

# PETROLEUM CHEMISTRY

**CHE 305**

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# Modern Petroleum Processing

A crude oil refinery is a group of industrial facilities that turns crude oil and other inputs into finished petroleum products.

**All refineries are different.** They have different *histories, locations, and market drivers*.

Therefore, no single illustration can capture all of the possible combinations and permutations of the processes that fit together to comprise an oil refinery. ***But despite their differences, most refineries perform the seven basic operations named in Table 6.***

*Table 6. Seven Basic Operations in Petroleum Processing*

<b>Separation</b>	<b>Combination</b>
<ul style="list-style-type: none"><li>• Distillation</li><li>• Solvent refining</li></ul>	<ul style="list-style-type: none"><li>• Catalytic polymerization</li><li>• Alkylation</li></ul>
<b>Conversion</b>	<b>Treating, finishing, blending</b>
<ul style="list-style-type: none"><li>• Carbon removal</li><li>• Hydrogen addition</li></ul>	<ul style="list-style-type: none"><li>• Gasoline, kerosene and diesel</li><li>• Lubes and waxes</li><li>• Asphalt</li></ul>
<b>Reforming</b>	<b>Protecting the Environment</b>
<ul style="list-style-type: none"><li>• Catalytic reforming</li><li>• Steam/hydrocarbon reforming</li></ul>	<ul style="list-style-type: none"><li>• Waste water treatment</li><li>• Disposal of solids</li><li>• Sulfur recovery</li></ul>
<b>Rearrangement</b>	
<ul style="list-style-type: none"><li>• Isomerization</li></ul>	

## 1: SEPARATION

### A Distillation

In terms of throughput, the biggest unit in most plants is the crude distillation unit. Many downstream conversion units also use distillation for production separation.

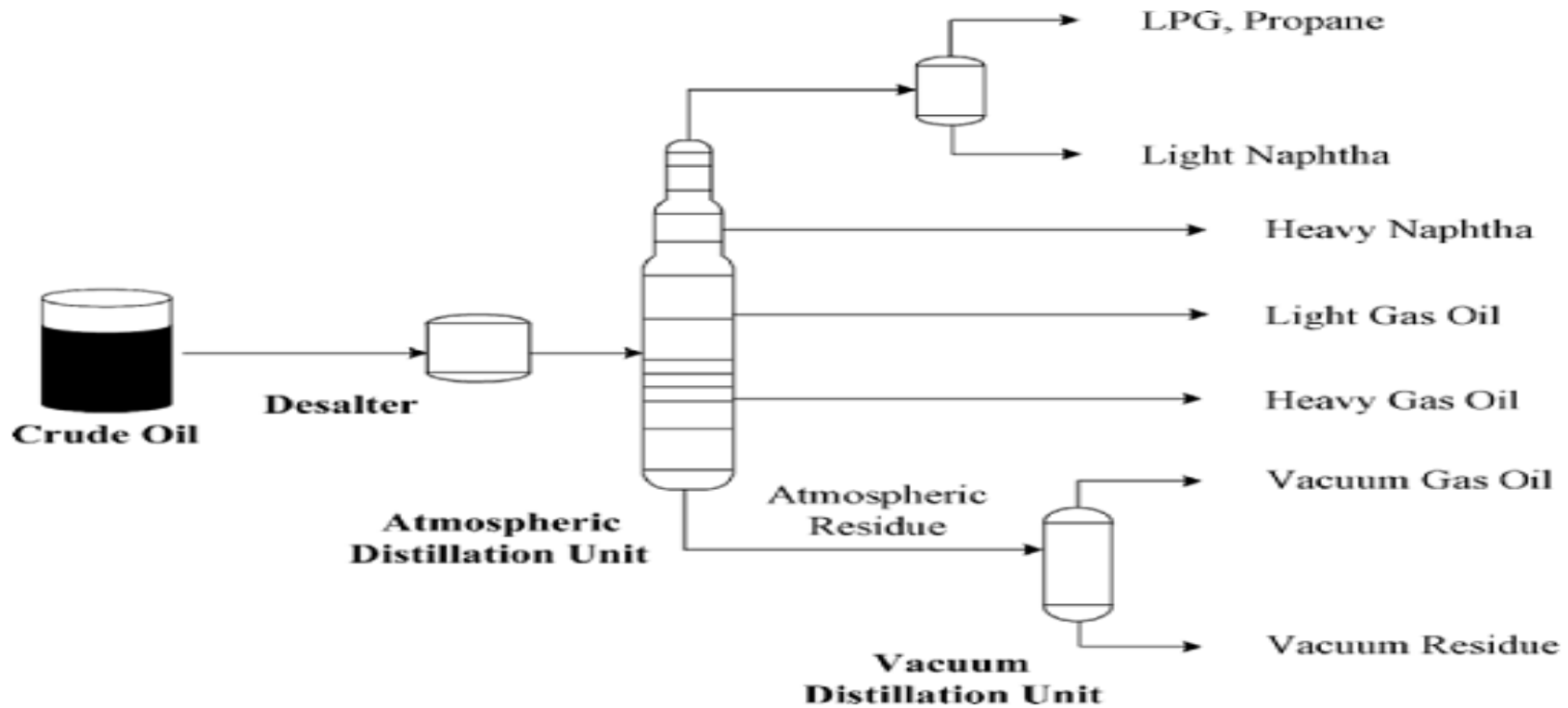
Low boiling fractions usually vaporize below 400 °C at atmospheric pressure without cracking the hydrocarbon compounds. Therefore, all the low boiling fractions of crude oil are separated by atmospheric distillation.

Crude oil distillation is more complicated than product distillation, in part because crude oils contain **water, salts, and suspended solids**. To reduce corrosion, plugging, and fouling in crude heaters and towers, and to prevent the poisoning of catalysts in downstream units, these contaminants are removed by a process called desalting.

The two most typical methods of crude-oil desalting – *chemical and electrostatic separation* – use hot water to dissolve the salts and collect suspended solids.

*\*In chemical desalting, water and surfactants are added to the crude, heated to dissolve salts and other impurities, and then sent to a settling tank where the water and oil separate.*

*\*In electrostatic desalting, chemicals are replaced with a strong electrostatic charge, which drives the separation of water from oil.*



*Figure 9. Crude distillation*

In some towers, the trays in the top section are replaced with structured packing. Before reaching the tower, desalted oil goes through a network of pre-heat exchangers to a fired heater, which brings the temperature up to about 650°F (343°C). If the oil gets much hotter than this, it starts to crack and deposit carbon inside the pipes and equipment through which it flows. The hot crude enters the distillation tower just above the bottom. Steam is added to enhance separation; it does so largely by decreasing vapor pressure in the column. When hot oil enters the tower, most of it vaporizes. Unvaporized heavy fuel oil and/or asphalt residue drops to the bottom of the tower, where it is drawn off.

Products are collected from the top, bottom and side of the column. Side draw products are taken from trays at which the temperature corresponds to the cut point for a desired product. In modern towers, a portion of each side draw stream is returned to the tower to control tray temperatures and further enhance separation.

After leaving the tower, product streams go to holding tanks or directly to downstream process units. As shown in Figure 9and Table 7, products can include heavy fuel oil, heating oil, kerosene, gasoline, and uncondensed gases.

Table 7. Destinations for Straight-Run Distillates				
Fraction	Approx. Boiling Range		Next Destination	Ultimate Product(s)
	°C	°F		
LPG	-40 to 0	-40 to 31	Sweetener	Propane fuel
Light Naphtha	39 - 85	80 - 185	Hydrotreater	Gasoline
Heavy Naphtha	85 - 200	185 - 390	Cat. Reformer	Gasoline, aromatics
Kerosene	170 - 270	340 - 515	Hydrotreater	Jet fuel, No. 1 diesel
Gas Oil	180 - 340	350 - 650	Hydrotreater	Heating Oil, No. 2 diesel
Vacuum Gas Oil	340 - 566	650 - 1050	FCC	Gasoline, LCO, gases
			Hydrotreater	Fuel oil, FCC feed
			Lube Plant	Lube basestock
			Hydrocracker	Gasoline, jet, diesel, FCC feed, lube basestock
Vacuum Residue	>540	>1000	Coker	Coke, coker gas oil
			Visbreaker	Visbreaker gas oil, resid
			Asphalt Unit	Deasphalted oil, asphalt
			Hydrotreater	FCC feed

Atmospheric distillation of the best crudes yields about 60% naphtha plus middle distillates (kerosene and gas oil), but the average is closer to 40%.

*Table 8. Typical Straight-run Yields from Various Crudes<sup>26,27</sup>*

<b>Source field</b>	<b>Brent</b>	<b>Bonny Lt.</b>	<b>Green Canyon</b>	<b>Ratawi</b>
<b>Country</b>	<b>Norway</b>	<b>Nigeria</b>	<b>USA</b>	<b>Mid East</b>
API gravity	38.3	35.4	30.1	24.6
Specific gravity	0.8333	0.8478	0.8752	0.9065
Sulfur, wt%	0.37	0.14	2.00	3.90
<b>Yields, wt% feed</b>				
Light ends	2.3	1.5	1.5	1.1
Light naphtha	6.3	3.9	2.8	2.8
Medium naphtha	14.4	14.4	8.5	8.0
Heavy naphtha	9.4	9.4	5.6	5.0
Kerosene	9.9	12.5	8.5	7.4
Atmospheric gas oil	15.1	21.6	14.1	10.6
Light VGO	17.6	20.7	18.3	17.2
Heavy VGO	12.7	10.5	14.6	15.0
Vacuum residue	12.3	5.5	26.1	32.9
Total naphtha	30.1	27.7	16.9	15.8
Total middle distillate	25.0	34.1	22.6	18.0

## A2 Vacuum Distillation

The residue from an atmospheric distillation tower can be sent to a vacuum distillation tower, which recovers additional liquid at 0.7 to 1.5 psia (4.8 to 10.3 kPa). The vacuum, which is created by a vacuum pump or steam ejector, is pulled from the top of the tower. Relative to atmospheric columns, vacuum columns have larger diameters and their internals are simpler. Often, instead of trays, random packing and demister pads are used.

## B Solvent Refining

Distillation splits a mixture into fractions according to the boiling points of the mixture constituents. In contrast, solvent refining segregates compounds with similar compound types, such as paraffins and aromatics. The three main types of solvent refining are **solvent deasphalting, solvent extraction, and solvent dewaxing**

### Solvent Deasphalting

Solvent deasphalting (SDA) is a separation process in which residues are selectively separated by molecular type by mixing with paraffinic solvents and precipitating out of solution asphaltenes and other residue heavy components. SDA produces a low-contaminant, relatively high hydrogen deasphalted oil product (DAO) and a pitch product that contains the majority of the residue's contaminants (metals, asphaltenes, CCR).

Depending on the DAO quality, it can be used for lubes base oil feedstock, for vacuum gas oil (VGO) conversion feedstock or for residue hydrocracking feedstock. The pitch product is typically used for delayed coking feedstock, as a fuel oil blending component, gasifier feed, or in some cases can be blended into asphalts. Solvents range from propane for lubes applications through pentane for residue hydrocracking applications.

### Solvent Extraction

Solvent extraction is used to remove aromatics and other impurities from lube and grease stocks. The feedstock is dried, then contacted with the solvent in a counter-current or rotating disk extraction unit (Figure 11). The solvent is separated from the product stream by heating, evaporation, or fractionation.

Remaining traces of solvent are removed from the raffinate by steam stripping or flashing. Electrostatic precipitators may be used to enhance separation of inorganic compounds. The solvent is then regenerated and recycled.

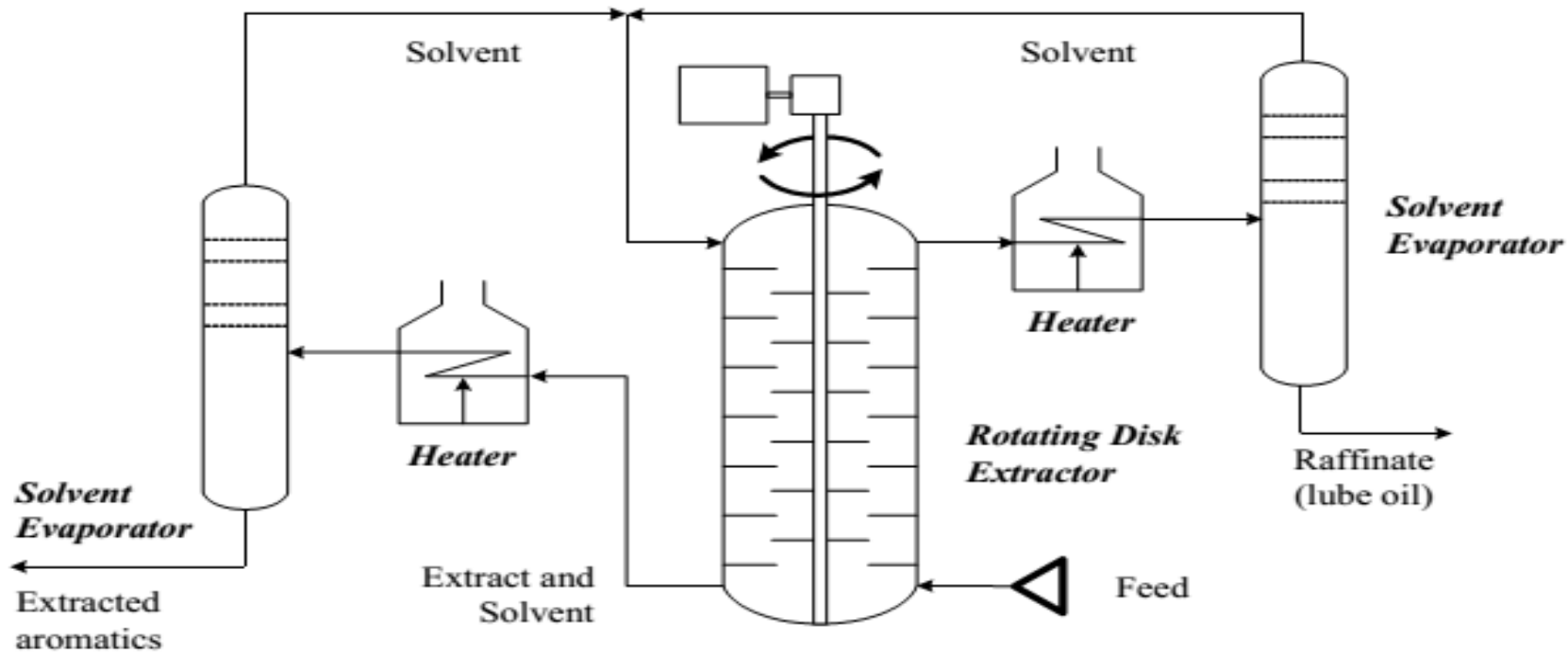


Figure 11. Rotating-disk solvent extraction

**Solvent Dewaxing, Wax Deoiling**

Solvent dewaxing removes wax (normal paraffins) from deasphalted lube base stocks. The main process steps include mixing the feedstock with the solvent, chilling the mixture to crystallize wax, and recovering the solvent. Commonly used solvents include toluene and methyl ethyl ketone (MEK). Methyl isobutyl ketone (MIBK) is used in a wax deoiling process to prepare food-grade wax.

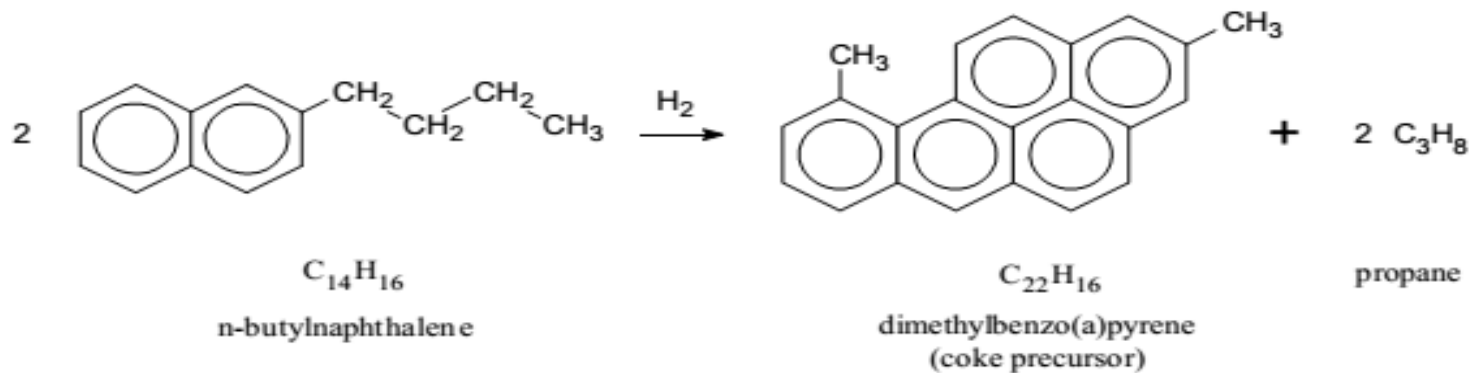


2. CONVERSION

**Table 10** illustrates the fundamental principle behind conversion. For a given class of hydrocarbons, “lighter” means lower molecular weight, lower boiling point, lower density, and higher hydrogen-to-carbon ratios (H/C). Methane, the lightest hydrocarbon, has an H/C of 4.0. Benzopyrene has an H/C of 0.6. The H/C of commonly used crude oils ranges from 1.5 to 2.0, and the H/C for as phaltenes is 1.15.

Table 10. Molecular Weight, H/C and Boiling Point for Selected Hydrocarbons					
Compound	Molecular Weight	Formula	H/C	Boiling Point	
				°C	°F
Paraffins					
Methane	16.04	CH <sub>4</sub>	4.0	-164	-263.2
Ethane	30.07	C <sub>2</sub> H <sub>6</sub>	3.0	-88.6	-127.5
Propane	44.10	C <sub>3</sub> H <sub>8</sub>	2.67	-42.1	-43.7
Butane (iso)	58.12	C <sub>4</sub> H <sub>10</sub>	2.50	-6.9	19.6
Octane (iso)	114.23	C <sub>8</sub> H <sub>18</sub>	2.25	99.2	210.6
Cetane (normal)	226.44	C <sub>16</sub> H <sub>34</sub>	2.13	287	548.6
Aromatics					
Benzene	78.11	C <sub>6</sub> H <sub>6</sub>	1.0	80.1	176.2
Naphthalene	128.17	C <sub>10</sub> H <sub>8</sub>	0.8	218	424.4
Benzopyrene	252.32	C <sub>20</sub> H <sub>12</sub>	0.6	—	—

Most conversion processes – FCC (fluidized catalytic cracking), thermal cracking, and deasphalting – increase the H/C by rejecting carbon. *A few processes – hydrotreating to a small extent and hydrocracking to a great extent – increase* the H/C by adding hydrogen. In this context, “rejecting carbon” does not mean that a little bit of carbon is removed from every molecule. Rather, it means that heavy molecules are split (“cracked”) into a smaller molecule with a higher H/C and another smaller molecule with a lower H/C. Molecules with low H/C – polyaromatic hydrocarbons (PAH) – can condense to form coke (Figure 12). Condensation reactions release hydrogen, lowering H/C even more.



*Figure 12.* Representative thermal-cracking reaction. The reaction shown here is the sum of a condensation reaction, which generates hydrogen, and dealkylation, which consumes hydrogen.

## 2A Visbreaking

Visbreaking is a mild form of thermal cracking that achieves about 15% conversion of atmospheric residue to gas oils and naphtha. At the same time, a low-viscosity residual fuel is produced.

Visbreaking comes in two basic flavors – **“short-contact”** and **“soaker.”** In short-contact visbreaking, the feed is heated to about 900°F (480°C) and sent to a “soaking zone” (reactor) at 140 to 300 psig (1067 to 2170 kPa). The elevated pressure allows cracking to occur while restricting coke formation. To avoid over-cracking, the residence time in the soaking zone is short – several minutes compared to several hours in a delayed coker – and the hot oil is quenched with cold gas oil to inhibit further cracking and sent to a vacuum tower for product separation. “Soaker” visbreaking keeps the hot oil at elevated temperature for a longer time to increase the yield of middle distillates. The low-viscosity visbreaker gas oil can be sent to an FCC unit or hydrocracker for further processing, or used as heavy fuel oil.

A **visbreaker** is a processing unit in an oil refinery whose purpose is to reduce the quantity of residual oil produced in the distillation of crude oil and to increase the yield of more valuable middle distillates (heating oil and diesel) by the refinery. A visbreaker thermally cracks large hydrocarbon molecules in the oil by heating in a furnace to reduce its viscosity and to produce small quantities of light hydrocarbons (LPG and gasoline).

### Process objectives

- Reduce the viscosity of the feed stream
- Reduce the amount of residual fuel oil produced by a refinery
- Increase the proportion of middle distillates in the refinery output

## 2B Coking

Coking processes come in two basic forms – delayed coking, which is a semi-batch process, and fluid-bed coking, which is continuous.

Coking is a refinery unit operation that upgrades material called bottoms from the atmospheric or vacuum distillation column into higher-value products and, as the name implies, produces petroleum coke—a coal-like material.

Two types of coking processes exist—**delayed coking and fluid coking**.

Both are physical processes that occur at pressures slightly higher than atmospheric and at temperatures greater than 900°F that thermally crack the feedstock into products such as naphtha and distillate, leaving behind petroleum coke. Depending on the coking operation temperatures and length of coking times, petroleum coke is either sold as fuel-grade petroleum coke.

## Delayed Coking

The main objective of the delayed coking unit is to convert low value residual products to lighter products of higher value and to produce a coke product.

In a delayed coker, vacuum residue feed is heated to about 900 to 970°F (487 to 520°C) and sent to a large coke drum. Cracking begins immediately, generating coke and cracked, vaporized products. Coke stays behind in the drum while the vapors rise to the top and flow to the product fractionator. Liquid products include coker naphtha, light coker gas oil (LCGO), and heavy coker gas oil (HCGO). All of these require further processing due to direct blending into finished products. The coker naphtha and LCGO are hydrotreated. The HCGO can go either to an FCC unit or a hydrocracker.

Different kind of coke can be obtained from this process, this includes:

***Sponge Coke:*** Sponge coke is named for its sponge-like appearance. It is produced from feeds that have low-to-moderate asphaltene concentrations. If sponge coke meets certain specifications, it can be used to make carbon anodes for the aluminum industry. Otherwise, it is used for fuel. “Green” sponge coke must be calcined before it can be used for anodes. Fuel coke may not require calcination.

***Needle Coke:*** Needle coke, named for its needle-like structure, is made from feeds that contain nil asphaltenes, such as hydrotreated FCC decant oils. Needle coke is a high-value product used to make graphite electrodes for electric-arc furnaces in the steel industry.

**Shot Coke:** Shot coke is an undesirable product because it is inconsistent and in some cases dangerous. It is produced when the concentration of feedstock asphaltenes and/or coke-drum temperatures are too high. Excessive feedstock oxygen content can also induce its formation. Shot coke begins to form as the oil flows into the coke drum. As light ends flash away, small globules of heavy tar are left behind. These globs of tar coke rapidly grow due to the heat produced by asphaltene polymerization, producing discrete mini-balls 0.1 to 0.2 inches (2 to 5 mm) in diameter.

### *Fluid Coking*

Fluid coking, also called continuous coking, is a moving-bed process for which the operating temperature is higher than the temperatures used for delayed coking. In continuous coking, hot recycled coke particles are combined with liquid feed in a radial mixer (reactor) at about 50 psig (446 kPa). Vapors are taken from the reactor, quenched to stop any further reaction, and fractionated. The coke goes to a surge drum, then to a classifier, where the larger particles are removed as product. The smaller coke particles are recycled to a preheater, where they mix with fresh feed. Coking occurs both in the reactor and in the surge drum.

*\*Installation costs for fluid coking are somewhat higher than for delayed coking, but feeds can be heavier and heat losses are lower\*.*

# Fluid Catalytic Cracking

Fluid catalytic cracking (FCC) produces more than half the world's gasoline. A typical FCC unit comprises three major sections – *riser/reactor, regenerator, and fractionation*. Table 12 provides important details on FCC.

*Table 12. FCC in a Nutshell*

<b>Purpose</b>	Convert heavy oils into gasoline and/or light olefins	
<b>Licensors</b>	Axens (IFP) KBR UOP	ExxonMobil Stone & Webster
<b>Catalysts and Additives</b>	Zeolite (highly acidic, catalyzes cracking) Rare-earth oxide (increases catalyst stability) ZSM-5 (increases octane and production of light olefins) Pt (promotes combustion of CO to CO <sub>2</sub> in regenerator) Desox (transfers SO <sub>x</sub> from regenerator to riser/reactor)	
<b>Feeds</b>	Atmospheric gas oil Coker gas oil Lube extracts	Vacuum gas oil Deasphalted oil Vacuum resid (up to 20 vol%)
<b>Typical Feed Properties</b>	Nitrogen Carbon residue Nickel + Vanadium 90% boiling point	<3000 wppm <5.0 wt% <50 wppm <1300°F (704°C)
<b>Typical Process Conditions</b>	Feed temperature Reactor temperature Regenerator temperature Catalyst/Oil ratio Reactor pressure	300 – 700°F (150 – 370°C) 920 – 1020°F (493 – 550°C) 1200 – 1350°F (650 – 732°C) 4.0 – 10.0 10 – 35 psig (170 – 343 kPa)
<b>Typical Product Yields</b>	Conversion H <sub>2</sub> , H <sub>2</sub> S, methane, ethane Propane and propylene Butanes and butenes Gasoline LCO Slurry oil Coke Total C <sub>3</sub> -plus	70 – 84 vol% 3.0 – 3.5 wt% 4.5 – 6.5 wt% 9.0 – 12.0 wt% 44 – 56 wt% 13 – 20 wt% 4 – 12 wt% 5 – 6 wt% 106 – 112 vol%

## *FCC Process Flow*

Figure 13 shows a sketch for the riser/reactor section of an FCC unit. In the reaction section, preheated oil is mixed with hot, regenerated catalyst. The mixture acts as a fluid because the catalyst particles are small – about the size of sifted flour. The hot catalyst vaporizes the oil, and the vaporized oil carries the catalyst up the riser/reactor.

The cracking reaction is very fast. It produces light gases, high-octane gasoline, and heavier products called light cycle oil (LCO), heavy cycle oil (HCO), slurry oil, and decant oil. It also leaves a layer of coke on the catalyst particles, making them inactive.

At the top of the riser, the temperature can reach 900 to 1020°F (482 to 549°C). The temperature at the riser outlet is a key factor in determining conversion and product selectivity, so FCC operators control it as tightly as possible. Higher temperatures favor production of olefin-rich light gas at the expense of gasoline, moderate temperatures favor gasoline production, and at lower temperatures gasoline yields decrease in favor of middle distillates.

In the disengaging section, steam is used to help separate the now deactivated catalyst from the reaction products. The catalyst goes to the regenerator, where the coke is burned away by fluidized combustion in the presence of air. The hot catalyst at temperatures up to 1350°F (732°C) returns to the riser/reactor, where the cycle begins again.

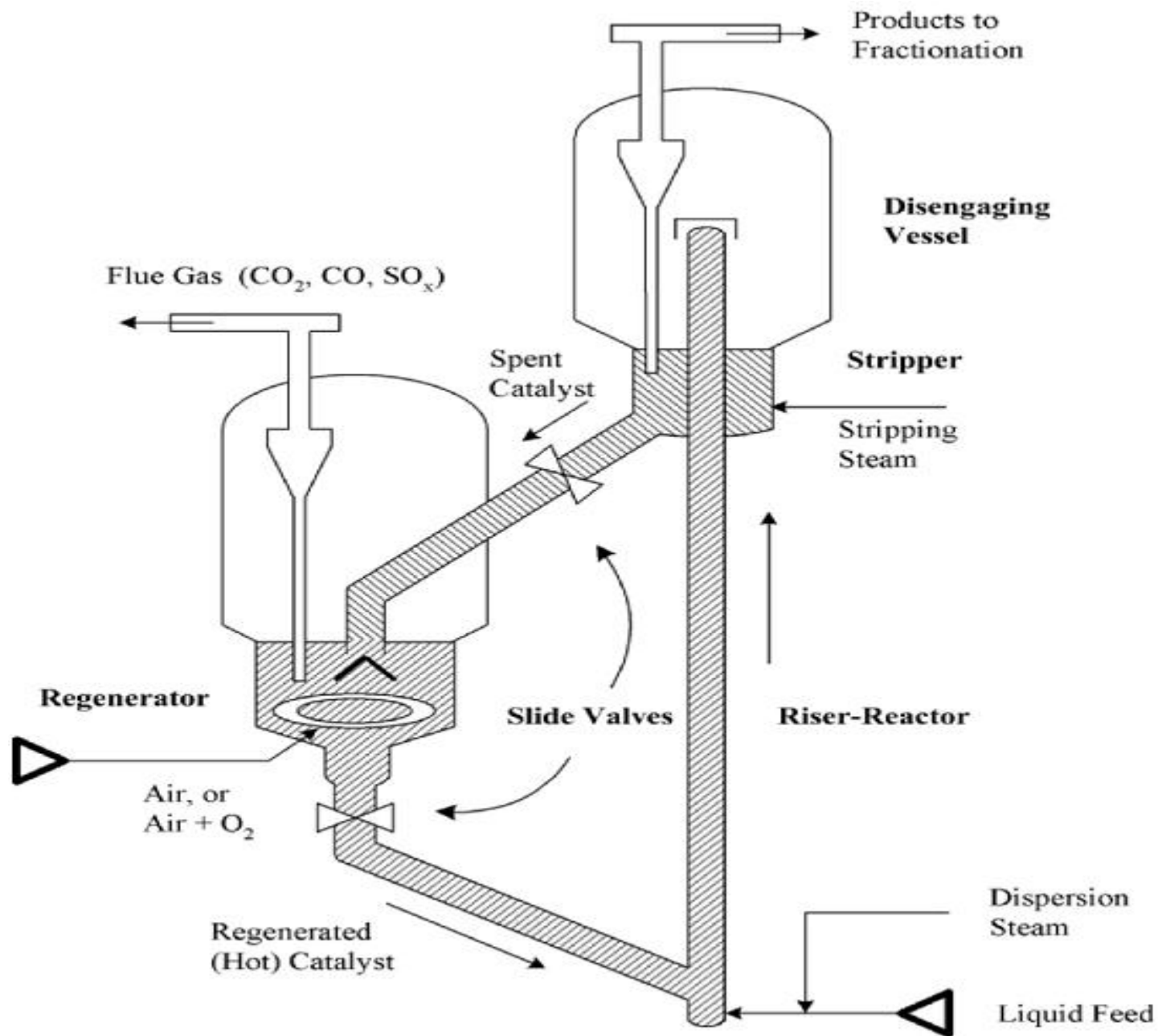


Figure 13. FCC riser-reactor and regenerator sections



## Houdry Catalytic Cracking (HCC)

The Houdry Catalytic Cracking (HCC) process was a precursor to FCC. Houdry catalyst particles are pellets, which are carried to a storage hopper by a conveyor belt or pneumatic lift tubes. The pellets flow down from the hopper through the reactor, and from the reactor to a regenerator. The HCC product slate is similar to that for FCC, but FCC conversions and gasoline yields are significantly higher.

## Hydrotreating and Hydrocracking

A modern petroleum refinery may have four or more hydrotreating units. Strictly speaking, hydrotreaters are not conversion units because the breaking of carbon-to-carbon bonds is minimal. However, it is convenient to discuss hydrotreating together with hydrocracking and mild hydrocracking because they employ similar catalysts and process flow schemes.

The key differences are presented in Table 14. Hydrocrackers tend to operate at higher pressure, using different catalysts, and with lower linear hourly space velocity (LHSV). LHSV is equal to the volume of feed per hour divided by the catalyst volume. A lower required LHSV means that a given volume of feed requires more catalyst. In terms of process conditions and conversion, mild hydrocracking lies somewhere between hydrotreating and full-conversion hydrocracking.

*Table 14. Comparison of Hydrotreating, Hydrocracking and Mild Hydrocracking*

Process, Feedstock Types	H <sub>2</sub> Partial Pressure		Conversion
	psig	kPa	
<i>Hydrotreating</i>			
Naphtha	250 – 300	1825 – 2170	0 – 5%
LGO (Kerosene)	250 – 600	1825 – 4238	0 – 5%
HGO (Diesel), LCO	600 – 800	4238 – 5617	5 -15%
VGO, VBGO, CGO, HCO	800 – 2000	5617 – 13,890	5 -15%
Residual Oil	2000 – 3000	13,890 – 20,786	5 -15%
<i>Mild Hydrocracking</i>			
VGO, VBGO, CGO, LCO, HCO	800 – 1500	5617 – 10,443	20 – 40%
<i>Hydrocracking</i>			
VGO, VBGO, CGO, LCO, HCO	1500 – 2000	10,443 – 13,890	60 – 99%
Residual Oil	2000 – 3000	13,890 – 20,786	15 – 25%

LGO = Light Gas Oil

HGO = heavy Gas Oil

LCO = FCC Light Cycle Oil

HCO = FCC Heavy Cycle Oil

VGO = Vacuum Gas Oil

VBGO = Visbreaker Gas Oil

CGO = Coker Gas Oil

*per square inch gauge (psig)*

*Kilopascal (kPa)*

**Purpose**

Hydrotreating	Hydrocracking
Remove hetero atoms & saturate carbon-carbon bonds <ul style="list-style-type: none"><li>Sulfur, nitrogen, oxygen, metals removal</li><li>Olefinic &amp; aromatic bonds saturated</li></ul>	Severe forms of hydroprocrsses <ul style="list-style-type: none"><li>Break carbon-carbon bonds</li><li>Drastic reduction of molecular weight</li></ul>
Minimal cracking	Reduce average molecular weight & produce higher yields of fuel products
Minimal conversion – 10 – 20% typical	50% plus conversion
Product suitable for further processing or final blending <ul style="list-style-type: none"><li>Reforming, cracking, hydrocracking</li></ul>	Products more appropriate for diesel than gasoline

**Chemistry of Hydrotreating and Hydrocracking**

To one extent or another, all of the chemical reactions listed in Table 15 occur in hydrotreaters and hydrocrackers.

*Table 15. List of Hydrotreating and Hydrocracking Reactions*

<b>Hydrotreating (C-C bond breaking is minimal)</b>	<b>Hydrocracking (C-C bond breaking is significant)</b>
Hydrodesulfurization (HDS)	Dealkylation of aromatic rings
Hydrodenitrogenation (HDN)	Opening of naphthene rings
Hydrodemetallation (HDM)	Hydrocracking of paraffins
Saturation of aromatics	
Saturation of olefins	
Isomerization	

### *Hydrotreating Process Flow*

**Figure 14** illustrates the process flow for a fixed-bed hydrotreater. At moderate-to-high pressure – 300 to 1800psig (2170 to 12,512 kPa) – mixtures of preheated oil and hydrogen pass down over fixed beds of catalyst, in which the desired reactions occur. Hydrotreating is exothermic (heat-releasing), so many commercial units comprise several catalyst beds separated by quench zones. In a quench zone, hot process fluids from the preceding bed are mixed with relatively cold, hydrogen-rich quench gas before passing to the next bed.

HDS and HDN reactions produce H<sub>2</sub>S and NH<sub>3</sub>, respectively. Wash water is injected into the effluent from the last reactor to remove ammonia, which goes into the aqueous phase as ammonium bisulfide, NH<sub>4</sub>HS(aq). The NH<sub>4</sub>HS(aq) is rejected from the unit as sour water in downstream flash drums. In the high-pressure flash drum, liquid products are separated from the hydrogen-rich gas, which is recycled to the reactors. In most hydrotreaters designed for deep desulfurization, H<sub>2</sub>S is removed from the recycle gas with a high-pressure amine absorber. The liquids go to a stripping column, which removes entrained H<sub>2</sub>S and other light gases. These go to a low-pressure amine absorber and then to either a gas plant or the refinery fuel-gas system.

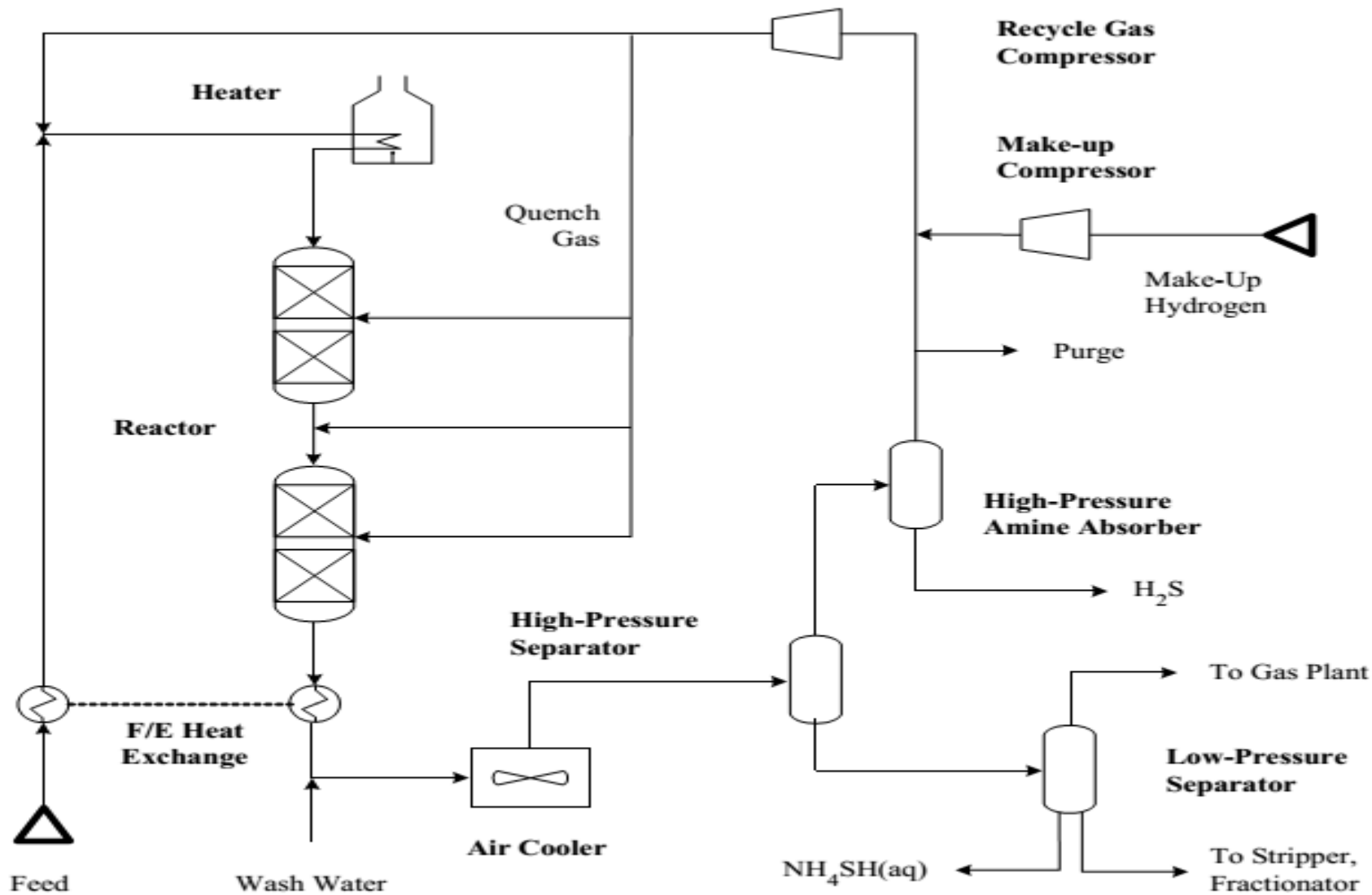


Figure 14. Gas-oil hydrotreating and once-through hydrocracking

The destination of the liquid is unit-specific. In some hydrotreaters, the stripped liquid goes directly to product blending. In others, it goes to one or more fractionation towers.

The objective of the Hydrotreating processes is to remove **sulphur** as well as other compounds which are undesirable and detrimental to the stability and meeting specifications of the product with respect to its performance and environment. Such compounds for example are - *unsaturated hydrocarbons, nitrogen from refinery process streams*. More stringent specifications, particularly those related to environment impact, has resulted in extensive application of hydrotreating processes.

Moreover the catalyst used in the reforming of gasoline to boost octane number can only handle sulphur in the very low ppm level necessitating hydrotreating of naphtha. The necessity for hydrotreating of middle distillates (kerosene/gasoil) originates from pressure to reduce sulfur emissions into the environment. Overall, this situation resulted in an increased necessity for high sulphur removal capability in many refineries.

Hydrotreating is a term loosely used for a wide variety of processes starting with removal of sulphur (**Hydrodesulphurisation**) to mild treatment of lube oils for final finishing and decolourisation (**Hydrofinishing**).

In certain conventions **Hydrodesulphurisation** is treated as a distinct term from milder form **Hydrotreating**.

Hydrodesulphurisation has been extensively used commercially for treating naphtha as feedstock for catalytic reformers to meet the very stringent sulphur specification of less than 1 ppm wt to protect the platinum catalyst. It has also been widely used for removal of sulphur compounds from kerosine and gasoils to make them suitable as blending components. In cases where products are from catalytic or thermal crackers, hydrogen treatment is used to improve product quality specifications like colour, smoke point, cetane index, etc.

## Process Description:

For Hydrotreating, two basic processes are applied:

- Liquid phase process for kerosine and heavier straight-run, cracked distillates and vacuum gas oil
- Vapour phase process for light straight-run and cracked fractions.

The basic configuration of the process is as follows:

The feedstock is mixed with hydrogen-rich make up gas and recycle gas from the reactor. The mixture exchanges heat with the reactor effluent and is heated in a furnace. It enters a reactor loaded with catalyst. In the reactor, the sulphur and the nitrogen compounds present in the feedstock are converted into hydrogen sulphide and ammonia respectively. The olefins present are saturated with hydrogen to become di-olefins and part of the aromatics will be hydrogenated. For hydrogenation of aromatics, a higher pressure is needed in the reactor compared to the normal operating conditions.

The reactor operating conditions are:

- Temperatures in the range of 300-380 degrees C
- Pressure ranging from 10-20 bar for naphta to 30-45 bar for gasoil.
- The catalyst used is normally cobalt, molybdenum and nickel finely distributed on alumina extrudates. It slowly gets deactivated by coke deposit. It is renewed every 2/3 years. It can be regenerated (by burning off the coke) and reused typically once or twice before its activity degenerates. Catalyst regeneration is, nowadays, mainly carried out ex- situ by specialised firms.

The reaction products leave the reactor and, after having been cooled to a low temperature, typically 40-50 degrees C, enter a liquid/gas separation stage. The hydrogen-rich gas from the high pressure separation is recycled to combine with the feedstock, and the low pressure off-gas stream rich in hydrogen sulphide is sent to a gas-treating unit, where hydrogen sulphide is removed. The clean gas is used as refinery fuel. The liquid stream is sent to a stripping column where H<sub>2</sub>S and other undesirable components are removed, and to a vacuum drier for removal of water.

Hydrotreating process

Process Function	Nomenclature	Remarks
Removal of Sulfur from product	Hydrosulphurization (HDS)	
Removal of Sulfur to meet stringent Sulfur specification in products	Deep Dehydrosulphurization(DHDS)	
Removal of contaminants to protect catalyst	Pretreatment	Example: Pretreatment of gasoline before Catalytic Reforming
Raising smoke point of kerosene	Hydrotreatment	Converts smoky aromatics to naphthenes
Denitrification or saturation of olefins in products to give stability	Hydrotreatment, Hydrofinishing	Extensively used for unstable cracked products
Hydrogenation of lube oil to meet color and stability of product	Hydrofinishing	

Hydrocracking

As shown in Table 14, the major difference between hydrotreating, hydrocracking, and mild hydrocracking is the extent to which conversion occurs. In a hydrocracking unit designed for high conversion of vacuum gas oil, the process flow is more complex.



The unit probably operates at a much higher pressure. It may include an additional reactor, a hot high-pressure separator, and a multiple-column fractionation section. To achieve near-total conversion of fresh feed, unconverted oil may be recycled. Some details about hydrocracking are given in Table 17.

*Table 17. Hydrocracking in a Nutshell*

<b>Purpose</b>	Convert heavy hydrocarbons into lighter hydrocarbons	
<b>Uses for Unconverted Oil</b>		
	FCC feed	Lube base stock
	Olefin plant feed	Recycle to extinction
<b>Other Reactions</b>		
	Sulfur removal (HDS)	Nitrogen removal (HDN)
	Olefin saturation	Aromatic saturation
<b>Licensors</b>		
	Axens (IFP) (IFP)	Chevron Lummus
	ExxonMobil	KBR
	Shell Global Solutions	UOP
<b>Catalysts</b>		
	NiMo on $\gamma$ -alumina (HDS, HDN, aromatic saturation)	
	NiMo or NiW on zeolite (hydrocracking)	
	NiMo or NiW on amorphous silica-alumina (hydrocracking)	
	Pd on zeolite (hydrocracking)	
<b>Feeds</b>		
	Heavy gas oil	Vacuum gas oil
	Coker gas oil	Residual oils
<b>Typical Process Conditions</b>		
	Reactor temperature	600 – 800°F (315 – 425°C)
	Reactor pressure	1200 – 2500 psig (8375 – 17,338 kPa)
<b>Range of Product Yields</b>		
	Conversion (once-through)	20 – 90 vol%
	Conversion (with recycle)	90 – 99 vol% fresh feed
	C <sub>4</sub> -plus naphtha	Up to 120 vol% fresh feed
	Middle distillates	Up to 90 vol% fresh feed
	Hydrogen consumption	1000 to 3000 scf/bbl
		175 to 525 Nm <sup>3</sup> /m <sup>3</sup>

## Hydrocracking Objectives

For a given hydrocracker, process objectives can include:

- Maximum production of naphtha
- Maximum production of middle distillate fuels
- Flexibility to swing between production of naphtha and middle distillates
- Production of ultra-clean lube base stocks
- Production of olefin plant feeds.

**Hydrocracking** is a catalytic chemical process used in petroleum refineries for converting the high-boiling constituent hydrocarbons in petroleum crude oils to more valuable lower-boiling products such as gasoline, kerosene, jet fuel and diesel oil. The process takes place in a hydrogen-rich atmosphere at elevated temperatures (260 – 425 °C) and pressures (35 – 200 bar).

Basically, the process cracks the high-boiling, high molecular weight hydrocarbons into lower-boiling, lower molecular weight olefinic and aromatic hydrocarbons and then hydrogenates them. Any sulfur and nitrogen present in the hydrocracking feedstock are, to a large extent, also hydrogenated and form gaseous hydrogen sulfide ( $\text{H}_2\text{S}$ ) and ammonia ( $\text{NH}_3$ ) which are subsequently removed. The result is that the hydrocracking products are essentially free of sulfur and nitrogen impurities and consist mostly of paraffinic hydrocarbons.

## Chemistry and catalysts

Basically, catalytic hydrocracking involves three primary chemical processes:

- Cracking of high-boiling, high molecular weight hydrocarbons found in petroleum crude oil into lower-boiling, lower molecular weight hydrocarbons.
- Hydrogenating unsaturated hydrocarbons (whether present in the original feedstock or formed during the cracking of the high-boiling, high molecular weight feedstock hydrocarbons) to obtain saturated hydrocarbons usually referred to as paraffins or alkanes
- Hydrogenating any sulfur, nitrogen or oxygen compounds in the original feedstock into gaseous hydrogen sulfide, ammonia and water

The above primary processes include too many complex reactions to describe each of them in detail. The following four reactions are provided as examples of those complex reactions:

Reaction 1: Addition of hydrogen to aromatics converts them into hydrogenated rings. These are then readily cracked using acid catalysts.

Reaction 2: Acid catalyst cracking opens paraffinic rings, breaks larger paraffins into smaller pieces and creates double bonds.

Reaction 3: Addition of hydrogen to olefinic double bonds to obtain paraffins.

Reaction 4: Isomerization of branched and straight-chain paraffins.

Hydrocracking catalysts consist of active metals on solid, acidic supports and have a dual function, specifically a cracking function and a hydrogenation function. The cracking function is provided by the acid catalyst support and the hydrogenation function is provided by the metals.

The solid acidic support consists of amorphous oxides such as silica-alumina, crystalline zeolite or a mixture of amorphous oxides and crystalline zeolite. Cracking and isomerization reactions (reactions 2 and 4 above) take place on the acidic support. Metals provide the hydrogenation reactions (reactions 1 and 3 above).

The metals that provide the hydrogenation functions can be the noble metals palladium and platinum or the base metals (i.e., non-noble metals) molybdenum, tungsten, cobalt or nickel.

As the name implies, Hydrocracking is cracking in presence of hydrogen. It is a catalytic process at high temperature and high pressure. The initial development of the process had the limitation of operation at very high pressures (above 200 bar). The development of improved catalyst made it possible to operate the process at considerably lower pressure, about 70-150 bar at temperatures of 350 to 430°C.

The main advantages of hydrocracking process are:

- its flexibility with respect to production of gasoline and middle distillates,
- quality of its products
- ability to handle a wider range of feedstock like cycle oils from other cracking units
- does not yield any coke as by-product
- better conversion of the gas oil and residues into useful products.

Although more expensive than other cracking processes, it is competitive and often advantageous compared to other cracking processes depending on market parameters.

# Catalytic Reforming

## Catalytic Reforming Objectives

Catalytic reforming converts low-octane heavy naphtha into a high-octane product (reformate) that is an excellent gasoline blend stock. Reformate has a high content of BTX (benzene-toluene-xylene), so it also serves as a great source of aromatics for petrochemical plants. In addition to making aromatic compounds, catalytic reformers produce hydrogen, which is used in hydrotreaters, hydrocrackers, and other hydrogenaddition processes.

## Chemistry of Catalytic Reforming

The chemistry of catalytic reforming includes the reactions listed in Table 18. All are desirable except hydrocracking, which converts valuable C5-plus molecules into light gases. The conversion of naphthenes to aromatics and the isomerization of normal paraffins provide a huge boost in octane. H<sub>2</sub> is produced by dehydrocyclization of paraffins and naphthene dehydrogenation, which are shown in Figure 15.

Table 18. List of Catalytic Reforming Reactions

Naphthene Reactions	Paraffin Reactions
Dehydrogenation to form aromatics	Dehydrocyclization to form aromatics
Isomerization to form different naphthenes	Isomerization to form other paraffins
	Hydrocracking to form C <sub>4</sub> -minus

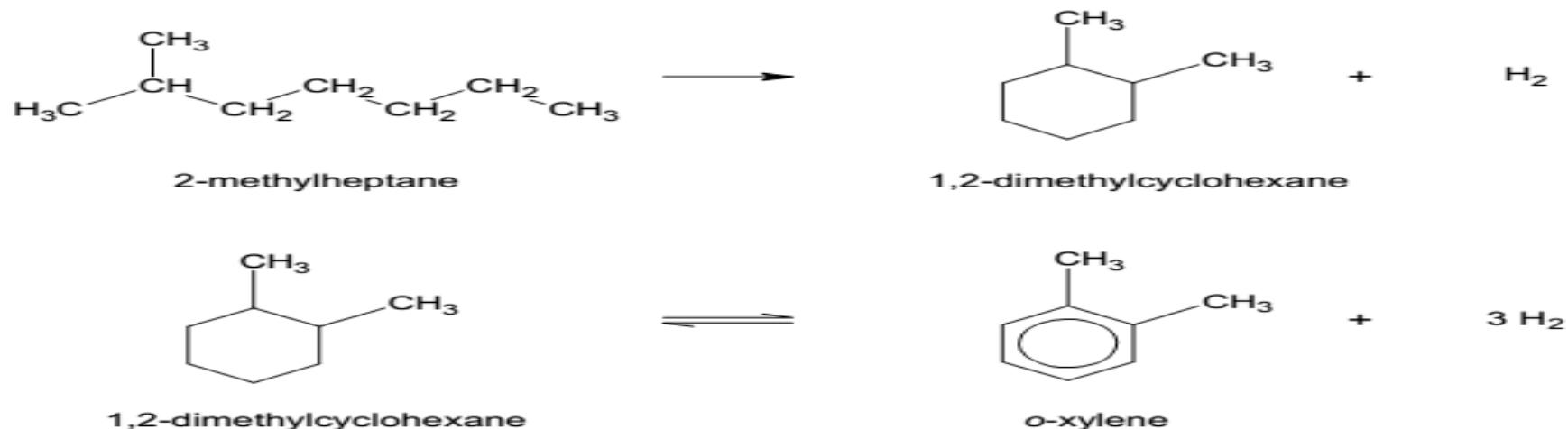


Figure 15. Dehydrocyclization and dehydrogenation

Hydrocracking and isomerization reactions are shown in *Figure 16* and *Figure 17*, respectively. Hydrocracking, which is undesirable in this process, occurs to a greater extent at high temperatures.

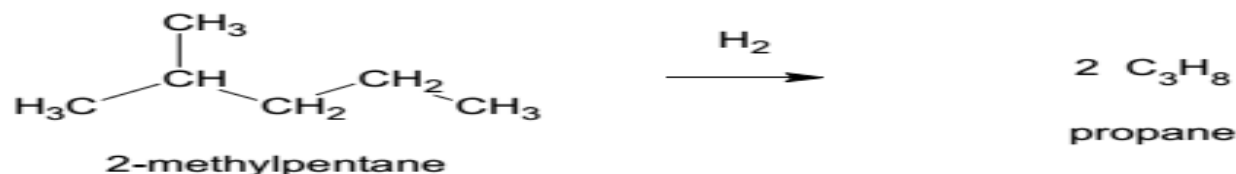


Figure 16. Hydrocracking in catalytic reformers.

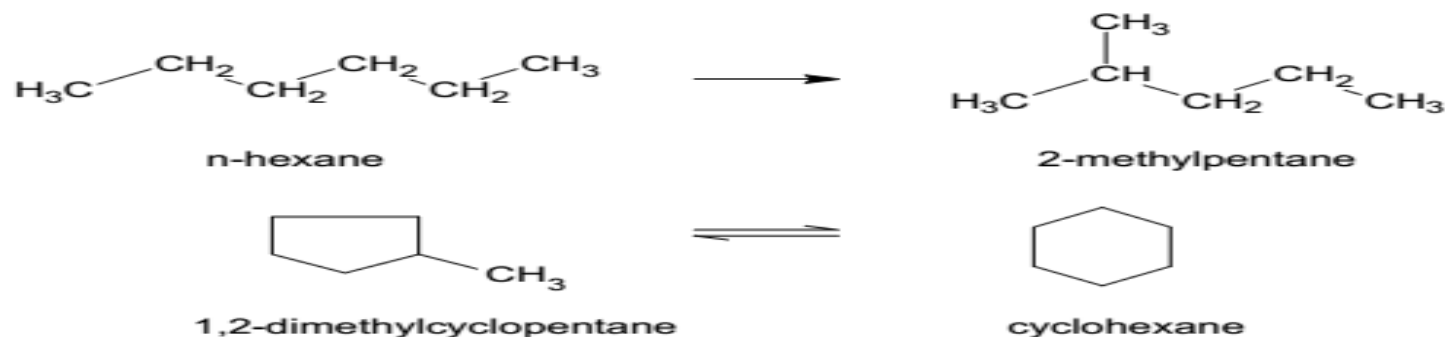


Figure 17. Isomerization of paraffins and naphthenes in catalytic reformers.

Additional details about catalytic reforming are given in *Table 19*.

*Table 19. Catalytic Reforming in a Nutshell*

<b>Purpose</b>	Increase heavy-naphtha octane	
<b>Other</b>	Produce aromatics (BTX) for petrochemical plants	
	Produce hydrogen	
<b>Licensors</b>	Axens (IFP)	BP
	ExxonMobil	UOP
<b>Catalysts</b>	Pt on $\gamma$ -alumina	Pt-Re on $\gamma$ -alumina
	Pt-Re-Sn on $\gamma$ -alumina	
<b>Promoters</b>	HCl	
<b>Feeds</b>	Hydrotreated heavy naphtha, 40 to 62 RON	
<b>Typical Process Conditions</b>		
	H <sub>2</sub> /HC ratio	Up to 6.0
	Reactor inlet temperature	900 – 970°F (482 – 521°C)
	Pressure (Semi-regen., Cyclic)	200 – 500 psig (1480 – 3549 kPa)
	Pressure (CCR)	100 – 150 psig (791 – 1136 kPa)
<b>Typical Product Yields and Properties</b>		
	Total C <sub>5</sub> -plus	84 to 85 vol%
	H <sub>2</sub> production	650 – 1100 scf/bbl (115 – 195 Nm <sup>3</sup> /m <sup>3</sup> )
	RONC (Semi-regen., Cyclic)	85 to 95
	RONC (CCR)	Up to 105

## Catalytic Reforming Catalysts

Catalytic reforming catalysts contain highly dispersed platinum (Pt), the activity of which is inhibited by sulfur. Therefore, an upstream hydrotreater lowers the sulfur content of reformer feeds to <1 wppm. In addition to Pt, modern multi-metallic catalysts contain highly dispersed rhenium (Re) and in some cases tin (Sn).

## Process Flows

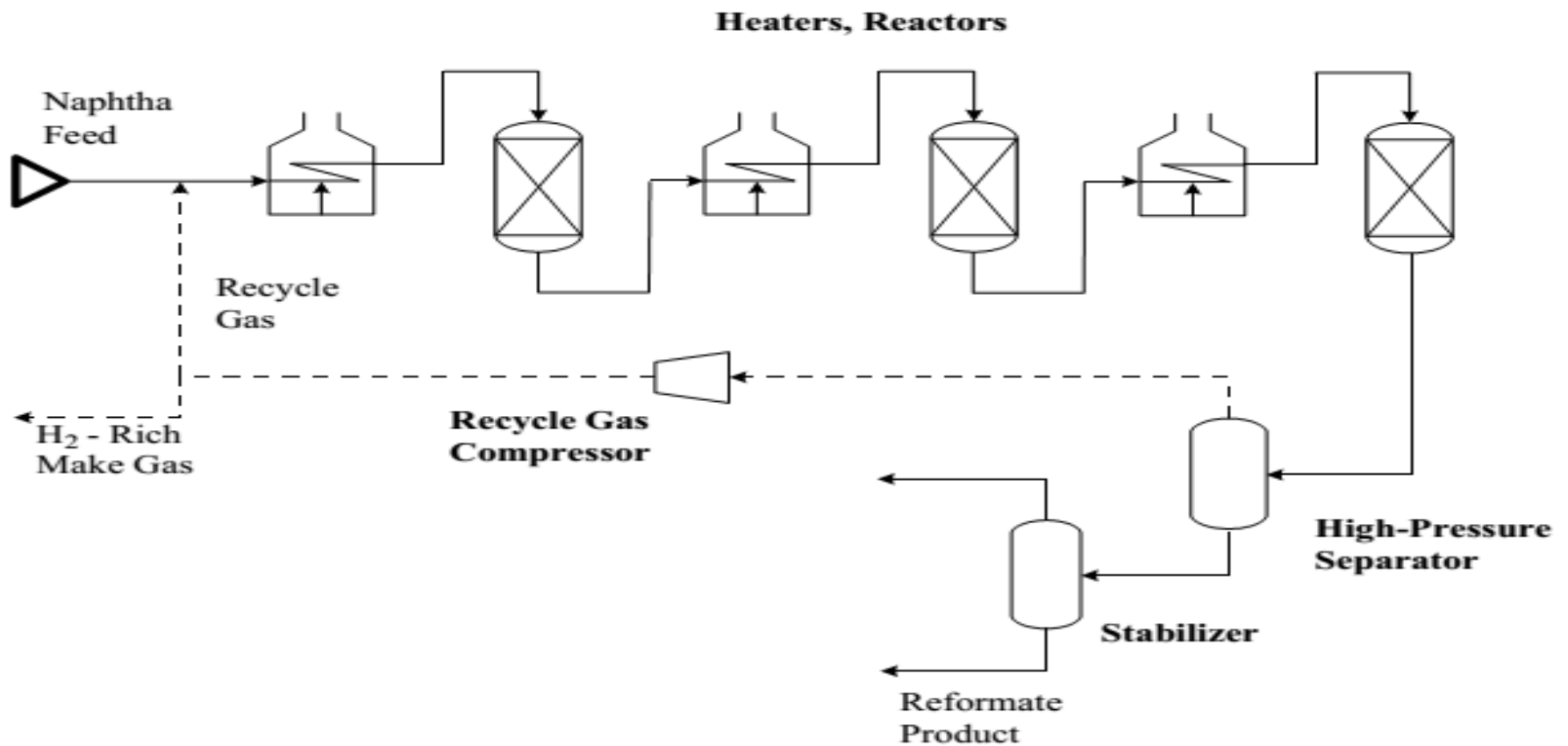
There are three major process flows for catalytic reforming:

- Semi-regenerative
- Cyclic
- Continuous catalyst regeneration (CCR)

Figure 18 shows a semi-regenerative reformer, a fixed-bed unit in which catalyst cycles last from 6 to 12 months. A catalyst cycle ends when the unit is unable to meet its process objectives – typically octane and overall C5-plus yields. At the end of a cycle, the entire unit is brought down and catalyst is regenerated. In a cyclic reformer, catalyst cycles are shorter – 20 to 40 hours – but they are staggered so that only one reactor goes down at a time. In a CCR unit, the catalyst is slowly but constantly moving from the reactor to the regenerator and back again.

In a semi-regenerative unit, desulfurized naphtha is mixed with hydrogen, heated to  $>900^{\circ}\text{F}$  ( $>480^{\circ}\text{C}$ ) and passed through a series of fixed-bed reactors. The major chemical reactions – dehydrogenation and dehydrocyclization – are endothermic (heat absorbing), and the reactors themselves are essentially adiabatic. This means that heat can't enter or leave except by the cooling or heating of reaction fluids. Consequently, the temperature drops as reactants flow through a reactor. Between reactors, fired heaters bring the process fluids back to desired reactor inlet temperatures.



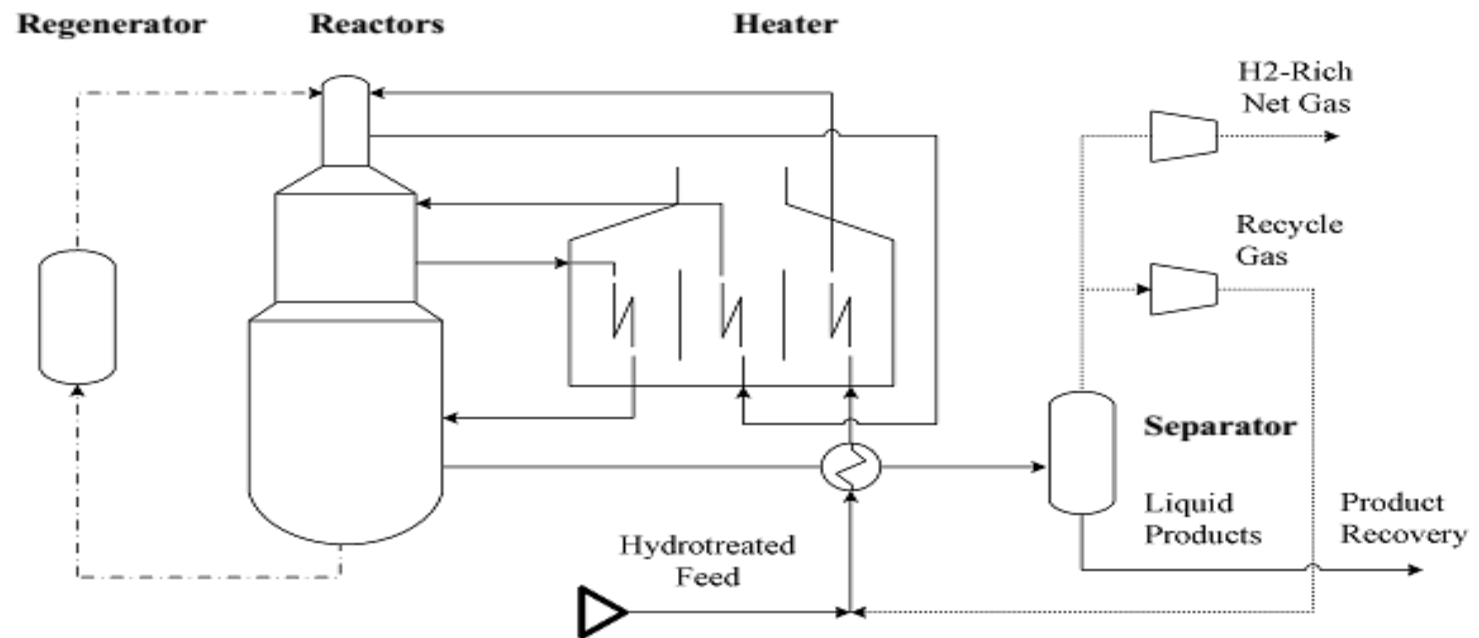


*Figure 18. Semi-regenerative catalytic reforming*

Some catalytic reformers operate at low pressure (100 psig, 791 kPa), while others operate at >500 psig(3549 kPa). Low operating pressure improves yields of aromatics and hydrogen, but it accelerates catalyst deactivation by increasing the rate at which coke forms on the catalyst. In a CCR reformer, the catalyst always is being regenerated, so increased coking is less problematic. Therefore, CCR units can operate at very low pressures. In most reformers, the feed is spiked with an organic chloride, which converts to hydrogen chloride (HCl) in the reactors. The HCl increases catalyst acidity and helps to minimize catalyst coking.

The effluent from the last reactor is cooled and sent to a separator, from which hydrogen-rich gas is removed and recycled to the reactors. The liquid product flows to a stabilizer column, where entrained gases are removed, before going to the gasoline blender or aromatics plant.

In a CCR unit (Figure 19), the hydrotreated feed mixes with recycle hydrogen and goes to series of adiabatic, radial-flow reactors arranged in a vertical stack. Catalyst flows down the stack, while the reaction fluids flow radially across the annular catalyst beds. The predominant reforming reactions are endothermic, so heaters are used between reactors to reheat the charge to reaction temperature. Flue gas from the fired heaters is typically used to generate steam.



*Figure 19. CCR catalytic reforming*

The effluent from the last reactor is cooled and sent to a separator. Part of the vapor is compressed and recycled to the reactors. The rest is compressed, combined with separator liquids, and sent to the product recovery section. Liquids from the recovery section go to a stabilizer, where light saturates are removed from the C6-plus aromatic products.

## **Isomerization**

### **Isomerization Objectives**

As we have seen, isomerization occurs as a side-reaction in all conversion processes. But in refining, when we say “isomerization process,” we are referring specifically to the on-purpose isomerization of n-butane, n-pentane, and n-hexane. The main purpose of n-paraffin isomerization is to produce isoparaffins with substantially higher octane numbers. An isomerization reaction for normal hexane was shown in Figure 17. Some details about paraffin isomerization processes are given in Table 20.

### **Isomerization Catalysts**

The most common catalyst for isomerising n-butane is platinum (Pt) on alumina promoted by chloride. The high activity of this catalyst allows operation at relatively low temperature. This is beneficial because the reaction is controlled by equilibrium; at low temperature, equilibrium favors isobutane. Pt/alumina catalysts can't be regenerated, and they are highly sensitive to water and other contaminants.

In units that isomerize n-pentane and n-hexane, the reactions are catalyzed either by Pt/alumina or Pt on zeolite. The zeolite catalysts require higher temperatures, but they are less sensitive to water. As with butane isomerization, the reactions are controlled by equilibrium, so lower reaction temperatures favor branched isomers. The high temperatures required by

zeolite catalysts reduce the octane of the product relative to products made at lower temperatures with chlorided alumina catalysts.

### Process Flow: C4Isomerization

The feed to a butane (C4) isomerization unit should contain maximum amounts of n-butane and only small amounts of isobutane, pentanes, and heavier material. The feed is dried, combined with dry makeup hydrogen, and charged to the reactor section at 230 to 340° F (110 to 170°C) and 200 to 300 psig (1480 to 2170 kPa). H<sub>2</sub> is not consumed by isomerization reactions, but it suppresses polymerization of the olefin intermediates that are formed during the reaction. A small amount of organic chloride promoter, which is added to maintain catalyst activity, converts completely to HCl in the reactors.

Often, two reactors in series are used to increase on-stream efficiency. The catalyst in one reactor can be replaced while the other continues to operate. The reactor effluent (isomerate) flows to a stabilizer. A caustic scrubber removes HCl from the separated light gases. The stabilized liquid product comprises a near-equilibrium mixture of n-butane and isobutanes, plus a small amount of heavier hydrocarbons. Losses due to cracking are less than 1 wt%.

The isomerate can be blended directly into gasoline or sent to an alkylation unit. N-butane from an alkylation unit can be recycled to a butane isomerization unit to achieve nearly total conversion of n-butane into isobutane or alkylate.

## Process Flow: C5C6Isomerization

Pentane/hexane (C5C6) isomerization processes increase the octane of light gasoline. In a typical unit, dried, hydrotreated feed is mixed with a small amount of organic chloride and recycled hydrogen, then heated to reaction temperature.

Process objectives determine whether one or two reactors are used. In two reactor units (Figure 20), the feed flows first to a saturation reactor, which removes olefins and (to a large extent) benzene. After saturation, the feed goes to an isomerization reactor, where normal paraffins are converted to isoparaffins.

The reactor effluent flows to a product separator, where hydrogen is separated from the other reaction products. Recovered hydrogen can go to a recycle compressor, which returns it to the reactors, or it can be treated and sent to the fuel gas system. Separator liquids go to a stabilizer column, which removes light gases and remaining dissolved hydrogen. The stabilized liquid goes to storage or gasoline blending. If sent to a fractionator, n-pentane and nhexane can be recycled to the isomerization unit for increased conversion.

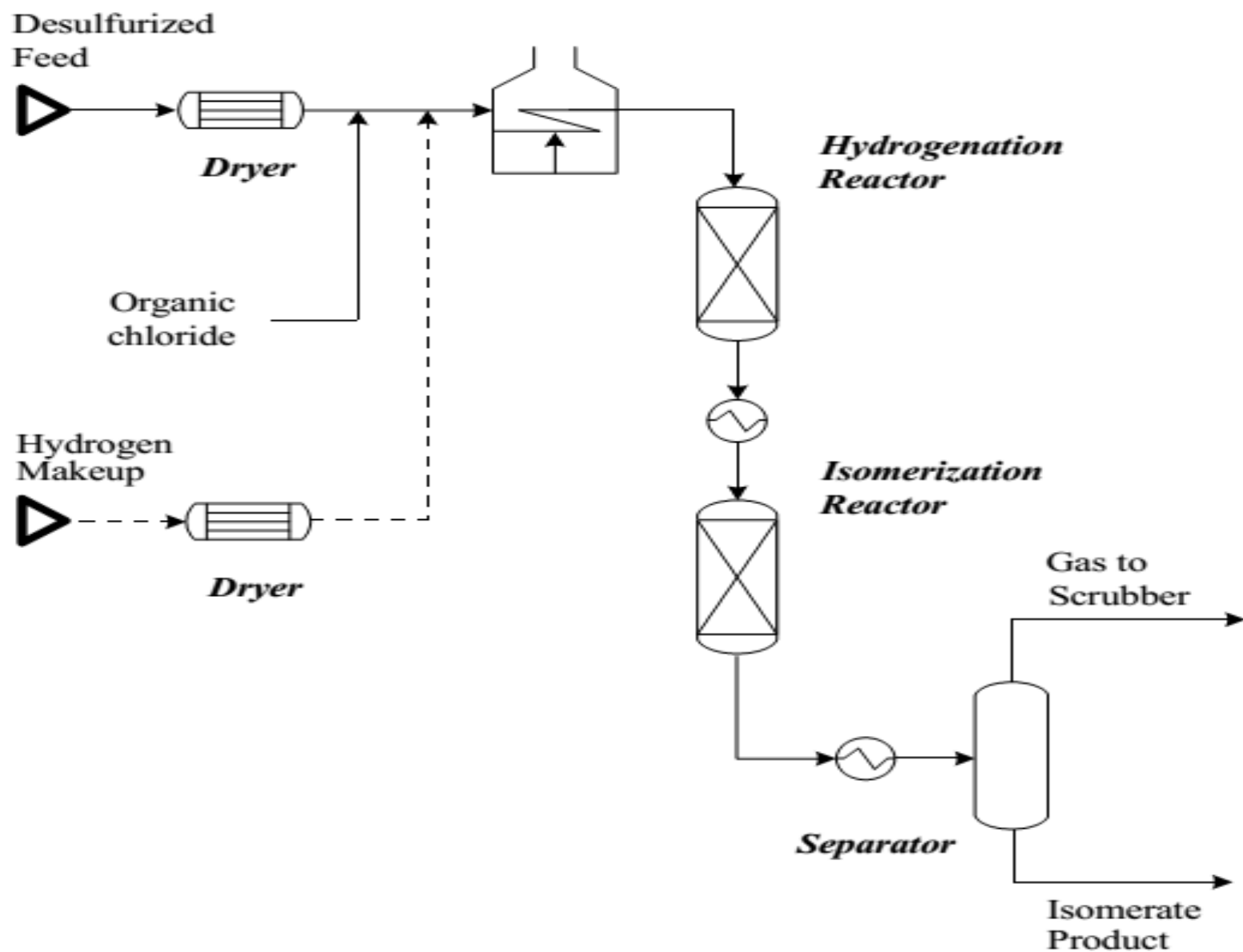


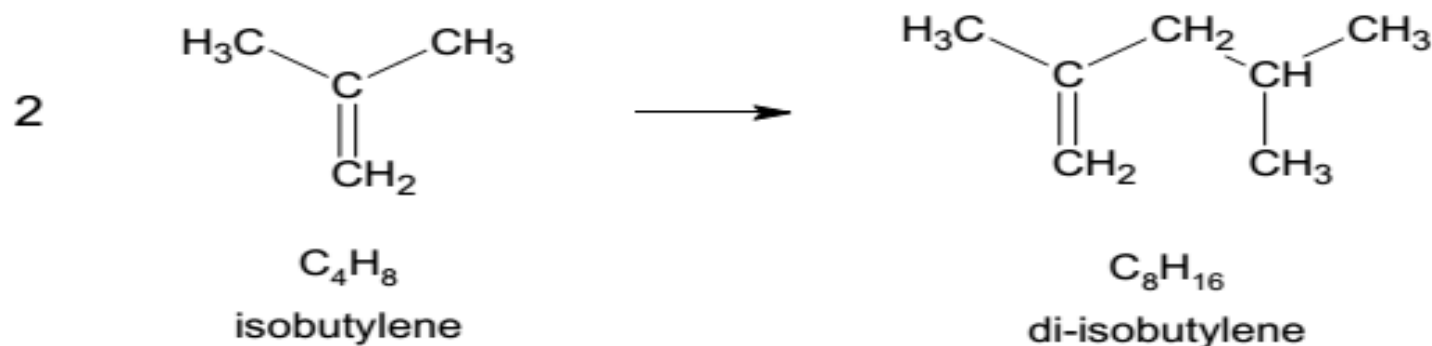
Figure 20.  $C_5C_6$  isomerization: two reactors, once-through hydrogen

# Catalytic Oligomerization

## Catalytic Oligomerization Objectives

Catalytic oligomerization also is called catalytic polymerization, catpoly, and catalytic condensation. The process converts  $C_3$  and  $C_4$  olefins into  $C_6$  to  $C_9$  olefins, which are excellent gasoline blend stocks. Per *Table 22*, the research octane numbers for  $C_6$  and  $C_8$  olefins such as methyl-2-pentenenes and 2,2,4-trimethylpentenes are greater than 97.

Variations on the process make higher olefins and aromatics such as cumene for petrochemical applications. *Figure 21* shows the main chemical reaction for the dimerization of isobutylene.



*Figure 21.* Dimerization of isobutylene

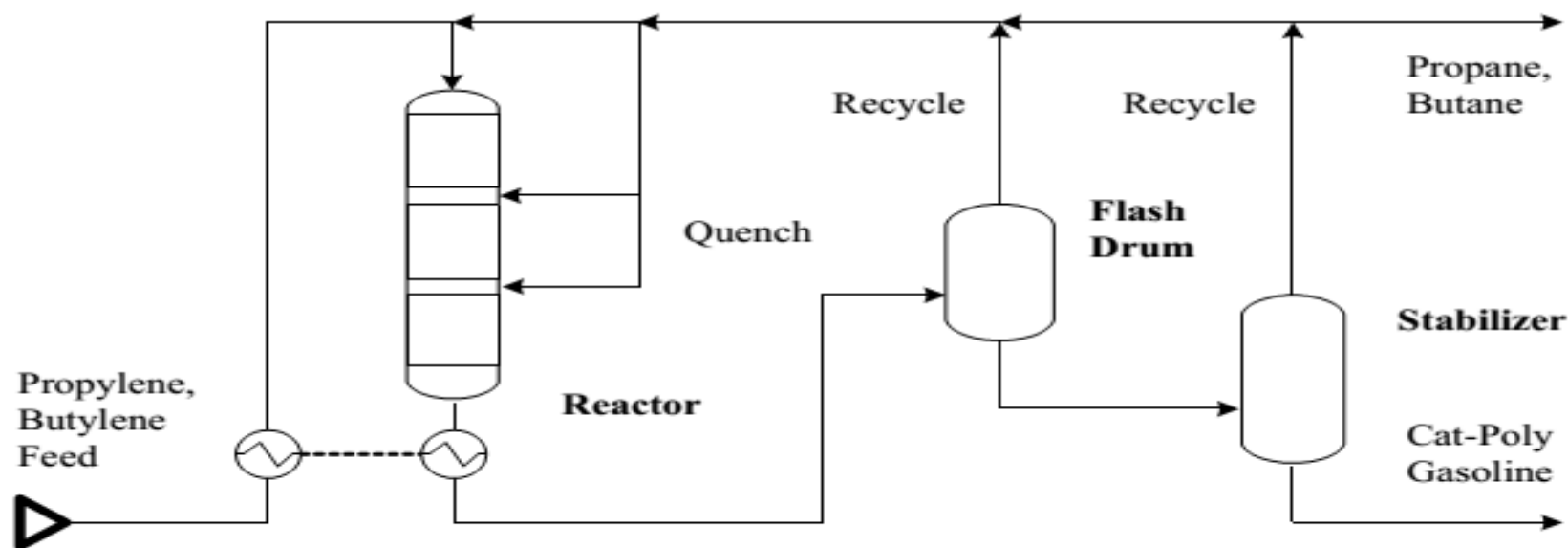
## Catalysts

Sulfuric acid, phosphoric acid, and solid phosphoric acid on kieselguhr pellets (SPA) are used as catalysts. The SPA catalyst is non-corrosive, so it can be used in less-expensive carbon-steel reactors.

## Process Flow

Figure 22 presents a sketch for a unit designed to use SPA catalysts. After pre-treatment to remove sulfur and other undesirable compounds, the olefin-rich feed is sent to the reactor. The reaction is exothermic, so temperatures are controlled by diluting the feed with product and by injecting relatively cold feedstock (quench) between beds in the reactor. Temperatures range from 300 to 450°F (150 to 230°F) and pressures range from 200 to 1,200 psig (1480 to 8375 kPa).

Reaction products go to stabilization and/or fractionator systems to separate gases – saturated and unsaturated C3-C4 compounds – from the liquid product. The gases are recycled to the reactor, and the liquid product goes to gasoline blending.



*Figure 22. Catalytic oligomerization of olefins*



# Alkylation

## Alkylation Objectives

Alkylation processes combine light olefins (primarily propylene and butylene) with isobutane in the presence of a highly acidic catalyst, either sulfuric acid or hydrofluoric acid. The product (alkylate) contains a mixture of high-octane, branched-chain paraffinic hydrocarbons. Figure 23 illustrates the reaction between isobutane and trans-2-butene. Alkylate is a highly desirable gasoline blend stock because, in addition to its high octane, it has a low vapor pressure. The octane of the product depends on the operating condition and the kinds of olefins used.

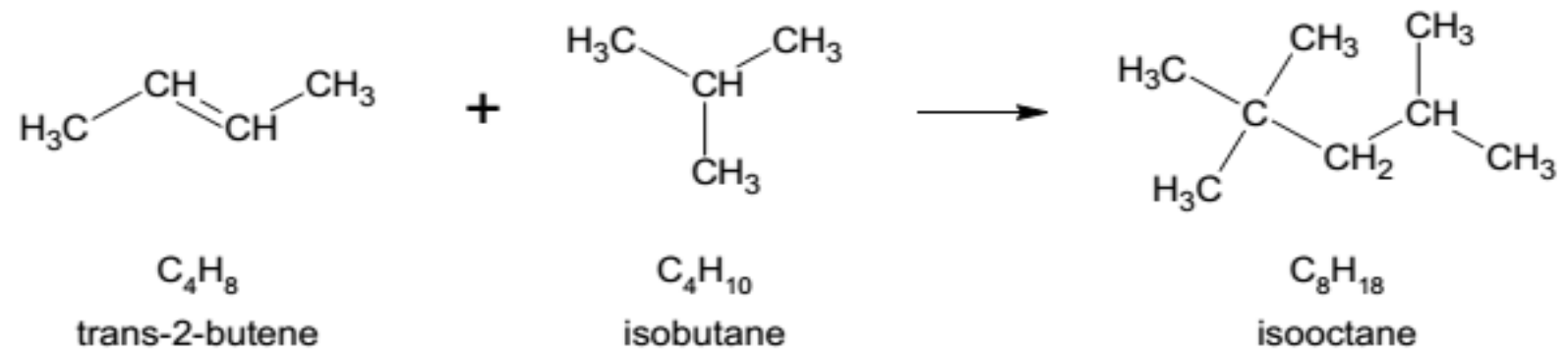


Figure 23. Alkylation of trans-2-butene

## Process Flow: Sulfuric Acid Alkylation

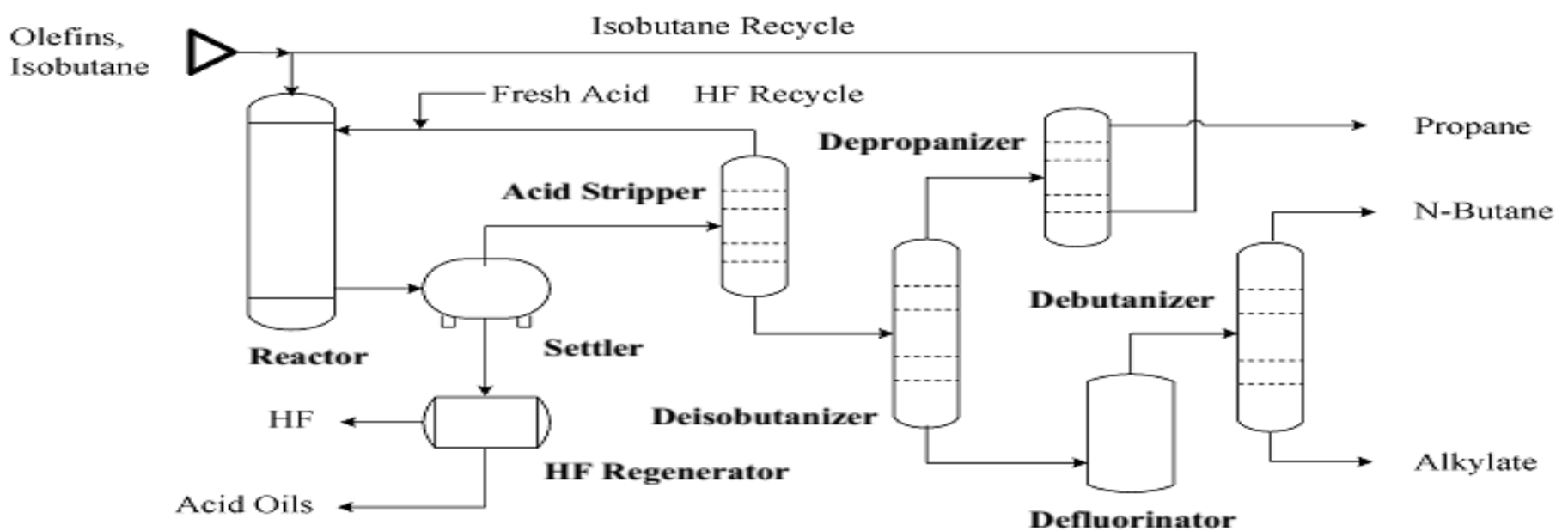
In sulfuric acid ( $\text{H}_2\text{SO}_4$ ) alkylation units, the feeds – propylene, butylene, Reactor Flash Stabilizer Drum 44 Robinson amylene, and fresh isobutane – enter the reactor and contact sulfuric acid with a concentration of 85 to 95%. The reactor is divided into zones.

Olefins are fed through distributors to each zone, and sulfuric acid and isobutanes flow over baffles from one zone to the next.

The reactor effluent goes to a settler, in which hydrocarbons separate from the acid. The acid is returned to the reactor. The hydrocarbons are washed with caustic and sent to fractionation. The fractionation section comprises a depropanizer, a deisobutanizer, and a debutanizer. Alkylate from the deisobutanizer can go directly to motor-fuel blending, or it can be reprocessed to produce aviation-grade gasoline. Isobutane is recycled.

### Process Flow: HF Alkylation

**Figure 24** shows a process schematic for hydrofluoric acid (HF) alkylation. Olefins and isobutane are dried and fed to a reactor, where the alkylation reaction takes place over the HF catalyst. The reactor effluent flows to a settler, where the acid phase separates from the hydrocarbon phase. The acid is drawn off and recycled. The hydrocarbon phase goes to a deisobutanizer (DIB). The overhead stream, containing propane, isobutane, and residual HF, goes to a depropanizer (DeC3). The DeC3 overhead goes to an HF stripper. It is then treated with caustic and sent to storage. Isobutane from the DIB main fractionator is recycled. The bottom stream from the debutanizer goes to product blending.



*Figure 24. HF alkylation*

## LUBES, WAXES AND GREASES

### Lube Base Stocks

Refiners prepare lube base stocks from residual oils by removing asphaltenes, aromatics, and waxes. Lube base stocks are hydrofinished, blended with other distillate streams for viscosity adjustment, and compounded with additives to produce finished lubricants.

### Catalytic dewaxing

Catalytic dewaxing (CDW) was developed by Exxon mobil in 1980s. The process employs a shape-selective zeolite called ZSM-5, which selectively converts waxy n-paraffins into lighter hydrocarbons. The Isodewaxing Process, commercialized in 1993 by ChevronTexaco,

catalytically isomerizes n-paraffins into iso-paraffins. This decreases the wax content and increases the concentration low-viscosity hydrocarbons, both of which are desirable. Isodewaxing also removes sulfur and nitrogen, and it saturates aromatics. Products have a high viscosity index (VI), low pour point, and excellent response to additives.

## Waxes

The raffinate from the solvent extraction unit in a traditional lube plant contains a considerable amount of wax. To recover the wax, the raffinate is mixed with a solvent, usually propane, and cooled in a series of heat exchangers. Further cooling is provided by the evaporation of propane in the chiller and filter feed tanks. The wax forms crystals, which are continuously removed, filtered, and washed with coldsolvent. The solvent is recovered by flashing and steam stripping. The wax is purified by heating with hot solvent, after which it is re-chilled, re-filtered and given a final wash.

Paraffin waxes are used to make candles and coated papers for use as bread wrappers, cold-drink cups, and beverage cartons. They are also used in building materials. The market for packaging is declining, but other uses are on the rise, especially in construction.

## Greases

Greases are made by blending salts of long-chained fatty acids into lubricating oils at temperatures of 400 to 600°F (204 to 315°C). Antioxidants are added to provide stability. Some greases are batch-produced, while others are made continuously. The characteristics of a grease depend to a great extent on the counter-ion (calcium, sodium, aluminum, lithium, etc.) in the fatty-acid salt.

# ASPHALT PRODUCTION

Asphalt can be produced directly from vacuum residue or by solvent deasphalting.

**Road-Tar Asphalt.** Vacuum residue is used to make road-tar asphalt. To drive off remaining light ends, it is heated to about 750°F (400°C) and charged to a column where a vacuum is applied.

In road-paving, the petroleum residue serves as a binder for aggregate, which can include stone, sand, or gravel. The aggregate comprises about 95% of the final mixture. Polymers are added to the binder to improve strength and durability.

The recommended material for paving highways in the United States is Superpave<sup>32</sup> hot-mix asphalt. Superpave was developed in 1987-93 during a US\$50 million research project sponsored by the Federal Highway Administration.

**Roofing Asphalt.** Roofing asphalt is produced by blowing, which involves the oxidation of asphalt flux by bubbling air through liquid asphalt at 260°C (500°F) for 1 to 10 hours. During this process, organic sulfur is converted to H<sub>2</sub>S and SO<sub>2</sub>. Catalytic salts such as ferric chloride (FeCl<sub>3</sub>) may be used to adjust product properties and increase the rates of the blowing reactions, which are exothermic. To provide cooling, water is sprayed into the top of the blowing vessel, creating a blanket of steam that captures sulfur-containing gases, light hydrocarbons, and other gaseous contaminants. These are recovered downstream. Cooling water may also be sprayed on the outside of the vessel.

The length of the blow depends on desired product properties, such as softening temperature and penetration rate. A typical plant blows four to six batches of asphalt per 24-hour day. There are two primary substrates for roofing asphalt – organic (paper felt) and fiberglass. The production of felt-based roofing shingles consists of:

- Saturating the paper felt with asphalt
  - Coating the saturated felt with filled asphalt
  - Pressing granules of sand, talc or mica into the coating
  - Cooling with water, drying, cutting and trimming, and packaging
- If fiberglass is used as the base instead of paper felt, the saturation step is eliminated.

## DRYING, SWEETENING, AND TREATING

Drying, sweetening and treating are not as glamorous as extraction and conversion, or even distillation, but they are essential to the performance and safety of finished products. In lubricating oils, traces of olefins and sulfur compounds can form gums and accelerate degradation. At high altitude, excess water in jet fuel can freeze and plug fuel lines. Traces of mercaptans and disulfides in “sour” gasoline can react with water in storage tanks to produce toxic levels of hydrogen sulfide.

### Drying and Sweetening

Light gas streams produced by various refinery units are collected and piped to treating plants, where:

- Propane is recovered for LPG
- Propylene is removed for use in petrochemical plants
- Butanes and butenes are removed for use as alkylation feeds
- Heavier components are recovered and sent to gasoline blending

Knock-out drums collect easy-to-condense liquids, but if necessary drying agents – alumina, silica, or molecular sieves – are used to remove the final traces of water. Some processes use

beds of molecular sieves to dry and sweeten at the same time. Gases containing hydrogen sulfide are scrubbed in trayed contactors with aqueous amines such as diethanolamine (DEA). Hydrogen sulfide is stripped from the “rich” amine with steam and recycled to the contactor. In a properly operating unit, the sweetened gas contains <10 wppm H<sub>2</sub>S.

## Treating

Treating improves the odor, color, and stability of straight-run liquids and conversion-unit products. Sulfuric acid treating removes olefins, sulfur, nitrogen, oxygen compounds, and other contaminants. Clay/lime treating of acid-treated oil removes any residual traces of asphaltenes. Caustic treating with sodium (or potassium) hydroxide removes naphthenic acids, phenols, mercaptans, and H<sub>2</sub>S.

If the concentration of organic sulfur exceeds the capacity of a caustic or acid treater, the stream must be sent to a hydrotreater.

## PRODUCT BLENDING

### Product Specifications

Liquid products from modern refineries comprise several individual streams, which are blended to meet desired specifications. Product specifications developed by ASTM – the American Society for Testing and Materials – are widely used throughout the world. Table 21 lists some common refinery products along with their ASTM designations.

*Table 21. ASTM Specification Numbers for Hydrocarbon Fuels*

<b>Product</b>	<b>ASTM Specification</b>	<b>Last Updated</b>	<b>Description</b>
Gasoline	D4814	2003	Standard Specification for Automotive Spark-Ignition Engine Fuel
Jet	D1655	2003	Standard Specification for Aviation Turbine Fuels
Kerosene	D3699	2003	Standard Specification for Kerosene
Diesel	D975	2004	Standard Specification for Diesel Fuel Oils
Fuel Oil	D396	1998	Standard Specification for Fuel Oils

Analogous institutions in other countries – for example, the Japanese Industrial Standards Committee (JISC) and the British Standards Institution (BSI) – serve similar functions. BSI developed the ISO9000 series of standards for managing manufacturing processes.

In addition to setting specifications, these institutions develop and publish test methods used to analyze a wide variety of materials. ASTM and its international cousins cooperate with each other, and they work closely with government regulators. For example, recent low-sulfur gasoline and diesel directives from the U.S. Environmental Protection Agency are incorporated into D975-04 and D4814-03a, respectively.

Other widely used tests and specifications are defined by licensors. For example, UOP's Laboratory Test Methods, distributed by ASTM, defines several hundred procedures for analyzing catalysts, chemicals and fuels. Axens (IFP), ChevronTexaco, ExxonMobil and other licensors also distribute test methods to process licensees.

Additives are an essential component of finished fuels. They increase stability, improve flow properties and enhance performance. For example, cetane-improvers are routinely added to diesel fuel, and additives that prevent intake-valve deposits are now required in all grades of gasoline in the United States.



## Gasoline Blending

Forty years ago, making gasoline was a relatively simple task. If a mixture of components met specifications for volatility and octane, it could be shipped to retail outlets and sold as-was. If the octane was low, the problem could be fixed by adding a little tetraethyl lead. Butanes could be added as needed to adjust volatility.

In fact, volatility and octane are still the two most important properties of gasoline. The volatility must be high enough to vaporize during cold weather; otherwise, engines won't start. And octane is still one of the best predictors of performance in a spark-ignition gasoline engine.

## Octane Numbers for Hydrocarbons

In a spark-ignition engine, some compounds start to burn before they reach the spark plug. This premature ignition causes knocking, which reduces the power of the engine, increases engine wear, and in some cases causes serious damage.

Octane number is a measure of the propensity of fuels to knock in gasoline engines. It is based on an arbitrary scale in which the octane number of n-heptane is zero and the octane number of isooctane (2,2,4-trimethylpentane) is 100. When a fuel is tested in a standard single-cylinder engine, mixtures of isooctane and n-heptane are used as standards. ASTM D2699 and ASTM D2700 describe methods for measuring research octane number (RON) and motor octane number (MON), respectively. The engine speed for the RON test is 600 rpm, while 900 rpm is used for the MON test. RONC and MONC are sometimes used instead to RON and MON. The "C" stands for clear, which means that the fuel does not contain lead or manganese additives.

Table 22 presents RON and MON values for several pure compounds. Aromatics, olefins, and branched isomers have higher octane numbers than straight-chain isomers with similar carbon numbers. Octane numbers for naphthenes are substantially lower than those for aromatics. Octane numbers do not blend linearly. For example, while the RON for pure 4-methyl-2-pentene is 99, its blended RON is 130.

In North America, the pump octane of gasoline is the average of RON and MON:  $(R+M)/2$ . This is the number displayed on pumps at filling stations. Typical grades are “regular” with a pump octane of 87, “mid-grade” with a pump octane of 89, and “premium” with a pump octane of 91 to 93. In some locales, customers can dial in any octane they want between 87 and 93.

Many refinery streams have the right vapor pressure, boiling range, and octane to end up in the gasoline pool. Table 23 shows properties for stocks recently used to make gasoline in a European refinery. The raffinate came from an aromatics extraction unit, and the pyrolysis gasoline came from a nearby ethylene plant.

Table 23. Gasoline Blend Stock Properties: Example

Component	Density (kg/m <sup>3</sup> )	RVP (bar)	Boiling Range		RON	MON
			°C	°F		
Butanes	0.575	3.6	-12 to -0.5	10.4 – 31	97	95
Straight-run Gasoline	0.64	1.15	27 – 80	81 – 176	80.2	76.6
Reformate	0.815	0.08	78 – 197	172 – 387	100.5	89.5
Raffinate	0.685	0.3	65 – 112	149 – 234	60.3	54.5
Hvy FCC Gasoline	0.76	0.2	43 – 185	109 – 365	90.5	79.5
Light FCC Gasoline	0.66	1.3	25 – 89	77 – 192	94.5	81.5
Pyrolysis Gasoline	0.845	0.3	47 – 180	117 – 356	101.5	86.5
Alkylate	0.705	0.3	39 – 195	102 – 383	98	93.5
MTBE	0.746	0.5	48 – 62	118 – 144	115	97

*Table 22. Octane Numbers for Selected Pure Compounds*

<b>Compound</b>	<b>Type</b>	<b>Formula</b>	<b>RON</b>	<b>MON</b>
n-Butane	n-Paraffin	C <sub>4</sub> H <sub>10</sub>	92	93
n-Pentane	n-Paraffin	C <sub>5</sub> H <sub>12</sub>	62	62
Cyclopentane	Naphthene	C <sub>5</sub> H <sub>10</sub>	101	85
2-Methylbutane	i-Paraffin	C <sub>5</sub> H <sub>12</sub>	92	90
2-Methyl-2-butene	Olefin	C <sub>5</sub> H <sub>10</sub>	97	85
n-Hexane	n-Paraffin	C <sub>6</sub> H <sub>14</sub>	25	26
Methylcyclopentane	Naphthene	C <sub>6</sub> H <sub>12</sub>	91	80
2,2-Dimethylbutane	i-Paraffin	C <sub>6</sub> H <sub>14</sub>	92	93
3-Methyl-2-pentene	Olefin	C <sub>6</sub> H <sub>12</sub>	97	81
4-Methyl-2-pentene	Olefin	C <sub>6</sub> H <sub>12</sub>	99	84
Benzene	Aromatic	C <sub>6</sub> H <sub>6</sub>	>100	106
n-Heptane	n-Paraffin	C <sub>7</sub> H <sub>16</sub>	-27	0
Methylcyclohexane	Naphthene	C <sub>7</sub> H <sub>14</sub>	75	71
2-Methylhexane	i-Paraffin	C <sub>7</sub> H <sub>16</sub>	42	46
2,2-Dimethylpentane	i-Paraffin	C <sub>7</sub> H <sub>16</sub>	93	96
2,2,3-Trimethylbutane	i-Paraffin	C <sub>7</sub> H <sub>16</sub>	116	101
Toluene	Aromatic	C <sub>7</sub> H <sub>8</sub>	>100	109
n-Octane	n-Paraffin	C <sub>8</sub> H <sub>18</sub>	<0	<0
Isooctane	n-Paraffin	C <sub>8</sub> H <sub>18</sub>	100	100
2,2,4-Trimethyl-1-pentene	Olefin	C <sub>8</sub> H <sub>16</sub>	>100	86
2,2,4-Trimethyl-2-pentene	Olefin	C <sub>8</sub> H <sub>16</sub>	>100	86
o-, m-, and p-Xylene	Aromatic	C <sub>8</sub> H <sub>10</sub>	>100	100
Ethylbenzene	Aromatic	C <sub>8</sub> H <sub>10</sub>	>100	98

## Reformulated Gasoline (RFG)

In 1970, gasoline blending became more complex. The U.S. Clean Air Act required the phase-out of tetraethyl lead, so refiners had to find other ways to provide octane. In 1990, the Clean Air Act was amended. It empowered EPA to impose emissions limits on automobiles and to require reformulated gasoline (RFG).

Phase I RFG regulations (Table 24) required a minimum amount of chemically bound oxygen, imposed upper limits on benzene and Reid Vapor Pressure (RVP), and ordered a 15% reduction in volatile organic compounds (VOC) and air toxics. VOC react with atmospheric NOx to produce ground level ozone. Air toxics include 1,3-butadiene, acetaldehyde, benzene, and formaldehyde.

Oxygen can be supplied as ethanol or C5to C7ethers. The ethers (Table 25) have excellent blending octanes and low vapor pressures. This makes them highly desirable gasoline blend stocks. Due to the detection of MTBE in ground water, the future for MTBE is questionable, especially since 1999, when the Governor of California issued an executive order requiring the phase-out of MTBE as a component of gasoline. But in Finland and many other European countries, MTBE is still considered a premium, relatively safe blend stock.

*Table 24. Simple Model RFG Specifications*

Property	Specification
Oxygen, wt%	2.0 max
Benzene, vol%	1.0 max
RVP, Summer	
Class B (psi)	7.2 max
Class B (kPa)	50 max
Class C (psi)	8.1 max
Class C (kPa)	56 max
VOC (summer)	15% reduction
Air toxics	15% reduction
Sulfur	Same as 1990
T90*, olefins, aromatics	Same as 1990

\*T90 is the temperature at which 90% of a gasoline blend evaporates.

RFG was implemented in two phases. The Phase I program started in 1995 and mandated RFG for 10 large metropolitan areas. Several other cities and four entire states joined the program voluntarily. In the year 2000, about 35% of the gasoline in the United States was reformulated.

The regulations for Phase II, which tookforce in January 2000, are based on the EPA Complex Model, which estimates exhaust emissions for a region.

Table 25. Blending octane and RVP of ethers and alcohols

Ether or Alcohol	Blending Octane (RON)	Blending RVP (psi)	Blending RVP (kPa)
Methanol	133	58-62	400-427
Ethanol	130	18-22	124-152
Methyl-t-butyl ether (MTBE)	118	8-10	55-69
Ethyl-t-butyl ether (ETBE)	118	3-5	21-34
t-Amyl methyl ether (TAME)	111	1-2	7-14

based on geography, time of year, mix of vehicle types, and – most important to refiners – fuel properties (Table 26).

By intent, Phase II is a regulation based on emissions instead of a formula. But refiners don’t have to measure the tail-pipe emissions of every gasoline blend. Instead, they can use EPA’s computer model – called MOBILE6 – to calculate emissions. By law, complex-model calculations are just as valid as dynamometer tests with vehicles.

Table 26. Example of Product Property Ranges Calculated by the Phase II Complex Model

Property	Reformulated gasoline		Conventional gasoline	
	Low end	High end	Low end	High end
Oxygen	0	3.7	0	3.7
Sulfur	0	500	0	1000
RVP	6.4	10	6.4	11
E200	30	70	30	70
E300	70	95	70	100
Aromatics	10	50	0	55
Olefins	0	25	0	30
Benzene	0	2	0	4.9
MTBE	0	3.7	0	3.7
ETBE	0	3.7	0	3.7
Ethanol	0	3.7	0	3.7
TAME	0	3.7	0	3.7

In practice, blending under the complex model can be less restrictive than blending to a recipe, because changing the amount of one blend-stock (for examples, due to a sudden increase or decrease in availability) can be offset by changes in others.

Gasoline Additives

**Table 27** lists the kinds of additives used to prepare finished gasoline. Additive packages vary from season-to-season, region-to-region, and retailer to retailer. “After-market” additives contain similar types of ingredients and usually are more concentrated. They are packaged so that they can be added by consumers to the fuel tanks of individual automobiles.

*Table 27. Additives Used in Gasoline*

Additive Type	Function
Anti-oxidation	Minimize oxidation and gum formation during storage
Metal passivation	Deactivate trace metals that can accelerate oxidation
Corrosion inhibition	Minimize rust throughout the gasoline supply chain
Anti-icing	Minimize ice in carburetors during cold weather
IVD control (detergent)	Control deposition of carbon on intake valves
CCD control	Control deposition of carbon in combustion chambers
Anti-knock	Methylcyclopentadienyl manganese tricarbonyl (MMT)

Low-Sulfur Gasoline and Ultra-Low-Sulfur Diesel

In recent years, the U.S. Environmental Protection Agency (EPA) and the European Parliament promulgated clean-fuel regulations that are lowering the sulfur content of gasoline and diesel fuel. New sulfur-content standards for several developed countries are shown in Table 28, which also shows the target dates for implementation.

Table 28. Clean Fuels: Limits on Sulfur

Country	2004 Level	Fuel Sulfur Content, wppm	
		Target Level	Target Date
US <sup>34-36</sup>			
Gasoline	>300	30	2004 – 2008
Diesel, on-road	500	15	July 1, 2006
	-	-	July 1, 2010
Diesel, off-road	2000 – 3500	500	2007
	-	15	2010
Canada <sup>37</sup>			
Gasoline	150	30	2005
Diesel	500	15	2006
Germany <sup>38</sup>			
Gasoline	10	10	2003
Diesel	10	10	2003
Sweden <sup>39</sup>			
Diesel	10	10	1995
Other EU <sup>38</sup>			
Gasoline	150	50	2005
	-	10	2008
Diesel	350	50	2005
	-	10	2008
Australia <sup>40</sup>			
Gasoline	500	150	2005
Diesel	500	30	2008
Korea (South) <sup>41</sup>			
Gasoline	100	30	2006
Diesel	300	50	2006
Japan <sup>42</sup>			
Gasoline	100	10	2008
Diesel	500	50	2004
	-	10	2008

Table 29 shows that, prior to 2004, FCC gasoline was by far the major source of sulfur in gasoline, typically accounting for 85 – 95% of the total sulfur in the blending pool. Obviously, to reduce the sulfur content of gasoline, sulfur either must be kept out of FCC feed or removed from FCC product(s). Both approaches are being used.

*Table 29. Sources of Sulfur in Gasoline (before 2004)*

Component	Contribution to the Gasoline Pool (vol%)	Contribution to Sulfur in the Pool (%)
Alkylate	12	0
Coker naphtha	1	1
Hydrocracker naphtha	2	0
FCC gasoline	36	98
Isomerase	5	0
Light straight-run naphtha	3	1
Butanes	5	0
MTBE	2	0
Reformate	34	0
Total	100	100

FCC Gasoline Post-Treating

**Hydrotreating FCC Gasoline.** Conventional hydrotreating does a good job of removing sulfur from FCC gasoline. Unfortunately, it also does a good job of reducing octane by saturating C6-C10olefins. In recent years, the industry has developed several processes to remove sulfur at minimum octane loss. Licensors include Axens (IFP), CDTECH, ExxonMobil, and UOP.

**Sulfur Removal by Selective Adsorption.** The ConocoPhillips S Zorb process uses selective adsorption to remove sulfur from FCC gasoline.



The feed is combined with a small amount of hydrogen, heated, and injected into an expanded fluid-bed reactor, where a proprietary sorbent removes sulfur from the feed. A disengaging zone in the reactor removes suspended sorbent from the vapor, which exits the reactor as a low-sulfur stock suitable for gasoline blending.

The sorbent is withdrawn continuously from the reactor and sent to the regenerator section, where the sulfur is removed as  $\text{SO}_2$  and sent to a sulfur recovery unit. The clean sorbent is reconditioned and returned to the reactor. The rate of sorbent circulation is controlled to help maintain the desired sulfur concentration in the product.

## Kerosene and Jet Fuel

Kerosene, jet fuel, and turbine fuel have similar boiling ranges. The key product properties are:

- Flash point
- Freezing point
- Sulfur content
- Smoke point

The flash point is the lowest temperature at which a liquid gives off enough vapor to ignite when an ignition source is present. The freezing point is especially important for jet aircraft, which fly at high altitudes where the outside temperature is very low. Sulfur content is a measure of corrosiveness. The measurement of smoke point goes back to the days when the primary use for kerosene was to fuel lamps. To get more light from a kerosene lamp, you could turn a little knob to adjust the wick. But if the flame got too high, it gave off smoke.

Even today, per ASTM D1322, smoke point is the maximum height of flame that can be achieved with calibrated wick-fed lamp, using a wick “of woven solid circular cotton of ordinary quality.” The smoke point of a test fuel is compared to reference blends. A standard 40%/60% (volume/volume) mixture of toluene with 2,2,4-trimethylpentane has a smoke point of 14.7, while pure 2,2,4-trimethylpentane has a smoke point of 42.8. Clearly, isoparaffins have better smoke points than aromatics. **Table 30** shows specifications for five grades of jet fuel, otherwise known as aviation turbine fuel. The JP fuels are for military aircraft.

<i>Table 30. Specifications for Aviation Turbine Fuels</i>					
<b>Specification</b>	<b>Jet A</b>	<b>Jet B</b>	<b>JP-4</b>	<b>JP-5</b>	<b>JP-8</b>
Flash point, °C (min)	38	-	-	60	38
Freeze point, °C (max)	-40 (Jet A) -47 (Jet A-1)	-50	-58	-46	-47
API Gravity	37 – 51	45 – 57	45 – 57	36 – 48	37 – 51
Distillation, °C					
10% max	205	-		205	205
20% max	-	145	145	-	-
50% max	-	190	190	-	-
90% max	-	245	245	-	-
EP	300	-	270	290	300
Sulfur, wt% max	0.3	0.3	0.4	0.4	0.3
Aromatics, vol% max	22	22	25	25	25
Olefins, vol% max	-	-	5	5	5

### Diesel Blending

Diesel blending is simpler than gasoline blending because the limitations are fewer. Only sulfur, cetane number, and (in some countries) aromatics and density are regulated for environmental reasons.

Sulfur contributes heavily to particulate emissions from diesel engines, and cetane number is a measure of burning quality in a diesel engine. As with octane number, cetane number measures the tendency of fuels to auto-ignite in a standard test engine. It is easier to start a diesel engine when the cetane number of the fuel is high. The reference fuels for ASTM D613, which describes the test method for cetane number, are n-cetane,  $\alpha$ -methyl-naphthalene, and heptamethyl-nonane, for which cetane numbers are defined to be 100, 0, and 15, respectively. Table 31 shows cetane numbers for selected pure compounds.

*Table 31. Cetane Numbers for Selected Pure Compounds*

Compound	Type	Carbons	Formula	Cetane No.
n-Decane	Paraffin	10	C <sub>10</sub> H <sub>22</sub>	76
Decalin	Naphthene	10	C <sub>10</sub> H <sub>18</sub>	48
$\alpha$ -Methylnaphthalene	Aromatic	11	C <sub>11</sub> H <sub>10</sub>	0*
n-Pentylbenzene	Aromatic	11	C <sub>11</sub> H <sub>16</sub>	8
3-Ethyldecane	Paraffin (iso)	12	C <sub>12</sub> H <sub>26</sub>	48
4,5-Diethyloctane	Paraffin (iso)	12	C <sub>12</sub> H <sub>26</sub>	20
3-Cyclohexylhexane	Naphthene	12	C <sub>12</sub> H <sub>24</sub>	36
Biphenyl	Aromatic	12	C <sub>12</sub> H <sub>10</sub>	21
$\alpha$ -Butylnaphthalene	Aromatic	14	C <sub>14</sub> H <sub>16</sub>	6
n-Pentadecane	Paraffin	15	C <sub>15</sub> H <sub>32</sub>	95
n-Nonylbenzene	Aromatic	15	C <sub>15</sub> H <sub>24</sub>	50
n-Hexadecane (cetane)	Paraffin	16	C <sub>16</sub> H <sub>34</sub>	100*
2-Methyl-3-cyclohexylnonane	Naphthene	16	C <sub>16</sub> H <sub>34</sub>	70
Heptamethylnonane	Paraffin (iso)	16	C <sub>16</sub> H <sub>34</sub>	15*
8-Propylpentadecane	Paraffin (iso)	18	C <sub>18</sub> H <sub>38</sub>	48
7,8-Diethyltetradecane	Paraffin (iso)	18	C <sub>18</sub> H <sub>38</sub>	67
2-Octylnaphthalene	Aromatic	18	C <sub>18</sub> H <sub>24</sub>	18
n-Eicosane	Paraffin	20	C <sub>20</sub> H <sub>42</sub>	110
9,10-Dimethyloctane	Paraffin (iso)	20	C <sub>20</sub> H <sub>42</sub>	59
2-Cyclohexyltetradecane	Naphthene	20	C <sub>20</sub> H <sub>40</sub>	57

\* Used as a standard for ASTM D976

Cetane index, as defined by ASTM D976, is not a measurement, but the result of a calculation based on density and mid-boiling point. It is nearly the same the as cetane number for diesel fuels comprised mostly of straight-run gas oils blended with lesser amounts of cracked stocks. Diesel index is a simpler calculation based on density and aniline point. The streams listed in **Table 32** are typical candidates for making diesel fuel.

<i>Table 32. Properties of U.S. Diesel Blend Stocks, Year 2000 (California Excluded)<sup>46</sup></i>				
<b>Blend Stock</b>	<b>Percent of Total U.S. Pool</b>	<b>Sulfur (wt%)</b>	<b>API Gravity</b>	<b>Cetane (no additives)</b>
Straight-run gas oil	12.4	0.222	30.3 – 42.2	40.3 – 45.0
Hydrotreated straight-run	51.9	0.036	29.9 – 42.9	44.5 – 50.4
FCC light cycle oil	3.1	0.532	22.3 – 33.1	<<30
Hydrotreated light cycle oil	19.4	0.087	30.7 – 45.0	42.7 – 44.1
Coker gas oil	1.0	0.342	32.3 – 42.4	<<30
Hydrotreated coker gas oil	8.2	0.026	29.9 – 34.8	36.1 – 45.3
Hydrocrackate	4.0	0.008	32.9 – 41.8	50.2

d poisons the converter catalyst. Similarly, sulfur poisons catalysts that may be used on future vehicles. Hence, the reduction of sulfur in gasoline and diesel fuel to ultra-low levels is a key requirement of Auto Oil II. Around the world, the transportation and fungibility of ultra-clean fuels is a major concern. For common-carrier pipelines, which transport various products made by different refiners, cross-contamination is a major concern.

The interface layer between shipments is called “trans mix.” If a shipment of gasoline containing 30 wppm of sulfur follows a batch of diesel containing 500 wppm of sulfur, the sulfur-contaminated trans mix could comprise more than 20% of the gasoline. Consequently, several pipeline companies have announced that in the future they will not transport any high-sulfur material.

Other important diesel-fuel properties include flash point, cloud point, pour point, kinematic viscosity, and lubricity. Cloud point and pour point indicate the temperature at which the fuel tends to thicken and then gel in cold weather. In addition to providing energy, diesel fuel also serves as a lubricant for fuel pumps and injectors, which prolongs the life of the engine. Viscosity measures the tendency of a fluid to flow. In a diesel engine, viscosity indicates how well a fuel atomizes in spray injectors. It also measures its quality as a lubricant for the fuel system. Lubricity measures the fuel’s ability to reduce friction between solid surfaces in relative motion. It indicates how the engine will perform when loaded.

Diesel Additives

Chemical additives improve the performance and extend the tank-life of diesel fuels. Typical types of additives are shown in Table 34.

*Table 34. Additives Used in Diesel Fuel*

Additive Type	Function
Anti-oxidation	Minimize oxidation and gum formation during storage
Cetane improvement	Increase cetane number
Dispersion	Improve behavior in fuel injectors
Anti-icing	Minimize ice formation during cold weather
Detergent	Control deposition of carbon in the engine
Metal passivation	Deactivate trace metals that can accelerate oxidation
Corrosion inhibition	Minimize rust throughout the diesel fuel supply chain
Cold-flow improvement	Improve flow characteristics in cold weather

# PROTECTING THE ENVIRONMENT

Environmental Pollution Control. In this section, we provide a brief overview of the methods used to improve air quality, prevent water pollution, and dispose of solid wastes.

## ***Air Quality***

In the 1970s and 1980s, environmental laws compelled refineries to reduce emissions of SO<sub>x</sub>, NO<sub>x</sub>, CO, and hydrocarbons. In the atmosphere, SO<sub>x</sub> reacts with water vapor to make sulfurous and sulfuric acids, which return to earth as acid rain. Volatile hydrocarbons react with NO<sub>x</sub> to make ozone. CO<sub>2</sub> is a major “green-house” gas. To reduce these pollutants, the industry tightened its operation by:

- Reducing fugitive hydrocarbon emissions from valves and fittings
- Removing sulfur from refinery streams and finished products
- Adding tail-gas units to sulfur recovery plants
- Reducing the production of NO<sub>x</sub> in fired heaters
- Scrubbing SO<sub>x</sub> and NO<sub>x</sub> from flue gases
- Reducing the production of CO<sub>2</sub> by increasing energy efficiency

## Sulfur Recovery

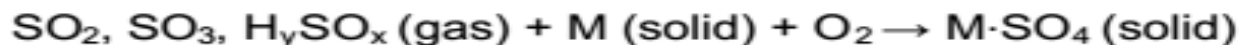
Conversion processes, hydrotreaters, and sweetening units remove chemically bound sulfur from petroleum fractions. That’s a good thing, but where does the sulfur go? The answer depends upon the form in which it is produced?

**SO<sub>x</sub> Abatement.** Fuel-oil fired heaters and the regenerators of FCC units are major sources of refinery SO<sub>x</sub> and NO<sub>x</sub> emissions. The most obvious way to reduce SO<sub>x</sub> emissions from a heater is to use low-sulfur fuels. Unfortunately, although that solution requires no investment, it is probably the most expensive due to the relatively high cost of buying low-sulfur fuel oil or hydrotreating high-sulfur fuel oil.

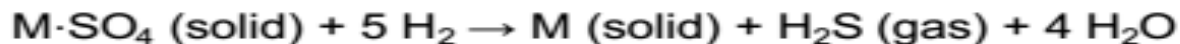
A large fraction of the sulfur in the feed to an FCC unit ends up in coke on the catalyst. SO<sub>x</sub> is formed in the regenerator when the coke is burned away. Therefore, removing sulfur from the feed decreases SO<sub>x</sub> emissions.

Using a hydrotreater or hydrocracker for feed HDS eliminates or minimizes the cost of post-FCC desulfurization equipment. Removing basic nitrogen decreases deactivation of acid sites on the FCC catalyst, which allows the FCC to reach a given conversion at lower temperatures. The saturation of aromatics in the feed pretreater provides the biggest benefit, because it converts hard-to-crack aromatics into easier-to-crack naphthenes. This alone can justify the installation of an FCC feed pretreater. Therefore, in addition to abating SO<sub>x</sub>, hydrotreating the feed to an FCC can generate a substantial return.

#### **FCC Regenerator (Oxidizing Environment)**



#### **FCC Riser/Reactor (Reducing Environment)**



*Figure 25. Mechanism of SO<sub>x</sub> transfer in FCC units.*

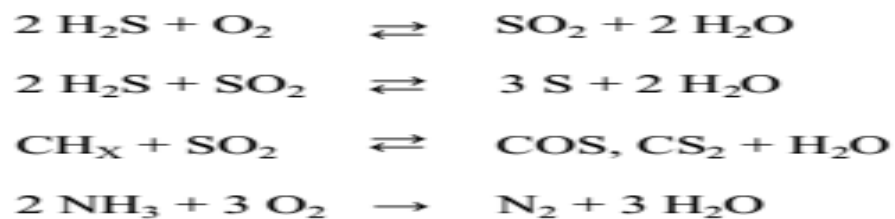
***SOx Transfer Additives.*** Arguably, SOx transfer additives are the most cost-effective way to lower SOx emissions in an FCC unit. These materials, first developed by Davison Chemical, react with SOx in the FCC regenerator to form sulfates (Figure 25). When the sulfated additive circulates to the riser/reactor section, the sulfate is reduced to H<sub>2</sub>S, which is recovered by amine absorption and sent to the sulfurplant. In some units, these additives reduce FCC SOx emissions by more than 70%. Consequently, if a pre-treater or post-treater still must be installed, its size can be reduced.

***Flue-Gas (Stack-Gas) Scrubbing.*** Flue-gas scrubbing is a refiner's last chance to keep NOx and SOx out of the air. In wet flue-gas desulfurization, gas streams containing SOx react with an aqueous slurry containing calcium hydroxide Ca(OH)<sub>2</sub> and calcium carbonate CaCO<sub>3</sub>. Reaction products include calcium sulfite (CaSO<sub>3</sub>) and calcium sulfate (CaSO<sub>4</sub>), which precipitate from the solution.

***NOx removal is more difficult.*** Wet flue-gas scrubbing removes about 20% of the NOx from a typical FCC flue gas. To remove the rest, chemical reducing agents are used. In the Selective Catalytic Reduction (SCR) process, anhydrous ammonia is injected into the flue gas as it passes through a bed of catalyst at 500 to 950°F (260 to 510°C). The chemical reaction between NOx and ammonia produces N<sub>2</sub> and H<sub>2</sub>O.

***Hydrogen Sulfide Removal.*** When sulfur-containing feeds pass through hydrotreaters or conversion units, some or most of the sulfur is converted into H<sub>2</sub>S, which eventually ends up in off-gas streams. Amine absorbers remove the H<sub>2</sub>S, leaving only 10 to 20 wppm in the treated gas streams. H<sub>2</sub>S is steam stripped from the amines, which are returned to the absorbers. The H<sub>2</sub>S goes to the refinery sulfur plant.

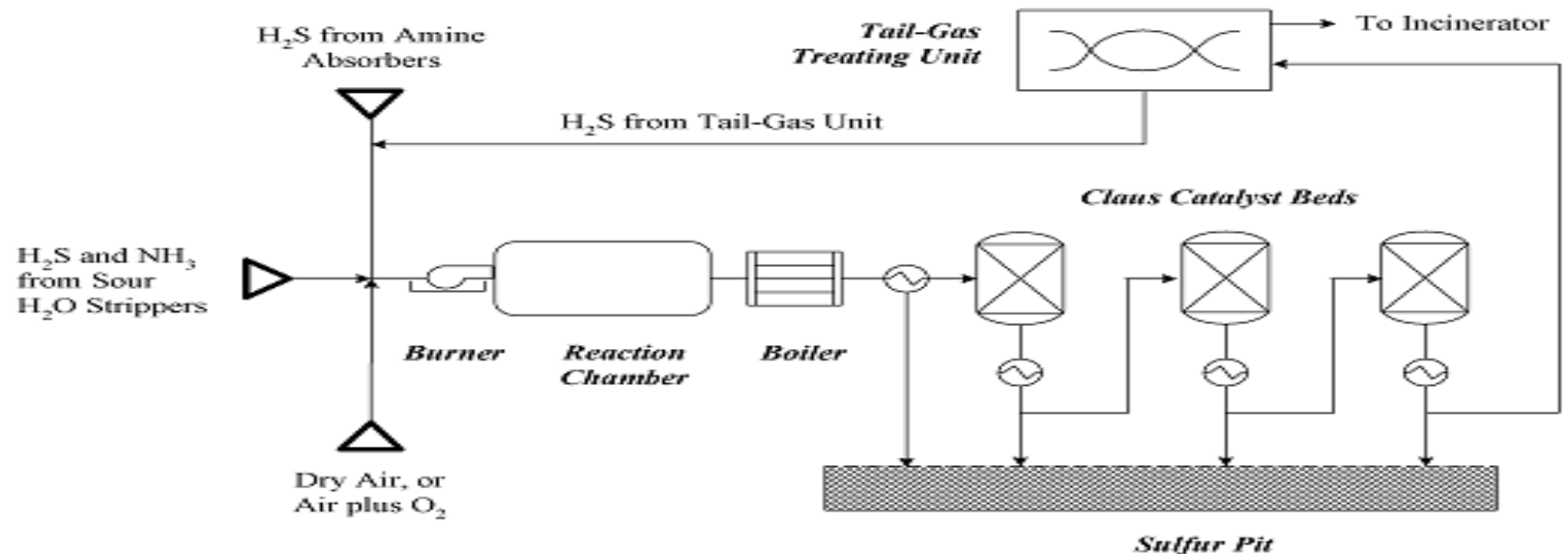




*Figure 26. Claus reactions.*

Claus Sulfur Recovery Process. At the sulfur plant, H<sub>2</sub>S is combined with sour-water stripper off-gas and sent to a Claus unit. Invented in 1881 by Carl Freidrich Claus, almost every refinery in the world uses some version of this process to convert H<sub>2</sub>S into elemental sulfur. A simplified version of Clausreaction chemistry is shown in Figure 26.

Figure 27shows a process schematic for a Claus unit. H<sub>2</sub>S and a carefully controlled amount of air are mixed and sent to a burner, where about 33% of the H<sub>2</sub>S is converted to SO<sub>2</sub>and water. From the burner, the hot gases go to a reaction chamber, where the reactions shown in Figure 26reach equilibrium. In several units, the air is enriched with oxygen to increase plant capacity.



*Figure 27. Claus process.*

As shown, elemental sulfur is produced by the reversible reaction between  $\text{SO}_2$  and  $\text{H}_2\text{S}$ .  $\text{COS}$  and  $\text{CS}_2$  appear in small amounts, but even traces of these compounds are hard to remove in tail-gas treating units. Ammonia comes in with the sour-water stripper off-gas. In the Claus process, it is thermally decomposed into nitrogen and water.

In the Claus burner, combustion temperatures reach  $2200^\circ\text{F}$  ( $1200^\circ\text{C}$ ). Needless to say, this generates a tremendous amount of heat. Much of the heat is recovered in a waste-heat boiler, which generates steam as it drops the temperature to  $700^\circ\text{F}$  ( $370^\circ\text{C}$ ). Next, the process gas goes to a condenser, where it is cooled to about  $450^\circ\text{F}$  ( $232^\circ\text{C}$ ). At this temperature, sulfur vapors condense, and the resulting molten sulfur flows through a drain to a heated sulfur-collection pit. At the bottom of the drain, a seal leg maintains system pressure and keeps unconverted gases out of the pit.

### ***Waste Water Treatment***

Waste water treatment is used to purify process water, runoff, and sewage. As much as possible, purified waste-water streams are re-used in the refinery. Wastewater streams may contain suspended solids, dissolved salts, phenols, ammonia, sulfides, and other compounds. The streams come from just about every process unit, especially those that use wash water, condensate, stripping water, caustic, or neutralization acids.

#### **Primary Treatment**

Primary treatment uses a settling pond to allow most hydrocarbons and suspended solids to separate from the wastewater. The solids drift to the bottom of the pond, hydrocarbons are skimmed off the top, and oily sludge is removed.

Difficult oil-in-water emulsions are heated to expedite separation. Acidic wastewater is neutralized with ammonia, lime, or sodium carbonate. Alkaline wastewater is treated with sulfuric acid, hydrochloric acid, carbon dioxide-rich flue gas, or sulfur.

## Secondary Treatment

Some suspended solids remain in the water after primary treatment. These are removed by filtration, sedimentation or air flotation. Flocculation agents may be added to consolidate the solids, making them easier to remove by sedimentation or filtration. Activated sludge is used to digest water-soluble organic compounds, either in aerated or anaerobic lagoons. Steam-stripping is used to remove sulfides and/or ammonia, and solvent extraction is used to remove phenols.

## Tertiary Treatment

Tertiary treatment processes remove specific pollutants, including traces of benzene and other partially soluble hydrocarbons. Tertiary water treatment can include ion exchange, chlorination, ozonation, reverse osmosis, or adsorption onto activated carbon. Compressed oxygen may be used to enhance oxidation. Spraying the water into the air or bubbling air through the water removes remaining traces of volatile chemicals such as phenol and ammonia.

## Solid Waste

Refinery solid wastes may include the following materials:

- Spent catalyst and catalyst fines
- Acid sludge from alkylation units
- Miscellaneous oil-contaminated solids

All oil-contaminated solids are treated as hazardous and sent to sanitary landfills. Recently, super-critical extraction with carbon dioxide has been used with great success to remove oil from contaminated dirt.

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