How Oil Refining Works

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Introduction to How Oil Refining Works

In movies and television shows -- *Giant*, *Oklahoma Crude*, *Armageddon*, *Beverly Hillbillies* -- we have seen images of thick, black crude oil gushing out of the ground or a drilling platform. But when you pump the gasoline for your car, you've probably noticed that it is clear. And there are so many other products that come from oil, including crayons, plastics, heating oil, jet fuel, kerosene, synthetic fibers and tires. How is it possible to start with crude oil and end up with gasoline and all of these other products?

Oil Refining Image Gallery

Photo courtesy Phillips Petroleum Company

Oil refineries take crude oil and turn it into products such as gasoline, jet fuel, crayons and plastics.
See more oil refining pictures.

Q: What is the primary compound in crude oil?

A: Carbon.

In this article, we will examine the chemistry and technology involved in refining crude oil to produce all of these different things.

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Crude Oil

Crude oil is the term for "unprocessed" oil, the stuff that comes out of the ground. It is also known as **petroleum**. Crude oil is a **fossil fuel**, meaning that it was made naturally from decaying plants and animals living in ancient seas millions of years ago -- most places you can find crude oil were once sea beds. **Crude oils vary in color**, from clear to tar-black, **and in viscosity**, from water to almost solid.

Crude oils are such a useful starting point for so many different substances because they contain **hydrocarbons**. Hydrocarbons are molecules that contain hydrogen and carbon and come in various lengths and structures, from straight chains to branching chains to rings.

There are two things that make hydrocarbons exciting to chemists:

- Hydrocarbons contain a lot of **energy**. Many of the things derived from crude oil like gasoline, diesel fuel, paraffin wax and so on take advantage of this energy.
- Hydrocarbons can take on many different forms. The smallest hydrocarbon is **methane** (CH_4), which is a gas that is a lighter than air. Longer chains with 5 or more carbons are liquids. Very

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

- **Carbon** - 84%
- **Hydrogen** - 14%
- **Sulfur** - 1 to 3% (hydrogen sulfide, sulfides, disulfides, elemental sulfur)
- **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)

long chains are solids like wax or tar. By chemically cross-linking hydrocarbon chains you can get everything from synthetic rubber to nylon to the plastic in tupperware. Hydrocarbon chains are very versatile!

- **Metals** - less than 1% (nickel, iron, vanadium, copper, arsenic)
- **Salts** - less than 1% (sodium chloride, magnesium chloride, calcium chloride)

The major classes 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

To see examples of the structures of these types of hydrocarbons, see the OSHA Technical Manual and this page on the Refining of Petroleum.

Now that we know what's in crude oil, let's see what we can make from it.

From Crude Oil

The problem with crude oil is that it contains hundreds of different types of hydrocarbons all mixed together. You have to separate the different types of hydrocarbons to have anything useful. Fortunately there is an easy way to separate things, and this is what **oil refining** is all about.

The oil refining process starts with a fractional distillation column.

Different hydrocarbon chain lengths all have progressively higher boiling points, so they can all be separated by distillation. This is what happens in an oil refinery - in one part of the process, crude oil is heated and the different chains are pulled out by their vaporization temperatures. Each different chain length has a different property that makes it useful in a different way.

To understand the diversity contained in crude oil, and to understand why refining crude oil is so important in our society, look through the following list of products that come from crude oil:

- **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 104 degrees Fahrenheit / 40 degrees Celsius
  - often liquified under pressure to create LPG (liquified petroleum gas)
- **Naphtha** or **Ligroin** - intermediate that will be further processed to make gasoline
  - mix of 5 to 9 carbon atom alkanes
  - boiling range = 140 to 212 degrees Fahrenheit / 60 to 100 degrees Celsius
- **Gasoline** - motor fuel
  - liquid
  - mix of alkanes and cycloalkanes (5 to 12 carbon atoms)
  - boiling range = 104 to 401 degrees Fahrenheit / 40 to 205 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 = 350 to 617 degrees Fahrenheit / 175 to 325 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 = 482 to 662 degrees Fahrenheit / 250 to 350 degrees Celsius
- **Lubricating oil** - used for motor oil, grease, other lubricants
  - liquid
  - long chain (20 to 50 carbon atoms) alkanes, cycloalkanes, aromatics
  - boiling range = 572 to 700 degrees Fahrenheit / 300 to 370 degrees Celsius
- **Heavy gas** 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 = 700 to 1112 degrees Fahrenheit / 370 to 600 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 1112 degrees Fahrenheit / 600 degrees Celsius

You may have noticed that all of these products have different sizes and boiling ranges. Chemists take advantage of these properties when refining oil. Look at the next section to find out the details of this fascinating process.

The Refining Process

As mentioned previously, a barrel of crude oil has a mixture of all sorts of hydrocarbons in it. Oil refining separates everything into useful substances. Chemists use the following steps:

1. The oldest and most common way to separate things into various components (called **fractions**), is to do it using the differences in boiling temperature. This process is called **fractional distillation**. You basically heat crude oil up, let it vaporize and then condense the vapor.
2. Newer techniques use **Chemical processing** on some of the fractions to make others, in a process called **conversion**. Chemical processing, for example, can break longer chains into shorter ones. This allows a refinery to turn diesel fuel into gasoline depending on the demand for gasoline.
3. Refineries must **treat** the fractions to remove impurities.
4. Refineries **combine** the various fractions (processed, unprocessed) into mixtures to make desired products. For example, different mixtures of chains can create gasolines with different octane ratings.

Photo courtesy Phillips Petroleum Company
An oil refinery

The products are stored on-site until they can be delivered to various markets such as gas stations, airports and chemical plants. In addition to making the oil-based products, refineries must also treat the wastes involved in the processes to minimize air and water pollution.

In the next section, we will look at how we separate crude oil into its components.

Fractional Distillation

The various components of crude oil have different sizes, weights and boiling temperatures; so, the first step is to separate these components. Because they have different boiling temperatures, they can be separated easily by a process called **fractional distillation**. The steps of fractional distillation are as follows:

Photo courtesy Phillips Petroleum
Distillation columns in an oil

1. You **heat** the mixture of two or more substances (liquids) with different boiling points to a high temperature. Heating is usually done with high pressure steam to temperatures of about 1112 degrees Fahrenheit / 600 degrees Celsius.
2. The mixture **boils**, forming vapor (gases); most substances go

into the vapor phase.

refinery

3. The **vapor** enters the bottom of a long column (**fractional distillation column**) that is filled with trays or plates.

    1. The trays have many holes or bubble caps (like a loosened cap on a soda bottle) in them to allow the vapor to pass through.
    2. The trays increase the contact time between the vapor and the liquids in the column.
    3. The trays help to collect liquids that form at various heights in the column.
    4. There is a temperature difference across the column (hot at the bottom, cool at the top).

4. The **vapor rises** in the column.
5. As the vapor rises through the trays in the column, it **cools**.
6. When a substance in the vapor reaches a height where the temperature of the column is equal to that substance's boiling point, it will **condense** to form a liquid. (The substance with the lowest boiling point will condense at the highest point in the column; substances with higher boiling points will condense lower in the column.).
7. The trays **collect** the various liquid fractions.
8. The collected liquid fractions may:

    1. pass to condensers, which cool them further, and then go to storage tanks
    2. go to other areas for further chemical processing

Fractional distillation is useful for separating a mixture of substances with narrow differences in boiling points, and is the most important step in the refining process.

The oil refining process starts with a fractional distillation column. On the right, you can see several chemical processors that are described in the next section.

Very few of the components come out of the fractional distillation column ready for market. Many of them must be chemically processed to make other fractions. For example, only 40% of distilled crude oil is gasoline; however, gasoline is one of the major products made by oil companies. Rather than continually distilling large quantities of crude oil, oil companies chemically process some other fractions from the distillation column to make gasoline; this processing increases the yield of gasoline from each barrel of crude oil.

In the next section, we'll look at how we chemically process one fraction into another.

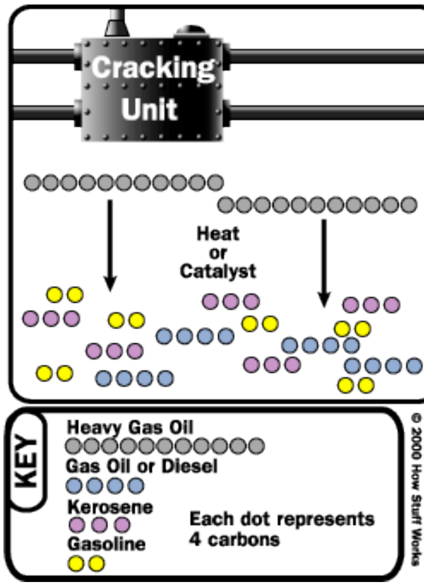
Chemical Processing

You can change one fraction into another by one of three methods:

- breaking large hydrocarbons into smaller pieces (**cracking**)
- combining smaller pieces to make larger ones (**unification**)
- rearranging various pieces to make desired hydrocarbons (**alteration**)

Cracking

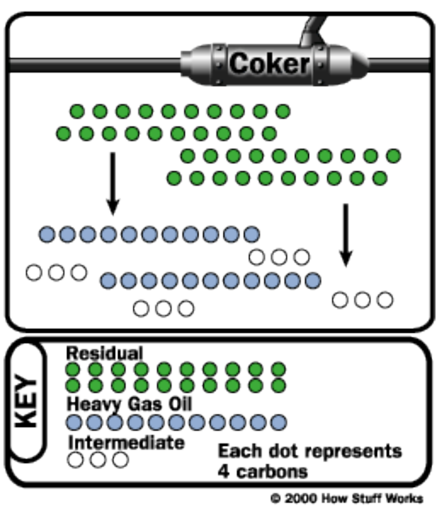
Cracking takes large hydrocarbons and breaks them into smaller ones.



Cracking breaks large chains into smaller chains.

There are several types of cracking:

- **Thermal** - you heat large hydrocarbons at high temperatures (sometimes high pressures as well) until they break apart.
    - **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** - uses a catalyst to speed up the cracking reaction. Catalysts include zeolite, aluminum hydrosilicate, bauxite and silica-alumina.
    - **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).

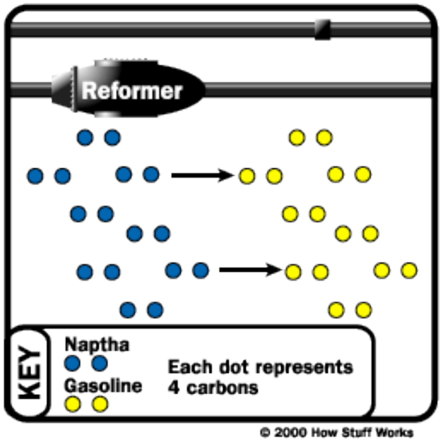
Photo courtesy Phillips Petroleum Company

Catalysts used in catalytic cracking or reforming

After various hydrocarbons are cracked into smaller hydrocarbons, the products go through another fractional distillation column to separate them.

Unification

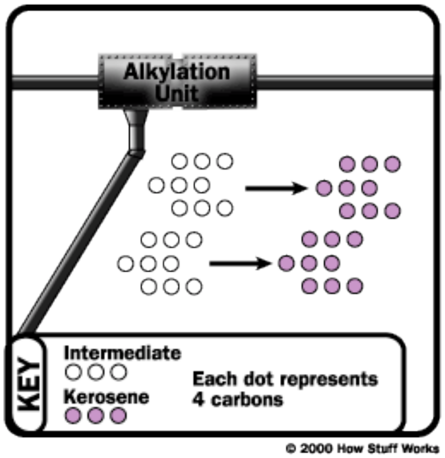
Sometimes, you need to combine smaller hydrocarbons to make larger ones -- this process is called **unification**. The major unification process is called **catalytic reforming** and uses a catalyst (platinum, platinum-rhenium mix) to combine low weight naphtha into aromatics, which are used in making chemicals and in blending gasoline. A significant by-product of this reaction is hydrogen gas, which is then either used for hydrocracking or sold.



A reformer combines chains.

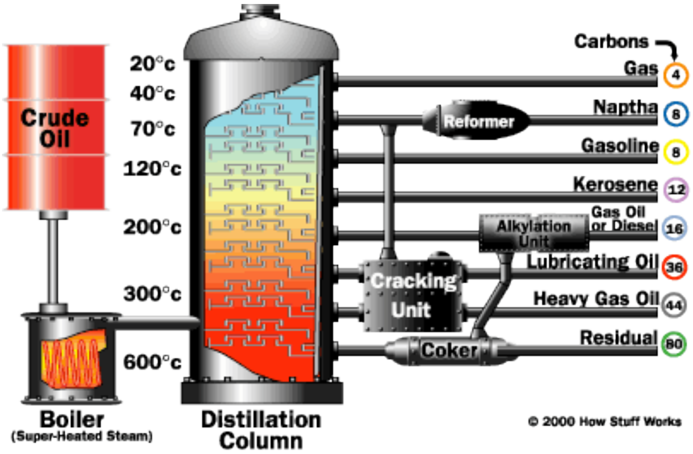
Alteration

Sometimes, the structures of molecules in one fraction are rearranged to produce another. Commonly, this is done using a process called **alkylation**. In alkylation, low molecular weight compounds, such as propylene and butylene, are mixed in the presence of a catalyst such as hydrofluoric acid or sulfuric acid (a by-product from removing impurities from many oil products). The products of alkylation are **high octane hydrocarbons**, which are used in gasoline blends to reduce **knocking** (see "What does octane mean?" for details).



Rearranging chains.

Now that we have seen how various fractions are changed, we will discuss the how the fractions are treated and blended to make commercial products.



An oil refinery is a combination of all of these units.

Treating and Blending the Fractions

Distilled and chemically processed fractions are treated to remove impurities, such as organic compounds containing sulfur, nitrogen, oxygen, water, dissolved metals and inorganic salts. Treating is usually done by passing the fractions through the following:

- a column of sulfuric acid - removes unsaturated hydrocarbons (those with carbon-carbon double-bonds), nitrogen compounds, oxygen compounds and residual solids (tars, asphalt)
- an absorption column filled with drying agents to remove water
- sulfur treatment and hydrogen-sulfide scrubbers to remove sulfur and sulfur compounds

After the fractions have been treated, they are cooled and then blended together to make various products, such as:

- gasoline of various grades, with or without additives
- lubricating oils of various weights and grades (e.g. 10W-40, 5W-30)
- kerosene of various various grades
- jet fuel
- diesel fuel
- heating oil
- chemicals of various grades for making plastics and other polymers

Photo courtesy Phillips Petroleum
Plastics produced from refined oil fractions

For more information on the fascinating world of oil refining and petroleum chemistry, check out the links on the next page.

Lots More Information

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