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

Louisiana Section
Air and Waste Management Association
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Diane H. Leche
Air Permit Coordinator
ExxonMobil Baton Rouge

So why do we need Refineries?

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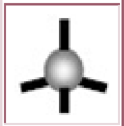
Because your car won't run on crude oil

- **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

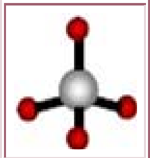
Five Minutes of Organic Chemistry

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:



Carbon forms 4 bonds

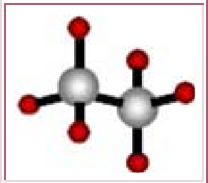
Organic chemicals get their diversity from the many different ways carbon can bond to other atoms. The simplest organic chemicals, called hydrocarbons, contain only carbon and hydrogen atoms; the simplest hydrocarbon (called methane) contains a single carbon atom bonded to four hydrogen atoms:



Methane - a carbon atom bonded to 4 hydrogen atoms

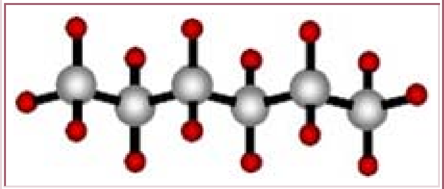
The Carbon Building Block

But carbon can bond to other carbon atoms in addition to hydrogen, as illustrated in the molecule ethane below:



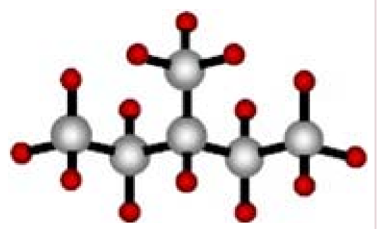
Ethane - a carbon-carbon bond

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:



Hexane - a 6-carbon chain

branched chains:



Isohexane - a branched-carbon chain

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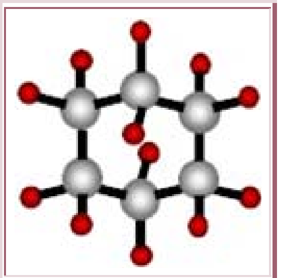
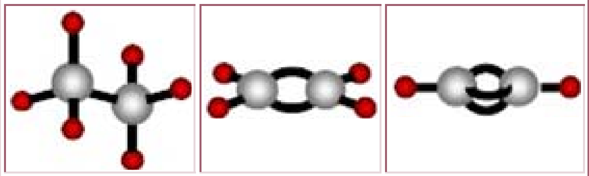
Did this inspire Tinkertoys?

rings:



Cyclohexane - a ringed hydrocarbon

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:



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Short hand

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).

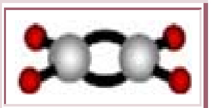
Simple Hydrocarbons

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.

Carbon Atoms	Prefix	Alkane Name	Chemical Formula	Structural Formula
1	Meth	Methane	CH_4	CH_4
2	Eth	Ethane	C_2H_6	CH_3CH_3
3	Prop	Propane	C_3H_8	$CH_3CH_2CH_3$
4	But	Butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$
5	Pent	Pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$
6	Hex	Hexane	C_6H_{14}	...
7	Hept	Heptane	C_7H_{16}	
8	Oct	Octane	C_8H_{18}	
9	Non	Nonane	C_9H_{20}	
10	Dec	Decane	$C_{10}H_{22}$	

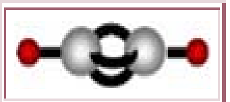
Not just fats are unsaturated . . .

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_nH_{2n}. Because one of the carbon pairs is double bonded, simple alkenes have two fewer hydrogen atoms than alkanes.



Ethene

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_nH_{2n-2}.



Ethyne

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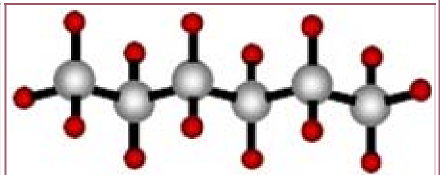
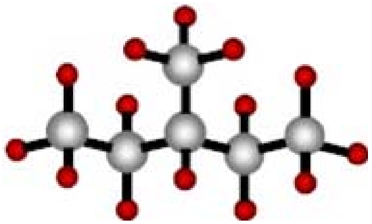
A rose by any other name? Not really . . . .

Isomers

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

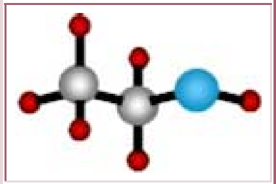
C_6H_{14}	 $CH_3CH_2CH_2CH_2CH_2CH_3$
C_6H_{14}	 CH_3 | $CH_3CH_2CHCH_2CH_3$

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

Ethanol, common drinking alcohol, is the active ingredient in "alcoholic" beverages such as beer and wine.

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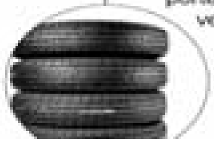
A Simple Guide to Oil Refining

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.

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SEPARATION

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**.

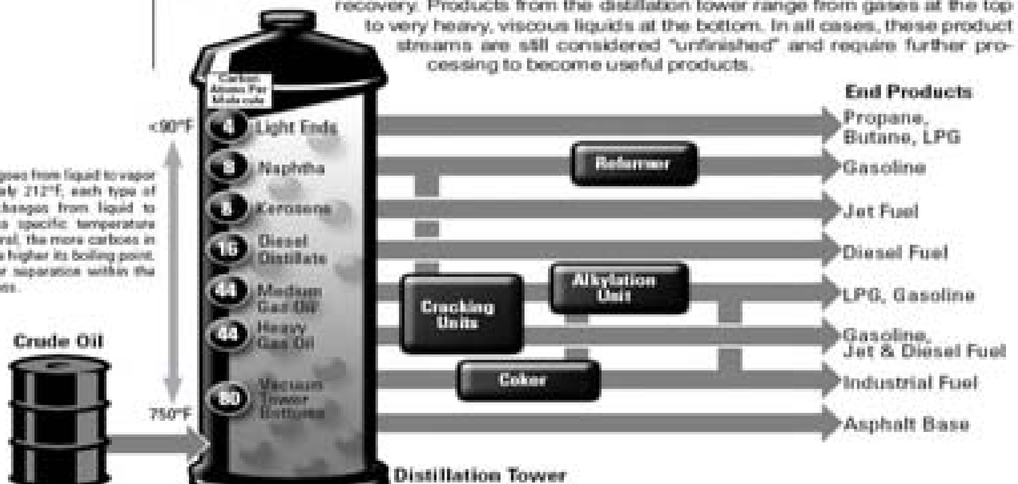
Light on the top. Heavy on the bottom.

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.

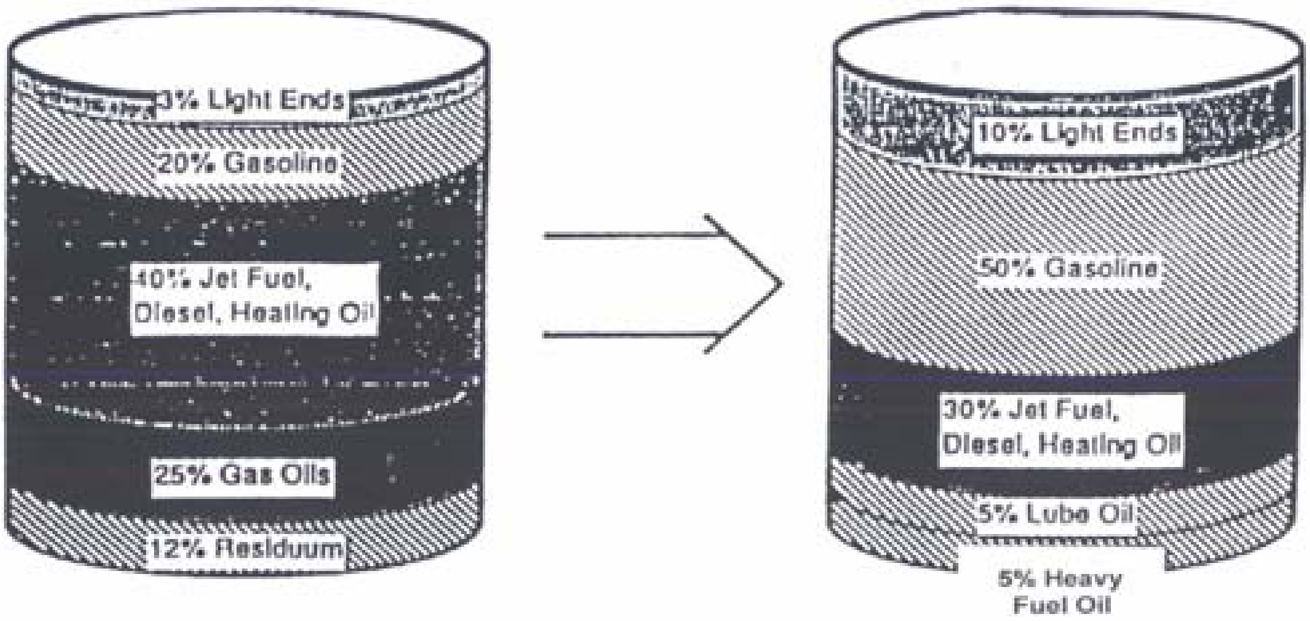
The "yield" from a distillation tower refers to the relative percentage of each of the separated components, know as "product streams." This will vary according to the characteristics of the crude being processed. Because a liquid's boiling point decreases at lower pressures, the final distillation steps 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.

Just as water goes from liquid to vapor at approximately 212°F, each type of hydrocarbon changes from liquid to vapor within a specific temperature range. In general, the more carbons in a molecule, the higher its boiling point. This allows for separation within the distilling process.



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 sold 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 is more likely sent to a Catalytic Reforming unit for octane improvement;
Kerosene: is generally treated and used 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 Fluidized Catalytic Cracking (FCC) and Hydrocracking. The routing of these streams will vary as product 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

CONVERSION Conversion

Distillation separates the crude oil into unfinished products. However, the 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.

Rearranging the molecules to add value.

All products in the refinery are based on the same 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 compositions differ. 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 hydrotreaters. 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 a barrel of crude oil makes.

Product	Gallons per Barrel
Gasoline	19.4
Distillate Fuel Oil *(Includes both home heating oil and diesel fuel)*	9.7
Kerosene-Type Jet Fuels	4.3
Coke	2.0
Residual Fuel Oil *(Heavy oils used as fuels in industry, marine transportation, and for electric power generation)*	1.9
Liquefied Refinery Gases	1.9
Still Gas	1.8
Asphalt and Road Oil	1.4
Petrochemical Feedstocks	1.1
Lubricants	0.5
Kerosene	0.2
Other	0.4

Source: API

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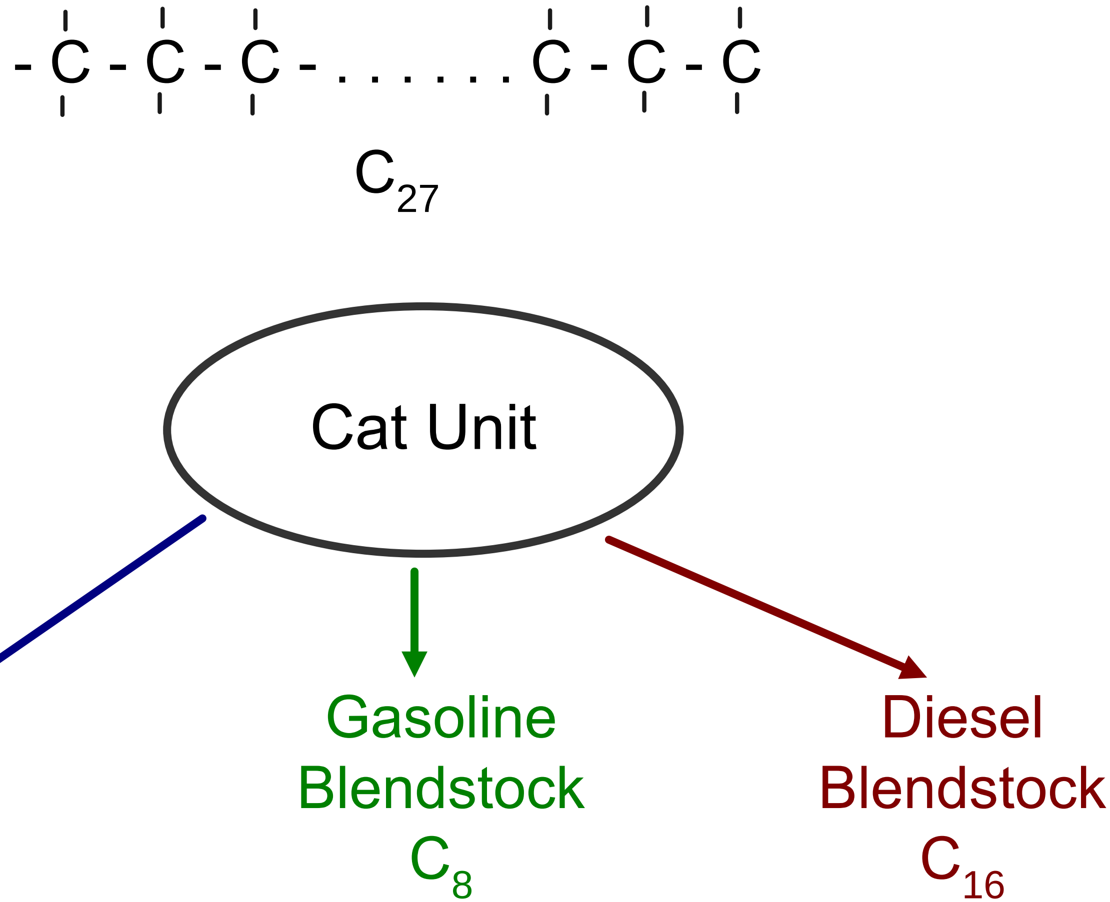
What does a Catalytic Cracking Unit do?

Fluid Catalytic Cracking
Unit Feed



PURIFICATION

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.

Sulfur out. Quality in.

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 industries. From lipstick to aspirin and diapers to roller blades, petrochemicals play a vital part. Here are just few examples:

Antiseptics	Crayons	Golf Balls	Roofing
Aspirin	Dentures	House Paint	Shampoo
Baby Strollers	Deodorant	Ink	Sunglasses
Balloons	Diapers	Jet Fuel	Telephones
Cameras	DVDs	Medical Equipment	Tires
Candles	Footballs	Motor Oil	Toothpaste
CD Players	Gasoline	Perfumes	Toys
Clothing	Garbage Bags	Photographs	Umbrellas
Compact Discs	Glue	Roller Blades	Vitamin Capsules

Source: API

How do you get the Sulfur out?

Typical diesel blending component with 500 ppmv sulfur

```
      H H S H H H H H              H S H H S H H H
H -  C-C-C-C-C-C-C-C . .........-C-C-C-C-C-C-C-C- H
      H H S H H H H H              H S H H S H H H
```

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

H_2 →

```
      H H S H H H H H            H S H H S H H H
 H -C-C-C-C-C-C-C-C . ......- C-C-C-C-C-C-C-C- H
      H H S H H H H H            H S H H S H H H
```

Resulting stream meets new EPA diesel sulfur specification of 15 ppmv

```
     H H H H H H H H            H S H H H H H H
H - C-C-C-C-C-C-C-C . .......-C-C-C-C-C-C-C-C- H
     H H H H H H H H            H H H H H H H H
```

→ H_2S

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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 SO_2 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

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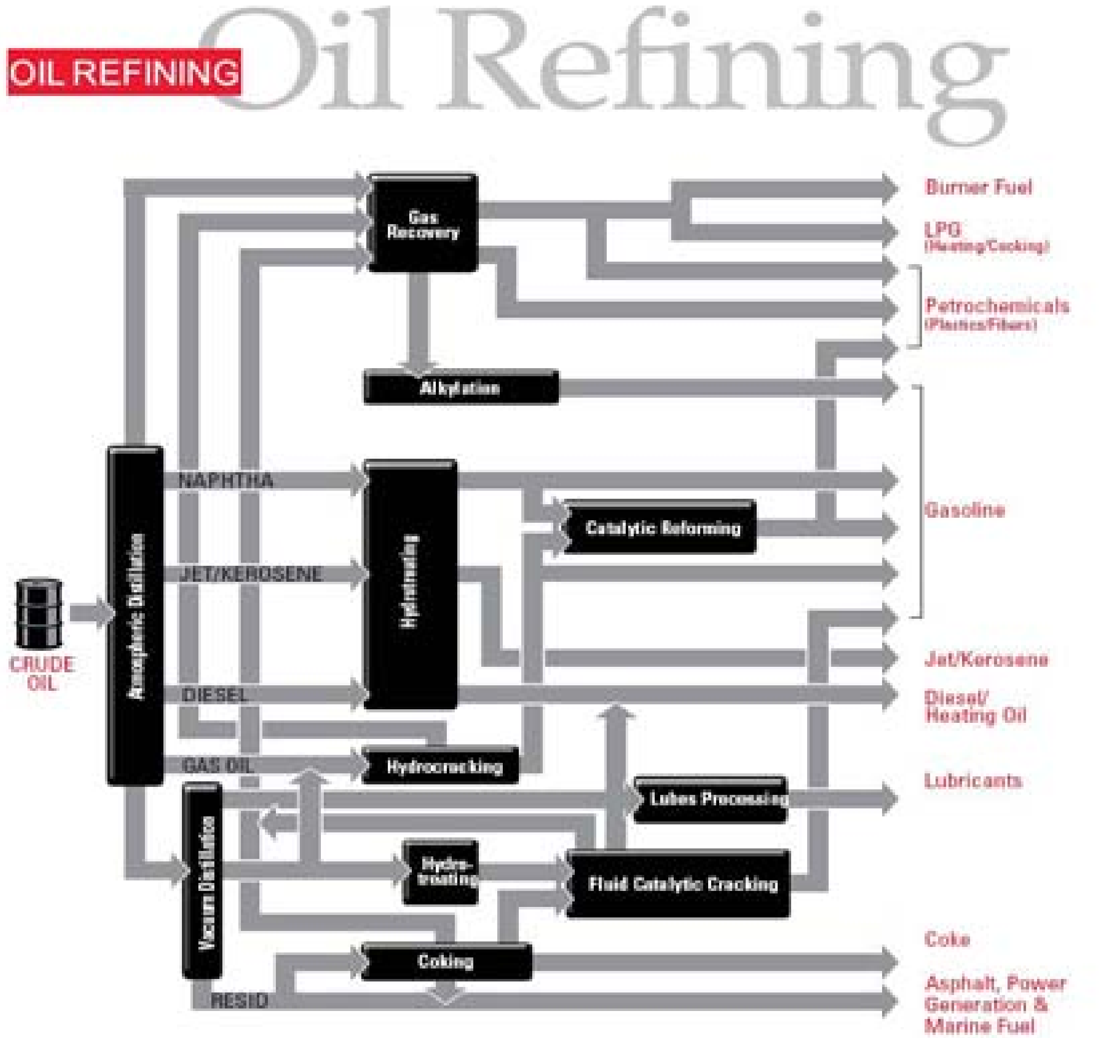
A Typical Refinery Flow Plan



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.

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