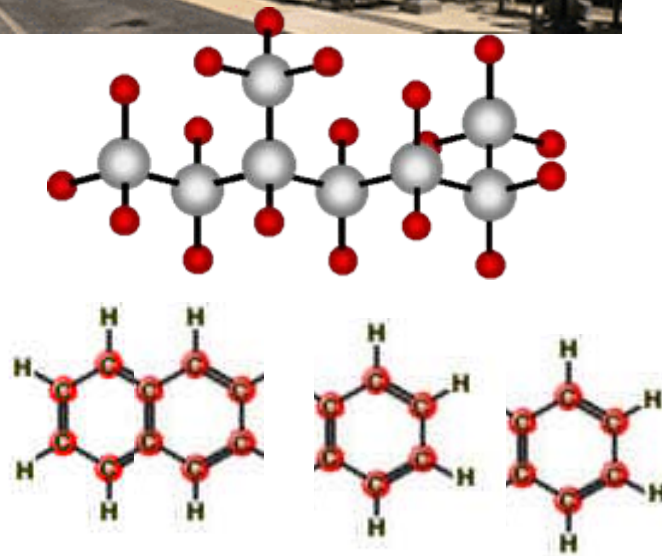


Refining Diesel Fuels

- Many different fuel products can be made to numerous, very broad specifications, from thousands of molecules
- Chemical compositions are a function of
 - Raw material source
 - Refining processes
 - Additives

Thermal Cracking

- Uses high pressure and temperature
- Converts heavy residues to lighter compounds
- Breaks Carbon-Carbon bonds
- Cuts off rings and side chains
- Produces free radicals

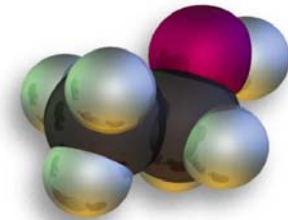


Fluid Catalytic Cracking

- Uses steam, heat and chemical catalyst
- Takes a few seconds
- Cyclone separates the products on reactor walls
- Products
 - Gasoline
 - “Cycle oil” for diesel
 - Heavy residue



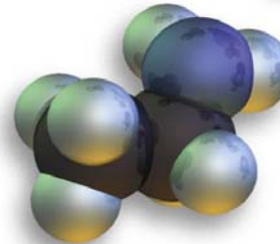
$\text{CH}_3\text{CH}_2\text{Cl}$



$\text{CH}_3\text{CH}_2\text{OH}$



CH_3OCH_3



$\text{CH}_3\text{CH}_2\text{NH}_2$



$\text{CH}_3\text{CH}_2\text{Br}$

Hydrocracking

- Used to produce Low Sulfur fuels
- Also removes nitrogen and oxygen atoms, contributing to instability
- Uses hydrogen in thermal processes
- Produces undesirable by-products

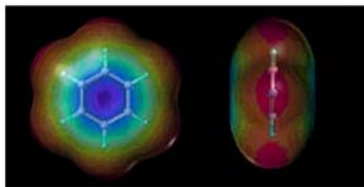
Downside of Hydrotreating

- Potential for incompatibility
- High temperatures may start reactions which actually contribute to gum and sludge formation
- Asphaltene fragments are introduced

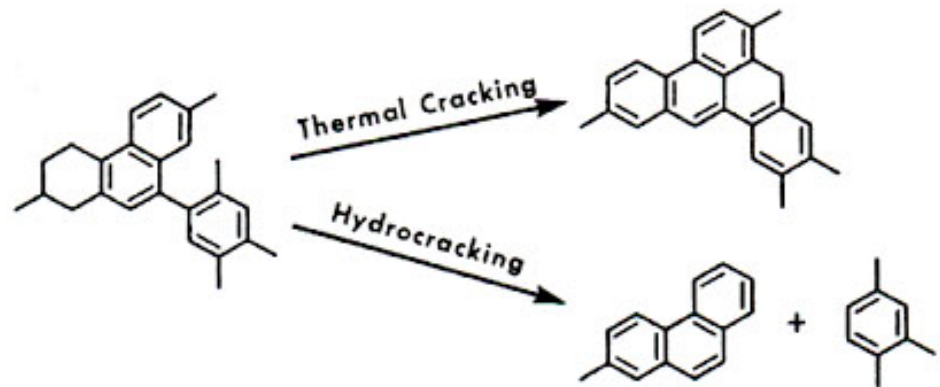
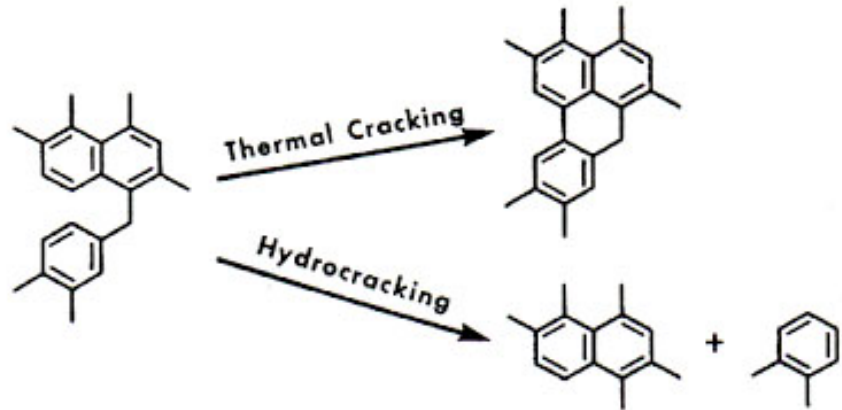
Products of Cracking

Major components

1. Paraffins
2. Olefins
3. Napthenes
4. Aromatics



Benezene Ring



Review of Diesel Refining

- Many different hydrocarbon sources
- Many different refining processes
- The Standard for “Diesel” is very broad
- Many different fuel “recipes”
- Like going to a chili cook-off

Low Sulfur Diesel

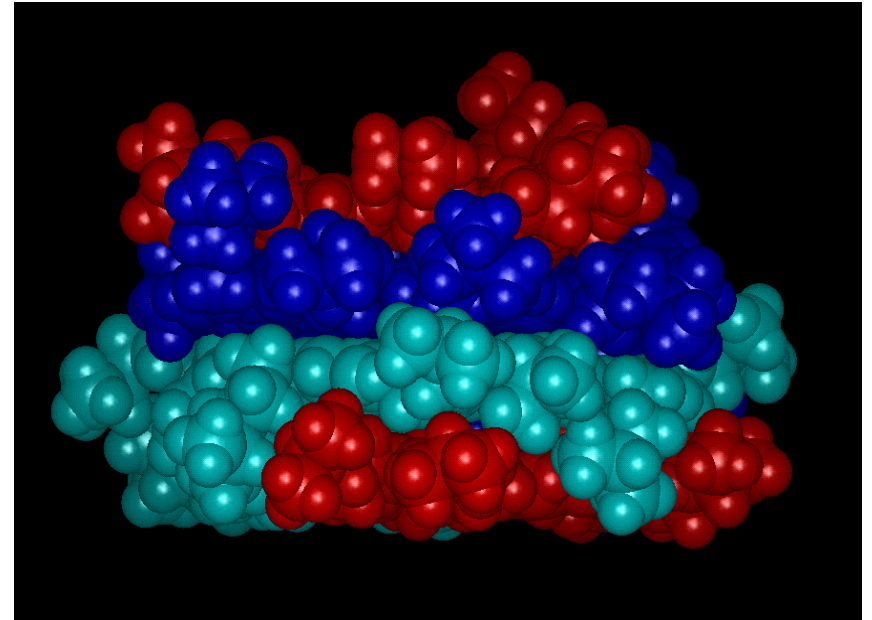
- Low Sulfur Diesel is a totally different product than High-Sulfur diesel
- High-Sulfur contains to 5,000 ppm of sulfur
- Low-Sulfur up to 500 ppm
- Ultra-Low-Sulfur contains 15 ppm or less
- Many other important chemical and performance differences

Differences of Ultra Low Sulfur

- Electrical conductivity is lower
- Corrosion properties are higher
- Lubricity coefficient is lower
- Paraffins have a lower heating value
- Elastomer compatibility issues
- Generally more unstable
- Tendency to form carbon deposits

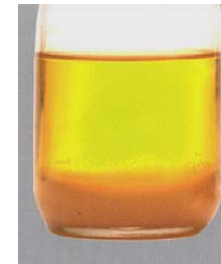
Review

- Modern diesel refining produces very complex fuels
- Cracking breaks up larger hydrocarbon molecules to be blended with the pure, distilled diesel
- Cracking leads to instability, incompatibility, and polymerization



Fuel Quality Degradation

- Instability
 - Formation of color, gum or sediment in liquid over time
- Incompatibility
 - Formation of precipitate or phase separation when two liquids are mixed



Incompatibility Reactions

- Inability to mix
- May result in phase separation
- Sediments, deposits, and sludge



Causes and Symptoms of Instability

Thermal Instability

- Seen in fuel used for engine cooling.
- Starts at temperatures above 100 C.
- Symptoms: darkening, filter clogging, sludge, poor combustion, carbon deposits in engine fuel system.

Storage Instability

- Starts during refining, storage, transport and end-user storage.
- Formation of color, sediment, gum or sludge over time
- Symptoms: darkening, poor filterability and poor combustion.

Instability Reactions

- Increased Peroxide level (promotes oxidation and more instability)
- Formation of dark-colored masses
- Formation of filterable and non-filterable sludge

Review of Diesel Degradation

- Many different raw products go into diesel
- Each batch is unique
- Many reactions begin to create slime, sludge
- Color change is a clue but not proof
- Accumulations on filter may be many things
- Some reactions cause phase change, similar to moisture turning to snow
- Some reactions cause weight and size growth, like rolling a snowball