- **Corrosion Inhibitors:** which protect the integrity of pipelines and storage equipment, as well as motor vehicle fuel systems, from attack by water and other acidic corrosive species.
- **Lubricity Improvers:** which improve the lubricating properties of distillate fuels and protect motor vehicle engines and pump components from metal-on-metal wear.
- **Cold Flow Improvers:** which prevent wax crystal agglomeration and precipitation upon cooling of diesel fuel and therefore extend the operating temperature range of the treated fuel and prevent fuel filter plugging.
- **Conductivity Improvers or Static Dissipators:** which help reduce the electrostatic hazards associated with the transfer, mixing and loading of petroleum fuels. Low fuel conductivity prevents charges leaking to earth and can result in electrostatic discharge, arcing or sparks inside tanks containing flammable vapour (fire or explosion hazard). A conductivity improver is added to low conductivity fuels (e.g. diesel and jet fuel) to allow electrostatic charges to dissipate.
- **Cetane Improvers:** which increase the cetane rating of diesel fuel, thereby improving the ignition and combustion characteristics of the fuel and help reduce toxic exhaust emissions.
- **Octane Improvers:** which increase the octane rating of gasoline fuel, thereby improving the anti-knocking characteristics of the fuel.
- **Anti Valve Seat Recession Additives:** which provide valve seat protection for vehicle engines designed to run on leaded petrol.
- **Detergents:** which improve engine performance and reduce vehicle maintenance expenses by preventing fuel system deposits.
- **Biocides:** which control microbiological (slime) growth in diesel storage tanks by establishing toxic residuals in both water and oil phases.
- **Dyes and Markers:** which are typically used for fuel identification purposes.

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