Crude Oil Composition

- **Crude oil** is the term for "unprocessed" oil petroleum
- Crude oil is a **fossil fuel**
- **Crude oils vary in color**, from clear to tar-black, **and in viscosity**, from water to almost solid.
- Crude oils are comprised of **hydrocarbons** molecules that contain hydrogen and carbon and come in various lengths and structures, from straight chains to branching chains to rings.

Crude Oil

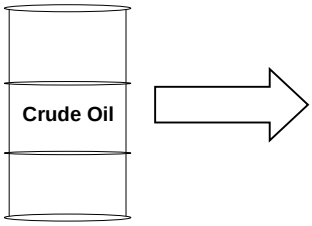
- A mixture of complex hydrocarbons-not a single compound or element
- Characterized by region, gravity, and sulfur content
- The poorer the quality (heavier-higher sulfur), the more complex refining required to make saleable motor fuel products

Crude Oil Characteristics

- **Crude density is commonly measured by API gravity**
  - **API gravity provides a relative measure of crude oil density.**
  - **The higher the API number, the lighter the crude**
  - **Classified as light >34, medium 24 – 26, or heavy <24)**
- **Sulfur content measures if a crude is sweet (low sulfur) or sour (high sulfur)**
  - **Less than 0.7% sulfur content = sweet**
  - **Greater than 0.7% sulfur content = sour**
  - **High sulfur crudes require additional processing to meet regulatory specifications**
- **Acid content measured by Total Acid Number (TAN)**
  - **High acid crudes are those with TAN > 0.7**
  - **Acidic crudes highly corrosive to refinery equipment**

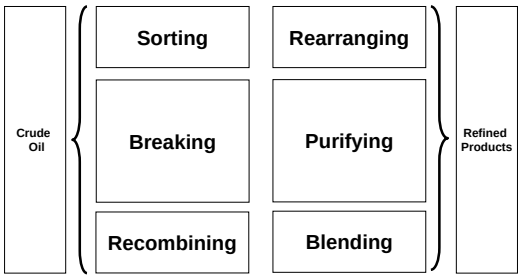
What do refineries do?

Refineries Convert Crude Oil Into a Wide Array Of Products

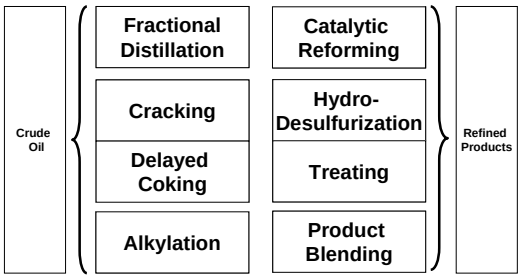


Fuel Gas (Consumed)
PG (Propane & Butane)
Gasoline
Jet Fuel
Kerosene
Diesel Fuel
Coke (Fuel & Specialty)

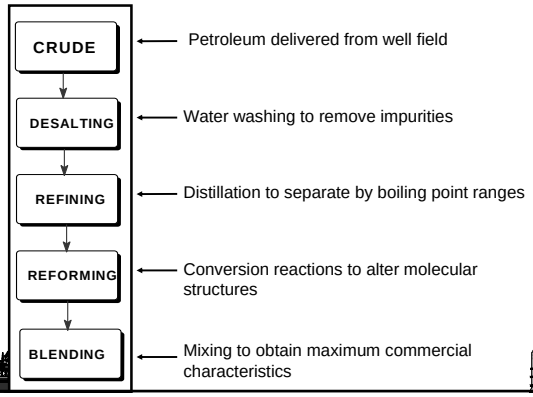
Refining Processes



Refining Processes



Refining Processes



Desalting

- **Crude oil often contains water, inorganic salts, suspended solids, and water- soluble trace metals**
- **As first step in the refining process, these contaminants must be removed by desalting (dehydration).**
- **Two most typical methods of crude- oil desalting using hot water as the extraction agent are**
  - **Chemical Desalting**
  - **ElectrostaticDesalting**

Desalting

- **Chemical desalting**: Water and chemical surfactant (demulsifiers) are added to the crude, heated to dissolve salts and other impurities in the water or and allowed to settle in a tank
- **Electrical desalting**: this is the application of high-voltage electrostatic charges to concentrate suspended water globules in the bottom of the settling tank.
  - Surfactants are added only when the crude has a large amount of suspended solids. Both methods of desalting are continuous.

Desalting

- The feedstock crude oil is heated to between 150° and 350°F to lower viscosity and surface tension for easier mixing and separation of the water.
- The temperature is limited by the vapor pressure of the crude-oil feedstock. In both methods other chemicals may be added.
  - Ammonia is often used to lower corrosion.
  - Caustic or acid may be added to adjust the pH of the water wash.
- Wastewater and contaminants are discharged from the bottom of the settling tank to the wastewater treatment facility.
- The desalted crude is continuously drawn from the top of the settling tanks and sent to the crude distillation (fractionating) tower.

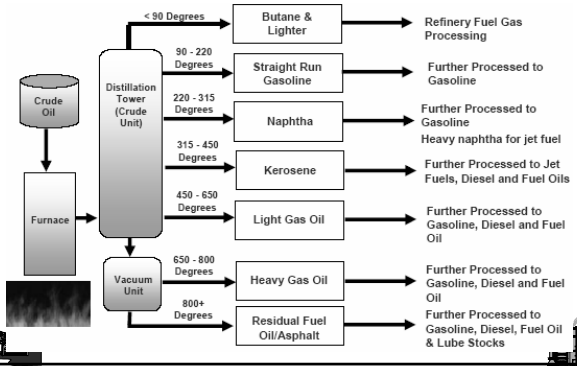
Separation

- **Fractions of the crude boil at different temperatures**
- **Components are separated by distillation and drawn off as they condense**
- **Distillation is found in every process area**
- **May be at high pressure, low pressure or under a vacuum**

Crude Oil Fractionation / Distillation

- Crude oil is heated to 750°F (399°C)
- Heated crude is separated into rough "cuts“
  - Different boiling point are drawn from the distillation tower
  - Light compounds (fuel gas and LPG) rise to the top of the tower, Heavy material (asphalt) falls to the bottom of the tower

Basic Refining Concepts

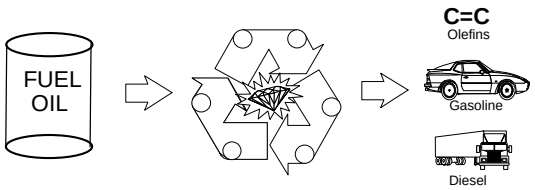


Conversion

- **Upgrading separation products by changing their chemical structure**
- **Temperature, pressure in presence of catalyst**
- **Re-arranging of molecules**
  - **Alkylation**
  - **Isomerization**
  - **Reformation**
- **Upgrading**
  - **Coking**
  - **Hydro Cracking**

Cracking

Using a powdered catalyst that behaves like a liquid when fluffed up with air, Cracking breaks up low-valued molecules (fuel oil) into gasoline, diesel and other processing unit feed stocks (Alkylation)



Cracking

- The term “cracking” refers to the process through which large hydrocarbon molecules are split into smaller ones in order to obtain lighter hydrocarbons.
- This process requires very high temperatures and sometimes the use of a “catalyst”.
- There are two types of cracking which have additional variations in the way they are implemented.
  - Thermal cracking
  - Catalytic cracking

Thermal Cracking

- It basically consists in heating the hydrocarbons until they reach high temperatures using also high pressures in some cases. This allows the hydrocarbons to break apart forming simpler hydrocarbons. The simple word “cracking” is often used to refer to this type of cracking as this is the oldest and most common type of cracking. However, thermal cracking can be achieved in different ways. There are three methods to implement thermal cracking:
  - **Steam**
  - **Visbreaking**
  - **Coking**

Thermal Cracking

- **Steam** - high temperature steam (1500 degrees Fahrenheit / 816 degrees Celsius) is used to break ethane, butane and naptha into ethylene and benzene, which are used to manufacture chemicals.
- **Visbreaking** - residual from the distillation tower is heated (900 degrees Fahrenheit / 482 degrees Celsius), cooled with gas oil and rapidly burned (flashed) in a distillation tower. This process reduces the viscosity of heavy weight oils and produces tar.
- **Coking** - residual from the distillation tower is heated to temperatures above 900 degrees Fahrenheit / 482 degrees Celsius until it cracks into heavy oil, gasoline and naphtha. When the process is done, a heavy, almost pure carbon residue is left (coke); the coke is cleaned from the cokers and sold

Catalytic Cracking

- This method of cracking generally uses zeolites as catalysts. Catalytic cracking can be also done through other catalyst such as aluminum hydrosilicate, bauxite and silica-alumina. As in the case of thermal cracking there are different methods to implement catalytic cracking:
  - Fluid catalytic cracking
  - Hydrocracking

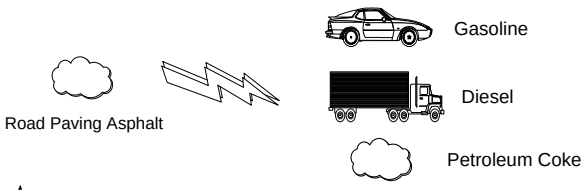
Catalytic Cracking

- **Fluid catalytic cracking** - a hot, fluid catalyst (1000 degrees Fahrenheit / 538 degrees Celsius) cracks heavy gas oil into diesel oils and gasoline
- **Hydrocracking** - similar to fluid catalytic cracking, but uses a different catalyst, lower temperatures, higher pressure, and hydrogen gas. It takes heavy oil and cracks it into gasoline and kerosene (jet fuel). Hydrocracking is basically a refining process that uses hydrogen and catalysts with relatively low temperatures and high pressures for converting middle boiling or residual material to high-octane gasoline, reformer charge stock, jet fuel, and/or high grade fuel oil. The process uses one or more catalysts, depending upon product output

Delayed Coking

Using time and high temperature to break large asphalt molecules into gasoline and diesel

Petroleum coke is a solid byproduct and is blended with coal for use as a solid fuel in power plants

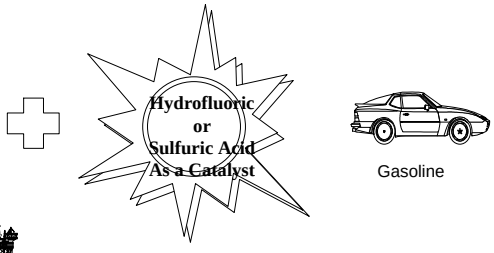


Alkylation

- **Alkylation** (alteration) is the rearranging and combining of molecules of different types to create more desirable products, such as very high octane gasoline

Recombining/Alkylation

Making high octane gasoline with an acid catalyst to combine isobutane with propylene and butylene produced in the cat cracker and coker

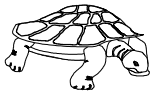


Reforming

- Reforming is changing hydrocarbons to create more desirable molecules
- Usually done using catalysts
  - platinum

Catalytic Reforming

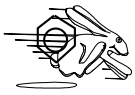
Using a precious metal catalyst to rearrange or change the shape of a gasoline molecule to improve the octane and liberate hydrogen



Straight Chain (low octane) Molecules

Platinum / Rhenium

High Temperature
Low Pressure

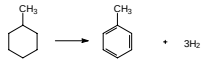


Branched Chain or Ring (high octane) Molecules plus Hydrogen

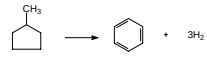
Catalytic Reforming

Conversion Reactions

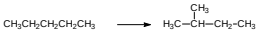
Dehydrogenation of cycloalkanes to aromatics



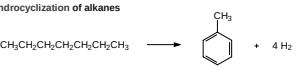
Dehydroisomerization of cyclopentanes to aromatics



Isomerization of alkanes

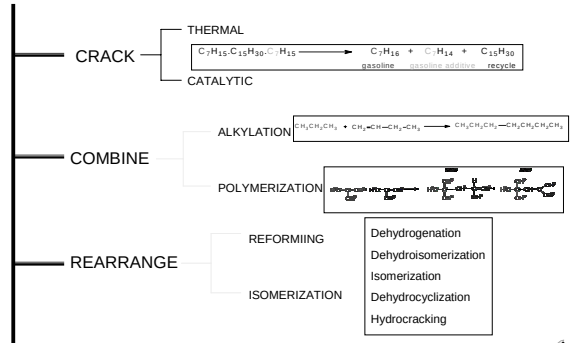


Dehdrocyclization of alkanes



Hydrocracking of alkanes

Conversion Reactions



Purification / Desulfurization

- **Molecules are purified using heat, hydrogen and catalysts**
- **Benefits**
  - **Reduces harmful emissions from vehicles**
  - **Reduces refinery emissions**
  - **Sulfur is recovered for use in other products**
    (Fertilizer, Paint, Textiles, Rubber, Medicines, etc.)
- **Purification Processes**
  - **Desulfurizers (Hydrotreaters)**
  - **Treating**
  - **Sulfur Recovery**

Product Blending

- Blend gasoline components to meet octane, vapor pressure, volatility, distillation, and sulfur specifications -- multiple grades
- Adjust operating parameters to ensure that Jet A / Kero product meets smoke point and freeze point specs
- Blend diesel components to balance cetane and cold flow properties (cloud point, pour point)

Oil Refinery

- An **oil refinery** is an industrial process plant where crude oil is processed and refined into more useful petroleum products, such as gasoline, diesel fuel, asphalt base, heating oil, kerosene, and liquefied petroleum gas.
- Oil refineries are typically large sprawling industrial complexes with extensive piping running throughout, carrying streams of fluids between large chemical processing units.

Oil Refinery Units

- **Desalter unit** washes out salt from the crude oil before it enters the atmospheric distillation unit.
- **Atmospheric Distillation unit** distills crude oil into fractions.
- **Vacuum Distillation unit** further distills residual bottoms after atmospheric distillation.
- **Naphtha Hydrotreater unit** uses hydrogen to desulfurize naphtha from atmospheric distillation. Must hydrotreat the naphtha before sending to a Catalytic Reformer unit.
- **Catalytic Reformer unit** is used to convert the naphtha-boiling range molecules into higher octane reformate (reformer product). The reformate has higher content of aromatics, olefins, and cyclic hydrocarbons). An important byproduct of a reformer is hydrogen released during the catalyst reaction. The hydrogen is used either in the hydrotreaters or the hydrocracker.
- **Distillate Hydrotreater unit** desulfurizes distillates (such as diesel) after atmospheric distillation.

Oil Refinery Units

- **Fluid Catalytic Cracker** (FCC) unit upgrades heavier fractions into lighter, more valuable products.
- **Hydrocracker unit** uses hydrogen to upgrade heavier fractions into lighter, more valuable products.
- **Visbreaking unit** upgrades heavy residual oils by thermally cracking them into lighter, more valuable reduced viscosity products.
- **Merox unit** treats LPG, kerosene or jet fuel by oxidizing mercaptans to organic disulfides.
- **Coking units** (delayed coking, fluid coker, and flexicoker) process very heavy residual oils into gasoline and diesel fuel, leaving petroleum coke as a residual product.
- **Alkylation unit** produces high-octane component for gasoline blending.

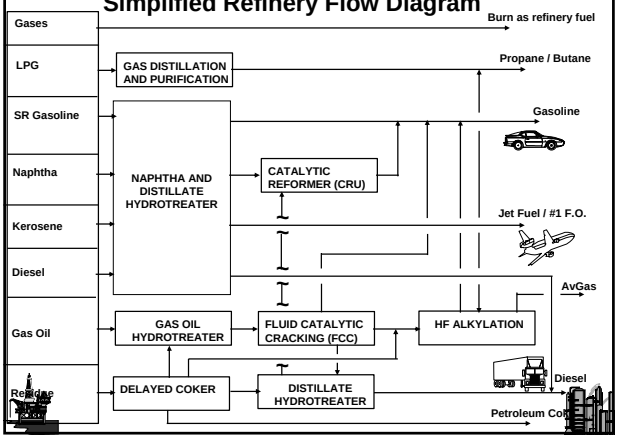
Oil Refinery Units

- **Dimerization unit** converts olefins into higher-octane gasoline blending components. For example, butenes can be dimerized into isooctene which may subsequently be hydrogenated to form isooctane. There are also other uses for dimerization.
- **Isomerization unit** converts linear molecules to higher-octane branched molecules for blending into gasoline or feed to alkylation units.
- **Steam reforming unit** produces hydrogen for the hydrotreaters or hydrocracker.
- **Liquified gas storage units** for propane and similar gaseous fuels at pressure sufficient to maintain in liquid form. These are usually spherical vessels or bullets (horizontal vessels with rounded ends.
- **Storage tanks** for crude oil and finished products, usually cylindrical, with some sort of vapor emission control and surrounded by an earthen berm to contain spills.

Oil Refinery Units

- **Amine gas treater**, Claus unit, and tail gas treatment for converting hydrogen sulfide from hydrodesulfurization into elemental sulfur.
- Utility units such as cooling towers for circulating cooling water, boiler plants for steam generation, instrument air systems for pneumatically operated control valves and an electrical substation.
- Wastewater collection and treating systems consisting of API separators, dissolved air flotation (DAF) units and some type of further treatment (such as an activated sludge biotreater) to make such water suitable for reuse or for disposal.[
- Solvent refining units use solvent such as cresol or furfural to remove unwanted, mainly asphaltenic materials from lubricating oil stock (or diesel stock).

Simplified Refinery Flow Diagram



Basic Refinery Operations

- **Separation - Distillation**
- **Conversion - Changing the size or shape of molecules**
  - **Re-shape molecules to improve product quality – eg reforming, isomerization alkylation**
  - **Upgrading – breaking large molecules into smaller**
    - **Carbon rejection – FCCU, Coking, visbreaking**
    - **Hydrogen addition - Hydrocracking**
- **Treatment / Blending – Making on specification products**
  - **Removal of impurities – desalting, desulfurization, denitrofication**
  - **Mixtures of components to meet specifications**