“What’s That Thang?”
Basics of a Petroleum Refinery

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So why do we need Refineries?
A Petroleum Refinery exists to take crude oil and refine it into finished products

- Major Refinery products: Motor Gasoline (MoGas), Diesel, Jet Fuel and Home Heating Oil – “Fuels” Business
- Some Refineries also produce motor oils, transmission fluids, waxes, etc. – “Lubes” or “Specialties” Business
- Some also have some Chemicals operations

Crude Oil is a mixture of hydrocarbons

- Includes hydrocarbon molecules ranging from C_2 to C_{40+}
- Multiple units are necessary to separate, convert and purify the crude into useful end products

Because your car won’t run on crude oil
Carbon (C) appears in the second row of the periodic table and has four bonding electrons in its valence shell. Similar to other non-metals, carbon needs eight electrons to satisfy its valence shell. Carbon therefore forms four bonds with other atoms (each bond consisting of one of carbon's electrons and one of the bonding atom's electrons). Every valence electron participates in bonding, thus a carbon atom's bonds will be distributed evenly over the atom's surface. These bonds form a tetrahedron (a pyramid with a spike at the top), as illustrated below:

Organic chemicals get their diversity from the many different ways carbon can bond to other atoms. The simplest organic chemicals, called hydrocarbons, contain only carbon and hydrogen atoms; the simplest hydrocarbon (called methane) contains a single carbon atom bonded to four hydrogen atoms.
But carbon can bond to other carbon atoms in addition to hydrogen, as illustrated in the molecule ethane below:

In fact, the uniqueness of carbon comes from the fact that it can bond to itself in many different ways. Carbon atoms can form long chains:

branched chains:
Did this inspire Tinkertoys?

rings:

There appears to be almost no limit to the number of different structures that carbon can form. To add to the complexity of organic chemistry, neighboring carbon atoms can form double and triple bonds in addition to single carbon-carbon bonds:
Keep in mind that each carbon atom forms four bonds. As the number of bonds between any two carbon atoms increases, the number of hydrogen atoms in the molecule decreases (as can be seen in the figures above).

**Simple Hydrocarbons**

The simplest hydrocarbons are those that contain only carbon and hydrogen. These simple hydrocarbons come in three varieties depending on the type of carbon-carbon bonds that occur in the molecule. Alkanes are the first class of simple hydrocarbons and contain only carbon-carbon single bonds. The alkanes are named by combining a prefix that describes the number of carbon atoms in the molecule with the root ending "ane". The names and prefixes for the first ten alkanes are given in the following table.

<table>
<thead>
<tr>
<th>Carbon Atoms</th>
<th>Prefix</th>
<th>Alkane Name</th>
<th>Chemical Formula</th>
<th>Structural Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Meth</td>
<td>Methane</td>
<td>CH₄</td>
<td>CH₄</td>
</tr>
<tr>
<td>2</td>
<td>Eth</td>
<td>Ethane</td>
<td>C₂H₆</td>
<td>CH₃CH₃</td>
</tr>
<tr>
<td>3</td>
<td>Prop</td>
<td>Propane</td>
<td>C₃H₈</td>
<td>CH₃CH₂CH₃</td>
</tr>
<tr>
<td>4</td>
<td>But</td>
<td>Butane</td>
<td>C₄H₁₀</td>
<td>CH₃CH₂CH₂CH₃</td>
</tr>
<tr>
<td>5</td>
<td>Pent</td>
<td>Pentane</td>
<td>C₅H₁₂</td>
<td>CH₃CH₂CH₂CH₂CH₃</td>
</tr>
<tr>
<td>6</td>
<td>Hex</td>
<td>Hexane</td>
<td>C₆H₁₄</td>
<td>...</td>
</tr>
<tr>
<td>7</td>
<td>Hept</td>
<td>Heptane</td>
<td>C₇H₁₆</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Oct</td>
<td>Octane</td>
<td>C₈H₁₈</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Non</td>
<td>Nonane</td>
<td>C₉H₂₀</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Dec</td>
<td>Decane</td>
<td>C₁₀H₂₂</td>
<td></td>
</tr>
</tbody>
</table>
Not just fats are unsaturated . . .

The second class of simple hydrocarbons, the alkenes, consists of molecules that contain at least one double-bonded carbon pair. Alkenes follow the same naming convention used for alkanes. A prefix (to describe the number of carbon atoms) is combined with the ending "ene" to denote an alkene. Ethene, for example is the two-carbon molecule that contains one double bond. The chemical formula for the simple alkenes follows the expression C\textsubscript{n}H\textsubscript{2n}. Because one of the carbon pairs is double bonded, simple alkenes have two fewer hydrogen atoms than alkanes.

Alkynes are the third class of simple hydrocarbons and are molecules that contain at least one triple-bonded carbon pair. Like the alkanes and alkenes, alkynes are named by combining a prefix with the ending "yne" to denote the triple bond. The chemical formula for the simple alkynes follows the expression C\textsubscript{n}H\textsubscript{2n-2}.
Isomers

Because carbon can bond in so many different ways, a single molecule can have different bonding configurations. Consider the two molecules illustrated here:

Both molecules have identical chemical formulas (shown in the left column); however, their structural formulas (and thus some chemical properties) are different. These two molecules are called isomers. Isomers are molecules that have the same chemical formula but different structural formulas.
It’s not just carbon and hydrogen

**Functional Groups**

In addition to carbon and hydrogen, hydrocarbons can also contain other elements. In fact, many common groups of atoms can occur within organic molecules, these groups of atoms are called functional groups. One good example is the hydroxyl functional group. The hydroxyl group consists of a single oxygen atom bound to a single hydrogen atom (-OH). The group of hydrocarbons that contain a hydroxyl functional group is called alcohols. The alcohols are named in a similar fashion to the simple hydrocarbons, a prefix is attached to a root ending (in this case "anol") that designates the alcohol. The existence of the functional group completely changes the chemical properties of the molecule. Ethane, the two-carbon alkane, is a gas at room temperature; ethanol, the two-carbon alcohol, is a liquid.

Ethanol, common drinking alcohol, is the active ingredient in "alcoholic" beverages such as beer and wine.
A Simple Guide to Oil Refining

We all know that motor oil and gasoline come from crude oil. What many people do not realize is that crude oil is also the starting point for many diverse products such as clothes, medical equipment, electronics, vitamin capsules and tires.

Whether on land or under the ocean, crude oil comes from deep underground where the remains of plants and animals from millions of years ago have been heated and pressurized over time. Generally blackish in color, crude oil has a characteristic odor that comes from the presence of small quantities of chemical compounds containing sulfur and nitrogen. There are different grades of crude oil. Each grade has a specific composition that is determined by the original decomposed source materials as well as the properties of the surrounding soil or rock formations.

It can be light or heavy, referring to density, and sweet or sour, referring to its sulfur content. However, in its raw state, crude oil is of little use. It must be refined to make it into useable products. Depending on the type of crude oil, it is treated via different refining processes to turn it into fuels, lubricating oils, waxes, chemicals, plastics and many other products used everyday in modern society.

The Refining Process

Once discovered, drilled and brought to the earth’s surface, crude oil is transported to a refinery by pipeline, ship or both. At the refinery, it is treated and converted into consumer and industrial products.

Three major refinery processes change crude oil into finished products:
• Separation,
• Conversion, and
• Purification.
Separation

The first step is to separate the crude oil into its naturally occurring components. This is known as separation and is accomplished by applying heat through a process called distillation.

Separation is performed in a series of distillation towers, with the bottom product from each tower feeding the next. A furnace in front of each distillation tower heats and vaporizes the crude oil mixture. The vapor and liquid mixture is then fed into the bottom section of the tower. The feed section is the hottest point in the distillation tower and can reach as high as 750 degrees Fahrenheit.

Components that are still liquid at this elevated temperature become the tower’s bottom product. Components that are in vapor form rise up the tower through a series of distillation stages. The temperature decreases as the vapors rise through the tower and the components condense.

The “yield” from a distillation tower refers to the relative percentage of each of the separated components, known as “product streams.” This will vary according to the characteristics of the crude being processed. Because a liquid’s boiling point decreases at lower pressures, the final distillation steps are performed in a vacuum to maximize liquid recovery. Products from the distillation tower range from gases at the top to very heavy, viscous liquids at the bottom. In all cases, these product streams are still considered “unfinished” and require further processing to become useful products.

End Products
- Propane, Butane, LPG
- Gasoline
- Jet Fuel
- Diesel Fuel
- LPG, Gasoline
- Gasoline, Jet, & Diesel Fuel
- Industrial Fuel
- Asphalt Base

Coker
Alkylation Unit
Reformer
Cracking Units
Vacuum Gas Oil
Heavy Gas Oil
Medium Gas Oil
Light Gas Oil
Naphtha
Kerosene
Diluent
Light Ends
<30°F

Distillation Tower

Crude Oil
750°F

Light products (light ends) are further separated into propane, normal butane and isobutane. This stream is often referred to as Liquefied Petroleum Gas (LPG) and is still as a cooking and heating fuel. Non-condensable gases (mostly hydrogen, methane and ethane) are subsequently treated to remove trace impurities and are often used as fuel within the refinery.

Naphtha could be blended into motor gasoline, but it is more likely sent to a Catalytic Reforming unit for octane improvement.

Kerosene is generally treated and sold as jet fuel.

Heavier distillate streams are also treated and blended into finished diesel fuel or home heating oil or are further processed in conversion units such as Fluid Catalytic Cracking (FCC) and Hydrocracking. The routing of these streams will vary in response to demand changes to either maximize diesel production or gasoline production.

Gas oil is routed to either FCC or Hydrocracking to be converted into higher value gasoline and diesel, and vacuum tower bottoms (VTB) are the final bottom product of distillation, which is processed in Cokers to be upgraded into gasoline, diesel and gas oil.
Straight Run vs Market Demand for Crude Products
Distillation separates the crude oil into unfinished products. However, these products do not naturally exist in crude in the same proportions as the product mix that consumers demand. The biggest difference is that there is too little gasoline and too much heavy oil naturally occurring in crude oil. That is why conversion processes are so important. Their primary purpose is to convert low valued heavy oil into high valued gasoline. All products in the refinery are based on the same basic building blocks, carbon and hydrogen chains, which are called hydrocarbons. The longer the carbon chain, the heavier the product will be. Converting heavier hydrocarbons to lighter hydrocarbons can be compared to cutting a link on a steel chain to make two smaller chains. This is the function of the Fluidized Catalytic Crackers (FCCs), Cokers and Hydrocrackers. In addition to breaking chains, there are times when we want to change the form of the chain or put chains together. This is where the Catalytic Reformer and Alkylation are necessary. Specialized catalysts are of critical importance in most of these processes.

The FCC is usually the key conversion unit. It uses a catalyst (a material that helps make a chemical reaction go faster, occur at a lower temperature, or control which reactions occur) to convert gas oil into a mix of Liquified Petroleum Gas (LPG), gasoline and diesel. The FCC catalyst promotes the reaction that breaks the heavier chains in the right place to make as much gasoline as possible. However, even with the catalyst, the reactions require a lot of heat; therefore the FCC reactor operates at about 1,000 degrees Fahrenheit.

The heaviest material in the refinery is Vacuum Tower Bottoms (VTB) or “resid.” If allowed to cool to room temperature, it would become a solid. Some resid is actually sold into the paving asphalt market as a blend component. Resid is too heavy and has too many contaminants to process in the FCC. The Delayed Coker is used to convert this heavy material into more valuable products. The delayed coker uses high temperature to break the hydrocarbon chains. Delayed coking reactions are less selective than FCC reactions. Delayed coking also produces a relatively low valued petroleum coke as a by-product.

In some refineries, the FCCs and Delayed Cokers are supplemented by Hydrocracking. Similar to the FCC, the Hydrocracker uses high temperature and a catalyst to get the desired reactions. In Hydrocracking, the catalyst stays in one place and the gas oil passes over the catalyst, whereas in the FCC the catalyst is much finer and moves together with the gas oil. The catalyst composition differs. In Hydrocracking, the reactions take place at high temperatures in the presence of high concentrations of hydrogen. The Hydrocracker produces products with low sulfur levels. The light liquid product can be sent directly to Catalytic Reforming and the other liquid products can be blended directly into jet fuel and diesel.

The conversion processes that have been discussed up to this point have focused on reducing the length of some hydrocarbon chains. However, there are other hydrocarbon chains that are too short. Butane is produced as a byproduct of other conversion units. The Alkylation Unit (Alky) takes two butanes and combines them into a longer chain using a catalyst.

The last conversion process is Catalytic Reforming. The purpose of the reformer is to increase the octane number of gasoline blend components and to generate hydrogen for use in the refinery hydrocrackers. The same length carbon chains can have very different octane numbers based on the shape of the chain. Straight chains, or paraffins, have a relatively low octane number, while rings, or aromatics, have high octane numbers. At high temperatures and in the presence of hydrogen, the catalyst will “reform” paraffins into aromatics, thus the name catalytic reforming. Some of the aromatics produced are sent to petrochemical manufacturers, where they are converted to plastics and fabrics.
What does a Catalytic Cracking Unit do?

Fluid Catalytic Cracking Unit Feed

\[ \text{C}_27 \]

Cat Unit

Gas
\[ \text{C}_3 \]

Gasoline
\[ \text{C}_8 \]

Diesel Blendstock
\[ \text{C}_{16} \]
Purification

Once crude oil has been through separation and conversion, the resulting products are ready for purification, which is principally sulfur removal. This is done by Hydrotreating, a process similar to Hydrocracking but without converting heavy molecules into lighter ones. In Hydrotreating, unfinished products are contacted with hydrogen under heat and high pressure in the presence of a catalyst, resulting in hydrogen sulfide and desulfurized product. The catalyst accelerates the rate at which the sulfur removal reaction occurs. In each case, sulfur removal is essential to meeting product quality specifications and environmental standards.

Other units in the refinery remove sulfur, primarily in the form of hydrogen sulfide, through extraction, which is a second method of purification.

Whether through hydrotreatment or extraction, desulfurization produces hydrogen sulfide. Sulfur recovery converts hydrogen sulfide to elemental sulfur and water. The residual sulfur is sold as a refinery by-product.

End Products
Modern refinery and petrochemical technology can transform crude oil into literally thousands of useful products. From powering our cars and heating our homes, to supplying petrochemical feedstocks for producing plastics and medicines, crude oil is an essential part of our daily lives. It is a key ingredient in making thousands of products that make our lives easier – and in many cases – help us live better and longer lives.

Oil does a lot more than simply provide fuel for our cars and trucks, keep our homes and offices comfortable, and power our factories.

Source: API
How do you get the Sulfur out?

Typical diesel blending component with 500 ppmv sulfur

\[
\text{H}_2\text{S} \quad \text{H}_2 \quad \text{H}_2\text{S} \quad \text{H}_2\text{S}
\]

Send the stream through a hydrofiner - hydrogen replaces most of the sulfur

Resulting stream meets new EPA diesel sulfur specification of 15 ppmv

\[
\text{H}_2\text{S}
\]
What are the major business drivers for Refineries?

• Process "heavier" crudes
  – Crudes are distinguished as "light", "intermediate" or "heavy"
  – This refers to the density of the crude
  – Lighter crudes are easier to process - but they are more expensive to buy
  – Some Refineries have installed additional equipment to process heavier crudes so that the cost of raw materials is lower

• Process “sour" crudes
  – Crudes that have less sulfur compounds are "sweet"; higher sulfur crudes are "sour"
  – Sour crudes require more processing to meet EPA product quality specs
  – Sulfur compounds in gasoline and diesel lead to SO2 emissions from engines
  – Sulfur compounds impact the vehicle’s catalytic converter, so higher sulfur fuels lead to more NOx emissions
  – Sweet crudes are more expensive to buy

• Meet EPA diesel product quality specs
  – 2005 - diesel in the market
    • On-road diesel - < 500 ppmv sulfur compounds
    • Nonroad diesel – ~ 2000 ppmv sulfur compounds
  – mid-2006 - diesel for on-road use was limited to 15 ppmv sulfur
  – mid-2007 - diesel for nonroad use - limited to 500 ppmv
  – mid-2010 - diesel for nonroad use - limited to 15 ppmv
  – Each of these steps requires a Petroleum Refinery to buy sweeter crudes, or install equipment to remove more sulfur from diesel blendstocks
A Typical Refinery Flow Plan

Crude oil arrives at the refinery by ship and by pipeline from sources near and far. However its journey does not end there. This diagram illustrates its travels in many forms to the variety of units throughout the refinery for processing by separation, conversion or purification. Finally, what started as crude oil leaves the refinery by pipeline, barge, rail or truck as a variety of petroleum products for use locally or across the country.